

Ruthenium-8-quinolinethiolate-phenylterpyridine versus ruthenium-bipyridine-phenyl-terpyridine complexes as homogeneous water and high temperature stable hydrogenation catalysts for biomass-derived substrates



Ryan J. Sullivan^a, Jin Kim^b, Caroline Hoyt^b, Louis A. (Pete) Silks III^b, Marcel Schlaf^{a,*}

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

^b Los Alamos National Laboratory, Biosciences Division, Group B11, MS E529, P.O. Box 1663, Los Alamos, NM 87545, United States

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ABSTRACT

[(4'-Ph-terpy)(bipy)Ru(L)](OTf)_n and [(4'-Ph-terpy)(quS)Ru(L)](OTf)_n (*n* = 0 or 1 depending on the charge of L, L = labile ligand, e.g., H₂O, CH₃CN or OTf, bipy = 2,2'-bipyridine, quS = quinoline-8-thiolate) have been evaluated as catalysts for the hydrogenation of the biomass-derivable C₆-substrates 2,5-dimethylfuran (obtainable from 5-hydroxymethylfurfural) and 2,5-hexanedione (the hydrolysis product of 2,5-dimethylfuran). Operating in aqueous acidic medium at *T* = 175–225 °C the bipy complex is only marginally active, while the quinoline-8-thiolate complex realizes yields of hydrogenated products up to 97% starting from 2,5-hexanedione and up to 66% starting from 2,5-dimethylfuran. The catalyst can also convert the 5-HMF derived acetone 4-(5-methyl-2-furanyl)-3-buten-2-one into 2,5,8-nonatriol, a potentially valuable cross-linker for polymer formulations. On the basis of DFT calculations, the higher activity of the quinoline-8-thiolate complex is proposed to be rooted in a metal–ligand bifunctional mechanism for the heterolytic activation and transfer of dihydrogen to the carbonyl substrate with the hydride-thiol complex [(4'-Ph-terpy)(quSH)Ru(H)]⁺ as the active catalyst.

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1. Introduction

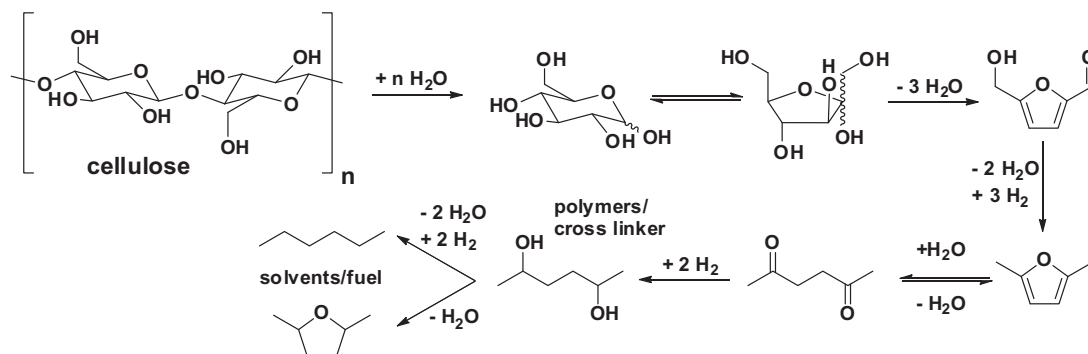
We recently demonstrated the use of the complexes [(4'-Ph-terpy)Ru(H₂O)₃](OTf)₂ (**1**) and [(4'-Ph-terpy)Ir(OTf)₃] (**2**) (4'-Ph-terpy = 4'-phenyl-2,2':6':2''-terpyridine, OTf = trifluoromethanesulfonate) as homogeneous catalysts for the hydrodeoxygenation (HDO) of 2,5-hexanedione (2,5-HD) and 2,5-dimethylfuran (2,5-DMF) to 2,5-hexane-diol (2,5-HDO) and 2,5-dimethyltetrahydrofuran (2,5-DMTHF) in aqueous acidic medium in up to 69% and 80% yield, respectively. Hexane can also be generated by catalyst **1** in up to 10% yield as the total HDO product [1]. These substrates form part of the value chain shown in Scheme 1 leading from glucose (obtainable from starch, sugarcane/beets or, in principle, cellulose) via the key intermediates 5-hydroxymethylfurfural (HMF) and 2,5-DMF to ultimately hexane [2], with the ultimate goal of our research approach being the development of a robust, recyclable and promiscuous homogeneous acid/metal-based binary catalyst system that through an iterative dehydration/hydrogenation

