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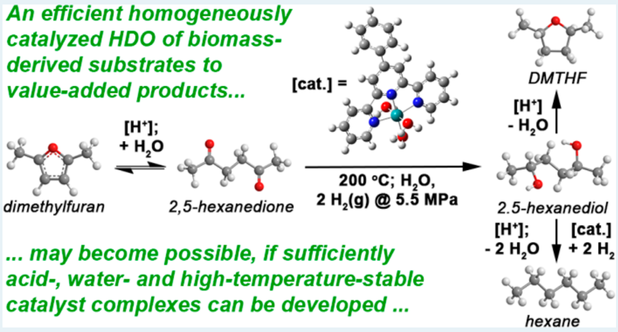
Hydrodeoxygenation of 2,5-Hexanedione and 2,5-Dimethylfuran by Water-, Air-, and Acid-Stable Homogeneous Ruthenium and Iridium Catalysts

Ryan J. Sullivan, Elnaz Latifi, Benjamin K.-M. Chung, Dmitriy V. Soldatov, and Marcel Schlaf*

Department of Chemistry, University of Guelph, The Guelph-Waterloo Centre for Graduate Work in Chemistry (GWC)^2, 50 Stone Road East, Guelph, Ontario, Canada, N1G 2W1

Supporting Information

ABSTRACT: The complexes $[(4'\text{-Ph-terpy})Ru(H_2O)_3](OTf)_2$ and $[(4'\text{-Ph-terpy})Ir(OTf)_3]$ have been evaluated as catalysts for the conversion of 2,5-hexanedione and 2,5-dimethylfuran to hydrodeoxygenated products in aqueous acidic medium at elevated temperature (150−225 °C) under hydrogen gas (5.5 MPa). These two substrates form part of a value chain leading from C_6 sugars to 2,5-hexanediol, 2,5-dimethyltetrahydrofuran, and hexane, which can be generated by the homogeneously acting ruthenium catalyst in up to 69%, 80%, and 10% yield, respectively, while at $T > 175$ °C the iridium system decomposes to a highly active but heterogeneously acting coating in the reactor defeating the premise of a homogeneous catalyst system. The deactivation and decomposition pathway of both catalysts leads to the formation of a series of isostructural complexes $[M(4'\text{-Ph-terpy})_2]^{n+}$ (M = Fe, Ni, Ru, Ir; $n = 2, 3$) characterized by ESI-MS and single crystal X-ray crystallography, in which the source of the Fe and Ni is the 316SS reactor body.



KEYWORDS: *homogeneous catalysis, aqueous media, hydrogenation, hydrodeoxygenation, biomass conversion, catalyst decomposition*

INTRODUCTION

In the last two decades enormous progress has been made in the development of new catalysts and processes for the conversion of biomass into chemicals and fuels by hydrodeoxygenation, i.e., the iterative combination of acid-catalyzed loss of water and metal catalyzed hydrogenations, which has emerged as one of the main strategies toward reducing the oxygen content of overfunctionalized biomass-derived substrates. Starting from the seminal work by Descotes,[1] advances in these processes have mainly focused on the use of heterogeneous catalyst systems,[2−7] while attempts to use and integrate homogeneous hydrodeoxygenation catalysts into value chains originating from biomass-derived C_5 and C_6 molecules identified as platform molecules remain comparatively few.[8−10] Examples are the hydrogenation of levulinic acid (LA) to γ-valerolactone (GVL) using ruthenium or iridium phosphine complexes,[11,12] the conversion of LA to 1,4-pentanediol and 2-methyltetrahydrofuran by an *in situ* generated ruthenium phosphine complex combined with an acidic ionic liquid,[13,14] the principal demonstration of a reaction cascade leading from sucrose to GVL, 1,4-pentanediol, 2-methyl-THF, and alkanes,[15] and the direct conversion of fructose to 2,5-dimethyltetrahydrofuran by RhI_3/HI with successful catalyst recycling but at very high acid/sugar substrate ratios.[16,17] Ladipo et al. have reported the use of *cis*-$[Ru(6,6'\text{-}Cl_2bpy)_2(OH_2)_2](BArF)_2$ ($6,6'\text{-}Cl_2bpy$ = 6,6′-dichloro-2,2′-bipyridine) as an effective catalyst for the selective hydrogenation of furfural to tetrahydrofurfurylalcohol in ethanol solvent.[18] The same catalyst (as the corresponding trifluoromethanesulfonic acid salt) had previously been introduced by Lau as a water-soluble alkene hydrogenation catalyst and used by us for the partial and total deoxygenation of terminal diols to primary alcohols, alkenes, and alkanes in aqueous acidic medium.[19−21] A further interesting alternative approach is the methyltrioxorhenium mediated deoxygenation of polyols.[22−27]

While the use of homogeneous systems for the hydrodeoxygenation of sugars and sugar derived substrates poses substantial challenges in catalyst recovery and reuse, it may offer advantages with respect to long-term catalyst stability, activity, and selectivity as well as mass transport limitations. Specifically, the operation of heterogeneous hydrogenation catalysts based on a combination of a hydrogenating metal (e.g., Ru, Rh, Ni, Pd, Pt) with a typical support (e.g., Al_2O_3, SiO_2) in the necessarily aqueous acidic medium of hydrodeoxygenation reactions can lead to rapid catalyst coking and fouling due to polymerization and decomposition of the typically highly polar sugar(-derived) substrates.[28] In contrast, single metal-site

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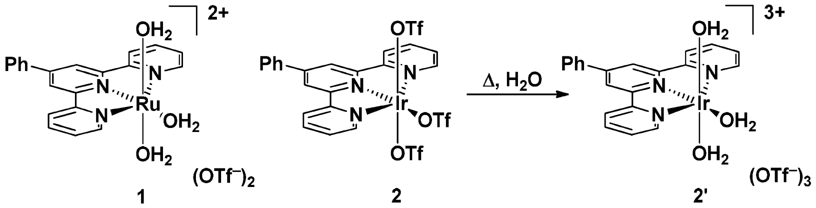
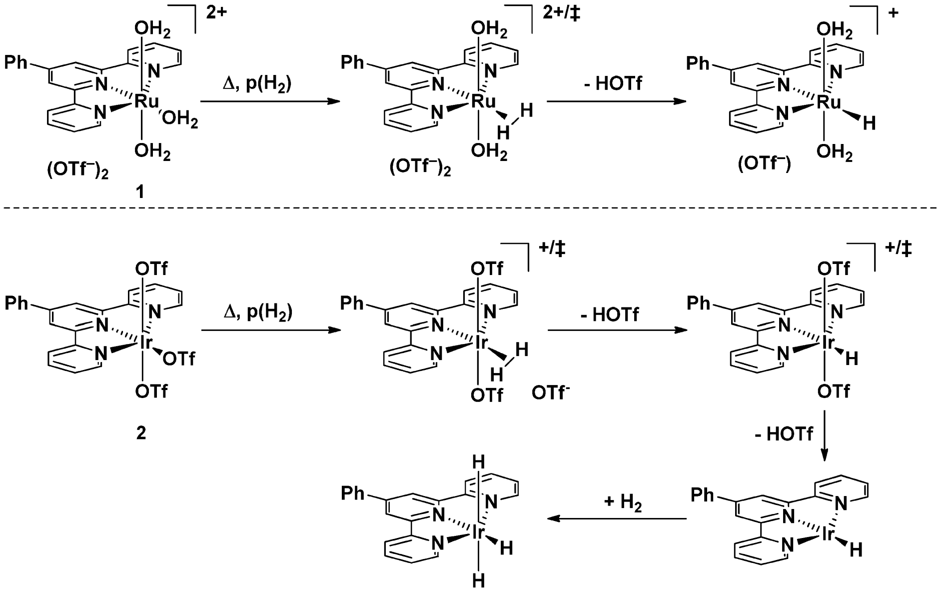
Chart 1. Structures of the Two Isoelectronic Ruthenium and Iridium Complexes Evaluated As HDO Catalysts



Scheme 1. Conceivable Modes of Hydrogen Activation by Catalysts 1 and 2



homogeneous catalysts are not susceptible to this type of deactivation process but may instead suffer from substrate, (side-) product or—for cationic complexes—counterion specific irreversible coordinative inhibition.[29]

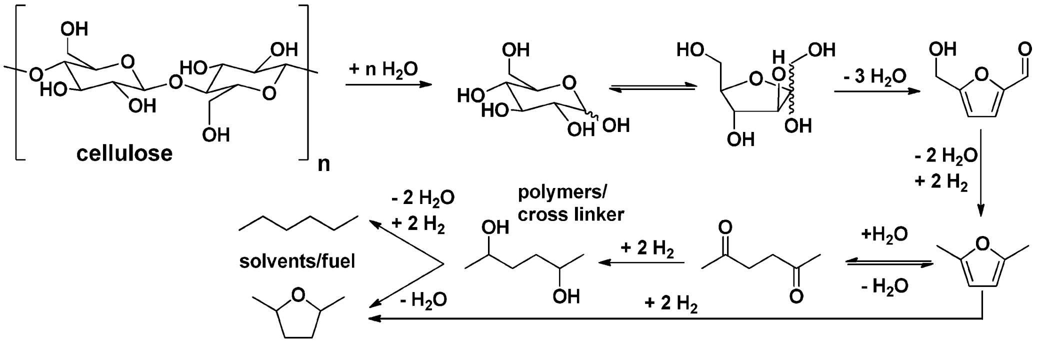
By definition homogeneous catalysts to be used in hydrodeoxygenation reactions must be water- and acid-stable and—for ease of use, handling—should also be air-stable, at least in their *pro-catalyst* form (i.e., the species actually added to the reaction mixture). Empirically, the acid-catalyzed loss of water from polyalcohols and other biomass derived substrates and the ring-opening of biomass-derived furans to diketones also requires temperatures of ≥150 °C, which then constitutes the lower limit of temperature stability for the catalysts used.[30−32] Together these criteria constitute a remarkable challenge to the design and synthesis of suitable catalysts that we chose to address through the combination of ruthenium(II) centers stabilized by air-stable nonphosphine containing chelate ligands based on pyridine donors and one or several easily dissociated labile ligands to allow for the activation of hydrogen gas and/or the substrate.[33] Postulating that cationic complexes containing aquo ligands would both be stable and soluble in aqueous medium while at the same time allowing heterolytic activation of hydrogen gas by facile displacement of one or several aquo ligands at a d^6 transition metal center,[34] this type of ruthenium complexes was specifically targeted.[21]

