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Partial Deoxygenation of 1,2-Propanediol Catalyzed by Iridium Pincer Complexes

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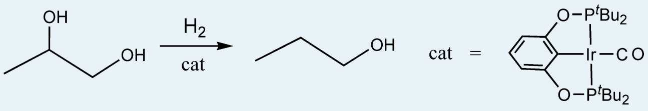
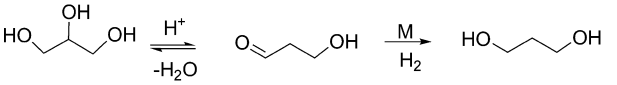


ABSTRACT: Iridium pincer complex (POCOP)IrH_2 (**1**; POCOP = κ^3-C_6H_3-1,3-[OP(tBu)$_2$]$_2$) catalyzes hydrogenolysis of 1,2-propanediol to *n*-propanol in good yield under mild conditions (acidic aqueous dioxane, 50−125 °C, 100−600 psi H_2). Studies of catalyst speciation revealed that the catalyst reservoir species is (POCOP)Ir(CO) (**2**), formed by decarbonylation of the substrate. Complex **2** is a superior catalyst precursor, since it is air-stable and readily prepared by treating complex **1** with CO.

KEYWORDS: *diol deoxygenation, catalysis, hydrogenation, hydrogenolysis*

The use of biomass and biomass-derived feedstocks in the production of fine and commodity chemicals is hindered by the lack of cost-effective purification and conversion processes. The development of efficient and selective catalytic transformations should allow biomass feedstocks to become economically competitive with traditional petroleum-based feedstocks. Ideally, the conversion reactions will be applicable to a range of substrates and tolerant of crude biomass inputs.

Glycerol is of particular interest as a renewable raw material because it is currently being generated in vast quantities as a byproduct of biodiesel production. The partial hydrogenolysis of glycerol has been envisioned as a new, direct route to 1,3-propanediol for the production of polyesters, polyurethanes, and polyethers with high renewable resource content.[1−6] One strategy for selective reduction of glycerol is a tandem catalytic sequence involving the dehydration of secondary alcohols followed by hydrogenation of the resulting carbonyl groups (eq 1).[1,2]



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Efficient conversion of glycerol to higher value products will require the development of highly active, selective catalysts. It will be crucial to identify robust catalysts that are tolerant of water and acid at the high temperatures required for the dehydration step.

Using terminal vicinal diols as a model system, Schlaf and coworkers have explored deoxygenation to *n*-alcohols using homogeneous Ru ionic hydrogenation catalysts.[7] These studies have provided insight into various factors that control deoxygenation selectivity. The use of diol models, which have less complex reactivity than their polyol analogs, enabled kinetic analysis and more thorough characterization of product profiles. The most selective of the Ru hydrogenation catalysts was [Cp*Ru(CO)$_2$(H_2)][OTf], which achieved a 54% yield of 1-propanol in sulfolane solvent at 110 °C and 710 psi H_2 using trifluoromethanesulfonic acid (HOTf) as the catalyst for the initial dehydration step.[8] In addition to the 1-propanol hydrogenation product, the formation of several ether condensation products was observed, including significant yields of propylene glycol propyl ether (11%) and di-*n*-propyl ether (15%). The overall selectivity for reduction of the secondary hydroxyl group is 99%. The high regioselectivity of the ruthenium catalyst was impressive, but the catalyst is deactivated by water, which is a byproduct of the reaction.[8] Several ruthenium containing ionic hydrogenation catalysts with N-donor ligands have demonstrated greater solubility and stability in aqueous solution; however, significant thermal decomposition or reduced selectivities (or both) were observed.[9,10]

The homogeneous ruthenium systems reported to date represent significant advances in the development of selective polyol deoxygenation catalysts, demonstrating unprecedented regioselectivity in partial diol deoxygenation. In addition, studies of these systems have delineated many of the competitive equilibria and condensation pathways that are common to alcohols in acidic medium and must be minimized for effective conversion. Because vicinal diol groups are common to all sugar polyols, the lessons learned using these model substrates are expected to be broadly applicable. To fully develop and optimize effective polyol deoxygenation technologies, catalysts that exhibit greater stability at high temperatures in the presence of water are needed.

