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[Cp*Ru(CO)₂]₂-Catalyzed Hydrodeoxygenation and Hydrocracking of Diols and Epoxides

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Supporting Information

ABSTRACT: The hydrogenolysis of glycols to hydrocarbons is a reaction of potential value for the production of chemicals and fuels from biomass-derived polyols. We find that $[Cp*Ru(CO)_2]_2$ (Cp* = 1,2,3,4,5-pentamethylcyclopentadienyl) catalyzes the hydrogenolysis of glycols to alkanes and of epoxides to alkanes/alkenes by molecular hydrogen at 170–200 °C and 4–27 atm; the product yields range from moderate to excellent. Moreover, we also established a



novel process that produces alkanes with a lower number of carbons from glycols: e.g., toluene from 1-phenyl-1,2-ethanediol.

The development of new, effective processes for the preparation of reduced-oxygen-content products from polyols and carbohydrates is an important step toward the practical utilization of these renewable resources to produce fuels and value-added chemicals.^{1,2} Metal-catalyzed deoxygenation of glycols and epoxides is much less developed than the reverse oxygenation reactions, epoxidation and dihydroxylation of alkenes, which have been extensively applied in organic synthesis and industry.³ Recently hydrodehydroxylation (hydrogenolysis) of polyols has been reported employing various heterogeneous catalyst systems, usually resulting in removal of one hydroxyl group, in some cases with significant regioselectivity.⁴ Homogeneous catalytic monodehydroxylation of glycols has also been recently achieved by Bullock and Fagan, who found that $\{[Cp*Ru(CO)_2]_2(\mu-H)\}^+OTf^-$ is a precatalyst for the selective hydrogenolysis of 1,2-propanediol to 1propanol (Scheme 1).⁵ Schlaf and co-workers reported the

Scheme 1



total hydrodeoxygenation of glycerol and 1,2-hexanediol to saturated hydrocarbons by $[LRu(H_2O)_x(diimine)]^{2+}$ and $[Cp^*Ru(OH_2)(N-N)]^+$.

Deoxydehydration (DODH) reactions, which remove two adjacent hydroxyl groups, are attractive for producing unsaturated hydrocarbons (Scheme 1). There are several multistep stoichiometric methods for glycol DODH,⁷ but single-step⁸ and catalytic methods are few, and the latter are almost entirely based on oxo-rhenium complexes. Metal-catalyzed DODH reactions of glycols were first discovered by Andrews and Cook⁹ using PPh₃ as the reductant and Cp*ReO₃ as the catalyst. Experimental and computational studies by

Gable and co-workers provided mechanistic insights into the catalytic process involving LReO₃ complexes, especially the olefin-producing metallo-glycolate fragmentation step.¹⁰ Recently, Abu-Omar and co-workers achieved the deoxygenation of epoxides and deoxydehydration of glycols to alkenes and alkanes with MeReO₃ as catalyst and the more practical reductant H₂.¹¹ An Au–C catalyst has also been found to be effective for the epoxide to alkene hydrogenolysis under mild conditions.¹² Contemporaneously, the Nicholas group reported sulfite-driven glycol DODH to olefins catalyzed by MeReO₃ and Z⁺ReO₄⁻ and examined its scope and catalytic pathway (Scheme 1).¹³ Finally, Bergman et al. disclosed that Re₂(CO)₁₀ (in air) catalyzes glycol DODH with secondary alcohols as reductants.¹⁴

In view of the efficacy of ruthenium catalysts in hydrogenation and hydrogenolysis reactions,¹⁵ we initiated a project seeking the development of new DODH reaction systems that would utilize readily available catalysts and the practical reductant H₂. Hydrogen is a valuable reductant due to its low cost and low toxicity, its strong reducing potential, and its production of water as a benign byproduct. In this report we reveal the first examples of glycol hydro-didehydroxylation and epoxide deoxygenation catalyzed by a low-valent ruthenium complex. Also uncovered is a novel C–C hydrogenolysis (cracking) process that produces reduced-carbon-number alkanes.