Previously we reported that the complex $[(4'\text{-Ph-terpy})\text{Ru}(H_2O)_3](\text{OTf})_2$ (terpy = 2,2′:6′,2″-terpyridine) (**1**) is an active and very robust catalyst for the total deoxygenation of glycerol to propene/propane in acidic sulfolane solution.[35] Catalyst **1** is a logical evolution of the bis-chelate complex *cis*-$[\text{Ru}(6,6'\text{-}Cl_2\text{bpy})_2(OH_2)_2](\text{OTf})_2$, which in our hands decomposed to Ru(0) by loss of ligand at temperatures >125 °C.[21] In contrast the tris-chelate complex **1** is stable in aqueous acidic medium up to 250 °C, which we interpreted to be a direct consequence of the enhanced chelate effect. This emphasizes that the key role of the ligand in these systems operating at such elevated temperatures is not the induction of reaction selectivity or specificity but rather the stabilization of the metal center against reduction to bulk metal which would then act as a heterogeneous rather than homogeneous catalyst.

Here we report the application of **1** and its iridium analogue $[(4'\text{-Ph-terpy})\text{Ir}(\text{OTf})_3]$ (**2**) to the hydrodeoxygenation of 2,5-hexanedione (2,5-HD) and 2,5-dimethylfuran (2,5-DMF). The structures of the two (pro)-catalysts are shown in Chart 1. In these complexes trifluoromethanesulfonate (OTf^-; triflate) and its corresponding acid (HOTf; triflic acid) were chosen as the counterion and acid cocatalysts (see below), as HOTf is the strongest known nonoxidizing acid and consequently its anionic form one of the weakest anionic ligands resulting in minimal coordinative inhibition of the catalysts by competition with also only weakly coordinating $H_2(g)$ and substrates.[36,37] On this basis we postulated that the tris-triflate iridium complex **2** would in hot aqueous conditions be converted into the corresponding aquo-complex **2′**, i.e., generate a species completely analogous to **1** as also shown in Chart 1.

The previously described complex **2** was targeted as a catalyst on the basis of its isoelectronic relationship ($\text{Ru}^{II}/d^6 \rightarrow \text{Ir}^{III}/d^6$) to complex **1** and hypothesizing that in oxidation state +3 slightly stronger metal−ligand bonds and therefore an even more stable catalyst would result.[38] For both catalysts an ionic

Scheme 2. Value Chain from Cellulose to Deoxygenated Value-Added Products via the Two Target Substrates 2,5-Dimethylfuran and 2,5-Hexanedione



hydrogenation *modus operandi* is postulated,[39] in which the base taking up the proton generated by a heterolytic splitting of dihydrogen would be the counterion, substrate, product or in the solvent-leveled aqueous reaction mixture most likely water resulting in the formation of H_3O^+ as the strongest possible corresponding acid.[35] For catalyst **2** we also considered the possibility of an *in situ* reduction to Ir^I as shown in Scheme 1 with the generation of two equivalents of free acid. In this scenario the activation of hydrogen would then occur via oxidative addition of H_2 to form the corresponding iridium trihydride as an active species.

The choice of the targeted substrates is based on the value chain *cellulose → HMF → 2,5-dimethylfuran →2,5-hexanedione →2,5-hexanediol →2,5-dimethyltetrahydrofuran and/or hexane* shown in Scheme 2. 2,5-DMF has been suggested as a possible fuel, and routes to 2,5-DMF from glucose/fructose (mainly by use of heterogeneous catalysts and ultimately to be derived from cellulose) have been proposed by several authors.[40−44] Further value could be added to this product by conversion into 2,5-hexanediol (2,5-HDO) − a potential polyester or polyurethane component or cross-linker in paint and resin formulations—or 2,5-methyltetrahydrofuran (2,5-DMTHF) and hexane (HEX) that could serve as biomass derived solvents or high energy density fuels.[16,17,44−46]

With the goal of developing a homogeneous catalyst system capable of the hydrodeoxygenation of the components of this value chain to 2,5-DMTHF or ultimately hexane, we here present a study of the application of the catalysts **1** and **2** to 2,5-hexanedione and 2,5-dimethylfuran.

■ EXPERIMENTAL SECTION

General. All reagents and solvents were purchased from readily available commercial sources and used as received unless otherwise specified. 2,5-Hexanedione, 2,5-dimethylfuran, and 1,4-dioxane were passed through a short plug of neutral Al_2O_3 (Brockmann Activity I) immediately before use to remove any peroxides or stabilizers present. All water used was HPLC grade. Trifluoromethanesulfonic (triflic) acid was stored under argon atmosphere in a Rotaflo Schlenk tube sealed with a Teflon stopcock and dispensed into reaction mixture using a microliter syringe. Catalyst syntheses were performed under argon atmosphere using standard Schlenk-line techniques. All NMR spectra were obtained on 300, 400, or 600 MHz spectrometers and calibrated to the residual protonated solvent signal. GC analyses were performed on a Varian 3800 with FID detectors using a 30 m Rtx-1701 (14% cyanopropylphenyl/86% dimethyl polysiloxane) column or a 30 m Stabilwax-da (acid-deactivated polyethylene glycol) column. Quantification was carried out using internal standard calibration against 100 mmol L^{-1} dimethyl sulfone (DMS) in a three level calibration. GC-MS analyses were performed on a Varian Saturn 2000 GC/MS using a 30 m Rtx-1701 (14% cyanopropylphenyl/86% dimethyl polysiloxane) column or a 30 m Stabilwax-da (acid-deactivated polyethylene glycol) column running in CI mode. Reaction products were identified by comparison to the retention times and MS fragmentation patterns of authentic samples. Head-space gas analyses were carried out on a SRI 8610 micro-GC with a TCD detector against authentic gas samples (1000 ppm of C_1−C_6 alkanes and C_2−C_6 alkenes in helium, GRACE Davison Discovery Sciences). For those reactions where phase separation of an organic product layer occurred the organic layer was weighed, diluted with MeOH, and analyzed by GC. No partitioning of the internal standard from the polar phase into these phase separated layers was observed. Assuming equal FID responses for all components of the organic layers (mainly 2-hexanone, 2,5-dimethyltetrahydrofuran, and hexane) they were quantified by relative peak areas on the basis of their equal carbon numbers (C_6).[47] Normalization to the molecular weights of each component allowed calculation of the mass of each component in the phase separated layer. These amounts were then added to those quantified in the aqueous phase, and the sum was reported as a percentage (by mole) of the starting material.

All hydrogenation experiments employed industrial grade H_2 gas (99.995%) and were carried out in an Autoclave Engineers (AE) Mini-reactor with a 50 mL 316 stainless steel (316SS) reactor vessel and impeller. At a total reaction solution volume of 25 mL the reactor has a gas-phase headspace of 50 mL (unused reactor body space and enclosed and pressurized magnet-drive stirring assembly). Unless otherwise specified (cf. control experiments) reactor vessel and impeller were thoroughly cleaned and polished after every run by lathe at 600 rpm with 3 M Abrasive pads and sand-blasting, respectively. Regular control reactions without addition of catalyst showed only marginal conversion (<5%) of substrate to hydrogenated products (see main text) caused by the background activity of the reactor walls.[48]

