Catalytic Deoxygenation of 1,2-Propanediol to Give *n*-Propanol

Marcel Schlaf,^{a,d} Prasenjit Ghosh,^{a,e} Paul J. Fagan,^c Elisabeth Hauptman,^c and R. Morris Bullock^{a,b,*}

^b Chemical Sciences Division, Pacific Northwest National Laboratory, P.O. Box 999, K2-57, Richland, WA 99352, USA Fax: (+1)-509-375-6660; e-mail: morris.bullock@pnl.gov

^e Current address: Department of Chemistry, Indian Institute of Technology Bombay, Powai, Mumbai 400 076, India

Received: November 5, 2008; Revised: February 24, 2009; Published online: March 20, 2009

Abstract: Deoxygenation of 1,2-propanediol (1.0M in sulfolane) catalyzed by bis(dicarbonyl)(μ -hydrido)(pentamethylcyclopentadiene)ruthenium trifluoromethanesulfonate ({[Cp*Ru(CO)₂]₂(μ -H)}+OTf⁻) (0.5 mol%) at 110 °C under hydrogen (750 psi) in the presence of trifluoromethanesulfonic acid (HOTf) (60 mM) gives *n*-propanol as the major product, indicating high selectivity for deoxygenation of the internal hydroxy group over the terminal hydroxy group of the diol. The deoxygenation of 1,2-propanediol is strongly influenced by the concentration of acid, giving faster rates and proceeding to higher conversions as the concentration of HOTf is increased. Propionaldehyde was observed as an intermediate, being

Introduction

Carbohydrates and other biomass-derived compounds are abundant, renewable resources that offer a very appealing alternative to the use of petroleum-based feedstocks.^[1] The development of efficient reactions to convert biomass-derived resources into chemicals or fuels on a large scale requires the discovery of new catalytic reactions that can carry out the transformations required for the effective use of this resource. The problem of converting biomass-derived materials into useful chemicals or fuels can, in some ways, be viewed as the *opposite* challenge faced in efforts to convert readily available hydrocarbons (e.g., methane) into fuels. Conversion of hydrocarbons to fuels requires reactions that will selectively introduce functionalization. Sugars and related compounds, in contrast, are "overfunctionalized,"^[2,3] with an OH group on nearly every carbon, so new reactions are needed that will selectively remove some of the oxygen-containing functionalities.

formed through acid-catalyzed dehydration of 1,2propanediol. This aldehyde is hydrogenated to *n*propanol through an ionic pathway involving protonation of the aldehyde, followed by hydride transfer from the neutral hydride, dicarbonyl(pentamethylcyclopentadiene)ruthenium hydride [Cp*Ru(CO)₂H]. The proposed mechanism for the deoxygenation/hydrogenation reaction involves formation of a highly acidic dihydrogen complex [Cp*Ru(CO)₂(η^2 -H₂)]⁺ OTf⁻.

Keywords: deoxygenation; dihydrogen complexes; heterolytic reaction; homogeneous catalysis; metal hydrides; ruthenium

Several studies of homogeneous as well as supported heterogeneous metal catalysts have been reported for deoxygenation reactions of diols or glycerol. Dicationic, mononuclear complexes such as [cis-Ru(6,6'- $Cl_2-2,2'-bipy)_2(OH_2)_2]^{+2}$ catalyze the deoxygenation of diols: alcohols were formed in most cases but in some cases further hydrogenation to alkanes was observed.^[4,5] 1,3-Propanediol is one of the components used in the manufacture of textile fibers with the tradenames Sorona[®] (DuPont) and Corterra[®] (Shell). If chemoselective deoxygenation of glycerol to 1,3propanediol could be achieved, this could be economically and environmentally attractive, as there is a large oversupply of glycerol generated as the by-product of bio-diesel production. Glycerol was converted to 1,3-propanediol and 1,2-propanediol at 200°C under CO/H₂ (4600 psi) using Rh(CO)₂(acac) and H₂WO₄ as the catalyst precursors.^[6] Reaction of glycerol with (CO)₄RuI₂ with added HI under H₂/CO pressure produced n-propanol and several ether products.^[7] Tomishige and co-workers discovered several supported Ru catalysts for the hydrogenolysis of glyc-



^a Chemistry Department, Brookhaven National Laboratory, Upton, New York 11973-5000, USA

^c Central Research and Development, E. I. DuPont de Nemours & Co. Inc., Experimental Station, Wilmington, Delaware 19880, USA

^d Current address: Department of Chemistry, University of Guelph, Guelph, ON, Canada N1G 2W1

erol.^[8] The major product was 1,2-propanediol, with smaller amounts of 1,3-propanediol, *n*-propanol and isopropyl alcohol also being observed. Drent and Jager patented a palladium catalyst, (diphosphine)Pd- $(OAc)_2$, for the deoxygenation of glycerol at 175 °C under CO/H₂ in the presence of added acids; they obtained 1,3-propanediol, 1,2-propanediol and *n*-propanol in addition to acrolein.^[9] Supported catalysts of Ru, Pt and Cu were reported for the catalytic hydrogenolysis of glycerol; they generally favor the formation of 1,2-propanediol.^[10] A Pt on TiO₂ catalyst was reported to hydrogenate hydroxypropionaldehyde (available from the dehydration of glycerol) to 1,3-propanediol with good selectivity.^[11]

As shown in generalized form in Eq. (1), one approach to the deoxygenation of diols or polyols is sequential treatment with H^+ and H^- sources, releasing

$$\begin{array}{c} OH \\ R \\ \hline R \\ \hline R' \\ \hline -H_2O \\ \hline R \\ \hline R' \\ \hline H^{-} \\ \hline H^{-} \\ \hline H^{-} \\ \hline R \\ \hline R' \\ \hline R'$$

 $\mathsf{R}, \mathsf{R}' = \mathsf{CH}_{3}, \mathsf{CH}_2\mathsf{OH}, \ldots$

water and formally resulting in the conversion of OH to H.^[12] A homogeneous metal catalyst capable of heterolytic cleavage of $H_2^{[13]}$ could potentially enable use of H_2 as the source of both H^+ and H^- . Metal complexes with dihydrogen ligands can function as acids, and have been shown to exhibit a wide range of acidities.^[13,14] Proton transfer from a cationic dihydrogen complex $[M(\eta^2-H_2)]^+$ would produce a neutral metal hydride (MH). From studies of the kinetics of hydride transfer to Ph_3C^+ , we have shown that neutral metal hydrides exhibit more than six orders of magnitude of range in their rate constants of kinetic hydricity.^[15,16] Extensive studies of the thermodynamic hydricity of metal hydride complexes by DuBois and coworkers has shown that the range of thermodynamic hydricity of metal hydrides spans more than 40 kcalmol⁻¹.^[17] Achieving catalytic deoxygenation of diols would require that proton and hydride transfer steps occur, followed by metal catalyst regeneration through heterolytic activation of H₂ to "H⁺" (as a Brønsted acid) and "H⁻" (as a metal hydride).