We began our investigation with 1-phenyl-1,2-ethanediol as a representative glycol substrate (Scheme 2; R = Ph) and readily available $[Cp*Ru(CO)_2]_2^{16}$ (1; $Cp* = \eta^5-C_5Me_5$) as precatalyst. The reaction between the glycol and H₂ (4 atm) was first conducted in benzene with 10 mol % of $[Cp*Ru(CO)_2]_2$ in a steel autoclave at 170 °C. GC and GC-MS analysis of the reaction mixture over 30 h indicated the gradual and nearly simultaneous formation of ethylbenzene and,

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Scheme 2



remarkably, toluene (ca. 2:1), with one less carbon than the starting glycol (entry 1, Table 1);¹⁷ neither styrene nor monoalcohols were detected.

Table 1. Glycol and Epoxide Deoxygenation by $H_2/$ [Cp*Ru(CO)₂]₂^{*a*}

entry	substrate	major products	yield (%)	P _{H2} (atm)	time (h)
	Ph	$\bigcirc \frown$	40		
1	ОН	$\tilde{\bigcirc}$	31	4	30
2	C ₄ H ₁₁ OH	C ₄ H ₁₁	70	4	8
3	С ₆ Н ₁₃ ОН	C ₆ H ₁₃	4	4	48
4		C ₆ H ₁₃ C ₆ H ₁₃ -CH ₃	10 16	20	23
5		C ₆ H ₁₃ C ₆ H ₁₃ -CH ₃	46 49	6 (200 °C)	80
6	С ₁₂ Н ₂₅ Он	C ₁₂ H ₂₅	3		
		C ₁₁ H ₂₃	4	26 (200 °C)	47
		C ₉ H ₁₉	4		
		C ₈ H ₁₇	4		
	Qн	C ₇ H ₁₅	5		
7	ОН	\bigcirc	56	6	49
ō	\bigcup^{\wedge_0}		68	4	23
8			25		
9	\bigcirc	\bigcirc	44	4	8
10	\sim	$\sim \sim$	70	6	8
11	но он	$\langle \rangle$	12	6	72

"Reaction conditions: 0.14 mmol of glycol or epoxide in benzene (6–10 mL), 0.014 mmol of $[Cp*Ru(CO)_2]_2$, 170 °C, 4 atm or as indicated in the table. Product yields were determined by GC and GC-MS with *n*-dodecane as internal standard.

The hydrogenolysis reactions promoted by **1** of representative aliphatic glycols, better models for biomass-derived polyols, were also examined to determine the products, selectivity, and efficiency (Table 1). When it was subjected to the standard reaction conditions (170 °C, 4 atm of H₂, 10 mol % **1**), 1,2hexanediol produced hexane in 70% yield (entry 2) as the only detected product.¹⁸ The reaction of 1,2-octanediol under the same conditions was sluggish and produced only 4% octane in 48 h (entry 3). At 200 °C with a hydrogen pressure of 6 atm, 10% octane and 16% of the cracking product heptane were produced (entry 4); at 20 atm H₂ and 170 °C, the octane and heptane yields increased substantially to 46% and 49%, respectively (entry 5). The long-chain 1,2-tetradecanediol was even less reactive, with no hydrocarbons being detected at 200 °C and 6 atm H₂ in 48 h. However, when the reaction was conducted at 200 °C with 26 atm of H₂, tetradecane (3%) and truncated linear alkanes were produced in low yield: i.e., nonane (4%), decane (4%), undecane (5%), and tridecane (4%) after 47 h (Table 1, entry 6). In contrast, the cyclic glycol cis-1,2-cyclohexanediol was converted to cyclohexene (56%), with no detectable alkane or cracking products (entry 7). We also investigated the reaction of 1,4-anhydroerythritol (a biomass-derived glycol). When 1,4-anhydroerythritol was hydrogenated by 1 under our reaction conditions, it afforded THF in modest yield (12%) (entry 11).

The hydrodeoxygenation of epoxides is also catalyzed by 1. Thus, styrene oxide was converted to ethylbenzene (68%) and toluene (25%) at 170 °C/4 atm of H₂ (Table 1, entry 8), the same products as formed from the corresponding glycol. Similarly, cyclohexene oxide (entry 9), like the corresponding diol (entry 7), afforded the alkene cyclohexene in 44% yield after 8 h (entry 9), again with no alkane detected. 1,2-Hexene oxide (like the corresponding glycol) was converted to *n*-hexane in good yield (70%, entry 10).