Ir(III) pincer complexes have exhibited remarkable thermal stability and excellent catalytic efficiency in the dehydrogenation of alkane,[11,12] alcohol, diol,[13] and amine[14−16] substrates at temperatures up to 250 °C. More recently, PNP- and PCP-ligated Ir(III) dihydrides were shown to rapidly hydrogenate CO_2 to potassium formate in aqueous KOH between 120 and 200 °C.[17]

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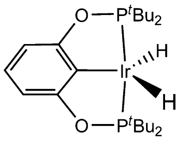
In this work, the Ir pincer complex (POCOP)IrH$_2$ (**1**), previously reported by Brookhart and co-workers,[18,19] has been utilized to catalyze the selective deoxygenation of 1,2-propanediol (1,2-PD). The hydrolytic and thermal stability of the (POCOP)Ir core enabled detailed optimization studies in which key variables that controlled deoxygenation selectivity were identified. In addition, the speciation of the catalyst was investigated, which led to the discovery of the superior *water- and air-stable* Ir(I) carbonyl precatalyst **2**. The significant stability of this catalyst system combined with high selectivity points to the viability of catalytic polyol deoxygenation processes.



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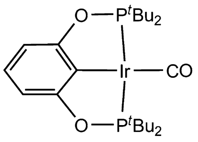

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RESULTS AND DISCUSSION

Hydrogenation of 1,2-Propanediol. Using (POCOP)-IrH$_2$ and trifluoromethanesulfonic acid, 1,2-PD was reduced to *n*-propanol in up to 95% yield in aqueous dioxane at 125 °C under 100 psi H_2. The relatively mild conditions of the reaction and the high selectivity observed are promising. Even more remarkable is the stability of this catalyst to the aqueous environment. In fact, the presence of water is actually required to achieve high deoxygenation selectivity and hydrogenation efficiency, which also increased as the acid concentration in the reaction system was decreased.

As shown in Figure 1, the combined yield of 1-propanol and *n*-propyl ether generated in the Ir-catalyzed deoxygenation of 1,2-PD increased from 2% to 95% as the percent of water initially present in the solution was increased from zero to 20% by volume and as the acid concentration was reduced from 1 to 0.05 equiv with respect to 1,2-PD.

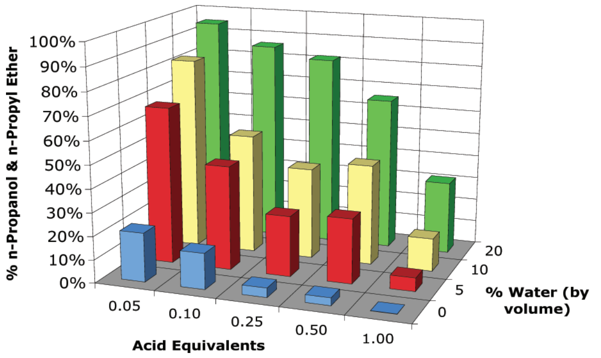
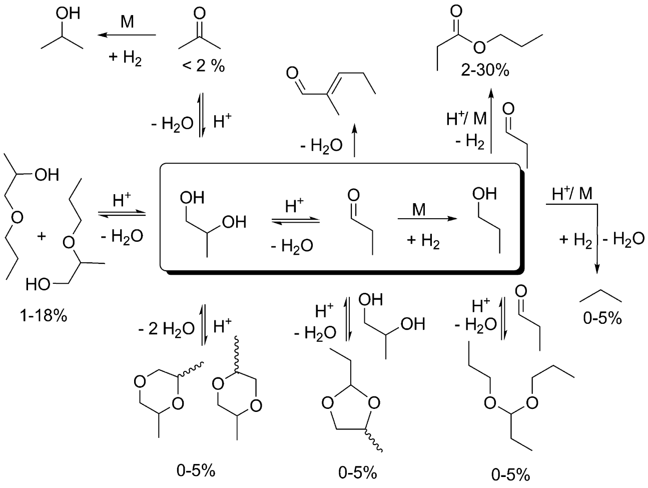


