ACS Catalysis

Research Article

pubs.acs.org/acscatalysis

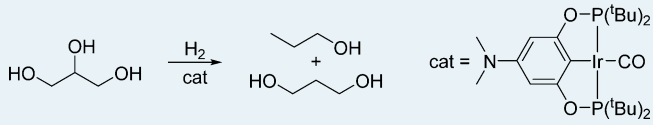
Partial Deoxygenation of Glycerol Catalyzed by Iridium Pincer Complexes

David B. Lao, Alisa C. E. Owens, D. Michael Heinekey,* and Karen I. Goldberg*

Department of Chemistry, University of Washington, Box 351700, Seattle, Washington 98195-1700, United States

Supporting Information

ABSTRACT: Iridium pincer complexes (POCOP)Ir(CO) (POCOP = κ^3-C_6H_3-1,3-[OP(^{t}Bu)$_2$]$_2$) and substituted POCOP derivatives catalyze deoxygenation of glycerol to *n*-propanol and 1,3-propanediol in good yield under moderate conditions (acidic aqueous dioxane, 200 °C, 80 bar H_2). Catalyst solubility in the polar reaction mixture is improved by incorporation of a polar moiety in the para position of the POCOP phenyl ring, with the best results obtained with a dimethylamino substituent.

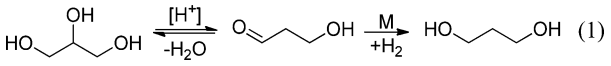


KEYWORDS: *glycerol, catalysis, deoxygenation*

INTRODUCTION

Dwindling petroleum reserves have led to significant focus on the development of renewable sources for fuels and commodity chemicals. Because of its infrastructure compatibility with current transportation fuels, biodiesel has drawn considerable interest, and production has grown significantly in recent years. The rapid growth in biodiesel production has resulted in the generation of large quantities of byproduct glycerol. While glycerol has many uses as a commodity chemical, the production scale of transportation fuels far exceeds that of commodity chemicals. As a result of high production quantities that exceed market demand and high purification costs, waste glycerol from biodiesel production is often burned onsite as fuel for the production process. The transformation of waste stream glycerol into a C-3 platform chemical would improve upon the atom efficiency and the economics of the biodiesel industry.[1−5]

Potential C-3 target chemicals from glycerol are 1,3-propanediol (1,3-PD) and 1-propanol (1-PO). 1,3-PD is utilized in the production of polyesters, polyurethanes, and polyethers. The conversion of glycerol to 1,3-PD can be envisioned as a net deoxygenation via a tandem catalytic sequence with an initial acid catalyzed dehydration followed by metal catalyzed hydrogenation (eq 1).



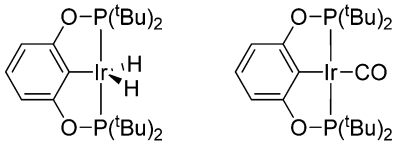
(1)

Deoxygenation of glycerol in the C2 and C3 positions would afford 1-PO, a useful solvent. Although 1-PO has lower value than 1,3-PD, it is still a value-added chemical made from glycerol, particularly so if generated from crude biodiesel byproduct glycerol.

Catalysts capable of selectively deoxygenating glycerol must be stable in aqueous acidic solutions at high temperatures. There have been many recent heterogeneous catalysts reported for glycerol deoxygenation with various transition metals including Pt,[6−9] Rh,[10−12] Ru,[4,5] and Cu.[4,5] Despite all the examples of heterogeneous catalysts, there are relatively few examples of homogeneous catalysts. Braca has reported a ruthenium iodocarbonyl catalyst for the deoxygenation of glycerol to 1-PO with up to 90% selectivity.[13] Schlaf has recently reported ruthenium aqua complexes with cocatalyst triflic acid for the deoxygenation of glycerol to 1-PO with up to 18% yield.[14,15]

We recently reported the deoxygenation of the glycerol model substrate 1,2-propanediol (1,2-PD) to 1-PO using a bis(phosphinite) (POCOP) iridium pincer catalyst (**1**).[16] Speciation studies showed that under the reaction conditions, the iridium carbonyl complex (**2**) was formed by alcohol decarbonylation. Complex **2** was then shown to be an effective catalyst for the deoxygenation of 1,2-PD.

Herein, we report an extension of this work for catalytic deoxygenation of glycerol to 1-PO and 1,3-PD using POCOP iridium carbonyl complex **2** and derivatives.



1 **2**

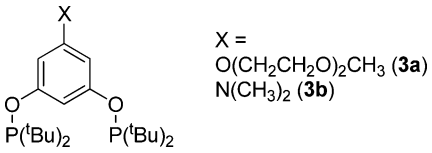
RESULTS AND DISCUSSION

Increasing Solubility in Polar Reaction Mixtures. Consistent with our previous studies of deoxygenation of 1,2-PD, it was found that dioxane is a suitable solvent for this chemistry. However, in glycerol/water/dioxane mixtures, complex **2** has limited solubility at room temperature and at

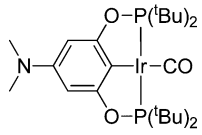
Received: July 12, 2013
Revised: August 30, 2013
Published: September 5, 2013

   dx.doi.org/10.1021/cs400551g | ACS Catal. 2013, 3, 2391−2396

elevated temperatures. A series of pincer ligands were prepared to increase catalyst solubility in polar reaction mixtures containing glycerol and water. Novel ligands containing diethylene glycol monomethyl ether (**3a**) and dimethyl amine (**3b**) were prepared by synthesizing the corresponding 5-substituted resorcinol[17,18] followed by diphosphorylation.[19]



Iridium carbonyl catalysts prepared from these ligands showed improved solubility over **2** in reaction mixtures containing glycerol in aqueous dioxane. Complete catalyst solubility in reaction mixtures at room temperature enabled reliable reaction optimization experiments to be performed. Because of ease of ligand synthesis and improved solubility in acidic polar solutions, the dimethyl amine complex **4** formed from ligand **3b** was used in all catalytic reactions described here.