Stoichiometric ionic hydrogenations of ketones can be accomplished under mild conditions by addition of a strong acid (HOTf; $OTf=OSO_2CF_3$) to solutions containing ketones and metal hydrides.^[18] These reactions document that transition metal hydrides can function as hydride donors in the presence of a strong acid. As shown in generalized form in Eq. (2), these proton and hydride transfer reactions are related to those outlined for the deoxygenation of diols in Eq. (1). Similar reactions were found for ionic hydrogena-



tion of alkenes,^[19] α , β -unsaturated ketones,^[20] and acyl chlorides,^[20] as well as conversion of acetals to ethers.^[21] Catalytic ionic hydrogenations^[22] were developed using molybdenum and tungsten complexes, in which both the proton as well as the hydride were delivered from a metal hydride bond, with regeneration of the metal hydrides being carried out through reaction with H₂.^[23]

These reactivity patterns suggest that deoxygenation of diols might be possible by using acidic and hydridic reactions catalyzed by organometallic complexes. Many ruthenium complexes react with H₂ and elicit heterolytic cleavage reactions of H₂ that have been used in a variety of catalytic hydrogenations.^[24] We reported in a communication that $\{[Cp*Ru(CO)_2]_2\}$ $(\mu-H)$ ⁺ OTf⁻ under H₂ in the presence of acid catalyzes the deoxygenation of 1,2-propanediol to produce *n*-propanol.^[12] This paper reports a complete mechanistic study of this reaction, including evidence that the reaction involves the heterolytic activation of H₂ gas through a highly acidic dihydrogen complex of ruthenium. Intermediates observed in the catalytic reaction are subjected to the reaction conditions to give a better understanding of the role of the ruthenium catalyst and the added acid.

Results and Discussion

Consideration of possible molecular catalysts for the catalytic deoxygenation of diols as outlined in Eq. (1) suggests the need for an acidic metal dihydrogen (or dihydride) complex. Heinekey and co-workers have shown that the ruthenium hydride complex Cp*Ru- $(CO)_{2}H$ reacts with HBF₄·Et₂O at low temperature to dihydrogen complex generate the cationic $[Cp*Ru(CO)_2(\eta^2-H_2)]^+$ BF₄^{-.[25]} This complex is highly acidic, as indicated by its deprotonation by Et₂O to give Cp*Ru(CO)₂H. Not only did the cationic complex $[Cp^*Ru(CO)_2(\eta^2-H_2)]^+$ appear to be ideal for deoxygenation due to its high acidity, but in addition, our studies of the hydricity of the neutral hydride Cp*Ru(CO)₂H showed that it was an excellent hydride donor.^[16] Studies of the kinetics of hydride transfer from $Cp^*Ru(CO)_2H$ to $Ph_3C^+BF_4^-$ showed that the rate constant for hydride transfer in CH₂Cl₂ at 25 °C was $k > 10^6 \text{ M}^{-1} \text{s}^{-1}$.

The potential viability of catalytic reactions using $[Cp*Ru(CO)_2(\eta^2-H_2)]^+$ as the proton donor and $Cp*Ru(CO)_2H$ as the hydride donor was, however, not obvious, since Heinekey had found^[25] that

 $[Cp*Ru(CO)_2(\eta^2-H_2)]^+ BF_4^-$ decomposes at temperatures above -38 °C to form the bridging hydride complex $\{[Cp*Ru(CO)_2]_2(\mu-H)\}^+ BF_4^-$, a reaction that releases H_2 and $H^+ [Eq. (3)]$.^[26]

$$2 \left[Cp^{*}(CO)_{2}Ru - \begin{matrix} H \\ H \end{matrix} \right]^{\bigoplus} BF_{4} \stackrel{\bigcirc}{\longrightarrow} \xrightarrow{-38 \ ^{\circ}C} \xrightarrow{(3)}$$

$$\begin{bmatrix} Cp^{*}(CO)_{2}Ru & H \\ H \\ Ru(CO)_{2}Cp^{*} \end{bmatrix} \stackrel{\bigoplus}{}_{BF_{4}} \stackrel{\bigoplus}{}_{+} H_{2} + HBF_{4} \cdot Et_{2}O$$

Study of {[Cp*Ru(CO)₂]₂(µ-H)}⁺OTf⁻ Under H₂

Although the dihydrogen complex $[Cp*Ru(CO)_2(\eta^2-H_2)]^+$ had been shown to decompose at low temperatures, it would be accessible from $\{[Cp*Ru(CO)_2]_2(\mu-H)\}^+$ if suitable conditions could be found to reverse the reaction shown in Eq. (3). A pathway for the formation of the acidic dihydrogen complex $[Cp*Ru(CO)_2(\eta^2-H_2)]^+$ OTf⁻ from $\{[Cp*Ru(CO)_2]_2(\mu-H)\}^+$ OTf⁻ under catalytic conditions, in the presence of HOTf, is shown in Scheme 1. In an attempt to di-





rectly observe the dihydrogen complex involved in the equilibria postulated in Scheme 1, variable temperature ¹H NMR experiments were carried out under H₂. In one experiment a 50 mM solution of $\{[Cp*Ru(CO)_2]_2(\mu-H)\}^+$ OTf⁻ in CD₂Cl₂ was employed, and in another experiment an additional 0.5 equivalent of HOTf was added to the solution. In both cases the spectra showed a small linear temperature dependence of the chemical shift of the bridging hydride ligand of $\{[Cp*Ru(CO)_2]_2(\mu-H)\}^+$ OTf⁻ over a temperature range from 25°C ($\delta = -17.75$) to 85°C ($\delta = -18.15$). No dihydrogen complex or any other new hydride resonances were observed, even when the experiment was carried out in a sapphire NMR tube at pressures of 50 atm H₂. The temperature dependence of the hydride shift is reversible and independent of the presence or absence of added HOTf. The small range of the chemical shift, as well as its direction (upfield with increasing temperature, that is, away from the shift ($\delta = -5.7$) of the postulated active catalyst [Cp*Ru(CO)₂(η^2 -H₂)]⁺ OTf⁻) suggests that it is not due to an intermolecular chemical exchange reaction, but is merely the temperature dependence of the chemical shift.

Even though neither the dihydrogen complex nor any other reactive intermediate could be directly observed in the variable temperature NMR experiment, evidence supporting the accessibility of $[Cp*Ru(CO)_2$ $(\eta^2-H_2)]^+$ under H_2 came from experiments on $\{[Cp*Ru(CO)_2]_2(\mu-H)\}^+$ OTf⁻ conducted under D_2 . When a solution of $\{[Cp*Ru(CO)_2]_2(\mu-H)\}^+$ OTf⁻ (40 mM) in CH_2Cl_2 was heated at 100 °C under of D_2 (4 atmospheres), incorporation of deuterium occurred, as evidenced by the formation of a bridging deuteride complex, $\{[Cp*Ru(CO)_2]_2(\mu-D)\}^+$ OTf⁻, observed by ²H NMR spectroscopy after 30 min (Scheme 2). The bridging deuteride (μ -D) resonance



appeared at $\delta = -17.78$ in the ²H NMR spectrum, essentially the same chemical shift as that of the bridging hydride complex ($\delta = -17.79$) in the ¹H NMR spectrum. A similar experiment in CD₂Cl₂ solution was monitored by ¹H NMR and showed a triplet at $\delta = 4.58$ (J = 45 Hz), indicative of HD gas. These experiments show that {[Cp*Ru(CO)₂]₂(µ-H)}+ under H₂ is in equilibrium with the cationic dihydrogen complex [Cp*Ru(CO)₂(η^2 -H₂)]⁺ (Scheme 2). Under the experimental conditions for catalysis described below, the neutral hydride, Cp*Ru(CO)₂H, would be converted to the cationic dihydrogen complex [Cp*Ru(CO)₂(η^2 -H₂)]⁺, indicating that the reaction shown as a decomposition in Eq. (3) is actually a re-

versible equilibrium in the presence of H^+ , heat, and sufficient pressure of H_2 .