Figure 1. Yield of (1-propanol + *n*-propyl ether) in the deoxygenation of 1,2-PD as a function of [acid]/[1,2-PD]$_o$) and percent water by volume. *n*-Propyl ether yield was <9% in all reactions.

Reactions containing no water or more than 0.25 equiv of triflic acid gave poor selectivity toward the *n*-alcohol and yielded up to 15 distinct products that were identified by ^{1}H NMR spectroscopy or GC/MS. Several of these products along with pathways that have been proposed for their generation are shown in Scheme 1. In addition to compounds shown in Scheme 1, dipropylene glycol, *n*-propyl ether, and isopropyl ether were also identified and reasonably result from condensation of the respective alcohols. In addition, some decomposition of the dioxane solvent was observed, leading to the generation of ethanol and ethylene glycol (<5%), which were not observed in the absence of dioxane. With the exception of propane, isomers of 2,5- and 2,6-dimethyldioxane, and dipropoxypropane, which were observed by NMR spectroscopy or GC/MS, all major byproducts were quantified using a GC assay method developed and verified with authentic samples. The product profiles obtained under each set of reaction conditions were characterized by NMR spectroscopy and GC/MS or comparison to authentic compounds prepared by independent synthesis.

Scheme 1. Conversion of Propanediol to 1-Propanol and the Competing Pathways to Various Byproducts Observed



The selectivity trend shown in Figure 1 may be attributed to both thermodynamic and kinetic factors. A higher water concentration will give lower steady state concentrations of dehydrated species and, thus, limit formation of byproducts arising from condensation reactions (see Scheme 1). The reversible formation of condensation byproducts, such as ethyl methyl dioxolane, in aqueous solution (>10% water) is apparent in the kinetic trace of the reaction mixture (Figure 2). It is reasonable to suggest that the relative rate of hydrogenation of propionaldehyde to that of dehydration is much higher at the optimal reaction conditions, leading to

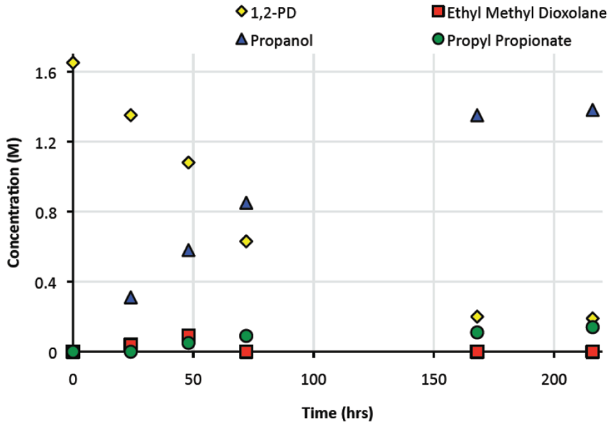
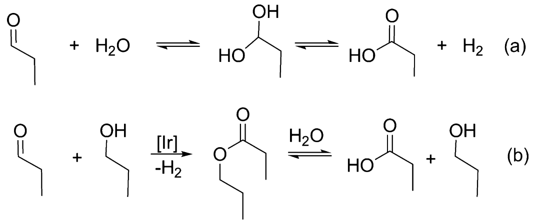


Figure 2. Time course of 1,2-propanediol deoxygenation showing reversible formation of ethyl methyl dioxolane.