4

Deoxygenation of Glycerol. In a typical experiment, glycerol was converted to 1-PO and 1,3-PD in aqueous dioxane solutions with 0.125 mol % **4** relative to glycerol and 1 mol % sulfuric acid relative to glycerol at 200 °C under 80 bar H_2. Reaction progress was monitored by quantitative $^{13}C\{^1H\}$ NMR spectroscopy of neat reaction solutions (see Experimental Section for details). Approximately 45% conversion of glycerol to 1-PO and 1,3-PD was observed after 48 h (Figure 1). Bubbling the reaction headspace gas through acetone-d_6 and characterizing by ^1H NMR spectroscopy showed formation of small amounts of propane and propylene. Weighing reaction vessels before and after heating and venting showed good mass balance suggesting that propane and propylene were formed in trace amounts. No appreciable amounts of 1,2-PD were observed in these reactions.

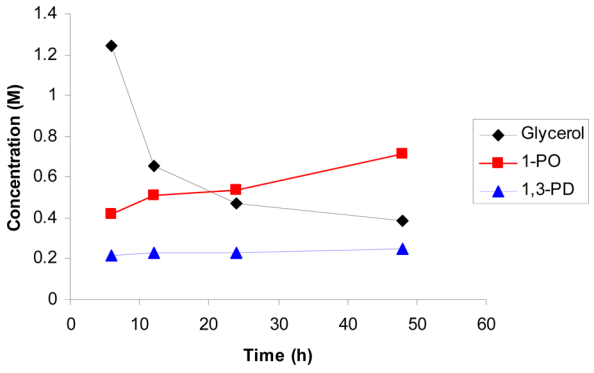


Figure 1. Time course of glycerol conversion to 1-propanol and 1,3-propanediol. Reactions with 0.0065 mmol of **4**, 5.2 mmol of glycerol, and 0.052 mmol of H_2SO_4 in deionized water (0.197 g) and dioxane (1.22 g) under 80 bar H_2. Reactions heated to 200 °C. Concentrations measured by quantitative ^{13}C NMR spectroscopy (see Experimental Section for details).

We propose that 1,2-PD was not observed because of the rapid deoxygenation of 1,2-PD to 1-PO as determined in our previous studies[16] and in control reactions. Control reactions have also shown that under our reaction conditions, 1,3-PD was not deoxygenated to 1-PO. It is reasonable to then suggest that 1-PO is formed via deoxygenation at the glycerol C1 position followed by a subsequent deoxygenation at the C2 position of 1,2-PD. Our previous studies have shown that deoxygenation of 1,2-PD to 1-PO occurs at much lower temperatures (125 °C) than the reaction conditions used for the deoxygenation of glycerol. Deoxygenation at the glycerol C2 position leads to formation of 1,3-PD.

The selectivity of product formation appears to change over time. In the first 6 h, 1,3-PD and 1-PO are formed in an approximate 1:2 ratio, respectively. Over the course of 48 h, the 1,3-PD: 1-PO selectivity diminishes to 1:4. As noted previously, this decrease in 1,3-PD selectivity is not because of conversion of 1,3-PD to 1-PO or decomposition of products as shown by overall mass balance. One possible explanation for the change in selectivity may be a change in the catalyst over the course of the reaction. A change in the reaction medium over the course of the reaction may also result in the different selectivity with time.

The effect of reaction temperature on conversion and selectivity was investigated (Figure 2). Lowering the reaction

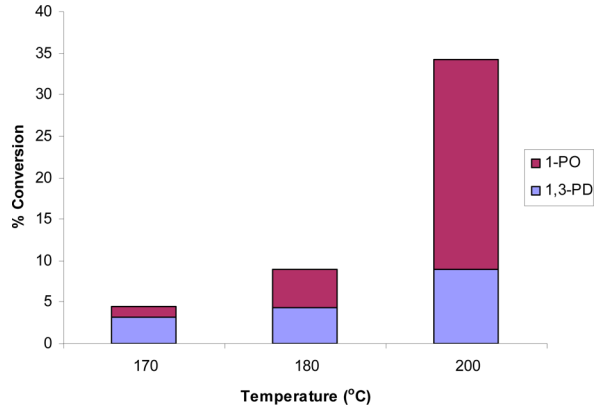


Figure 2. Conversion of glycerol to 1-propanol and 1,3-propanediol at different temperatures. Reactions with 0.0065 mmol of **4**, 5.2 mmol of glycerol, and 0.052 mmol of H_2SO_4 in deionized water (0.197 g) and dioxane (1.22 g) under 80 bar H_2. Reactions heated for 24 h. Concentrations measured by qualitative ^{13}C NMR spectroscopy (see Experimental Section for details).

temperature from 200 to 180 °C for 24 h resulted in the reduction of glycerol conversion from about 35% to 9%. Further lowering the temperature to 170 °C resulted in reduction of glycerol conversion to 4%.