Initial Experiments on Catalytic Deoxygenation of 1,2-Propanediol and Choice of Solvent

Initial experiments on the deoxygenation of 1,2-propanediol catalyzed by $\{[Cp*Ru(CO)_2]_2(\mu-H)\}^+$ OTfwere carried out in NMR tubes in CD₂Cl₂ under H₂ (4 atm). It was established that 1,2-propanediol was slowly catalytically deoxygenated to give *n*-propanol at temperatures above 85 °C with added HOTf. Experiments in NMR tubes were convenient to examine the reaction under different conditions, but it became clear that the complexity of products formed made NMR unsuitable for quantitative determination of the reaction products. Subsequent experiments required monitoring of the reaction by quantitative gas chromatography (GC) with an internal standard, to provide an accurate determination of organic intermediates and products.

One of the long-term goals of this work is the development of catalytic ionic deoxygenations/hydrogenations for the conversion of naturally abundant polyols and monosaccharides to chemical feedstocks with reduced oxygen content. An important consideration is the choice of a suitable solvent to dissolve both diols or polyols (which have high solubility in water) and organometallic catalysts (which are normally used in organic solvents of lower polarity). Seminal work by Andrews has shown that NMP (N-methylpyrrolidinone) can be used as the solvent in the decarbonylation of carbohydrates with ruthenium or rhodium catalysts.^[27] We were concerned that the basicity of NMP, even if rather low, might be a drawback for ionic deoxygenation reactions under acidic conditions. An ideal solvent should have high thermal stability in the presence of acids and high polarity to dissolve the diol and promote ionic reactions (proton and hydride transfers). It should be non-coordinating, or at most weakly coordinating, so that it does not compete with H₂ binding to the metal catalyst. Sulfolane (tetramethylenesulfone, bp 285 °C, dielectric constant $\varepsilon = 43.3$) fulfills all these conditions. An initial small-scale reaction under conditions comparable to those in CD₂Cl₂ established that the catalytic system is indeed active in sulfolane solvent [Eq. (4)], generating *n*-propanol



and di-*n*-propyl ether along with other intermediates described in detail below. Subsequent studies on these deoxygenation reactions were carried out in sulfolane.

Quantitative Study of the Catalytic Deoxygenation of 1,2-Propanediol

Figure 1 shows the products formed in the deoxygenation of 1,2-propanediol (1.0M) in sulfolane catalyzed by 5 mM {[Cp*Ru(CO)₂]₂(μ -H)}⁺ OTf⁻ (0.5 mol% catalyst loading) with 60 mM added HOTf (i.e., 6 molar equivalents of acid per Ru). Acid-catalyzed dehydration of 1,2-propanediol would produce propionaldehyde, as shown in Eq. (5). Catalytic hydrogena-

$$\begin{array}{c} OH \\ -H_2O \end{array} \qquad \begin{array}{c} Cat. H^* \\ H \end{array}$$
 (5)

tion of the C=O bond of the aldehyde generates the observed product, n-propanol [Eq. (6)]. Mechanistic

$$\begin{array}{c} & \quad \{ [Cp^{^{\bullet}}Ru(CO)_{2}]_{2}(\mu-H) \}^{+}OTf^{-} \\ & \quad (catalyst) \end{array}$$

considerations will be discussed in more detail in a later section. Condensation of two molecules of n-



Figure 1. Time-dependence of the major products formed from the deoxygenation of 1,2-propanediol (1.0M in sulfolane with 0.1M toluene as an internal standard) at 110 °C. Initial conditions were 5 mM { $[Cp*Ru(CO)_2]_2(\mu-H)$ }⁺ OTf⁻, 60 mM HOTf under 750 psi H₂ (before heating).

792

asc.wiley-vch.de

© 2009 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

propanol gives di-*n*-propyl ether. Propylene glycol propyl ether (two isomers as shown in Figure 1) is generated from acid-catalyzed cross-condensation of the product *n*-propanol with the starting material diol [Eq. (7)].

$$\begin{array}{c} OH \\ \downarrow \\ OH \end{array}^{+} OH \xrightarrow{\text{cat. }H^{+}} O \\ \hline -H_{2}O \end{array} \xrightarrow{O} OH \end{array} + \begin{array}{c} OH \\ \downarrow \\ OH \end{array}$$
(7)

The concentration of 1,2-propanediol had dropped from its initial value of 1.0 M to 82 mM (92% conversion) after 30 h, as determined by quantitative GC. The concentration of *n*-PrOH was 538 mM (54%, 108 turnovers based on the bimetallic Ru catalyst precursor), that of *n*-Pr₂O was 74 mM, and 110 mM of propylene glycol propyl ether was detected. Defining the products as [deoxygenation products] = [*n*-propanol] + 2 [di-*n*-propyl ether] + [propylene glycol propyl ether] gives a total of 796 mM, corresponding to an 80% yield of deoxygenation and hydrogenation products, accounting for about 160 turnovers of the catalyst.

Careful examination of the reaction mixture by GC revealed additional observable intermediates (not shown in Figure 1) that provide further information about the reaction mechanism. In addition to the observation of propionaldehyde (maximum concentration observed 38 mM), small amounts of the acetal, *cis/trans*-2-ethyl-4-methyl-1,3-dioxolane [Eq. (8)] were

observed (maximum concentration observed 16 mM). This substituted dioxolane is formed under the catalytic reaction conditions through acid-catalyzed condensation of 1,2-propanediol with propionaldehyde, and its identity was verified [two isomers as shown in Eq. (8)] by independent synthesis using this route. An alternative mechanism for production of propylene glycol propyl ether would be through hydrogenation of the acetal, as outlined in Eq. (9). A related reac-



tion of *n*-propanol with propionaldehyde to give a hemiacetal, followed by deoxygenation of the hemiacetal, would provide an alternate mechanism to generate di-*n*-propyl ether.

The regioselectivity of the deoxygenation is excellent, owing to the high preference for dehydration at the secondary OH of the diol rather than the less reactive primary OH. An upper limit of about 0.5%yield is estimated for the alternative product isopropyl alcohol. The absence of detectable isopropyl alcohol does not entirely preclude its formation, as it would be more reactive under the reaction conditions. We did not, however, detect any products derived from isopropyl alcohol, such as di(isopropyl) ether, the mixed ether, *n*-propyl isopropyl ether, or isopropyl triflate.