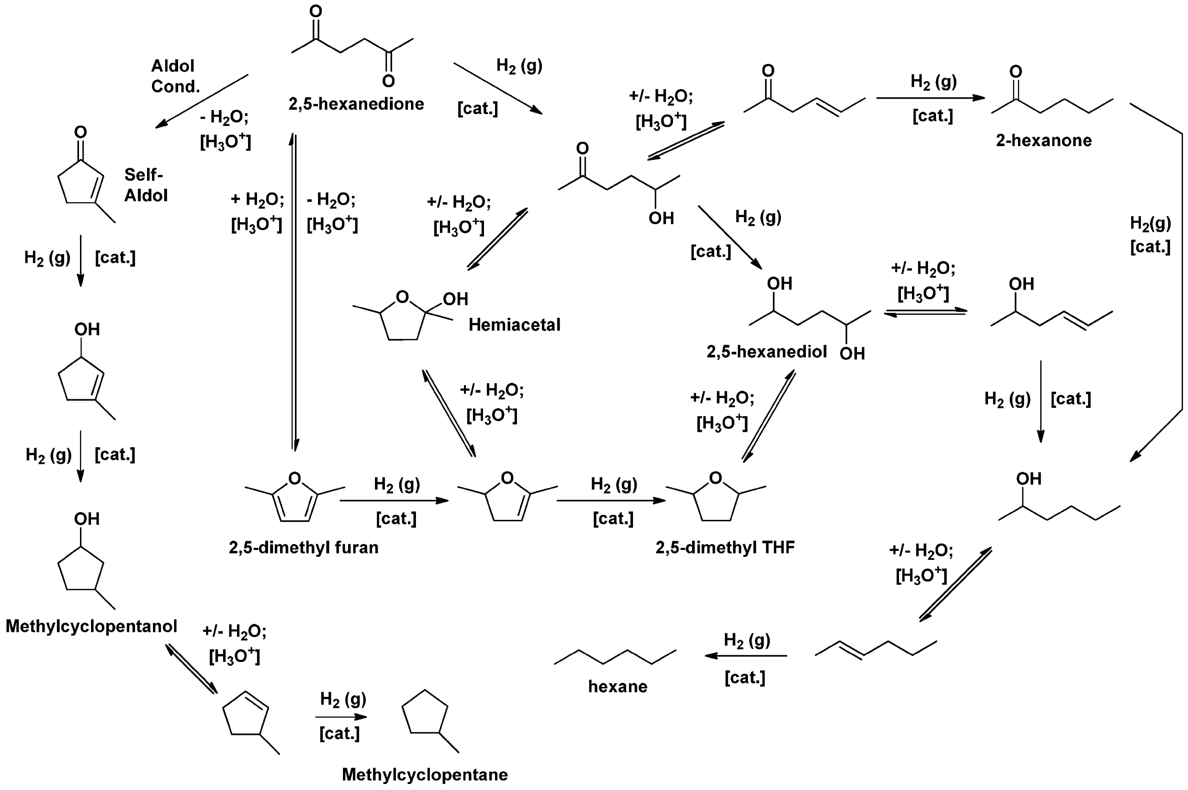
4′-Phenyl-2,2′:6′,2″-terpyridine was prepared following the solvent-less procedure developed by Cave and Raston.[49] In our hands this protocol consistently generated a product containing an orange contaminant of unknown structure and without a discernible NMR signature. Passing a $CHCl_3$ solution of this crude orange product through a short plug of basic Al_2O_3 (Brockman Activity I) efficiently removes this impurity rendering a snow-white product in 67% overall yield after

Table 1. Hydrogenation of 2,5-Hexanedione by Catalysts 1 and 2 in Water

entry[a]	cat.	T [°C]	cat. decomp. [Y/N]	2,5-HD[b] [%]	2,5-HDO[b] [%]	2,5-DMTHF[b] [%]	HMA[b] [%]	HXO[b] [%]	HEX[b] [%]	MBD[b] [%]	phase sep.
1	**1**	150	N	8	45	17	6	0	0	24	N
2	**1**	175	N	0	69	25	1	0	0	4	N
3	**1**	200	N	2	14	80	3	0	0	1	N
4	**1**	225	N	6	0	78	2	2	3	9	Y
5	**2**	200	N	0	13	80	0	0	0	7	N
6	*c*	225	n/a	60	1	0	2	0	0	37	N

[a] Reaction conditions: 2,5-hexanedione [1000 mmol/L] in water, 5.5 MPa (800 psi) $H_2(g)$, dimethylsulfone (ISTD) [100 mmol/L], catalyst load [1 mmol/L= 0.1 mol % w.r.t substrate], reaction time = 16 h. [b] By quant. GC; ± 1%; 2,5-HD = 2,5 hexanedione; 2,5-HDO = 2,5-hexanediol; 2,5-DMTHF = 2,5-dimethyltetrahydrofuran (sum of *cis* and *trans* isomers); HMA = hemiacetal = 2-hydroxy-2,5-dimethyl-tetrahydrofuran; HXO = 2-hexanone; HEX = hexane; MBD = mass balance deficiency: gas phase products and substrate decomposition to solids not quantifiable by GC. [c] Control reaction without catalyst added.

Scheme 3. Overall Reaction Cascades and Observed Reaction Products for the Hydrodeoxygenation of 2,5-Hexanedione and 2,5-Dimethylfuran in Aqueous Acidic Medium



removal of solvent *in vacuo*. $[(4'\text{-Ph-terpy})Ru(H_2O)_3](OTf)_2$ (terpy =2,2′:6′,2″-terpyridine) (**1**) was prepared as previously described (the final purple solid is *air-stable* for extended periods, i.e., hours or days, but should be stored under inert atmosphere for the longer term).[35] $[(4'\text{-Ph-terpy})Ir(OTf)_3]$ (**2**) was prepared according to the method developed by Lo et al.[38]

Single Crystal X-ray Diffraction Analyses. Crystals were taken directly from the samples recovered from the reactor and studied at 150 K. Ruthenium complex (CCDC deposition number: 1018797): dark-red truncated prism; $[RuL_2](triflate)_2{*}(H_2O){*}0.5$(*trans*-2,5-diMeTHF), where L = 4′-phenyl-2,2′:6,2″-terpyridine; FW = 1086.02; triclinic, *P*-1; a = 12.4822(2), b = 12.5899(2), c = 16.3218(2) Å, α = 85.1949(13)°, β = 73.0090(14)°, γ = 67.1062(17) °, V = 2258.47(7) Å^3; Z = 2; $R1$ = 0.038; GOF = 1.114. Mixed FeNiIr crystal I (CCDC deposition number: 1018795): dark-red prism; $[ML_2](triflate)_2{*}(H_2O){*}0.5$(*trans*-2,5-diMeTHF), where M = Fe:Ni:Ir with 61.29(8):26.27(4):12.4(1) %, respectively; FW = 1058.52; triclinic, *P*-1; a = 12.5227(3), b = 12.5493(4), c = 16.3000(4) Å, α = 85.591(2)°, β = 73.366(2)°, γ = 67.274(3) °, V = 2262.17(12) Å^3; Z = 2; $R1$ = 0.052; GOF = 1.053. Mixed FeNiIr crystal II (CCDC deposition number: 1018796): dark-red prism; $[ML_2](triflate)_2{*}(H_2O){*}0.5$(*trans*-2,5-diMeTHF), where M = Fe:Ni:Ir with 65.46(8):28.06(3):6.5(1) %, respectively; FW = 1050.45; triclinic, *P*-1; a = 12.5186(5), b = 12.5124(4), c = 16.2959(5) Å, α = 85.669(2)°, β = 73.376(3)°, γ = 67.447(3) °, V = 2257.13(15) Å^3; Z = 2; $R1$ = 0.055; GOF = 1.121.

Representative Procedure for a Catalytic Hydrodeoxygenation Reaction. In a 25 mL volumetric flask were combined catalyst **1** (0.0197 g, 0.025 mmol) and ~10 mL of HPLC water to form a dark purple solution. Methylsulfone (0.2333 g, 2.5 mmol, GC internal standard), 2,5-hexanedione

Table 2. Hydrogenation of 2,5-Hexanedione by **1** and **2** in the Presence of Added Acid

entry[a]	cat.	*T* [°C]	acid	acid [equiv w.r.t. Ru]	cat. decomp.[Y/N]	2,5-HD[b] [%]	2,5-HDO[b] [%]	2,5-DMTHF[b] [%]	SA[b] [%]	HMA[b] [%]	HXO[b] [%]	HEX[b] [%]	MBD[b] [%]	phase sep.
1	**1**	125	HOTf	10	N	82	2	10	3	3	0	0	0	N
2	**1**	150	HOTf	10	N	15	4	37	7	2	0	0	35	N
3	**1**	175	HOTf	10	N	8	1	41	1	0	1	1	46	Y
4	**1**	200	HOTf	10	N	7	0	33	0	0	9	12	39	Y
5	**1**	225	HOTf	10	N	24[c]	0	7	0	0	12	3	53	Y
6	**2**	200	HOTf	10	Y[d]	0	0	29	0	0	0	19	52	Y
7	**2**	200	HOTf	5	Y[d]	4	0	65	0	0	0	15	16	Y
8	**2**	200	HOTf	1	Y[d]	0	1	56	0	0	0	0	43	Y
9	**2**	200	H_3PO_4	5	Y[d]	0	0	91	0	0	0	3	6	Y
10	**2**	200	H_3PO_4	1	Y[d]	0	1	55	0	0	0	3	41	Y
11	-[e]	225	HOTf	10	n/a	46	0	1	0	0	0	0	53	N

[a] Reaction conditions: 2,5-hexanedione [1000 mmol/L] in water, 5.5 MPa (800 psi) H2(g), dimethylsulfone (ISTD) [100 mmol/L], catalyst load [1 mmol/L = 0.1 mol % w.r.t substrate], HOTf 10 mmol/L = 10 equiv w.r.t. Ru metal, reaction time = 16 h. [b] By quant. GC; ± 1%; 2,5-HD = 2,5 hexanedione; 2,5-HDO = 2,5-hexanediol; 2,5-DMTHF = 2,5-dimethyltetrahydrofuran (sum of *cis* and *trans* isomers); SA = self-aldol products; HMA = hemiacetal = 2-hydroxy-2,5-dimethyltetrahydrofuran; HXO = 2-hexanone; HEX = hexane; MBD = mass balance deficiency: gas phase products and substrate decomposition to polymers and solids not quantifiable by GC. [c] <1% of 2,5-DMF also formed. [d] Black coating formed on reactor wall. [e] Control reaction without catalyst added.

(2.853 g, 25 mmol), or 2,5-dimethylfuran (2.4105 g, 25 mmol) and (where applicable) triflic acid were added, and the volume made up to 25.00 mL with water. The solution was thoroughly mixed, then placed in an Autoclave Engineers MiniReactor, and purged three times with hydrogen. The reactor was pressurized to 5.5 MPa (800 psi) H_2, sealed, and then heated to the set temperature (125–238 °C), which in all cases was reached in ≤30 min. The reaction was stirred at temperature for 16 h and then cooled to ambient. A sample of the headspace gas was taken for micro-GC-TCD analysis before the reactor was vented. The reaction products were analyzed by GC-FID.