The reaction selectivity is also a function of temperature. Reactions carried out at 180 °C show a 1:1 ratio of 1,3-PD to 1-PO. The selectivity increased to a 2:1 ratio of 1,3-PD to 1-PO when the reaction was carried out at 170 °C.

We have previously shown that deoxygenation of 1,2-propanediol at 185 °C requires H_2 pressures above 40 bar to achieve high selectivities (90%) to 1-PO.[16] Comparable selectivities and conversions for glycerol deoxygenation at 200 °C for 20 h were observed when H_2 pressures between 40 and 80 bar were used (Figure 3). Notably, the use of a mixture of 40 bar CO and 40 bar H_2 in our reactions resulted in a decrease of conversion from 24% to 3%, but maintained a 1,3-

dx.doi.org/10.1021/cs400551g | ACS Catal. 2013, 3, 2391−2396

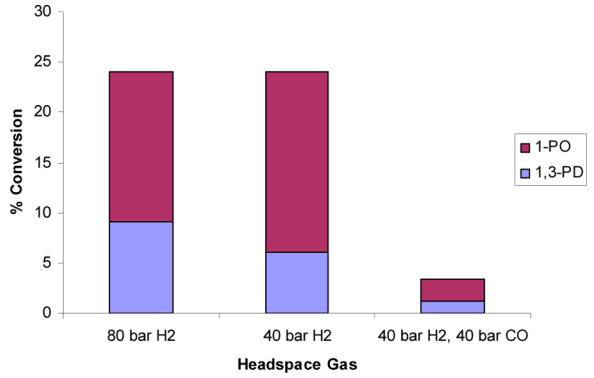


Figure 3. Conversion of glycerol to 1-propanol and 1,3-propanediol at different headspace pressures. Reactions with 0.0065 mmol of **4**, 5.2 mmol of glycerol, and 0.052 mmol of H_2SO_4 in deionized water (0.197 g) and dioxane (1.22 g). Reactions heated at 200 °C for 20 h. Concentrations measured by qualitative ^{13}C NMR spectroscopy (see Experimental Section for details).

PD: 1-PO selectivity of about 1:4. The decrease in conversion in the presence of CO suggests that catalysis is hindered by CO coordination to the catalyst. The proposed reaction mechanism is discussed below.

The effect of acid concentration was also studied (Figure 4). Acid concentration was varied from 0.25% to 4.0% versus

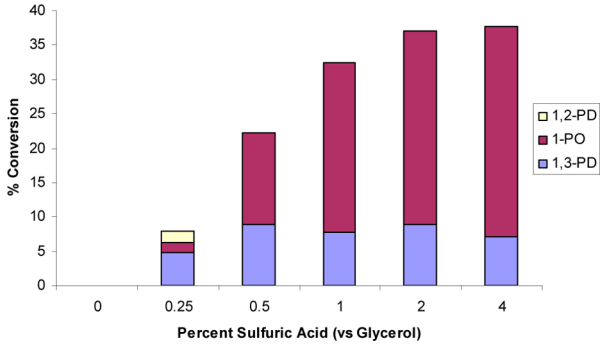


Figure 4. Conversion of glycerol to 1-propanol, 1,2-propanediol, and 1,3-propanediol with varying acid equivalents. Reactions with 0.0065 mmol of **4** and 5.2 mmol of glycerol in deionized water (0.197 g) and dioxane (1.22 g) under 80 bar H_2. Reactions heated to 200 °C for 24 h. Concentrations measured by quantitative ^{13}C NMR spectroscopy (see Experimental Section for details).

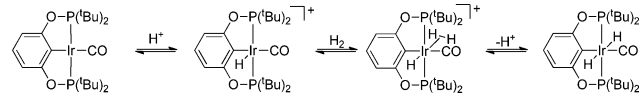
glycerol. Acid concentrations below 4.0% were used to limit the formation of acid catalyzed side products. An increase in acid concentration results in an increase in glycerol conversion from 8 to 38% over 24 h at 200 °C. The increase in conversion with acid concentration is consistent with an initial acid catalyzed dehydration step. Selectivity for 1,3-PD decreased with increasing acid concentration. Increasing acid concentration from 0.25% to 4.0% led to a decrease in 1,3-PD:1-PO selectivity from 2:1 to 1:4. Notably, with 0.25% acid, formation of 1,2-PD was also observed as a product. 1,2-PD was not observed with higher acid concentrations.

The dependence of selectivity on acid concentration is not fully understood at this time. A change in the protonation level of the catalyst may account for the increased selectivity for 1-PO at higher acid concentration. Studies are currently underway to determine the role of the catalyst on product selectivity.

To test the applicability of our reaction conditions to the development of a practical process, the deoxygenation of waste glycerol from biodiesel production was also studied. Waste stream glycerol contains impurities such as sodium hydroxide and methanol necessary for the transesterification process as well as carboxylates. While distillation is the most common method for purification on an industrial scale, it is an energy intensive process. In lieu of distillation, we have found that waste glycerol can be purified by acidifying with 1 M sulfuric acid, allowing the biphasic mixture to settle, and decanting the impurity layer containing various free acids. The resulting solution of water, methanol, and glycerol can be diluted in dioxane and used directly in deoxygenation reactions. In our initial test reactions, recycled waste glycerol was deoxygenated in 20% yield over 24 h, with a 1,3-PD to 1-PO selectivity of 1:9. The high selectivity for 1-PO in these reactions is due to the high acid concentration employed in the purification of crude glycerol.