reaction cascade can directly convert sugars or sugar alcohols to value-added HDO products in a single reactor with water as the only side-product. By definition, this goal requires the catalyst used to be stable to both acid and water, as well as the high temperatures needed – empirically *T* > 150 °C – to trigger the acid catalyzed dehydration reactions of the (poly-) alcohol substrates [3,4].

As a result of our study we found that while complexes **1** and **2** are active and stable in aqueous-acidic medium at temperatures up to 175 °C, they decompose to the inactive bis-tridentate [M(4'-Ph-terpy)₂]ⁿ⁺, M = Ru/*n* = 2 or M = Ir/*n* = 3 complexes at *T* > 175 °C, which were recovered from the reaction mixtures and analyzed by MS and single-crystal X-ray analysis. Furthermore, re-addition of fresh substrate to recovered clear-red reaction solutions of **1** showed only marginal catalytic activity, which – in addition to the formation of the bis-tridentate complex – was attributed to catalyst inhibition by irreversible coordination of organic (by-) products in the reaction, possibly dimers formed by aldol condensation or Diels–Alder adducts acting as chelating ligands. As **1** is postulated to operate as an ionic hydrogenation catalyst with water acting as the base deprotonating a transient η²-H₂ ligand it intrinsically generates one equivalent of acid, giving H₃O⁺ as

* Corresponding author. Tel.: +1 519 824 4120x53002.

E-mail address: mschlaf@uoguelph.ca (M. Schlaf).



Scheme 1. Value chain from cellulose to deoxygenated value-added products via the two target substrates 2,5-dimethylfuran and 2,5-hexanedione [1].

the strongest possible solvent-leveled acid in aqueous medium. However, increased concentrations of an acid co-catalyst (HOTf) and/or the use of organic co-solvents also suppressed catalyst activity. The inhibition by additional acid can then be understood by disfavoring this deprotonation step, i.e., higher concentrations of H_3O^+ push the hydrogen activation equilibrium $[\text{M}(\eta^2\text{-H}_2)]^+ + \text{H}_2\text{O} \rightleftharpoons \text{M} - \text{H} + \text{H}_3\text{O}^+$ to the left side, away from the hydride complex as the active reducing agent.

On the basis of the established catalyst decomposition pathway to $[\text{Ru}(4'\text{-Ph-terpy})_2]^{2+}$ and the postulated catalyst inhibition by chelating organic species we hypothesized that blocking two of the three coordination sites in **1** occupied by labile ligands (i.e., H_2O , solvent, substrate, etc.) by adding a second bidentate chelating ligand would prevent the decomposition to the bis-tridentate complexes, while still leaving one coordination site for the heterolytic activation of dihydrogen. An obvious and logical choice for this is the complex $[(4'\text{-Ph-terpy})(\text{bipy})\text{Ru}(\text{L})](\text{OTf})_n$ (**3**) ($n = 1$ or 2 depending on the charge of L, L = labile ligand, e.g., H_2O , CH_3CN or OTf, bipy = 2,2'-bipyridine), as Creutz et al. have previously established that the analogous hydride complex cation $[(\text{terpy})(\text{bipy})\text{Ru}(\text{H})]^+$ can rapidly transfer the hydride ligand to carbonyl acceptors in aqueous medium [5–7]. A further extension is the incorporation of the quinoline-8-thiolate ligand resulting in the complex $[(4'\text{-Ph-terpy})(\text{quS})\text{Ru}(\text{L})](\text{OTf})_n$ (**4**) ($n = 0$ or 1 depending on the charge of L, L = labile ligand, e.g., H_2O , CH_3CN or OTf, quS = quinoline-8-thiolate). For this system we anticipated that the coordination of the soft anionic sulfur donor to the soft ruthenium centre would result in strong binding of the quS ligand in a stable 5-membered metallacycle and lead to an increased electron density on the metal. This in turn should result in a higher hydride donor ability of the corresponding hydride complex $[(4'\text{-Ph-terpy})$