The color of the samples removed from the reaction solution progresses from the pale yellow color of $\{[Cp*Ru(CO)_2]_2(\mu-H)\}^+$ OTf⁻ to the orange color of $[Cp*Ru(CO)(\mu-CO)]_2$ as the catalyst activity decreases, indicating that the overall rate is dependent on the amount of water present in the reaction mixture. The catalyst is deactivated through deprotonation by water generated in the reaction [Eq. (10)]. Addition



of water to a yellow solution of $\{[Cp*Ru(CO)_2]_2(\mu-H)\}^+ OTf^-$ in CD_2Cl_2 leads to deprotonation, and precipitation of the neutral dimer $[Cp*Ru(CO)(\mu-CO)]_2$ as an orange solid. Deprotonation of $\{[Cp*Ru(CO)_2]_2$ $(\mu-H)\}^+ OTf^-$ was also observed in DMSO- d_6 containing small amounts of water. Even with no acid added, reaction of H₂ with $\{[Cp*Ru(CO)_2]_2(\mu-H)\}^+ OTf^-$ generates one equivalent of highly acidic dihydrogen complex $[Cp*Ru(CO)_2(\eta^2-H_2)]^+ OTf^-$ (Scheme 1), but the catalytic reactions proceed faster, and to much higher conversions, in the presence of added acid. We therefore studied catalyst activity as a function of acid concentration, as described below.

Dependence on Acid Concentration

The deoxygenation of 1,2-propanediol (1.0M) catalyzed by $\{[Cp*Ru(CO)_2]_2(\mu-H)\}^+$ OTf⁻ was studied using variable amounts of added HOTf (Figure 2).

Reaction of {[Cp*Ru(CO)₂]₂(μ -H)}⁺ OTf⁻ with H₂ produces 0.5 equivalent of the acidic dihydrogen complex [Cp*Ru(CO)₂(η^2 -H₂)]⁻ OTf⁻, but additional acid is needed to obtain higher turnovers of the catalyst. This is because the water formed in the deoxygenation, together with any formed through the condensa-



Figure 2. Deoxygenation products as a function of added HOTf for catalytic deoxygenation of 1,2-propanediol (1.0 M in sulfolane) at 110 °C. Initial conditions were 5 mM $\{[Cp*Ru(CO)_2]_2(\mu-H)\}^+$ OTf⁻, under 750 psi H₂ (before heating), with [HOTf] as labeled in the figure.

tion reactions [Eqs. (7) and (8)] deprotonates the catalyst precursor $\{[Cp*Ru(CO)_2]_2(\mu-H)\}^+$ OTf⁻ to give the dimer $[Cp*Ru(CO)(\mu-CO)]_2$ that does not react with H₂. In addition to promoting the acid-catalyzed pathways for the organic transformations [e.g., Eqs. (5), (7), (8)] additional acid thus maintains a higher precursor concentration of the catalyst ${[Cp*Ru(CO)_2]_2(\mu-H)}^+$ OTf⁻ by converting the water to H_3O^+ [Eq. (10)]. Thus little reactivity is observed in the absence of added acid, and the rate of the reaction is much faster with larger acid concentrations; at the highest acid concentration (60 mM) shown in Figure 2, about 400 mM of deoxygenation products were detected after 1.4 h, corresponding to an initial turnover frequency of about 28 h^{-1} . As can be clearly seen from Figure 2, the overall conversion achieved is also strongly dependent on the acid concentration, with the run carried out with only 6 mM added HOTf leveling off at about 210 mM of deoxygenation products.

Dependence on Temperature

Most of the catalytic experiments reported here were carried out at 110 °C. An experiment at 85 °C gave much slower rates of catalysis, suggesting that this temperature may be close to the lowest one at which the equilibrium that generates the postulated catalytically active mononuclear species by breaking up the bimetallic complex { $[Cp*Ru(CO)_2]_2(\mu-H)$ }⁺ OTf⁻ is thermally accessible. Reactions at 135 °C were faster than those at 110 °C, but above 150 °C the catalyst suffers some decomposition, based on the visual observation of black products that deposited in the reaction vessel. A reaction temperature of 110 °C was chosen to provide reasonable ability to monitor the early



Figure 3. Pressure dependence study of deoxygenation of 1,2-propanediol by $\{[Cp*Ru(CO)_2]_2(\mu-H)\}^+$ OTf⁻ at 110°C, at 750 psi (diamonds), 500 psi (circles), and 250 psi (triangles). [1.0M 1,2-propanediol in sulfolane containing 0.1M toluene as an internal standard; 5 mM $\{[Cp*Ru(CO)_2]_2(\mu-H)\}^+$ OTf⁻; 60 mM HOTf.]

30

Time (hours)

20

40

50

60

stages of the reaction, while preventing decomposition of the catalyst.

Dependence on H₂ Pressure

Deoxygenation Products (mM)

0

10

Experiments were carried out at 750, 500, and 250 psi initial pressure of H₂ to determine any pressure dependence of the catalytic deoxygenation, using conditions described in Figure 3. No significant dependence of the reaction rate on pressure was observed. Considering that the reaction showed little or no dependence on pressure, experiments were designed to carry out the catalytic reaction under 1 atmosphere of H_2 , by bubbling hydrogen through the reaction mixture in normal glassware (vs. a high-pressure autoclave). These experiments were carried out on a solution that was initially 0.93 M in 1,2-propanediol in sulfolane, at 110°C concentrations of 5 mM at initial of $\{[Cp*Ru(CO)_2]_2(\mu-H)\}^+$ OTf⁻ and 60 mM HOTf, very similar to the conditions at higher pressure.

Conversions from the atmospheric pressure reactions were, however, inferior to the high-pressure reactions. For example, the concentration of the deoxygenation products was only 0.37 M (39%) after 5 h, substantially less than that of the 51% yield observed after 4.4 h at 750 psi. The *n*-propanol concentration showed similar trends, reaching 0.23 M (5 h at 1 atm), *vs.* 0.32 M (after 4.4 h at 750 psi). Another substantial difference between the atmospheric and the highpressure reactions is the higher amount of 2-ethyl-4-

asc.wiley-vch.de

methyl-1,3-dioxolane isomers in the atmospheric pressure experiments (0.34 M, 36%, after 5 h) than in the high-pressure experiments (0.016 M, after 4.4 h at 750 psi). This difference is due to the volatile dioxolane being removed from the atmospheric pressure reaction since it distills, whereas in the high-pressure experiment it remains in the reaction solution and undergoes further reaction.

Synthesis of the Triflate Complex Cp*Ru(CO)₂OTf, and Comparison of Cp*Ru(CO)₂OTf *vs.* {[Cp*Ru(CO)₂]₂(µ-H)}⁺ OTf⁻ as Catalyst Precursors

The triflate complex, $Cp*Ru(CO)_2OTf$, was previously reported as an oil.^[28] We prepared it from the reaction of $Cp*Ru(CO)_2Cl$ with AgOTf in CH_2Cl_2 , and isolated it in 89% yield as a yellow solid [Eq. (11)].

 $Cp^{*}(CO)_{2}Ru - CI + AgOTf \rightarrow Cp^{*}(CO)_{2}Ru - OTf + AgCI$ (11)

Bands for the ruthenium carbonyls appeared the IR spectrum at 2050 cm⁻¹ and 1999 cm⁻¹, significantly higher energies than the corresponding v(CO) bands for Cp*Ru(CO)₂Cl (2032, 1978 cm⁻¹) or Cp*Ru(CO)₂H (2005, 1939 cm⁻¹), thus indicating, as expected, much less electron density on the metal in the metal triflate compared to ether the chloride or hydride. The identity and purity of the triflate complex were further confirmed by elemental analysis.