Mechanistic Studies. In our previous work, we reported that the air and water stable iridium carbonyl precatalyst, (POCOP)Ir(CO), could be used in place of (POCOP)Ir$(H)_2$ for the deoxygenation of 1,2-propanediol. We also discovered that upon the completion of these reactions, both (POCOP)-Ir(CO) and *trans*-(POCOP)Ir(CO)$(H)_2$ were present in the reaction mixture. The presence of these two species was confirmed by NMR (^1H and $^{31}P\{^1H\}$) and IR spectroscopy. The proposed mechanism for formation of *trans*-(POCOP)Ir-(CO)$(H)_2$ from (POCOP)Ir(CO) is shown in Scheme 1.

Scheme 1. Proposed Mechanism for Formation of *trans*-(POCOP)Ir(CO)$(H)_2$ from (POCOP)Ir(CO)



Initial protonation of (POCOP)Ir(CO) forms a cationic monohydride species. Dihydrogen association and deprotonation affords *trans*-(POCOP)Ir(CO)$(H)_2$. It is hypothesized that the iridium dihydride and/or dihydrogen-hydride species are the active catalysts for the deoxygenation of glycerol.

The formation of *trans*-(POCOP)Ir(CO)$(H)_2$ from (POCOP)Ir(CO) has been verified by pressurizing a tetrahydrofuran (THF) solution of (POCOP)Ir(CO) under H_2 for 24 h in the presence of 0.5 equiv of anilinium tetrafluoroborate. In the absence of catalytic acid, the formation of *trans*-(POCOP)Ir(CO)$(H)_2$ is not observed. A linear relationship was observed for H_2 pressure and conversion to *trans*-(POCOP)Ir(CO)$(H)_2$. Under 110 bar of H_2, up to 80% conversion to *trans*-(POCOP)Ir(CO)$(H)_2$ could be achieved, but complete conversion was never observed. These observations are consistent with an equilibrium between *trans*-(POCOP)Ir(CO)$(H)_2$ and (POCOP)Ir(CO), with equilibration facilitated by acid. Upon neutralization of the acid, the resulting mixture is stable for weeks at ambient temperature without any change in composition.

Reaction of (POCOP)Ir(CO) with the bis-etherate of tetrakis[3,5-bis(trifluoromethyl)phenyl]boric acid ([H-$(OEt_2)_2$]B$(C_6H_3(CF_3)_2)_4$) affords the cationic Ir(III) complex [(POCOP)Ir(CO)(H)]$^+$, identified by the observation of a triplet resonance in the ^1H NMR spectrum at −36 ppm (J = 10.4 Hz). The structure of this cationic complex was determined by X-ray diffraction (Figure 5).

dx.doi.org/10.1021/cs400551g | *ACS Catal.* 2013, 3, 2391−2396

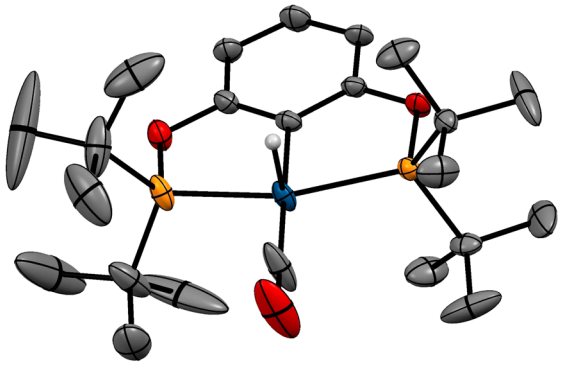


Figure 5. ORTEP of $[(POCOP)Ir(CO)(H)]^+$.(50% probability ellipsoids) Counter-anion and non hydride H atoms omitted for clarity. Significant bond distances: Ir−P = 2.3209(14) Å, 2.3196(12) Å; Ir−C_{Ph} = 2.033(5) Å; Ir−C_{CO} = 1.929(6) Å; Ir−H = 1.58(7) Å.

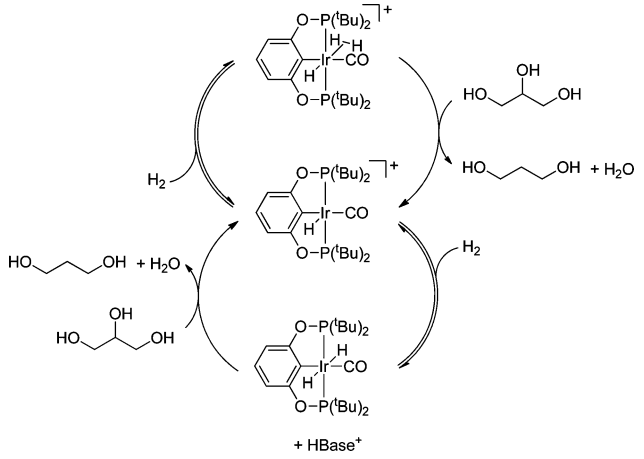
The cationic complex $[(POCOP)Ir(CO)(H)]^+$ is a rare example of a structurally characterized five coordinate Ir(III) complex.[20,21] For comparison, the structure of the neutral Ir(I) complex **2** was also determined. The structure of **2** is very similar, with Ir−P = 2.2785(3) Å, 2.2800(3) Å; Ir−C_{Ph} = 2.0488(12) Å; Ir−C_{CO} = 1.8658(14) Å. Details of the X-ray data collection are found in the Supporting Information.