lower steady-state concentrations of aldehyde intermediate and minimal competition from subsequent acid-catalyzed conversions. In fact, no propionaldehyde intermediate is observed by NMR spectroscopy in reaction mixtures containing more than 20% water (by volume) and 0.10 equiv or less of acid. In these cases, the propionaldehyde intermediate is rapidly hydrogenated to *n*-propanol by the Ir catalyst with excellent overall selectivity. As the acid concentration increases, acid-catalyzed pathways become competitive with hydrogenation, resulting in significant formation of ether, ester, carboxylic acid, and aromatic byproducts. In the latter case, mesitylene (5−10%) is formed via acid-catalyzed trimerization of the ketone intermediate at high acid concentration.[20] This mechanism was confirmed by an experiment using 1,2-pentanediol, which leads to formation of 1,3,5-tripropylbenzene.

Carboxylate-containing byproducts were significant, formed in up to 30% yield in reactions containing more than 0.5 equiv of triflic acid. Carboxylic acid could result from dehydrogenation of 1,1-geminal diols produced in the reaction (Scheme 2a). This pathway would be facilitated at higher water concentrations; however, dehydrogenative coupling of the aldehyde intermediate with the 1-alcohol product, followed by acid-catalyzed hydrolysis (Scheme 2b) would also be consistent with experimental findings.

Scheme 2. Proposed Pathways to Propionic Acid: (a) Dehydrogenation of 1,1-Propanediol, (b) Dehydrogenative Coupling of Propionaldehyde and 1-Propanol



We have examined the iridium-catalyzed hydrogenation of propionaldehyde in dioxane solvent. In addition to 1-propanol, we find that propyl propionate is formed, with the amount of ester formed increasing with the yield of 1-propanol. No ester is observed in a control experiment starting from propionaldehyde in the absence of dihydrogen and water, which rules out a Tischenko-type aldehyde coupling. However, addition of water to a solution of propionaldehyde and (POCOP)IrH$_2$ under Ar leads to formation of equimolar amounts of propionic acid and propanol, indicating that under aqueous conditions, propionaldehyde can act as a hydrogen acceptor in the dehydrogenation of its 1,1-propanediol hydration product (Scheme 2b).

The yield of carboxylate products decreases with increasing hydrogen pressure, but trace amounts of propionic acid (<1.5%) are observed at pressures as high as 600 psi in the aqueous-phase diol deoxygenations. Examination of the hydrogenation of propionaldehyde to 1-propanol shows that the selectivity decreases with increasing water content (Figure 3) as a result of the competing dehydrogenation pathways to propionic acid (Scheme 2). This effect of increased water is opposite that previously noted for the diol substrate, in which deoxygenation selectivity improves with a concomitant decrease in carboxylic acid yield with more water. The high selectivity to 1-propanol from 1,2 propanediol in the face of the opposing effects of water on the overall deoxygenation reaction and the hydrogenation step can be attributed to the low steady state concentrations of aldehyde intermediate generated in the course of the reaction.

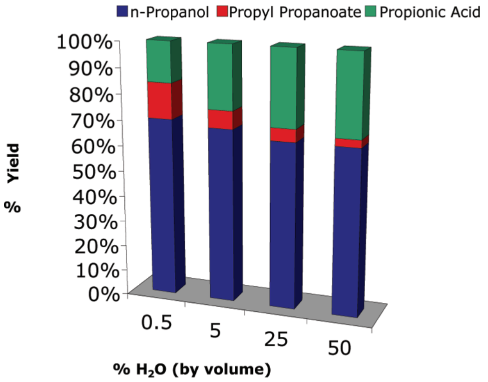


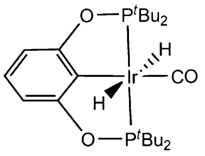
Figure 3. Percent yield of *n*-propanol, propyl propionate, and propionic acid in the (POCOP)IrH$_2$-catalyzed hydrogenation of propionaldehyde as a function of percent water by volume (1.5 mol % (POCOP)IrH$_2$, 100 psi H$_2$, 50 °C, aqueous dioxane).