Complex **1** is freely soluble in water forming initially purple solutions that turn red after the reaction. Complex **2** is not soluble in water at ambient temperature but forms pale yellow solutions in 5:1 1,4-dioxane/water. In either water or 5:1 1,4-dioxane purple-red solutions result after the reaction with **2**. With 2,5-dimethylfuran as the substrate initially biphasic reaction mixtures result. The appearance of the final reaction mixtures is discussed in the main text and indicated in the tables listing the observed conversion and yields.

■ RESULTS

Catalytic Hydrogenation Reactions. *Hydrodeoxygenation of 2,5-Hexanedione by 1 and 2.* Complexes **1** and **2** were evaluated as catalysts for the hydrogenation of 2,5-hexanedione (2,5-HD) exploring the influence of temperature and type and amount of acid cocatalyst added on catalyst activity and product distribution. Since 2,5-HD is freely soluble in water at the substrate concentration selected (1000 mmol/L), all reactions with this substrate were carried out in aqueous solution. Table 1 summarizes the results of experiments as a function of temperature and catalyst employed but without the addition of an acid cocatalyst. However, note that even in the absence of added acid the reaction mixtures are still acidic due to the generation of free HOTf by the heterolytic activation of hydrogen (cf. Scheme 1). Scheme 3 shows the overall reaction cascade observed with all pathways, inferred and actually observed intermediates and products.

Under the aqueous conditions no acid-catalyzed ring closure of the substrate to 2,5-DMF was observed in any of the reactions starting from 2,5-HD, but even in the absence of added acid cocatalyst a complex reaction network of iterative dehydration, cyclizations, and hydrogenations evolves in which 2,5-dimethyltetrafuran (2,5-DMTHF) and hexane (HEX) appear to be the terminal stable products. Small amounts of the partial hydrodeoxygenation intermediates 2-hydroxy-2,5-dimethyl-tetrahydrofuran (hemiacetal = HMA) and 2-hexanone (HXO) as well as the self-aldol products (SA, left-most branch in Scheme 3, ≪1%) were also observed in some of the reactions.

The best result for catalyst **1** is achieved at 200 °C (Entry 3, Table 1) realizing 94% of hydrogenated products 2,5-HDO (14%) and 2,5-DMTHF (80%) with no catalyst decomposition and an almost full mass balance (MBD ≤ 1%). Trace amounts of hexane (HEX) were identified in a gas phase sample from the head space of the reactor (by micro-GC). At the higher temperature 225 °C (Entry 4, Table 1) phase separation of the reaction mixture occurs into an aqueous polar and a small amount of an organic phase containing 2,5-DMTHF, 2-hexanone (HXO), and HEX as the total deoxygenation product. The mass balance deficiency (MBD) for this reaction (9%) and all others listed in the following is caused by partial condensation into and decomposition of the substrate and products into the reactor headspace and/or decomposition into nonvolatile oligo- or polymeric products in solution and—where applicable—partition of some of the hexane generated into the gas phase.[50] At the lower temperature of 175 °C a higher selectivity to 2,5-HDO is observed at comparable conversion, while at 150 °C substantial decomposition/polymerization of the substrate competes with hydrogenation indicating very low catalyst activity at this temperature. For comparison, a control reaction without added catalyst at 225 °C (Entry 6, Table 1) results in 37% decomposition to brown solids and 60% recovery of the substrate with only marginal conversion to hydrogenated products caused by the background activity of the 316SS reactor body.[48] Control reactions at lower temperatures equally gave no conversion to hydrogenated substrates but higher recoveries of unconverted substrate. In all reactions the initially purple solution of **1** turns red, i.e., a different color than the catalytically active yellow dimer $[((4'\text{-phenyl-}2,2'{:}6',2''\text{-terpy})Ru(CO))_2(\mu\text{-}OCH_3)_2](OTf)_2$ observed when **1** was employed in the hydrodeoxygenation of

Table 3. Hydrogenation of 2,5-Dimethylfuran by Catalyst 1 in Water

entry[a]	T [°C]	HOTf [equiv w.r.t. Ru]	cat. decomp. (Y/N)	2,5-DMF[b] [%]	2,5-HD[b] [%]	2,5-HDO[b] [%]	2,5-DMTHF[b] [%]	SA[b] [%]	HMA[b] [%]	HXO[b] [%]	HEX[b] [%]	MBD[b] [%]	phase sep.
1	150	n/a	N	47	0	7	4	0	0	0	0	41	Y
2	175	n/a	N	0	22	19	14	2	8	0	0	34	N
3	200	n/a	N	0	3	12	55	0	4	0	0	27	N
4	225	n/a	N	0	12	0	48	0	3	3	2	32	Y
5[c]	225	n/a	n/a	2	50	0	0	0	0	0	0	48	N
6	200	1	N	0	47	0	8	0	5	0	0	40	N
7[d]	225	1	Y	1	16	0	40	0	3	8	4	28	Y
8[d]	225	5	Y	1	40	0	3	0	0	6	0	49	Y
9[e]	225	1	Y	0	49	0	6	0	2	0	0	43	N
10[c]	225	1	n/a	2	83	0	6	0	0	0	0	9	N

[a] Reaction conditions: 2,5-dimethylfuran [1000 mmol/L] in water, 5.5 MPa (800 psi) $H_{2(g)}$, dimethylsulfone (ISTD) [100 mmol/L], catalyst load [1 mmol/L = 0.1 mol % w.r.t. substrate], reaction time = 16 h. [b] By quant. GC; ± 1%; 2,5-HD = 2,5 hexanedione; 2,5-HDO = 2,5-hexanediol; 2,5-DMTHF = 2,5-dimethyltetrahydrofuran (sum of *cis* and *trans* isomers); SA = self-aldol products; HMA = hemiacetal = 2-hydroxy-2,5-dimethyltetrahydrofuran; HXO = 2-hexanone; HEX = hexane; MBD = mass balance deficiency: gas phase products and substrate decomposition to polymers and solids not quantifiable by GC. [c] Control reactions without catalyst added. [d] Catalyst decomposition to blue metallic coating in reactor body observed. [e] Control reaction with blue coating from reaction of Entry 7.

Table 4. Hydrogenation of 2,5-Dimethylfuran by Catalyst 2 in Water

entry[a]	*T* [°C]	acid	acid [equiv w.r.t. Ru]	cat. decomp. (Y/N)	2,5-DMF[b] [%]	2,5-HD[b] [%]	2,5-HDO[b] [%]	2,5-DMTHF[b] [%]	HEX[b] [%]	MBD[b] [%]	phase sep.
1	175	n/a	n/a	N	0	0	23	46	0	31	Y
2	200	n/a	n/a	Y	0	0	1	74	1	24	Y
3	225	n/a	n/a	Y	0	0	0	38	7	55	Y
4	175	HOTf	1	Y	0	0	0	87	2	12	Y
5	225	HOTf	1	Y	0	0	0	69	13	18	Y
6[c]	225	HOTf	1	Y	0	0	0	71	7	23	Y
7	225	HOTf	5	Y	0	0	0	17	29	54	Y
8	225	HOTf	10	Y	0	4	0	9	25	62	Y
9	225	H_3PO_4	1	Y	0	0	0	61	13	26	Y
10	225	H_3PO_4	5	Y	0	0	0	47	31	23	Y

[a] Reaction conditions: 2,5-dimethylfuran [1000 mmol/L] in water, 5.5 MPa (800 psi) $H_{2(g)}$, dimethylsulfone (ISTD) [100 mmol/L], catalyst load [1 mmol/L = 0.1 mol % w.r.t. substrate], reaction time = 16 h. [b] By quant. GC; ± 1%; 2,5-HD = 2,5 hexanedione; 2,5-HDO = 2,5-hexanediol; 2,5-DMTHF = 2,5-dimethyltetrahydrofuran (sum of *cis* and *trans* isomers); HEX = hexane; MBD = mass balance deficiency: gas phase products and substrate decomposition to polymers and solids not quantifiable by GC. [c] Control reaction with black coating generated from the reaction of Entry 5.

glycerol.[35] At 200 °C the iridium catalyst **2** achieves very similar results (Entry 5, Table 1) resulting in a clear purple-red solution and was not further evaluated under these conditions.

With reference to Scheme 3 and as observed for Entry 4, Table 1, an iterative hydrodeoxygenation sequence can in principle result in the total deoxygenation of the substrate to hexane, which requires further acid-catalyzed dehydration of the initial products of 2,5-HD hydrogenation. We therefore evaluated both catalysts in the presence of added HOTf. Table 2 summarizes the results of the 2,5-HD reactions with added HOTf. For **1** with 10 equiv of acid added no catalyst decomposition (as evidenced by the formation of Ru^0 or a metallic coating in the reactor − *vide infra*) was observed, and depending on the temperature used the original purple ($T \leq 150$ °C) to orange-red ($T \geq 150$ °C) homogeneous solutions were recovered with some organic substrate decomposition to brown solids (humins) observed at the higher reaction temperatures. For $T \geq 175$ °C phase separation of an organic nonpolar layer from the aqueous polar reaction mixture was observed. In the presence of acid overall lower conversions to hydrodeoxygenated products result, and higher amounts of acid-catalyzed decomposition to nonvolatile products, reaching 53% for $T = 225$ °C, are observed, which is the same amount of decomposition as in the control reaction (Entry 11, Table 2) .