The possible intermediacy of cationic *trans*-$[(POCOP)Ir(CO)(H_2)(H)]^+$ was investigated by low temperature ^{1}H NMR spectroscopy. At 180 K, a solution containing *trans*-$(POCOP)Ir(CO)(H)_2$ in CD_2Cl_2 was treated with 1 equiv of $[H(OEt_2)_2]B(C_6H_3(CF_3)_2)_4$. New broad resonances at −18.7, −23.0, and −23.3 ppm are observed upon mixing. Upon warming the solution to 223 K, hydrogen was evolved, and the resonances at −23.0 and −23.3 ppm disappear. The resonance at −18.7 ppm disappears upon warming the sample to 273 K. Complete formation of $[(POCOP)Ir(CO)(H)]^+$ was indicated by the appearance of a resonance at −36 ppm in the ^{1}H NMR spectrum. The highly transient nature of these intermediates hampers accurate determination of the relaxation times (T_1) of the hydride resonances, but an approximate value of about 300 ms for all three hydride signals was measured at 180 K. This value is not consistent with the presence of a dihydrogen ligand. Further studies are currently underway to confirm the intermediacy of the proposed dihydrogen complex.

Proposed Mechanism for Deoxygenation. *trans*-$[(POCOP)Ir(CO)(H_2)(H)]^+$ is hypothesized to be a possible proton and hydride source for the deoxygenation of glycerol. A proposed catalytic cycle for glycerol deoxygenation to 1,3-propanediol via *trans*-$[(POCOP)Ir(CO)(H_2)(H)]^+$ is shown in the top portion of Scheme 2. Initial protonation of $(POCOP)Ir(CO)$ to $[(POCOP)Ir(CO)(H)]^+$ followed by reaction with hydrogen generates *trans*-$[(POCOP)Ir(CO)(H_2)(H)]^+$. *trans*-$[(POCOP)Ir(CO)(H_2)(H)]^+$ can act as a proton and hydride source for the deoxygenation of glycerol. An alternative pathway is shown in the bottom of Scheme 2. Deprotonation of *trans*-$[(POCOP)Ir(CO)(H_2)(H)]^+$ affords *trans*-$(POCOP)Ir(CO)(H)_2$. An external acid can serve as a proton source, and *trans*-$(POCOP)Ir(CO)(H)_2$ can serve as a hydride source for the deoxygenation of glycerol.

Formation of 1-propanol is hypothesized to proceed through an analogous mechanism for deoxygenation at the C1 position, leading to 1,2-PD, which is then rapidly deoxygenated to 1-propanol. The selectivity of the reaction (1,3-PD vs 1-PO product) was found to depend on the acid concentration, the reaction temperature, and the reaction time. Whether this is due to changes in the reaction medium as the reaction progresses or decomposition of the catalyst is not yet clear and is under further investigation.

Scheme 2. Proposed Mechanism for Formation of 1,3-Propanediol from Glycerol with *trans*-$[(POCOP)Ir(CO)(H_2)(H)]^+$



CONCLUSION

The catalyzed deoxygenation of glycerol to 1,3-propanediol and 1-propanol has been achieved with sulfuric acid and an iridium pincer complex. Conversions of up to 45% glycerol and selectivities of 1:4 1,3-propanol to 1-propanol have been achieved. The catalytic reactions can also be performed using acidified waste glycerol from biodiesel production.

The transient *trans*-$[(POCOP)Ir(CO)(H_2)(H)]^+$ is proposed to be the active catalyst for these reactions.

EXPERIMENTAL SECTION

General Procedures. All experiments were performed under an inert atmosphere using standard glovebox or Schlenk techniques. All NMR solvents were dried using appropriate drying agents. All reaction solvents and reagents were used as received.

^{1}H, ^{31}P, and ^{13}C NMR spectra were obtained using a Bruker 500 MHz spectrometer. IR spectra were obtained using a Bruker Vector 33 FT-IR spectrometer. X-ray crystal structures were collected at −173 °C on a Bruker APEX II single crystal X-ray diffractometer, Mo-radiation.

Reaction Quantification by ^{13}C NMR Spectroscopy. Qualitative studies were performed by collecting ^{13}C NMR spectra of neat reaction mixtures. Intensity enhancement due to the nuclear Overhauser effect (NOE) was nullified by integration of carbons with an equal number of protons.

Reaction mixtures were quantified by collecting ^{13}C NMR spectra of neat reaction mixtures. A similar procedure for quantitative analysis of reaction mixtures was recently reported by Gagne et al.[22] Quantitative spectra were obtained by collecting inverse-gated decoupled NMR spectra to avoid NOE enhancement. To minimize integration problems associated with long relaxation times, delay times of 3 s were employed, and the paramagnetic additive $Cr(acac)_3$ was used as a relaxation agent.[23] Sodium *p*-toluenesulfonate was used as an internal standard.

dx.doi.org/10.1021/cs400551g | *ACS Catal.* 2013, 3, 2391−2396

After the reaction is complete, approximately 300−400 mg of material comes to rest in the reactor head assembly. Rinsing the reactor head with D_2O and examining the resulting solution by ^1H NMR spectroscopy showed 1-propanol and solvent dioxane. Since the exact amount of lost material was not quantified, reported conversion percentages only account for the material in the reactor vessels.

Synthesis. (POCOP)Ir(H)(Cl),[19] (POCOP)Ir(CO),[24] Ir(CO)$_2$(Cl)(*p*-toluidine),[25] and [H(OEt$_2$)$_2$]B(C$_6$H$_3$(CF$_3$)$_2$)$_4$[26] were prepared as previously described in the literature.