Effect of Temperature and Pressure. Increasing the reaction temperature from 125 to 200 °C at 100 psi H$_2$ led to a significant decrease in 1,2-propanediol deoxygenation selectivity from 95% to 12% 1-propanol, even in 20% aqueous dioxane. At this higher temperature, the product mixture also contained propionaldehyde (17%), 2-methyl-2-pentenal (8%), ethyl methyl dioxolane (6%), propylene glycol propyl ether (2%), dipropylene glycol (6%), propionic acid (3%), and acetone (2%) upon complete consumption of the diol. The high concentration of propionaldehyde suggests that the rate of the aldehyde hydrogenation step is not competitive with alternative reversible reactions of the aldehyde at this temperature. Notably, at 185 °C, increasing the hydrogen pressure to 600 psi restored the deoxygenation selectivity to 90% 1-propanol. The only byproducts observed were propionaldehyde (0.5%), propylene glycol propyl ether (PGPE, 1%), dipropylene glycol (3%), and a trace amount of ethanol from dioxane decomposition.

The use of only water as solvent was briefly explored. Limited screening showed that yields of PGPE (7%) and dipropylene glycol (5%) were significantly higher (results from 66% conversion using 0.5 mol % Ir, and 0.6% triflic acid at 185 °C for 6 h with 100 psi H$_2$). The selectivity for 1-propanol remained relatively high (43% yield), and minor amounts of *n*-propyl ether (1.6%), isopropyl alcohol (0.4%), propionaldehyde (0.1%), propionic acid (0.2%), and ethyl methyl dioxolane (0.4%) were observed. Further optimization to improve selectivity and efficiency with variation of acid concentration, hydrogen pressure, and temperature of the reactions is in progress.

Catalyst Speciation. Monitoring catalyst speciation reveals that the (POCOP)IrH$_2$ precatalyst is not observed during the course of the deoxygenation reaction. Upon completion of the reaction, two species were identified by ^{31}P NMR spectroscopy, with a resonance at δ = 199 assigned to the previously reported[19] carbonyl complex (POCOP)Ir(CO), (**2**). A resonance at δ = 183 is attributed to *trans*-(POCOP)-Ir(CO)(H)$_2$,(**3**), which also exhibits a triplet hydride resonance in the ^{1}H NMR spectrum at −9.53 ppm ($^2J_{P-H}$ = 15 Hz).

Upon completion of the deoxygenation reactions, an orange crystalline solid was isolated from the reactor. Dissolution of this solid gave the ^{31}P and ^{1}H NMR spectra shown in Figure 4. IR spectra of these crystals show CO bands at 1933 and 1988



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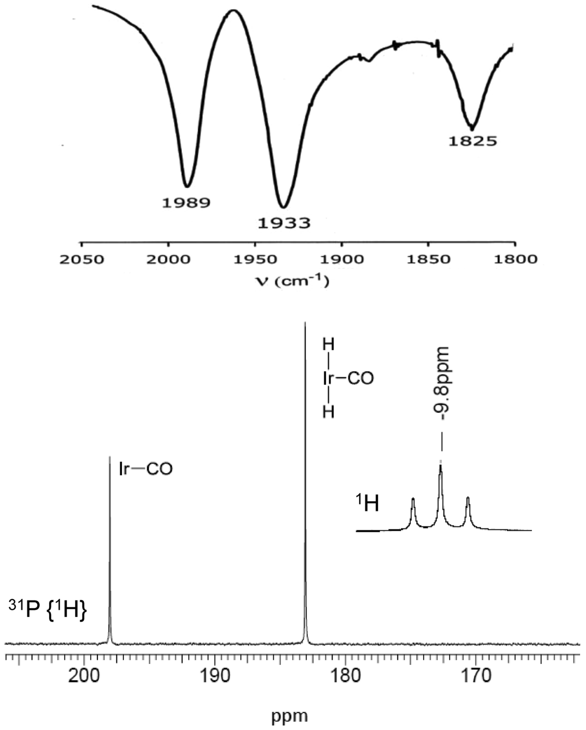


Figure 4. Data for catalyst sample isolated from deoxygenation reaction. Bottom: ^{1}H and ^{31}P{^{1}H} NMR spectra in THF-d_8. Top: IR spectrum (carbonyl region, KBr disk).