$(\text{quS})\text{Ru}(\text{H})]$ (**4a**) postulated to form under catalytic conditions (H_2 atmosphere and elevated temperature) and also potentially enable a metal–ligand bifunctional heterolytic activation of the transient $\eta^2\text{-H}_2$ ligand into a hydride and coordinated thiol assuming that a *cis* configuration between the hydride and thiol can be structurally realized. This was previously directly observed at low temperature for the complexes $[\text{M}(\eta^2\text{-H}_2)(\text{CO})(\text{quS})(\text{PPh}_3)_2]^+ \rightleftharpoons [\text{M}(\text{H})(\text{CO})(\text{quSH})(\text{PPh}_3)_2]^+$, $\text{M} = \text{Ru}, \text{Os}$ [8,9].

The structural evolution of the catalyst systems and the proposed metal–ligand bifunctional heterolytic activation of dihydrogen by **4** is summarized in Scheme 2.

Here we present the comparative evaluation of complexes **3** and **4** as catalysts for the conversions of the lower half of Scheme 1, i.e., the conversion of 2,5-dimethylfuran and 2,5-hexanedione to deoxygenated/hydrogenated products in aqueous acidic medium.

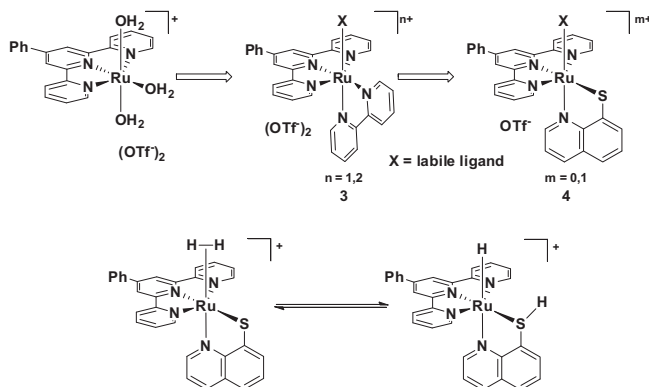
2. Materials and methods

2.1. General

All reagents and solvents were purchased from commercial suppliers and used as received unless otherwise specified. 2,5-HD and 2,5-DMF, 1,4-dioxane and γ -valerolactone were passed through a short plug of neutral Al_2O_3 (Brockmann Activity I) immediately before use to remove any peroxides or stabilizers present and, in the case of 2,5-dimethylfuran, a yellow contaminant of unknown identity (but possibly the 2 + 2 cycloaddition or 4 + 2 Diels–Alder dimer formed under the influence of light). All water used was HPLC grade. NMR spectra were collected on 400 or 600 MHz Bruker Avance spectrometers and calibrated to the residual solvent signals. IR spectra were collected on a Thermo-Fisher Nicolet 4700 FT-IR spectrometer. ESI-MS spectra were collected on Bruker AmaZone SL or Agilent 6540 UHD Accurate Mass Q-TOF spectrometers.

GC analyses were performed on a Varian 3800 with FID detector using a 30 m Stabilwax-da (acid deactivated polyethylene glycol) column. Quantification was carried out using dimethylsulfoxide as the internal standard (100 mmol L^{-1}) and linear 5 level calibration curves. GC–MS analyses were performed on a Varian Saturn 2000 GC/MS running in CI mode and using the same column and temperature programming used for quantification. Reaction products were identified by comparison to the retention times of authentic samples or by analysis of the mass spectra when authentic samples were unavailable (C_9 HDO products, see SI). Head space gas analyses were carried out on a SRI 8610 micro-GC fitted with a TCD detector against authentic gas samples (1000 ppm of $\text{C}_1\text{--C}_6$ alkanes and alkenes in helium, GRACE Davison Discovery Sciences).

All hydrogenation experiments employed industrial grade H_2 gas (99.995%) and were carried out in an Autoclave Engineers MiniReactor with a 50 mL 316SS reactor vessel and impeller. At a



Scheme 2. Structural evolution of complexes to be tested as catalysts and proposed metal–ligand bifunctional heterolytic activation of dihydrogen by the quinoline-8-thiol complex.

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