5-Diethylene Glycol Monomethyl Ether Resorcinol. Following a similar procedure as Marzo et al.,[17] to a stirring solution of phloroglucinol (0.63 g, 5.0 mmol), potassium fluoride (0.29 g, 5.0 mmol), and potassium carbonate (0.35 g, 2.5 mmol) in 4 mL of dimethylsulfoxide (DMSO) under argon was added 2-bromoethyl 2-methoxyethyl ether (0.92 g, 5.0 mmol) in 2 mL of DMSO. The slurry was stirred under argon. After 48 h, 10 mL of deionized water was added to the mixture to afford a clear orange solution. The solution was neutralized to pH 7 with 10% HCl, and the organic material was extracted with chloroform. The organic extractions were combined, dried over $MgSO_4$, and condensed under vacuum to afford an orange liquid. The crude product was purified by column chromatography on silica, eluted with 60:40 ethyl acetate:hexane to collect 0.090 g (8% yield) of an off-white solid. ^1H NMR (500 MHz, 25 °C, DMSO-d_6): δ 9.17 (s, 2H, 2 × OH); δ 5.82 (m, 1 H, 2-H); δ 5.77 (m, 2 H, 4- and 6-H); glycol: δ 3.92 (t, 2 H), δ 3.67 (t, 2 H), δ 3.56 (t, 2 H), δ 3.45 (t, 2 H), δ 3.25 (s, 3 H).

5-Dimethylamine Resorcinol. Following a similar procedure as Petrzilka and Lusuardi,[18] to a stirring solution of phloroglucinol (1.0 g, 7.9 mmol) in 9 mL of H_2O and 14 mL of DMF was added an aqueous solution of dimethylamine (1.3 mL 40% w:w solution, 10 mmol). The solution was stirred under argon for 48 h and then concentrated under vacuum to afford a dark red oil. A pink precipitate formed upon addition of about 30 mL of chloroform to the dark red oil. The mixture was filtered and washed with small portions of cold chloroform to afford 0.59 g (49% yield) of a pink solid. ^1H NMR (500 MHz, 25 °C, DMSO-d_6): δ 8.81 (s, 2 H, 2 × OH); δ 5.59 (s, 3 H, 2-, 4- and 6-H); δ 2.77 (s, 6 H, NC-H).

General Procedure for POCOP Ligand Synthesis by Brookhart.[24] 5-Diethylene glycol monomethyl ether POCOP (**3a**). From 0.090 g (0.39 mmol) of 5-diethylene glycol monomethyl ether resorcinol, 0.020 g (0.83 mmol) of NaH, and 0.150 g (0.83 mmol) of di-*tert*-butylchlorophosphine was obtained 0.20 g (99% yield) of **3c** as a light yellow oil. ^1H NMR (500 MHz, 25 °C, C_6D_6): δ 7.22 (m, 1 H, 2-H); δ 6.79 (m, 2 H, 4- and 6-H); glycol: δ 3.82 (t, 2 H), δ 3.50 (t, 2 H), δ 3.44 (t, 2 H), δ 3.32 (t, 2 H), δ 1.13 (s, 3 H); δ 3.82 (d, J = 11.7 Hz, 36 H, PCC-H). $^{31}P\{^1H\}$ NMR (202 MHz, 25 °C, C_6D_6): δ 151.

*5-Dimethylamine POCOP (**3b**).* From 0.153 g (1.0 mmol) of 5-dimethylamine resorcinol, 0.048 g (2.0 mmol) of NaH, and 0.36 g (2.0 mmol) of di-*tert*-butylchlorophosphine was obtained 0.44 g (99% yield) of **3b** as a light orange oil. ^1H NMR (500 MHz, 25 °C, C_6D_6): δ 7.10 (m, 1 H, 2-H); δ 6.52 (m, 2 H, 4- and 6-H); δ 2.55 (s, 6 H, NC-H); δ 1.18 (d, J = 12 Hz, 36 H, PCC-H). $^{31}P\{^1H\}$ NMR (202 MHz, 25 °C, C_6D_6): δ 149.

General Procedure for (5-X-POCOP)Ir(CO). A solution of 1 equiv of 5-X-POCOP and 1 equiv of Ir(CO)$_2$(Cl)(*p*-toluidine) in toluene was heated to reflux under argon for 16 h. After 16 h, the volatiles were removed under vacuum, and the solid was washed with small portions of cold pentane and methanol.

(5-Diethylene Glycol Monomethyl Ether POCOP)Ir(CO). Because of product solubility in pentane, the condensed residue was purified by neutral alumina column chromatography, eluted with 10:90 Et$_2$O:hexanes. From 0.192 g (0.37 mmol) of 5-diethylene glycol monomethyl ether POCOP and 0.132 g of Ir(CO)$_2$(Cl)(*p*-toluidine) in 8 mL of toluene was obtained 0.081 g (30% yield) of (5-diethylene glycol monomethyl ether POCOP)Ir(CO) as a yellow solid. ^1H NMR (500 MHz, 25 °C, CD_2Cl_2): δ 6.20 (s, 2H, 3- and 5-H); glycol: δ 4.05 (t, 2 H), δ 3.76 (t, 2 H), δ 3.65 (t, 2 H), δ 3.52 (t, 2 H), δ 3.34 (s, 3 H); δ 1.35 (v t, J = 7.3 Hz, 36 H, PCC-H). $^{31}P\{^1H\}$ NMR (202 MHz, 25 °C, CD_2Cl_2): δ 200. IR (pentane, cm^{-1}): 1946 (νCO).