The presence of added acid also causes the stable 2,5-DMTHF, most likely formed by acid-catalyzed dehydration ring-closure of 2,5-HDO, to dominate the product distribution. At the higher temperature traces of 2,5-DMF were also identified in the reaction mixture, i.e., even in aqueous solvent the acid catalyzed ring-closure of 2,5-HD to its cyclic bis-enol (i.e., the furan ring) is possible. The best result for **1** is achieved at 200 °C (Entry 4, Table 2) generating 12% of hexane.[51] Catalyst **2** was then evaluated at this temperature exploring the effect of different amounts of acid (Entries 6−8, Table 2). A high acid load (10 equiv as for **1**) not only gives the highest yield of the total deoxygenation product hexane but also results in excessive substrate decomposition. A better balance of total deoxygenation and overall conversion to hydrodeoyxgenated products is achieved at 5 equiv of HOTf added (Entry 7). In order to explore the possible effect of a weaker, noncoordinating and nonoxidizing acid two reactions with H_3PO_4 were also carried out giving a very high conversion and selectivity to 2,5-DMTHF (91%, Entry 9, Table 2) and low substrate decomposition. The buffering capacity of the $H_2PO_4^- \Leftrightarrow HPO_4^{2-} \Leftrightarrow PO_4^{3-}$ system likely plays an important role here and suggests that the reaction could be further optimized for the highly selective generation of 2,5-DMTHF. However, in all cases the reactions of **2** in the presence of acid generated a

Table 5. Hydrogenation of 2,5-Dimethylfuran by Catalyst 1 in 5/1 1,4-Dioxane/Water

entry[a]	*T* [°C]	time [h]	cat. load [% w.r.t. to substrate]	acid/base [eq w.r.t. Ru]	2,5-DMF[b] [%]	2,5-HD[b] [%]	2,5-HDO[b] [%]	2,5-DMTHF[b] [%]	SA[b] [%]	HMA[b] [%]	HXO[b] [%]	HEX[b] [%]	MBD[b] [%]
1	175	16	0.1	n/a	15	35	6	14	7	3	0	0	21
2	200	16	0.1	n/a	6	44	0	17	5	1	0	0	27
3	225	16	0.1	n/a	9	46	0	11	3	0	0	0	30
4	225	16	0.1	5/HOTf	8	41	0	9	1	0	3	1	38
5	225	16	0.1	1/HOTf	3	19	0	26	2	0	10	5	35
6	225	16	0.1	5/NaOH	64	2	0	2	1	1	0	0	30
7	225	16	0.1	1/NaOH	5	31	1	12	10	2	1	0	38
8	225	40	0.1	n/a	0	0	0	78	0	1	0	3	19
9	238[c]	16	0.1	n/a	0	1	0	71	0	1	0	4	24
10	225	16	0.25	n/a	0	1	0	44	0	0	3	11	41
11[d]	225	16	n/a	n/a	83	3	0	0	0	0	0	0	13

[a] Reaction conditions: 2,5-dimethylfuran [1000 mmol/L] in 5:1 1,4-dioxane:water, 5.5 MPa (800 psi) $H_{2(g)}$, dimethylsulfone (ISTD) [100 mmol/L], catalyst load [1 mmol/L = 0.1 mol % w.r.t. substrate], reaction time = 16 h. [b] By quant. GC; ± 1%; 2,5-HD = 2,5 hexanedione; 2,5-HDO = 2,5-hexanediol; 2,5-DMTHF = 2,5-dimethyltetrahydrofuran (sum of *cis* and *trans* isomers); SA = self-aldol products; HMA = hemiacetal = 2-hydroxy-2,5-dimethyltetrahydrofuran; HXO = 2-hexanone; HEX = hexane; MBD = mass balance deficiency: gas phase products and substrate decomposition to polymers and solids not quantifiable by GC. [c] Maximum sustained internal reactor temperature attainable by the equipment used. [d] Control reaction without catalyst.

black coating on the reactor walls along with clear purple solutions. The nature and activity of this coating and of the purple species in solution was further investigated in detail with 2,5-DMF as the substrate (*vide infra*) ultimately suggesting that all reactions at $T \geq 200$ °C and in the presence of acid with **2** as the starting catalyst are in fact heterogeneously catalyzed by this coating likely composed of Ir^0.

Hydrogenation of 2,5-Dimethylfuran. Taking "one step back" in the value chain illustrated in Scheme 2 the more challenging hydrodeoxygenation of 2,5-DMF was attempted as a function of temperature, solvent, and concentration of acid cocatalyst added. While 2,5-DMF is only marginally soluble in water at room temperature, both the relative permittivity (= dielectric constant ε_0) and surface tension σ [mN/m] of water drop substantially with rising temperature ($\varepsilon_0^{20} = 80.36 \rightarrow \varepsilon_0^{150} = 32.32$ and $\sigma^{20} = 72.74 \rightarrow \sigma^{150} = 48.75$, respectively),[52] which led us to postulate that the solubility of this substrate would be much higher at the temperatures required for catalyst activity and ring-opening of the substrate (≥150 °C) and that a homogeneous single-phase reaction solution be present at elevated temperatures inside the reactor.[31] It is also important to realize that at temperatures 150−250 °C the pK_w of water drops from 14.00 at 25 °C to 11.64−11.20, i.e., the relative concentration of hydronium H_3O^+ (and hydroxide OH^-) is approximately 3 orders of magnitude higher than at room temperature providing enhanced intrinsic acid/base-catalysis for the interconversion of 2,5-DMF and 2,5-HD (cf. Scheme 3) even without the addition of an acid cocatalyst above and beyond any acidic species generated by the heterolytic activation of $H_2(g)$ at the metal center (Scheme 1). A first series of experiments with 2,5-DMF as the substrate was therefore carried out in water as the reaction medium. Tables 3 and 4 list the results for catalysts **1** and **2**, respectively, with and without the addition of HOTf.

The results listed in Table 3 show that the hydrodeoxygenation of 2,5-DMF in water is in fact possible. The best results for **1** without added acid were achieved at 200 and 225 °C (Entries 3 and 4, Table 3), showing a small amount of hexane as the phase separated total deoxygenation product without catalyst decomposition occurring. As reactions with 10 equiv of added HOTf (cf. Table 2) led to complete catalyst inhibition and very high levels of substrate decomposition the amount of acid added was lowered to 5 and ultimately 1 equiv w.r.t. ruthenium content, which at 200 and 225 °C (Entries 6 and 7, Table 3) gave 8 and 40% of hydrodeoxygenated products, i.e., again lower conversion to desired products and/or higher decomposition of substrate than without acid added (Entries 3 and 4, Table 3). For the reactions at 225 °C in the presence of acid a blue coating with a metallic sheen was observed along with the clear red reaction solutions obtained at the end of the reaction, indicating at least partial catalyst decomposition. However, in a control reaction without cleaning the reactor this coating generated from **1** proved to be essentially inactive giving similar amounts of hydrodeoxygenated products as the control reaction without catalyst in a clean reactor (Entry 10, Table 3). The control reaction (Entry 11, Table 3) also clearly established that 2,5-DMF hydrolyzes to 2,5-HD under the reaction conditions as we also observed in a previous study employing HMF derived substrates with longer alkyl side-chains.[31] Control reactions at 225 °C with 2,5-DMTHF as the substrate with or without acid added showed no conversion to ring-opened products or further deoxygenation, i.e., once formed 2,5-DMTHF is stable under even the harshest reaction conditions tested here.

Table 4 lists the results for the reaction carried out with catalyst **2**. With the exception of the first reaction at 175 °C without added acid, which realized at total of 69% of hydrodeoxygenated products, catalyst decomposition to a black coating, very similar in appearance to that seen in the reactions with 2,5-HD, was observed in all cases. In contrast to the coating generated from **1**, the coating from the iridium system **2** is very active as a catalyst, achieving essentially the same conversion and product distribution as the homogeneous catalyst, i.e., the observed activities are likely heterogeneous in nature based on the formation of an Ir^0 species on the reactor wall surfaces (Entries 5 and 6, Table 4). The coating maintains ~50% of its activity even after twice charging the reactor with pure water only and heating to 225 °C for 16 h but is easily removed by mechanical polishing returning the reactor to its baseline activity (cf. control reaction, Entry 10, Table 3). In the presence of acids relatively high conversions to the hexane (up

Table 6. Hydrogenation of 2,5-Dimethylfuran by Catalyst 2 in 5/1 Azeotrope 1,4-Dioxane/Water or 9/1 Sulfolane/Water

entry[a]	*T* [°C]	solvent	cat. decomp. (Y/N)	2,5-DMF[b] [%]	2,5-HD[b] [%]	2,5-HDO[b] [%]	2,5-DMTHF[b] [%]	SA[b] [%]	HMA[b] [%]	HXO[b] [%]	HEX[b] [%]	MBD[b] [%]	phase sep.
1	175	1,4-diox/H_2O	N	49	22	1	2	1	1	0	0	24	N
2	200	1,4-diox/H_2O	Y	12	44	2	7	9	2	0	0	25	N
3	225	1,4-diox/H_2O	Y	7	32	0	16	8	1	0	0	36	N
4	175	sulfolane/H_2O	N	6	59	1	16	0	0	0	0	18	N
5	200	sulfolane/H_2O	Y	5	37	1	9	0	0	0	0	48	N
6	225	sulfolane/H_2O	Y	14	43	1	6	0	0	0	1	35	N

[a] Reaction conditions: 2,5-dimethylfuran [1000 mmol/L] in the solvent mixture indicated. 5.5 MPa (800 psi) $H_{2(g)}$, dimethylsulfone (ISTD) [100 mmol/L], catalyst load [1 mmol/L = 0.1 mol % w.r.t. substrate], reaction time = 16 h. [b] By quant. GC; ± 1%; 2,5-HD = 2,5 hexanedione; 2,5-HDO = 2,5-hexanediol; 2,5-DMTHF = 2,5-dimethyltetrahydrofuran (sum of *cis* and *trans* isomers); SA = self-aldol products; HMA = hemiacetal =2-hydroxy-2,5-dimethyltetrahydrofuran; HXO = 2-hexanone; HEX = hexane; MBD = mass balance deficiency: gas phase products and substrate decomposition to polymers and solids not quantifiable by GC.

to 29%, Entry 7, Table 4) were observed, however, also accompanied by high levels of substrate decomposition.