As shown in Figure 4, the performance of Cp*Ru-(CO)₂OTf was found to be nearly identical to that of $[Cp*Ru(CO)_2]_2(\mu-H)$ ⁺, verifying that Cp*Ru-(CO)₂OTf reacts with H₂ under the reaction conditions to produce $[Cp*Ru(CO)_2(\eta^2-H_2)]^+$ OTf⁻ (Eq.



Figure 4. Catalytic deoxygenation of 1,2-propanediol (1.0M) in sulfolane carried out at 110 °C under 750 psi hydrogen (initial pressure before heating). The squares represent 5 mM {[Cp*Ru(CO)₂]₂(μ -H)}⁺ OTf⁻ and 60 mM HOTf, and the circles represent 10 mM Cp*Ru(CO)₂OTf and 65 mM HOTf.



(12), *cf.* Scheme 1 for generation of $[Cp*Ru(CO)_2(\eta^2-H_2)]^+$ from { $[Cp*Ru(CO)_2]_2(\mu-H)$ }+OTf⁻)). To provide equivalent concentrations of total available acid equivalents, the experiment using Cp*Ru(CO)_2OTf was carried out with 65 mM HOTf added (*vs.* 60 mM HOTf in the experiment starting with the bimetallic complex { $[Cp*Ru(CO)_2]_2(\mu-H)$ }+ OTf⁻) to account for the incipient H⁺ present in { $[Cp*Ru(CO)_2]_2(\mu-H)$ }+ OTf⁻.

Comparison of OTf⁻ vs. BF₄⁻ Counterions

Most of our studies were conducted using the OTfcounterion for the starting Ru complex, along with HOTf as the added acid. A comparison with the use of briefly investigated, $BF_4^$ was using $\{[Cp*Ru(CO)_2]_2(\mu-H)\}^+ BF_4^-$ as the Ru catalyst precursor, along with HBF₄·OEt₂. An experiment using ${[Cp*Ru(CO)_2]_2(\mu-H)}^+$ $5 \,\mathrm{mM}$ BF_4^- , 60 mM HBF₄·OEt₂, 1.0M 1,2-propanediol at 110°C under an initial pressure of 750 psi H₂ did produce catalytic deoxygenation, but the reaction leveled off after producing 169 mM of deoxygenation products at 48 h, thus being significantly inferior to the performance of corresponding reactions with triflate. This may be caused by the somewhat lower acid strength of HBF₄·OEt₂ compared to HOTf influencing this change in reactivity, though on the basis of the limited study carried out, this cannot be distinguished from a lower stability of the Ru complexes with a BF₄⁻ counterion. An explanation for the lower reactivity of the BF₄⁻ salt is the possible hydrolysis of BF_4^- to $B(OH)_xF_y^-$, releasing fluoride ions that could act as a powerful catalyst inhibitor through coordination to the ruthenium center.

Reactivity of the Dioxolane and Aldehyde Intermediates Under Catalytic Conditions

In addition to the deoxygenated products *n*-propanol and di-*n*-propyl ether, small amounts of the intermediates propionaldehyde and *cis/trans*-2-ethyl-4methyl-1,3-dioxolane [formed by pathways shown in Eqs. (5) and (8)] were identified and quantitatively measured by GC of the reaction mixtures. Both the aldehyde and the dioxolane were subjected to the

Adv. Synth. Catal. 2009, 351, 789-800

same catalytic conditions; the deoxygenation of 1,2propanediol is also plotted in Figure 5 for comparison. Figure 5 shows that propionaldehyde is hydro-



Figure 5. Time-dependence of deoxygenation products formed in separate catalytic reactions, with starting materials shown in the figure. Initial concentrations were 1.0M for 1,2-propanediol, 1.0M for propionaldehyde, and 0.5M for 2-ethyl-4-methyl-1,3-dioxolane. Initial conditions were 5 mM $\{[Cp*Ru(CO)_2]_2(\mu-H)\}^+$ OTf⁻ under 750 psi H₂ (before heating) at 110°C in sulfolane. 30 mM HOTf was added in the deoxygenation of 1,2-propanediol and one experiment with 2-ethyl-4-methyl-1,3-dioxolane, as labeled. The hydrogenation of propionaldehyde and one experiment with 2-ethyl-4-methyl-1,3-dioxolane were carried out with no added acid.

genated by $\{[Cp^*Ru(CO)_2]_2(\mu-H)\}^+$ OTf⁻ in the absence of any added free acid, at rates faster than the rate of deoxygenation of 1,2-propanediol. After 25 h, 630 mM *n*-propanol, 75 mM di-*n*-propyl ether, and 16 mM propylene glycol propyl ether were formed, corresponding to 78% conversion of the substrate to deoxygenated/hydrogenated products. This result strongly supports the proposed hydrogenation of propionaldehyde under the reaction conditions by an ionic hydrogenation mechanism, and the rate of hydrogenation accounts for the small amounts of the aldehyde observed under the deoxygenation conditions.

In contrast to the reaction of the aldehyde in the absence of added acid, subjecting the 2-ethyl-4methyl-1,3-dioxolanes at an initial concentration of 0.5 M to the same reaction conditions leaves most of the dioxolane unreacted. After 0.75 h of reaction, about 50 mM of the dioxolane had been consumed, but after that early time the reaction essentially ceases, leaving the remaining dioxolane unreacted. When the dioxolane was reacted in the presence of added HOTf, however, a much faster reaction was observed, with the reaction being essentially complete in less than 2 h due to rapid acid-induced ring-opening of the dioxolane.

Mechanism of the Catalytic Deoxygenation and Hydrogenation

The proposed mechanism for the catalytic deoxygenation involves acid-catalyzed formation of propionaldehyde, which is then catalytically hydrogenated. Protonation of the diol results in dehydration, generating propionaldehyde [Eq. (5)]. This acid-catalyzed reaction could be initiated by the highly acidic dihydrogen complex, $[Cp*Ru(CO)_2(\eta^2-H_2)]^+$, but under the reaction conditions the acid-catalyzed dehydration would also readily occur from reaction with HOTf. Once the aldehyde is generated, the process for the hydrogenation of its C=O bond to an alcohol proceeds through an ionic hydrogenation pathway^[22] as reported earlier for a series of molybdenum and tungsten hydrides, with the cationic dihydride or dihydrogen complex serving as the proton source and the neutral hydride being the hydride donor.^[23] A series of experiments to be reported separately show that a variety of ketones can be hydrogenated using $\{[Cp*Ru(CO)_2]_2(\mu-H)\}^+$ OTf⁻ as a catalyst precursor.