The complete hydrodeoxygenation and hydrocracking reactions found in the glycol and epoxide reactions catalyzed by 1 have little precedent in homogeneous Ru catalysis. Aside from the glycol to alkane hydrogenation catalyzed by $[LRu(H_2O)_x(diimine)]^{2+}$ complexes,⁵ the hydrocracking of aldoses catalyzed by $H_2Ru(PMe_3)_4$ under basic conditions has been reported,¹⁹ but this reaction likely involves base-promoted retroaldol C–C cleavage of the β -hydroxy aldehyde, a pathway not available to saturated polyols. In fact, we can find no reports of complex 1 serving as a hydrogenation precatalyst for any class of substrates.

Although the catalytic pathways for the hydrodehydroxylation, deoxygenation, and hydrocracking reactions promoted by 1 are presently unclear, a few observations and conclusions can be noted at this time. The similar product profiles in both the glycol and epoxide hydrogenations are suggestive of the involvement of common intermediates. Regarding possible organic intermediates in the catalytic process leading to alkanes and cracking products, such as monoalcohols or olefins, we have found that both styrene and the mono-ol PhCH₂CH₂OH are completely converted to ethylbenzene (80%) and a small amount (4%) of toluene within 6 h under the standard catalytic reaction conditions. Hence, while these may be hydrogenation intermediates from the glycol, they are unlikely to be primary precursors to the hydrocracking products (e.g., via olefin metathesis/hydrogenation). With respect to intervening Ru complexes, the preponderance of alkane products (and absence of monoalcohols) together with the observed reduced-carbon alkanes in the reactions promoted by 1 appear to exclude the active involvement of $[Cp^*Ru(CO)_2(\mu-H)]_2^+$ or $[Cp^*Ru (CO)_2(H_2)]^+$, implicated in the Bullock-Fagan studies of glycol monohydrogenolysis.⁶ Under neutral conditions more likely ruthenium hydride intermediates are $Cp*Ru(CO)_2H^{20}$ or $[Cp^*Ru(\mu-H_4)RuCp^*]^{21}$ Since a sparingly soluble black material was present at the conclusion of the reactions, we sought to determine its role in the catalytic process. The material was largely soluble in DMSO, but its IR and ¹H NMR

spectra were inconclusive.²² Importantly, the material was itself catalytically inactive, as was ruthenium powder, indicating the former to be a catalytic dead end and suggesting that the active catalyst is homogeneous.

The production of both alkanes and truncated alkanes in the present system is most simply explained by the intermediacy of a metalloglycolate species (Scheme 3), which could undergo

Scheme 3. Possible Catalytic Pathway for Hydrogenolysis and Hydrocracking



alternative redox fragmentations either to $olefin^{10}$ (which is subsequently hydrogenated) or to reduced-carbon aldehydes²³ (which also are then reduced²⁴).²⁵ Both mono- and bimetallic (bridged) glycolate species (**A** and **B**) can be envisioned, the latter being precedented by $[Cp*Ru(L)(\mu-OR)_2]_2^{26}$

In conclusion, we have disclosed here a new system for glycol and epoxide conversion to alkanes which employs H_2 as reductant and $[Cp*Ru(CO)_2]_2$ as a precatalyst. A rare hydrocracking reaction is also promoted by 1. Future investigations will focus on elucidating the important catalytic species and mechanisms of these reactions and their application to biomass-derived polyols.

ASSOCIATED CONTENT

S Supporting Information

Text and figures giving experimental procedures and representative gas chromatograms. This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) GC analyses of aliquots provide yield of ethyl benzene/toluene, time: 20/10%, 8 h; 26/16%, 23 h; 40/31%, 30 h.

(18) The potential cracking product, pentane, would not be detectable because of its short GC retention time.

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(22) The black precipitate did not melt below 120 °C and almost entirely dissolved in DMSO (10 mg/mL). The decomposition temperature of $[Cp*Ru(CO)_2]_2$ is 297 °C;¹⁶ therefore, the black material does not likely result from simple thermal decomposition of 1. Its IR spectrum (KBr) showed no significant peaks in the 1800–2100 cm⁻¹ M–CO region; its ¹H NMR spectrum showed broad peaks at 1.091, 4.96, 2.5, 2.96, 5.9, and 7.4 ppm. When styrenediol (20 mg) and 15 mg of the black material were subjected to the usual reaction conditions (24 h, 4 atm of H₂), only the unreacted diol was detected. The same result was obtained when the diol (20 mg) and Ru powder (1.4 mg) were heated together under hydrogen.

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