Recognizing that both the catalyst and 2,5-DMF substrate decomposition (up 50%) in the aqueous reaction mixtures may be rooted in the fact that the system starts out as a biphasic aqueous/organic mixture, a series of reactions at 175−225 °C with and without added HOTf (1 and 5 equiv) was also attempted in a 5:1 mixture of 1,4-dioxane:water representing the azeotropic mixture of these two solvents. This mixture completely dissolves 2,5-DMF at the substrate concentration employed and ambient conditions. 1,4-Dioxane was selected as it was anticipated to be stable under the reaction conditions and chemically resembles the stable product 2,5-DMTHF (cf. control reaction with this substrate discussed above) with the azeotrope having a sufficiently different boiling point from 2,5-HDO, 2,5-DMTHF, and HEX to potentially allow separation by distillation. Table 5 gives the results of the reactions for catalyst **1** in the azeotrope solvent mixture as a function of temperature, reaction time, catalyst load, and cocatalyst, which—postulating that base catalysis could also lead to ring opening and hydrogenation—in this series was expanded to include addition of NaOH at 1 and 5 equiv w.r.t to catalyst. For **1** none of the reactions listed in Table 5 showed catalyst decomposition to solids or phase separation giving deep red homogeneous solutions in all cases.

Under otherwise identical reaction conditions overall lower conversions to hydrodeoxygenated products than in water were observed, while the amount of decomposition—if somewhat lower than in water—was still appreciable. E.g., at 200 °C without added acid the reaction in the dioxane mixture generated only 17% of 2,5-DMTHF with 27% decomposition (Entry 2, Table 5) compared to 55% and 34%, respectively in water (Entry 3, Table 3). At a longer reaction time of 40 h at 225 °C (Entry 8, Table 5) 78% of 2,5-DMTHF with 19% decomposition are realized compared to only 11% and 30%, respectively after 16 h (Entry 3, Table 5). Similar results were obtained by running the reaction at 238 °C (Entry 9, Table 5), the highest temperature reachable by the equipment currently available to us. These results can be rationalized by 1,4-dioxane causing coordinative inhibition of the catalyst, possibly by acting as a reversibly binding weak chelate from a boat conformation of the solvent and/or by some of the nonvolatile decomposition products not quantifiable by GC being formed reversibly and converted to volatile hydrodeoxygenation products over time. The large amounts of 2,5-HD and the presence of the self-aldol products in the reactions of Entries 1−4 suggest that reversibly formed aldol condensates (dimers etc.) of 2,5-HD constitute a substrate reservoir. At a higher catalyst load (Entry 10, Table 5) not only a moderate yield of 2,5-DMTHF but also a high amount of decomposition is observed, which we attribute to the higher amount of acid released by the catalyst in this case. The corresponding results for catalyst **2** are summarized in Table 6, which also lists the results of a temperature series in a 9:1 sulfolane/water mixture. Again catalyst **2** decomposed at temperatures >175 °C, and in both solvent systems only marginal conversions to hydrodeoxygenated products were observed indicating coordinative inhibition by either solvent.

Attempts at Catalyst Recycling and Catalyst Decomposition Pathways. On the basis of the results discussed that showed that catalyst **2** is not stable at $T > 175$ °C no attempts were made to recycle this catalyst. For catalyst **1** the overall best result was obtained by the reaction in water at 200 °C without addition of acid cocatalyst (Table 3, entry 3), which gave a total yield of 12 + 55 = 67% of the desired hydrodeoxygenation products 2,5-HDO and 2,5-DMTHF, respectively. Attempting to reuse the catalyst, fresh 2,5-DMF was added to the clear deep red single-phase solution obtained from repeats of this reaction. However, resubjecting this solution to the same reaction conditions gave only 3% conversion to 2,5-DMTHF (≈ reactor baseline activity) with 76% recovery of ring-opened substrate (2,5-HD) along with some substrate decomposition (18%), i.e., the recovered catalyst/product solution is completely inactive. Postulating that the red solution represents an irreversibly inhibited catalyst resting state, generated, e.g., by coordination of one of the intermediate or side-products listed in Scheme 3, we hypothesized that offering the catalyst system an alternative stable but reactivatable resting state may change this behavior. We therefore repeated the experiment in the presence of propanal (5 mol %) as an additional substrate and source of CO ligands, essentially recreating a reaction mixture that resembles more closely that with glycerol as the substrate,[35] where the dimer $[((4'\text{-phenyl-}2,2'\!:\!6',2''\text{-terpy})\text{Ru}(\text{CO}))_2(\mu\text{-OCH}_3)_2](\text{OTf})_2$ was identified as a reversibly

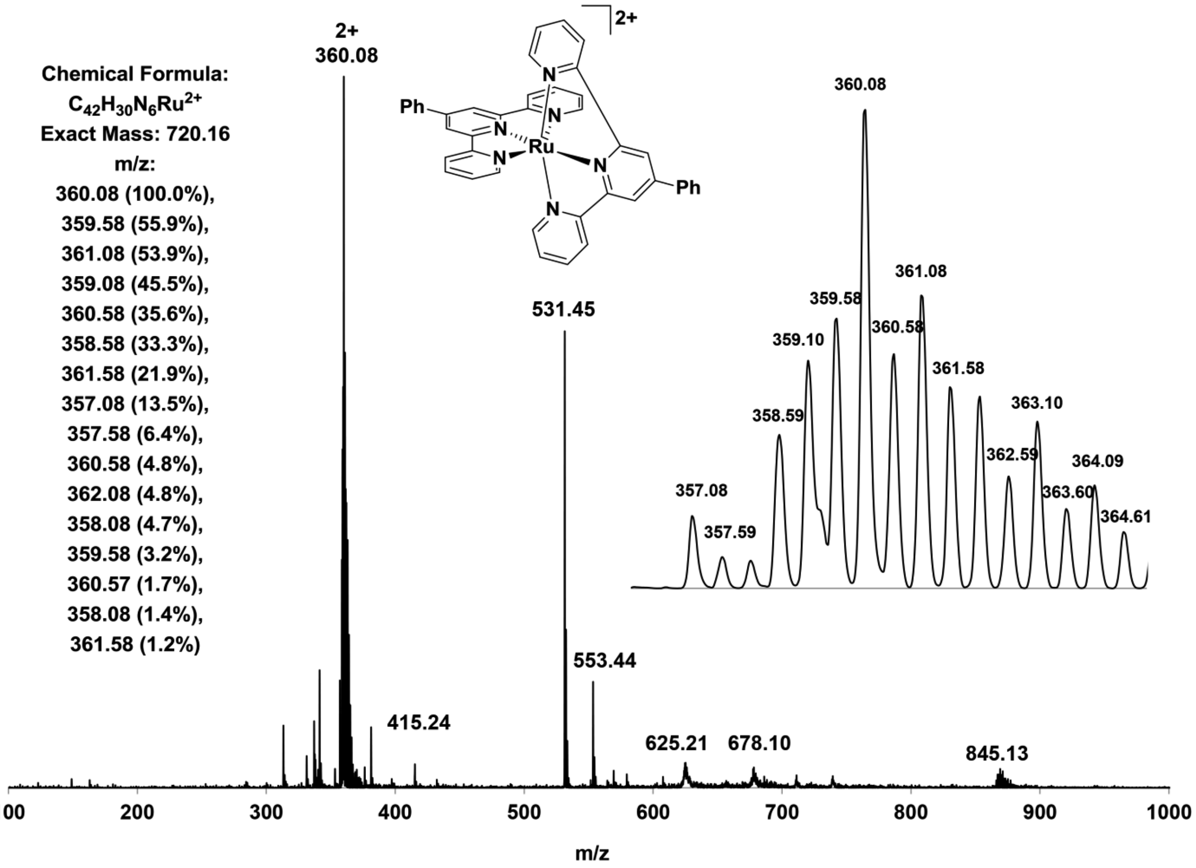


Figure 1. ESI-MS of $[Ru(4'\text{-Ph-terpy})_2]^{2+}$ (MeOH solution, +-ve ionization mode).

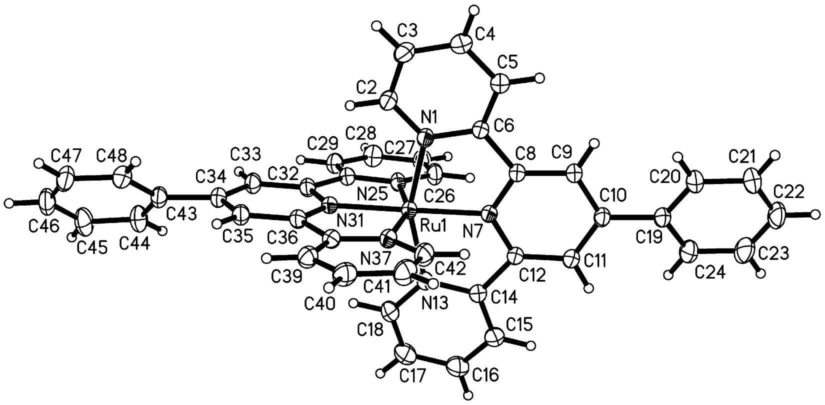


Figure 2. ORTEP drawing of the complex cation in the crystal structure of $[Ru(4'\text{-phenyl-}2,2'{:}6,2''\text{-terpyridine})_2](OTf)_2{\cdot}(H_2O){\cdot}0.5$(*trans*-2,5-DMTHF). Thermal ellipsoids are drawn at the 50% probability level.

formed resting state of the catalyst formed at $T > 200$ °C that can serve as a pro-catalyst equivalent to **1**. However, these reactions again resulted in deep red solutions with no catalytic activity.