*(5-Dimethylamine POCOP)Ir(CO) (**4**).* From 0.300 g (0.68 mmol) of 5-dimethylamine POCOP and 0.266 g (0.68 mmol) of Ir(CO)$_2$(Cl)(*p*-toluidine) in 10 mL of toluene was obtained 0.160 g (35% yield) of **4** as a bright yellow powder. ^1H NMR (500 MHz, 25 °C, CD_2Cl_2): δ 6.03 (s, 2H, 3- and 5-H); δ 2.90 (s, 6 H, NC-H); δ 1.36 (v t, J = 7.0 Hz, 36 H, PCC-H). $^{31}P\{^1H\}$ NMR (202 MHz, 25 °C, CD_2Cl_2): δ 200. IR (pentane, cm-1): 1941 (νCO).

trans-(POCOP)Ir(CO)(H)$_2$. To a stirring solution of 0.31 g (0.50 mmol) of (POCOP)Ir(H)(Cl) and 0.056 g (0.50 mmol) of potassium *tert*-butoxide in 6 mL of benzene under argon was added 0.015 g (0.50 mmol) of paraformaldehyde. The dark red solution was heated under static argon at 80 °C for 3 h. After cooling, the solution was filtered through Celite and condensed to afford a brown-yellow solid that was used without further purification. The isolated product consisted of an about 1.6:1 mixture of (POCOP)Ir(CO) to *trans*-(POCOP)Ir(CO)(H)$_2$ by ^1H- and ^{31}P NMR integration. ^1H NMR (500 MHz, 25 °C, CD_2Cl_2): δ 6.68 (t, J = 8.2 Hz, 1H, 4-H); δ 6.37 (d, J = 7.3 Hz, 2H, 3- and 5-H); δ 1.29 (v t, J = 7.1 Hz, 36 H, PCC-H); δ −10.08 (t, J = 14.8 Hz, 2 H, Ir−H). $^{31}P\{^1H\}$ NMR (202 MHz, 25 °C, CD_2Cl_2): δ 183.

[(POCOP)Ir(CO)(H)]$^+$. Reaction of 1 equiv of *trans*-(POCOP)Ir(CO)(H)$_2$ with 1 equiv of [H(OEt$_2$)$_2$]B(C$_6$H$_3$(CF$_3$)$_2$)$_4$ in dichloromethane affords [(POCOP)Ir(CO)(H)]$^+$. X-ray quality crystals were obtained upon standing for 24 h.

Glycerol Deoxygenation. Deoxygenation reactions were carried out in Parr reactors outfitted with gas-inlet valves and pressure sensors. In a typical reaction, 45 mL reactors equipped with Teflon stirbars were charged with (N(CH$_3$)$_2$POCOP)IrCO (4.3 mg, 0.0065 mmol) and a solution containing glycerol (0.479 g, 5.2 mmol), deionized water (0.197 g), and dioxane (1.22 g). A sulfuric acid solution (1.0 M) was added with a micropipet (52 μL, 0.052 mmol). Reactors were stirred at 400 rpm, purged with H_2 for 4 min, pressurized to 80 bar, and heated to 200 °C over 20 min (pressure increases to 110 bar). After 24 h, the reactor was allowed to cool to room temperature and then cooled in an ice water bath for 20 min before venting slowly. To analyze gaseous products, the vented gas was bubbled slowly through acetone-d_6 in a J. Young NMR tube and analyzed by ^1H NMR spectroscopy.

To ensure gaseous products were not produced in appreciable amounts, mass changes were detected using a solution balance (August Sauter KG, Ebingen, Germany). Prior to reaction, the reactor was charged with glycerol, solvent, and catalyst and balanced against an equivalent mass of water. After reaction, the reactor was cooled and vented, and this procedure was repeated. No change in mass was observed. Independent

dx.doi.org/10.1021/cs400551g | ACS Catal. 2013, 3, 2391−2396

experiments established that changes in mass of ±5 mg could be detected.

Reaction conditions of heating time, gas pressure, acid concentration, and reaction temperature were varied. Time course studies were performed by setting up a series of identical reactions and stopping reactions at different times. For reactions with CO and H_2 mixtures, the reactors were purged with CO for 4 min, pressurized to 40 bar of CO followed by 40 bar of H_2 to increase the total pressure to 80 bar. For studies involving varying acid concentration, the mass of deionized water was adjusted to maintain the total water concentration.

Crude Glycerol Purification and Deoxygenation. To a stirring solution of crude glycerol from biodiesel production was added concentrated sulfuric acid until the solution became cloudy (ca. pH = 0). The cloudy solution was left overnight to allow formation of two distinct layers. The clear, colorless bottom layer was collected and filtered to remove any particulates.

The solution of purified glycerol (1.0 g) was diluted with dioxane (5.1 g). Standard deoxygenation procedures were carried out with 2.0 g of this solution and $(N(CH_3)_2POCOP)$-Ir(CO) (6.8 mg, 0.010 mmol).