In the mechanism shown in Scheme 3 [where the $Cp^*(CO)_2$ ligands on Ru are omitted for clarity], the metal complex shown as Ru⁺ may have the alcohol





initially bound to the metal prior to displacement by H_2 . In our studies of related complexes of tungsten, we found that complexes with alcohol ligands, $[Cp(CO)_3W(ROH)]^+$ OTf⁻, are readily prepared by addition of HOTf to solutions of $Cp(CO)_3WH$ and ketones.^[29] These alcohol complexes have been isolated as kinetic products, and crystal structures have been obtained in some cases, but the counterion OTf⁻ displaces the alcohol to give $Cp(CO)_3WOTf$ and free

796 asc.wiley-

alcohol. Similar alcohol complexes of Ru may be formed in these reactions; Casey and co-workers have characterized related cationic alcohol complexes of ruthenium.^[30] However, if any alcohol complexes were formed under our reaction conditions, they would not be detected since they would be converted to Cp*Ru(CO)₂OTf, or directly to $[Cp*Ru(CO)_2(\eta^2 H_2$]⁺. Heating the bimetallic catalyst precursor ${[Cp^*Ru(CO)_2]_2(\mu-H)}^+$ OTf⁻ under hydrogen converts it to mononuclear species (cf. Scheme 1), the neutral ruthenium hydride Cp*Ru(CO)₂H and the cationic dihydrogen complex $[Cp*Ru(CO)_2(\eta^2-H_2)]^+$. The acid protonates the neutral hydride, so that both Ru complexes convert under these conditions to $[Cp*Ru(CO)_2(\eta^2-H_2)]^+$. Hydride transfer from the neutral ruthenium hydride, Cp*Ru(CO)₂H, to the protonated aldehyde then generates the alcohol and Cp*Ru(CO)₂OTf. Reaction of this triflate complex with H₂ regenerates the dihydrogen complex $[Cp*Ru(CO)_2(\eta^2-H_2)]$ +OTf⁻ [Eq. (12)]. Thus either Cp*Ru(CO)₂OTf or the bimetallic catalyst precursor ${[Cp*Ru(CO)_2]_2(\mu-H)}^+$ OTf⁻ would be converted to $[Cp*Ru(CO)_2(\eta^2-H_2)]^+$ under the reaction conditions.

Deoxygenation of Glycerol

Having shown that the internal OH of 1,2-propanediol could be deoxygenated by these Ru catalysts, we then carried out preliminary attempts on the catalytic deoxygenation of glycerol, using conditions similar to those discussed above for 1,2-propanediol. However, deoxygenation of glycerol (initial concentration 1.0M) catalyzed by {[Cp*Ru(CO)₂]₂(μ -H)}⁺ OTf⁻ (10 mM) in sulfolane at 110°C with added HOTf (20 mM) generated only 29 mM of the desired product, 1,3-propanediol, after 19 h, corresponding to 2.9 turnovers of the bimetallic catalyst [Eq. (13)]. In ad-



dition, *n*-propanol (31 mM) and 1,2-propanediol (9 mM) were observed, along with several other unidentified products. Another reaction using 120 mM HOTf, but otherwise conducted under the same conditions, produced 46 mM 1,3-propanediol (4.6 turnovers), 57 mM *n*-propanol (5.7 turnovers), a small amount (3 mM) of *n*-Pr₂O, but no detectable 1,2-propanediol. Thus, the deoxygenation of glycerol is catalyzed by the ruthenium catalyst, but in much lower yields of desired products compared to the deoxygenation of 1,2-propanediol. The beneficial effect of added acids may need to be balanced against acid-induced reactions that polyols such as glycerol can undergo.^[3] As noted in the introduction, catalysts developed by others for the deoxygenation of glycerol have also led to product mixtures.

Deoxygenation of 1-Phenyl-1,2-ethanediol

A few experiments were also conducted to compare the deoxygenation of 1-phenyl-1,2-ethanediol to that of 1,2-propanediol. Deoxygenation of 1-phenyl-1,2ethanediol (1.0M) in sulfolane at 110 °C catalyzed by- $\{[Cp*Ru(CO)_2]_2(\mu-H)\}^+$ OTf⁻ (5 mM) with added HOTf (60 mM) generated 0.66M (66% yield) of phenethyl alcohol after 8 h [Eq. (14)]. The phenyl group

may provide significant stabilization of some of the intermediates. More study would be needed to make a detailed comparison between the catalytic deoxygenation of this substrate with 1,2-propanediol.

Conclusions

The deoxygenation of 1,2-propanediol is catalyzed by $\{[Cp*Ru(CO)_2]_2(\mu-H)\}^+$ OTf⁻ under H₂ in the presence of acid. Addition of H₂ and removal of H₂O lead to the net removal of one O from the diol, giving an alcohol. These reactions are proposed to proceed through the formation of the highly acidic mononuclear dihydrogen complex $[Cp*Ru(CO)_2(\eta^2-H_2)]^+$ OTf⁻ that is formed from the bimetallic catalyst precursor ${[Cp*Ru(CO)_2]_2(\mu-H)}^+$ OTf⁻. The predominant product is *n*-propanol; condensation products derived from n-propanol are also observed. The deoxygenation of a diol is a simpler version of the type of reactivity that would be needed for the deoxygenation of higher polyols and carbohydrates that contain more OH groups. These results are therefore relevant to the need to develop new catalytic methods for deoxygenation of biomass-derived compounds to provide higher value chemicals or fuels. The high selectivity, giving *n*-propanol rather than isopropyl alcohol, is due to the acid-catalyzed dehydration preferring dehydration at the secondary over the primary OH in the diol. Added acid (HOTf) accelerates the reaction and leads to higher conversions. Most reactions were

carried out under high pressures of H_2 , but there is little or no dependence on H_2 pressure, and the reaction does proceed under 1 atm of H_2 . The proposed mechanism involves acid-catalyzed dehydration of 1,2-propanediol to produce propionaldehyde, which was observed in the reaction mixture as an intermediate. Catalytic hydrogenation of the propionaldehyde gives the alcohol product; this hydrogenation is proposed to occur by an ionic hydrogenation mechanism, involving proton transfer and hydride transfer steps. Regeneration of the catalyst occurs through reaction with H_2 , with the metal-mediated heterolytic cleavage of H_2 being a key step in the mechanism.

Experimental Section

General

All manipulations were carried out under an atmosphere of argon using Schlenk or vacuum-line techniques, or in a Vacuum Atmospheres drybox. Solvents were purified and deoxygenated by standard methods. Sulfolane, 1,2-propanediol and glycerol were degassed by multiple freeze-pumpthaw cycles, but otherwise were used as received from Aldrich. *cis/trans*-2-Ethyl-4-methyl-1,3-dioxolane was prepared from acid-catalyzed condensation of propionaldehyde with 1,2-propanediol, as previously described.^[4] NMR spectra were recorded on Bruker AM-300 (300 MHz for ¹H) and Bruker Avance (400 MHz for ¹H) spectrometers. IR spectra were recorded on a Mattson Polaris spectrometer. Elemental analyses were obtained from Schwarzkopf Microanalytical Laboratory, Woodside, NY. Cp*Ru(CO)₂H was prepared by either of the two methods reported previously.^[16,31]

Synthesis of {[Cp*Ru(CO)₂]₂(µ-H)}⁺ OTf⁻

HOTf (155 µL, 1.75 mmol) was added dropwise with stirring over a period of 5 min to a yellow solution of Cp*Ru-(CO)₂H (1.03 g, 3.51 mmol) in CH₂Cl₂ (1 mL). Hydrogen evolution was observed, and the color of the reaction mixture changed to orange. Yellow microcrystals of {[Cp*Ru(CO)₂]₂(µ-H)}⁺OTf⁻ precipitated upon addition of ether (10 mL) and were isolated by filtration and were dried under vacuum to obtain {[Cp*Ru(CO)₂]₂(µ-H)}⁺ OTf⁻; yield: 1.26 g (98%). ¹H NMR (CD₂Cl₂): δ =2.05 (s, 30H, C₅Me₅); -17.74 (s, 1H, Ru-H); IR (CH₂Cl₂): v(CO)=2047 (w), 2021 (s), 1990 (s) cm⁻¹.