Insight into the catalyst decomposition pathway for both **1** and **2** was gained by the observation that red or red-purple crystals, respectively, deposited from recovered aqueous reaction solutions of both catalyst systems after being stored under ambient conditions for several weeks. The ESI-MS spectrum of a crystal (redisolved in MeOH) deposited from a reaction solution of **1** showed a dominant peak with a distinct ruthenium isotope pattern at $m/z = 360.08$. The same crop of crystals also allowed a structure determination by single-crystal X-ray diffraction. Together these unambiguously established the identity of the material as the bis-chelate complex $[Ru(4'\text{-Ph-terpy})_2](OTF)_2$. Figure 1 shows the ESI-MS and Figure 2 the ORTEP of this bis-chelate complex, which—with different counterions and solvent inclusions—has previously been described by Constable and Housecroft as well as McMurtrie and Dance.[53,54]

The analogous analysis of a purple solution of redissolved crystals (in MeOH or acetone) obtained from a reaction solution of **2** by ESI-MS gave a dominant peak at $m/z = 337.08$. This species does on the basis of both its mass charge ratio and the absence of an iridium isotope pattern not contain iridium. Instead, we successfully modeled this complex as a 2.3:1 mixture of iron and nickel by overlaying the known isotope patterns of these two metals as shown in Figure 3.[55] Again the

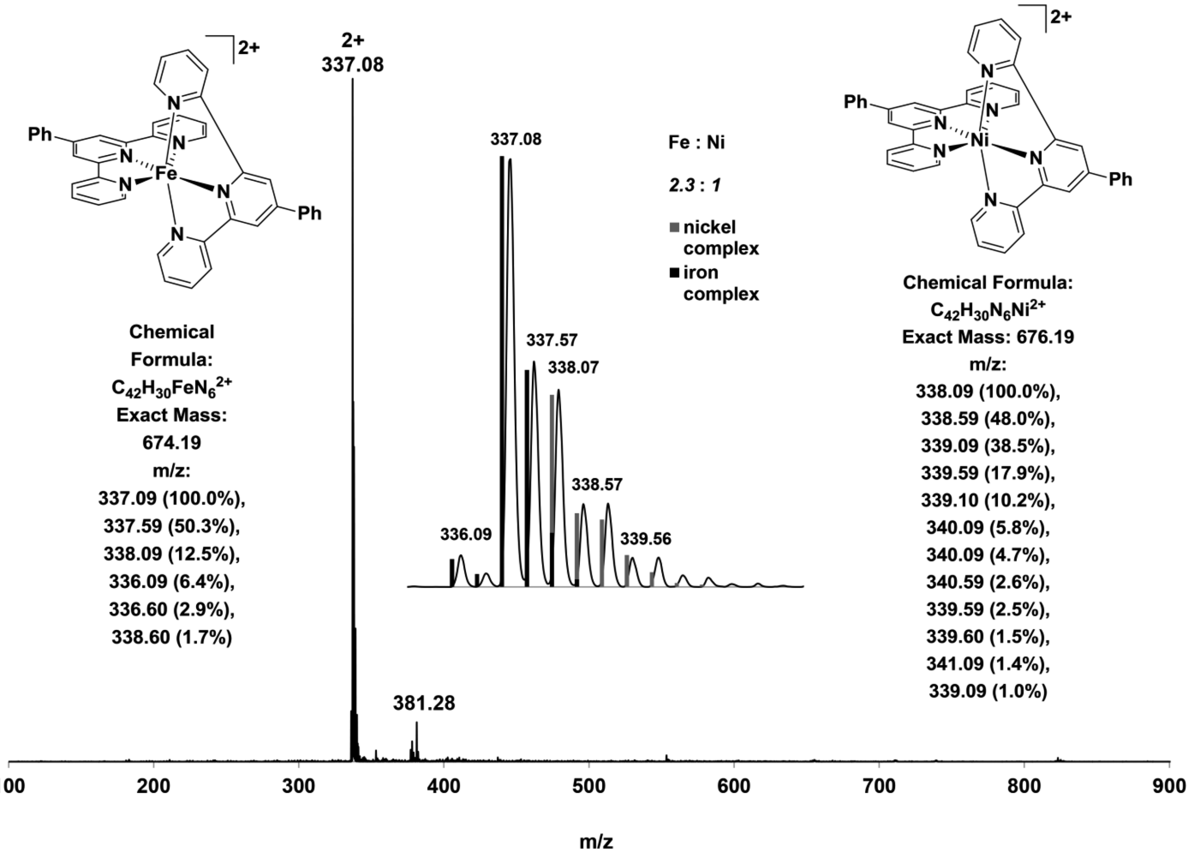


Figure 3. ESI-MS of $[(Fe)_{0.7}(Ni)_{0.3}(4'\text{-Ph-terpy})_2]^{2+}$ (MeOH solution, +-ve ionization mode).

same crop of crystals also allowed a structure determination by single-crystal X-ray diffraction from two different crystals, which—in agreement with the ESI-MS spectrum—showed these crystals to be a blend of the complexes $[Fe(4'\text{-Ph-terpy})_2](OTf)_2$ and $[Ni(4'\text{-Ph-terpy})_2](OTf)_2$, isostructural to those of **1** and to each other. However, the presence of relatively large amounts of unaccounted electron density required fixing the Fe:Ni ratio at 2.3:1 on the basis of the MS results (Figure 3) and incorporation of smaller proportions of Ir for optimal refinement, giving final crystal compositions of Fe, 61.29(8)%/Ni, 26.27(4)%/Ir, 12.4(1)% and Fe, 65.46(8)%/Ni, 28.06(3)%/Ir, 6.5(1)%, respectively.[56]

For both catalysts this established the ligand loss and redistribution deactivation/decomposition pathways shown in Scheme 4, which for ruthenium forms an inactive and for iridium a catalytically active coating in the reactor body. With **1** the bis-chelate complex $[Ru(4'\text{-Ph-terpy})2]^{2+}$ is formed by a ligand redistribution reaction generating the blue inactive coating in the reactor from ~50% of the original metal content. With **2** as the starting complex the black catalytically very active coating, presumably composed of Ir^0 is generated releasing free ligand into solution, which then captures Fe^{II}/Ni^{II} (and possibly small amout of Mn^{II}) ions leached into the reaction solution under the reducing aqueous-acidic conditions or directly scavenges metals from the 316SS of the reactor body, which in either case is the only source of iron and nickel in the reaction mixture.

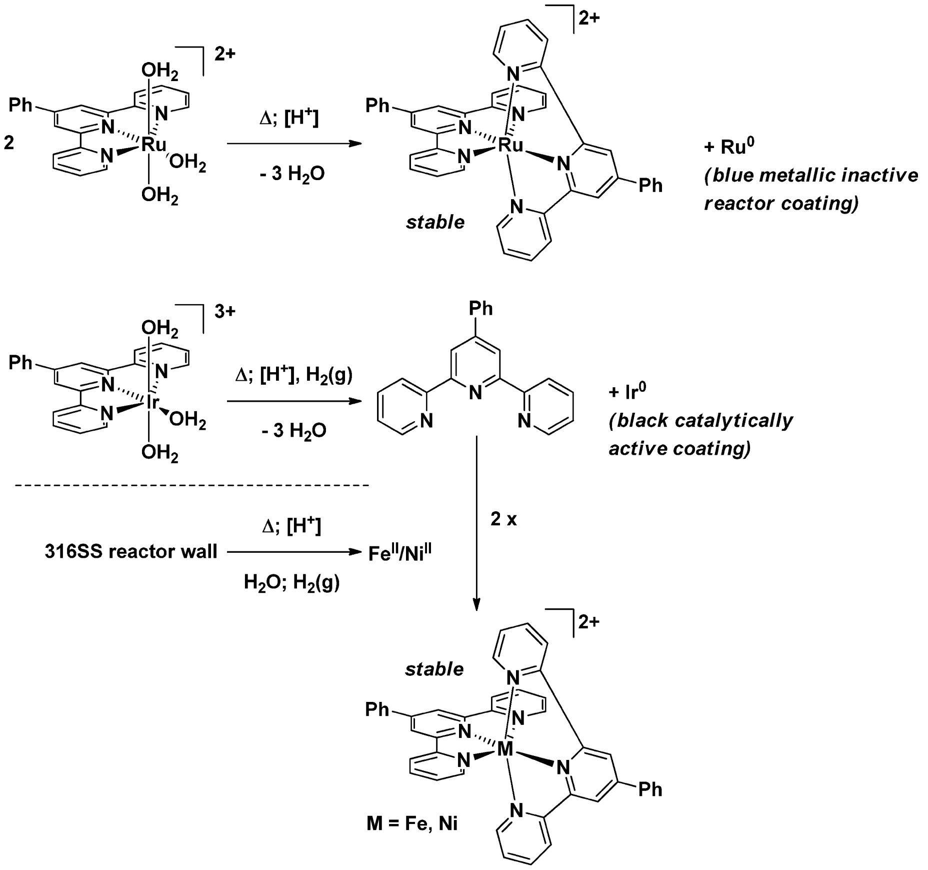
For all three metals the bis-chelate complexes $[M(4'\text{-Ph-terpy})2]^{2+}$; M = Ru, Fe, Ni, once formed are stable and inactive as a catalyst on the basis of the failed recycling experiments.