Low Temperature Protonation of *trans*-(POCOP)Ir-(CO)$(H)_2$. A J. Young NMR tube was charged with solid $[H(OEt_2)_2]B(C_6H_3(CF_3)_2)_4$ (9.8 mg, 0.0097 mmol) and *trans*-(POCOP)Ir(CO)$(H)_2$ (6.0 mg, 0.0097 mmol). The J. Young NMR tube was evacuated, and CD_2Cl_2 was vacuum distilled into the tube. The solution was kept frozen until immediately before NMR studies at which time, tubes were partially thawed quickly in a dry ice/isopropanol bath, inverted, and immediately injected into an NMR probe cooled to 180 K.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Text, tables, and CIF files giving X-ray crystallographic data for (POCOP)Ir(CO) and $[(POCOP)Ir(CO)(H)]^+$ and details of crystallographic data collection. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: heinekey@chem.washington.edu (M.H.).
*E-mail: goldberg@chem.washington.edu (K.I.G).

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the Center for Enabling New Technologies through Catalysis (CENTC, CHE-1205189). We thank Dr. Gene Wong, Mr. Alex Wallner, Dr. N. Malathi Weliange, and Mr. Eric Camp, for technical assistance and useful discussions. We thank Mr. William Levin for the waste glycerol from biodiesel production.

■ REFERENCES

(1) Schlaf, M. *Dalton Trans.* **2006**, *39*, 4645−4653.
(2) Johnson, T. D.; Taconi, K. A. *Environ. Prog.* **2007**, *26*, 338−348.
(3) Cheda, J. N.; Huber, G. W.; Dumesic, J. A. *Angew. Chem., Int. Ed.* **2007**, *46*, 7164−7183.
(4) Dam, J. T.; Hanefeld, U. *ChemSusChem* **2011**, *4*, 1017−1034.
(5) Ruppert, A, M.; Weinberg, K.; Palkovits, R. *Angew. Chem., Int. Ed.* **2012**, *51*, 2564−2601.
(6) Daniel, O. M.; DeLaRiva, A.; Kunkes, E. L.; Datye, A. K.; Dumesic, J. A.; Davis, R. J. *ChemCatChem* **2010**, *2*, 1107−1114.
(7) Gong, L.; Lu, Y.; Ding, Y.; Lin, R.; Li, J.; Dong, W.; Wang, T.; Chen, W. *Appl. Catal., A* **2010**, *390*, 119−126.
(8) Oh, J.; Dash, S.; Lee, H. *Green Chem.* **2011**, *13*, 2004−2007.
(9) Qin, L.; Song, M.; Chen, C. *Green Chem.* **2010**, *12*, 1466−1472.
(10) Shimao, A.; Koso, S.; Ueda, N.; Shinmi, Y.; Furikado, I.; Tomishige, K. *Chem. Lett.* **2009**, *38*, 540−541.
(11) Chaminand, J.; Djakovitch, L.; Gallezot, P.; Marion, P.; Pinel, C.; Rosier, C. *Green Chem.* **2004**, *6*, 359−361.
(12) Furikado, I.; Miyazawa, T.; Koso, S.; Shimao, A.; Kunimori, K.; Tomishige, K. *Green Chem.* **2007**, *9*, 582−588.
(13) Braca, G.; Galletti, A. M. R.; Sbrana, G. *J. Organomet. Chem.* **1991**, *417*, 41−49.
(14) Thibault, M. E.; DiMondo, D. V.; Jennings, M.; Abdelnur, P. V.; Eberlin, M. N.; Schlaf, M. *Green Chem.* **2011**, *13*, 357−366.
(15) Taher, D.; Thibault, M. E.; DiMondo, D.; Jennings, M.; Schlaf, M. *Chem.—Eur. J.* **2009**, *15*, 10132−10143.
(16) Ahmed-Foskey, T. J.; Heinekey, D. M.; Goldberg, K. I. *ACS Catal.* **2012**, *2*, 1285−1289.
(17) Brizzi, A.; Brizzi, V.; Cascio, M. G.; Corelli, F.; Guida, F.; Ligresti, A.; Maione, S.; Martinelli, A.; Pasquini, S.; Tuccinardi, T.; Marzo, V. D. *J. Med. Chem.* **2009**, *52*, 2506−2514.
(18) Petrzilka, T.; Lusuardi, W. G. *Helv. Chim. Acta* **1973**, *56*, 510−518.
(19) Göttker-Schnetmann, I.; White, P.; Brookhart, M. *J. Am. Chem. Soc.* **2004**, *126*, 1804−1811.
(20) Ghosh, R.; Emge, T. J.; Krogh-Jespersen, K.; Goldman, A. S. *J. Am. Chem. Soc.* **2008**, *130*, 11317−11327.
(21) Bernskoetter, W. H.; Hanson, S. K.; Buzak, S. K.; Davis, Z.; White, P. S.; Swartz, R.; Goldberg, K. I.; Brookhart, M. *J. Am. Chem. Soc.* **2009**, *131*, 8603−8613.
(22) McLaughlin, M. P.; Adduci, L. L.; Becker, J. J.; Gagne, M. R. *J. Am. Chem. Soc.* **2013**, *135*, 1225−1227.
(23) Lamar, G. N. *Chem. Phys. Lett.* **1971**, *10*, 230−232.
(24) Goettker-Schenetmann, I.; White, P.; Brookhart, M. *Organometallics* **2004**, *23*, 1766−1776.
(25) Roberto, D.; Cariati, E.; Psaro, R.; Ugo, R. *Organometallics* **1994**, *13*, 4227−4231.
(26) Brookhart, M.; Grant, B.; Volpe, A. F., Jr. *Organometallics* **1992**, *11*, 3920−3922.