Synthesis of Cp*Ru(CO)₂OTf

Cp*Ru(CO)₂Cl (0.250 g, 0.762 mmol) and AgOTf (0.216 g, 0.841 mmol) were stirred overnight in CH₂Cl₂ (30 mL) at room temperature. Formation of a white precipitate was observed. The solution was filtered and the filtrate was evaporated to obtain Cp*Ru(CO)₂OTf as a yellow solid; yield: 0.300 g (89%). ¹H NMR (CD₂Cl₂): δ =1.88 (s, 15 H, C₅Me₅); ¹³C NMR (CD₂Cl₂): δ =198.3 (s, CO), 119.3 (q, ¹J_{C,F}= 319 Hz, CF₃), 101.0 (s, C₅Me₅), 10.2 (q, ¹J_{C,H}=129 Hz, C₅Me₅); ¹⁹F NMR (CD₂Cl₂): δ =-77.6 (s); IR (CH₂Cl₂): v(CO)=2050 (s), 1999 (s) cm⁻¹; anal. calcd. for

 $C_{13}H_{15}O_5SF_3Ru\colon C$ 35.37%, H 3.42%; found: C 35.38%, H 3.37%.

Synthesis of $\{[Cp*Ru(CO)_2]_2(\mu-H)\}^+ [BF_4]^-$

This complex was previously synthesized by protonation of $[Cp*Ru(CO)(\mu-CO)]_2$ with HBF₄·Et₂O.^[32] We prepared it by the method described here. To a yellow solution of Cp*Ru-(CO)₂H (0.200 g, 0.682 mmol) in CH₂Cl₂ (*ca.* 1 mL) was added HBF₄·OEt₂ (50 µL of 85% solution) slowly dropwise with stirring. Hydrogen evolution was observed during the course of the addition and the color of the reaction mixture changed to orange. Yellow microcrystals of {[Cp*Ru(CO)₂]₂ (μ -H)]⁺ [BF₄]⁻ precipitated out upon addition of ether (10 mL) to the reaction mixture. These yellow microcrystals were isolated by filtration and were dried to obtain {[Cp*Ru(CO)₂]₂(μ -H)]⁺ [BF₄]⁻; yield: 0.189 g (82%). ¹H NMR (CD₂Cl₂): δ =2.05 (s, 30H, C₃Me₅), -17.76 (s, 1H, Ru-H); IR (CH₂Cl₂): v(CO)=2047 (w), 2021 (s), 1990 (s) cm⁻¹.

Procedure and Conditions for the Catalytic Hydrogenation of 1,2-Propanediol

Catalysis experiments were carried out in a 300-mL Parr (Model 4561) mini-reactor. In a glovebox {[Cp*Ru(CO)₂]₂ $(\mu$ -H)}⁺ OTf⁻ (0.184 g, 0.250 mmol) was weighed into a glass liner for the reactor, and dissolved in 50 mL of a degassed sulfolane solution that was 1.0M in 1,2-propanediol and 0.1 M in the internal GC standard toluene. HOTf (266 µL, 3.01 mmol) was added slowly dropwise to the reaction mixture. The reactor was sealed, brought outside the drybox. flushed twice with H₂ gas, and pressurized to 750 psi. The reaction was started by switching on the stirrer (stirring speed 600 rpm) and the heating, with this point taken as t=0.0 h. With the reaction volume used, about 10 samples of ~ 0.5 mL each can be obtained from the reactor, with a 1 mL flush of the dip-tube before each sample (except the first) to ensure authenticity of sampling. Reactor temperatures were verified by and calibrated using a thermocouple immersed into the reaction solutions. Analyses of the catalysis runs were carried out on Hewlett Packard Model 5890 Series II gas chromatograph with an flame ionization detector. A DB-Wax column (J & W Scientific, 30 m×0.25 mm, film thickness 0.25 µm) with a helium carrier flow of 2 mL min⁻¹ was used for the GC analyses at temperatures from 35 to 250 °C. To protect the column, samples from the reaction were neutralized with excess NaHCO₃ or Na₂CO₃, and filtered or decanted from the solid base prior to injection. Quantitative analysis of all components were based on calibrations with authentic samples of known concentrations using at least three levels over the concentration range of 10-1000 mM in sulfolane with 0.1 M toluene as the internal standard. Response factors showed excellent linearity with concentration. Reactions of glycerol were conducted in an analogous manner.

Deoxygenation of 1,2-Propanediol by $\{[Cp*Ru(CO)_2]_2(\mu-H)\}^+ [BF_4]^-$

This experiment was carried out in an analogous manner to those described above using ${[Cp*Ru(CO)_2]_2(\mu-H)}^+ OTf^-$ This experiment used ${[Cp*Ru(CO)_2]_2(\mu-H)}^+ [BF_4]^-$ (0.135 g, 0.200 mmol); 40 mL of 0.942 M solution of 1,2-propanediol (containing 0.1 M toluene as an internal standard) in sulfolane; HBF₄·Et₂O solution (54% by weight, 7.25 M; 331 μ L, 2.40 mmol), hydrogen pressure (750 psi), temperature 110 °C. After 72 h, 0.14 M (15%) of the 1,2-propanediol remained, and the concentrations and yields of hydrogenated products were *n*-propanol (0.089 M, 9%), and propylene glycol propyl ether (0.075 M, 8%). Di-*n*-propyl ether was not detected. The total yield of deoxygenation products from this experiment indicated 16 catalyst turnovers (17% yield).

Acknowledgements

Research at Brookhaven National Laboratory was carried out under contract DE-AC02–98CH10886 with the U.S. Department of Energy. Pacific Northwest National Laboratory is operated by Battelle for the U.S. Department of Energy. We thank the U.S. Department of Energy, Office of Science, Laboratory Technology Research Program, and the Office of Basic Energy Sciences, Division of Chemical Sciences, for support. We thank NSERC (Canada) for a postdoctoral fellowship to M.S.