■ DISCUSSION

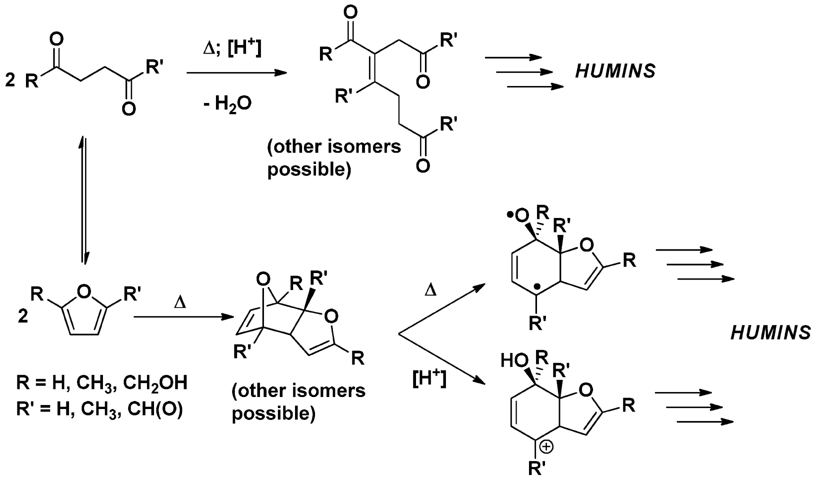
Hydrodeoxygenation Reaction Cascade. The complexity of the overall hydrodeoyxgenation reaction cascade of the 2,5-DMF/2,5-HD system (Scheme 3) is reflected in the complex product distributions observed, which are further complicated by acid-catalyzed substrate decomposition reactions that compete with the desired hydrodeoxygenation pathways. However, the product distribution data and the results of the control reactions without catalysts and for 2,5-DMTHF as the substrate allow some interpretation of the actually operating pathways as a function of substrate and reaction conditions. For 2,5-HD as the substrate a pathway via ring-closure to 2,5-DMF followed by hydrogenation of the furan ring to 2,5-DMTHF appears unlikely as only trace amounts of 2,5-DMF were observed in these reactions. The observation of ring-opening of 2,5-DMF to 2,5-HD in the presence of only acid or both acid and metal catalyst (with the catalyst also generating some acid by heterolytic H_2 activation—cf. Scheme 2) supports the notion that the actual initial hydrogenation substrate for 2,5-DMF as the starting point is likely also 2,5-HD. However, a direct furan ring hydrogenation cannot be excluded in this case. Other homogeneously catalyzed hydrogenations of substituted furans are well established and have been shown to proceed at much lower temperatures (albeit at typically high catalyst loads asking for <100 turnovers) under basic conditions and can be highly enantioselective, precluding a ring-opening as the first step.[57,58]

On the basis of our earlier study on the hydrodeoxygenation of HMF-acetone condensate 2-hydroxymethyl-5-butan-3′-one-furan to nonane by the heterogeneous Pd^0/C system in glacial HOAc,[31] the results of the control reaction with 2,5-DMTHF

Scheme 4. Catalyst Decomposition Pathways via Ligand Loss and Redistribution



Scheme 5. Possible Pathway for the Decomposition of Biomass Derived Furans to Humin via Aldol Condensations and Diels-Alder Reactions



that gave no substrate conversion at all and the fact that 2-hexanone (HXO) is only observed if hexane (HEX) is also formed suggest that for the open chain products 2,5-HD must be the initial hydrogen acceptor, as the formation of the very stable THF ring—while in principle hydrolyzable to the diol (2,5-HDO)[59] – is a "dead end" under the reaction conditions employed. As a trend, higher acid concentrations result in a higher degree of substrate loss due to formation of nonvolatile dimers, oligomers, and ultimately polymers (humins) as an acid catalyzed competition reaction to hydrodeoxygenation. As the hydrogenation of C=C and C=O bonds in the substrates and any of the intermediates lowers the overall reactivity of any intermediate and products toward humin formation, achieving better mass balances and higher conversion to the stable products 2,5-DMTHF and/or hexane will require a more active hydrogenation catalyst competing more effectively with acid catalyzed humin formation, which is believed to mainly occur through aldol condensation reactions.[60] In addition to the aldol pathway, we propose that—in particular under acidic conditions and high temperature—a Diels–Alder pathway starting by the dimerization of furans followed by ring-opening and aromatization to phenolic species as outlined in Scheme 5 may also play a role in humin formation. Such a pathway would also be applicable to furfural, HMF, and other biomass derived furans.

Acknowledging the relatively low solubility of hydrogen gas in water and postulating that either hydrogen activation or hydride transfer from the metal center to substrate are part of the rate-determining step in the hydrogenation reactions, a better hydrodeoxygenation:decomposition ratio may also be achieved by carrying out the reactions at (much) higher hydrogen pressures,[61] which does however pose substantial technical and economic challenges.[62]

Catalysts and Catalyst Deactivation. The two isostructural and isoelectronic catalysts tested combine a very open structure with three potential coordination sites for the activation of hydrogen and/or substrate with a strongly chelating meridional binding pocket, which does however still not sufficiently stabilize the catalysts. For **2** decomposition may also occur via a planar complex formed in situ by reduction to Ir^I and shown at the bottom right of Scheme 2. While the open structure is in principle desirable for an effective nonspecific and nonselective catalysis as targeted here, it also makes the metal center more susceptible to coordinative inhibition, either by the counterion of excess acid added, by coordination of two ligands forming the inert bis-chelate complexes discussed above, or by irreversible coordination of substrate or product condensates—in particular as chelating dimers, oligomer, or polymers, i.e., the humins or humin precursors or components referred to above (Scheme 5). In a reverse argument, the stability and inactivity of the bis-chelate complexes $[M(4'\text{-Ph-terpy})_2]^{2+}$ (M = Ru, Fe, Ni) is then a direct consequence of their lack of a free coordination site required for any kind of catalytic activity. The fact that the addition of excess acid appears to make both catalysts more susceptible to decomposition (Scheme 4) also suggests that the formation of the bis-chelate complexes may be acid-mediated, possibly starting with decoordination and protonation of one of the terminal pyridine-arms of the 4′-Ph-terpy ligand.

CONCLUSION AND OUTLOOK

The complex $[(4'\text{-Ph-terpy})Ru(H_2O)_3](OTf)_2$ (**1**) is a homogeneous catalyst for the hydrodeoxygenation of 2,5-hexanedione and 2,5-dimethylfuran in aqueous acidic medium at temperatures up to 225 °C but eventually decomposes to the inactive bis-chelate complex $[(4'\text{-Ph-terpy})_2Ru]^{2+}$ and a metallic but catalytically inactive ruthenium coating, making the system nonrecyclable. The analogous iridium system $[(4'\text{-Ph-terpy})Ir(H_2O)_3](OTf)_3$ (**2′**), postulated to form in situ from the tris-triflate precursor $[(4'\text{-Ph-terpy})Ir(OTf)_3]$ (**2**), decomposes at $T > 175$ °C, but in contrast to **1** forms—in particular in the presence of added acid—a catalytically highly active coating, i.e., in this case the complex merely serves as a precursor to a heterogeneous catalyst effectively defeating the purpose and premise of a homogeneous precursor. The 4′-Ph-terpy ligand liberated by the decomposition to Ir^0 reacts with iron and nickel from the 316SS reactor body to form a mixture of the stable and catalytically inactive bis-chelate complexes $[M(4'\text{-Ph-terpy})2]^{n+}$; M = Fe, Ni. The homogeneous system is inhibited by both the addition of acid or the use of a coordinating solvent (1,4-dioxane, sulfolane) and overall the activity of the coating formed by **2** is higher than that of **1** in homogeneous phase. Starting from 2,5-dimethylfuran the heterogeneous catalyst formed from **2** realizes—depending on reaction conditions—up to 87% conversion to 2,5-dimethyltetrahydrofuran (Entry 4, Table 4) or 29% of hexane (Entry 7, Table 4), while **1** at best achieves at best 78% (at extended reaction times: Entry 8, Table 5) and 11% (at increased catalyst load: Entry 10, Table 5), respectively.

The formation of even small amounts of hexane by the homogeneous system **1** is however intriguing, as it leads to phase separation of the nonpolar product from an aqueous or other highly polar reaction medium and thus offers in principle a pathway to recycling a homogeneous catalyst system based on water-soluble cationic complexes applicable to biomass hydrodeoxygenation. At the temperatures required for the dehydration and ring-opening reactions in a value chain leading from C_6 biomass-derived substrates to the desired deoxygenated solvent and fuel products, the present system is however still not sufficiently stable against decomposition to catalytically inactive species and—at the hydrogen pressures tested—also lacks sufficient overall activity to prevent substantial substrate decomposition by the competing humin forming side reactions. Catalysts that are both more stable against deactivation and overall more active may be accessible by a logical extension of the design sequence bipy → terpyridine to pyridine-based tetradentate ligands, possibly including coordinated or pendant amines that could act as proton shuttles in a metal—ligand bifunctional heterolytic activation of hydrogen gas under aqueous acidic conditions,[63] with the ultimate goal to be able to directly convert sugars and/or sugar alcohols to alkanes in a single reactor with recycling and reuse of the homogeneous catalyst enabled by phase separation of the reaction solution from the nonpolar products.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Details of the single crystal X-ray structure determination. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*Phone: 519-824-4120 x 53002. E-mail: mschlaf@uoguelph.ca.

Notes

The authors declare no competing financial interest.

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