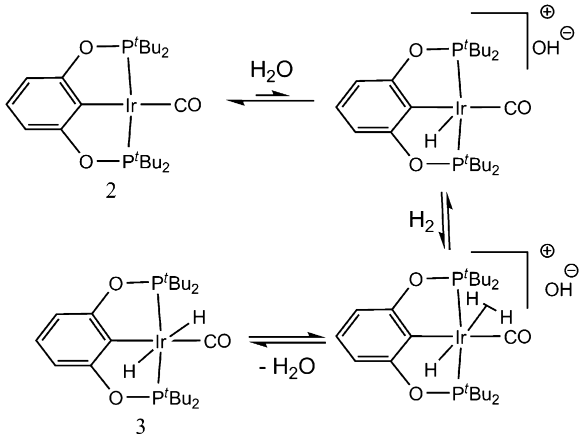
cm^{-1}, attributed to the Ir(I) and Ir(III) carbonyls, respectively. The Ir−H stretching frequency was observed at 1825 cm^{-1}. These observations suggest that a mixture of complexes **2** and **3** crystallized from the reaction.

Consistent with previous reports, we find that (POCOP)IrH$_2$ is rapidly converted to (POCOP)Ir(CO) upon exposure to CO at room temperature.[19] In contrast, addition of CO to (POCOP)IrH$_2$ in toluene at 0 °C resulted in a mixture of the Ir(I) and Ir(III) carbonyls, as indicated by the two ^{31}P signals at δ 199 and δ 183 and a triplet ($^2J_{P-H}$ = 15 Hz) hydride resonance at −9.53 ppm.

In the hydrogenation reactions examined, the Ir carbonyl complexes **2** and **3** are accessed via decarbonylation of the aldehyde intermediate. The generation of **2** and **3** is even faster when starting with the aldehyde as the substrate. This reactivity is analogous to a previous report[21] that decarbonylation of methanol led to cationic *trans*-[(PNP)Ir(H)$_2$CO]$^+$, presumably through a formaldehyde intermediate. Similar decarbonylation reactions leading to ruthenium carbonyl complexes were reported by Schlaf and co-workers in the course of hydrogenation of 1,2 hexanediol.[22]

Noting that (POCOP)Ir(CO) was observed in the catalytic deoxygenation reactions, we tested this species as a precatalyst. (POCOP)Ir(CO) has a significant advantage over (POCOP)IrH$_2$ in that it is air-stable. The presence of water was found to accelerate the rate of hydrogenation. Water likely aids in the formation of the active catalyst from (POCOP)Ir(CO) via a proton-assisted oxidative addition of hydrogen, affording *trans*-(POCOP)Ir(CO)(H)$_2$. Initial protonation of the basic (POCOP)Ir(CO) complex leads to formation of a cationic Ir(III) monohydride. Subsequent association of dihydrogen, followed by deprotonation of the cationic species results in formation of the *trans*-dihydride (Scheme 3).

Scheme 3. Proposed Mechanism for Water Assisted Hydrogen Addition to (POCOP)Ir(CO)



We have separately verified formation of **3** by the mechanism suggested in Scheme 3. At room temperature, a solution of complex **2** in THF was pressurized with 1200 psi hydrogen. No reaction to form **3** was observed after 24 h. Addition of acid (anilinium tetraphenylborate) led to the formation of a mixture of **3** and **2**. A similar proton-assisted hydrogen addition to the analogous (PONOP)Ir(CH$_3$) complex affording a *trans*-dihydride complex was recently demonstrated.[23]

■ CONCLUSION

Efficient hydrogenolysis of 1,2 propanediol to 1-propanol is catalyzed by acid in tandem with a pincer iridium complex. The presence of water in the reaction mixture gives improved selectivity for 1-propanol. In contrast to prior work with ruthenium catalysts in which catalyst deactivation by water was significant, the catalyst reservoir species is an air- and water-stable Ir(I) carbonyl complex that can be recovered from the reaction mixture.

■ EXPERIMENTAL SECTION

General Procedures. All experiments were performed under an argon atmosphere using standard glovebox or Schlenk techniques. All solvents were dried using appropriate drying agents. Alcohol and aldehyde substrates were purchased from Aldrich and used as received. The compounds (POCOP)IrH$_2$,[19] (POCOP)Ir(H)(Cl),[18] and (POCOP)Ir(CO)[19] were prepared as described in the literature.

All deoxygenation reactions were prepared in a glovebox under an atmosphere of argon in J.Young screw cap NMR tubes or Parr reactors. ^{1}H NMR spectra were obtained using a Bruker 500 or 300 MHz spectrometer and were integrated relative to the toluene internal standard resonances. Quantitative GC analyses were performed using a Hewlett-Packard 4890 gas chromatograph using a DB wax column with FID detector. GC/MS data were obtained using a Hewlett-Packard 5971A spectrometer. IR spectra were obtained using a Bruker Vector 33 FT-IR spectrometer.

Deoxygenation of 1,2-PD. Experiments conducted to investigate the effect of acid and water were performed in medium-walled J.Young tubes as follows: (POCOP)IrH_2 (0.005 g, 0.009 mmol) was added to an NMR tube. The remaining reagents were added in appropriate volume to achieve a total volume of 0.50 mL with a 1,2-propanediol concentration of 1.36 M while varying the acid (0.050−1.00 equiv relative to 1,2-PD) and water (0−20% by volume) content. Dioxane (0.280−0.437 mL) was added to give a dark red-brown homogeneous solution, which lightened upon addition of 1,2-propanediol (0.050 mL, 0.681 mmol) and water (0−0.100 mL). Toluene was added as an internal standard (0.010 mL, 0.096 mmol). Finally, trifluoromethanesulfonic acid (0.003−0.060 mL, 0.034−0.678 mmol) was added to the reaction mixture using a micropipet to give a light orange solution, and the tubes were sealed. The J.Young tubes were freeze−pump−thawed three times prior to addition of 100 psi of H_2. Pressurized tubes were then heated to 125 °C. At the end of the reaction, the tubes were cooled to room temperature. The mixtures were analyzed by gas chromatography.

Reactions conducted at pressures higher than 100 psi H_2 were carried out in Parr reactors. Water, acid, catalyst, and diol concentrations were varied. The order of additions was unchanged. In these cases, the reactor was purged with hydrogen gas for 1 min prior to charging with 600 psi H_2. At the end of the reaction, the Parr reactor was allowed to cool to room temperature and then cooled in dry ice/acetone prior to slow venting of the hydrogen atmosphere to minimize the mass loss. The average mass lost was 10%.

Propionaldehyde Hydrogenation. (POCOP)IrH_2 (0.0017 g, 0.0029 mmol) was added to a J.Young tube, followed by dioxane (0.198−0.448 mL). Propionaldehyde (0.0500 mL, 0.687 mmol) was added, and the red-brown solution turned orange. Toluene (2.00 μL, 0.0187 mmol) was added as an internal standard, and varying amounts of water were added (2.50−250 μL). The J.Young tube was sealed under an Ar atmosphere and freeze−pump−thawed on a vacuum line. The tube was pressurized with 100 psi H_2 and heated to 125 °C. The reaction was monitored by NMR spectroscopy, and the yields were determined by integration relative to toluene.

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Notes

The authors declare no competing financial interest.

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