References

- a) A. Corma, S. Iborra, A. Velty, *Chem. Rev.* 2007, 107, 2411–2502; b) J. N. Chheda, G. W. Huber, J. A. Dumesic, *Angew. Chem.* 2007, 119, 7298–7318; *Angew. Chem. Int. Ed.* 2007, 46, 7164–7183.
- [2] F. W. Lichtenthaler, S. Mondel, Pure Appl. Chem. 1997, 69, 1853–1866.
- [3] M. Schlaf, Dalton Trans. 2006, 4645-4653.
- [4] Z. Xie, M. Schlaf, J. Mol. Catal. A: Chem. 2005, 229, 151–158.
- [5] R. R. Dykeman, K. L. Luska, M. E. Thibault, M. D. Jones, M. Schlaf, M. Khanfar, N. J. Taylor, J. F. Britten, L. Harrington, J. Mol. Catal. A: Chem. 2007, 277, 233–251.
- [6] T. M. Che, (Celanese Corp.), U.S. Patent 4,642,394, issued Feb. 10, 1987.
- [7] G. Braca, A. M. Raspolli Galletti, G. Sbrana, J. Organomet. Chem. 1991, 417, 41–49.
- [8] a) Y. Kusunoki, T. Miyazawa, K. Kunimori, K. Tomishige, *Catal. Commun.* 2005, *6*, 645–649; b) T. Miyazawa, Y. Kusunoki, K. Kunimori, K. Tomishige, *J. Catal.* 2006, 240, 213–221; c) T. Miyazawa, S. Koso, K. Kunimori, K. Tomishige, *Appl. Catal. A* 2007, *329*, 30–35.
- [9] E. Drent, W. W. Jager, (Shell Oil Company), U.S. Patent 6,080,898, issued June 27, 2000.
- [10] a) E. P. Maris, R. J. Davis, J. Catal. 2007, 249, 328-337;
 b) J. Chaminand, L. Djakovitch, P. Gallezot, P. Marion, C. Pinel, C. Rosier, Green Chem. 2004, 6, 359-361;
 c) A. Alhanash, E. F. Kozhevnikova, I. V. Kozhevnikov, Catal. Lett. 2008, 120, 307-311.
- [11] D. Arntz, T. Haas, A. Schäfer-Sindlinger, (Degussa), U.S. Patent 5,364,984, issued Nov. 15, 1994.
- [12] For a preliminary report of these results, see: M. Schlaf, P. Ghosh, P. J. Fagan, E. Hauptman, R. M. Bul-

lock, Angew. Chem. 2001, 113, 4005–4008; Angew. Chem. Int. Ed. 2001, 40, 3887–3890.

- [13] a) G. J. Kubas, Metal Dihydrogen and σ-Bond Complexes: Structure, Theory, and Reactivity, Kluwer Academic/Plenum Publishers, New York, 2001; b) D. M. Heinekey, W. J. Oldham, Jr., Chem. Rev. 1993, 93, 913–926; c) P. G. Jessop, R. H. Morris, Coord. Chem. Rev. 1992, 121, 155–284.
- [14] a) G. Jia, R. H. Morris, J. Am. Chem. Soc. 1991, 113, 875–883; b) G. Jia, A. J. Lough, R. H. Morris, Organometallics 1992, 11, 161–171; c) K. Abdur-Rashid, T. P. Fong, B. Greaves, D. G. Gusev, J. G. Hinman, S. E. Landau, A. J. Lough, R. H. Morris, J. Am. Chem. Soc. 2000, 122, 9155–9171; d) G. J. Kubas, Chem. Rev. 2007, 107, 4152–4205; e) G. J. Kubas, Catal. Lett. 2005, 104, 79–101.
- [15] a) T.-Y. Cheng, B. S. Brunschwig, R. M. Bullock, J. Am. Chem. Soc. 1998, 120, 13121–13137; b) T.-Y. Cheng, R. M. Bullock, J. Am. Chem. Soc. 1999, 121, 3150– 3155.
- [16] T.-Y. Cheng, R. M. Bullock, Organometallics 2002, 21, 2325–2331.
- a) D. E. Berning, B. C. Noll, D. L. DuBois, J. Am. [17] Chem. Soc. 1999, 121, 11432-11447; b) C. J. Curtis, A. Miedaner, W. W. Ellis, D. L. DuBois, J. Am. Chem. Soc. 2002, 124, 1918-1925; c) D. E. Berning, A. Miedaner, C. J. Curtis, B. C. Noll, M. C. Rakowski DuBois, D. L. DuBois, Organometallics 2001, 20, 1832-1839; d) A. J. Price, R. Ciancanelli, B. C. Noll, C. J. Curtis, D. L. DuBois, M. R. DuBois, Organometallics 2002, 21, 4833-4839; e) R. Ciancanelli, B. C. Noll, D. L. DuBois, M. R. DuBois, J. Am. Chem. Soc. 2002, 124, 2984-2992; f) W. W. Ellis, R. Ciancanelli, S. M. Miller, J. W. Raebiger, M. R. DuBois, D. L. DuBois, J. Am. Chem. Soc. 2003, 125, 12230-12236; g) A. Miedaner, J.W. Raebiger, C. J. Curtis, S. M. Miller, D. L. DuBois, Organometallics 2004, 23, 2670-2679; h) W. W. Ellis, J. W. Raebiger, C. J. Curtis, J. W. Bruno, D. L. DuBois, J. Am. Chem. Soc. 2004, 126, 2738-2743; i) J. W. Raebiger, A. Miedaner, C. J. Curtis, S. M. Miller, O. P. Anderson, D. L. DuBois, J. Am. Chem. Soc. 2004, 126, 5502-5514.
- [18] J.-S. Song, D. J. Szalda, R. M. Bullock, C. J. C. Lawrie, M. A. Rodkin, J. R. Norton, *Angew. Chem.* **1992**, *104*, 1280–1282; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1233–1235.
- [19] R. M. Bullock, J.-S. Song, J. Am. Chem. Soc. 1994, 116, 8602–8612.
- [20] J.-S. Song, D. J. Szalda, R. M. Bullock, *Inorg. Chim. Acta* 1997, 259, 161–172.
- [21] J.-S. Song, D. J. Szalda, R. M. Bullock, J. Am. Chem. Soc. 1996, 118, 11134–11141.
- [22] a) R. M. Bullock, *Chem. Eur. J.* 2004, 10, 2366–2374;
 b) R. M. Bullock, in: *Handbook of Homogeneous Hydrogenation*, Vol. 1, (Eds.: J. G. de Vries, C. J. Elsevier), Wiley-VCH, Weinheim, Germany, 2007, Chapter 7, pp 153–197.
- [23] a) R. M. Bullock, M. H. Voges, J. Am. Chem. Soc. 2000, 122, 12594–12595; b) B. F. M. Kimmich, P. J. Fagan, E. Hauptman, W. J. Marshall, R. M. Bullock, Organometallics 2005, 24, 6220–6229; c) F. Wu, V. K. Dioumaev,

D. J. Szalda, J. Hanson, R. M. Bullock, *Organometallics* **2007**, *26*, 5079–5090.

- [24] M. Ito, T. Ikariya, Chem. Commun. 2007, 5134–5142.
- [25] M. S. Chinn, D. M. Heinekey, N. G. Payne, C. D. Sofield, *Organometallics* **1989**, *8*, 1824–1826.
- [26] For simplicity, the symmetrically bridging hydride in Eq. (3) and elsewhere in this paper is drawn with a line between the two Ru atoms, as well as for the Ru–H bond. This is potentially misleading, as the number of lines drawn exceeds the number of electron pairs involved in the bonding, since bridging hydrides have 3-center, 2-electron bonds. For a cogent discussion of the confusion that has arisen in the literature over such bonding, see: M.-H. Baik, R. A. Friesner, G. Parkin, *Polyhedron* 2004, 23, 2879–2900.
- [27] a) M. A. Andrews, S. A. Klaeren, J. Am. Chem. Soc. 1989, 111, 4131–4133; b) M. A. Andrews, Organometallics 1989, 8, 2703–2708.
- [28] K.-H. Griessmann, A. Stasunik, W. Angerer, W. Malisch, J. Organomet. Chem. 1986, 303, C29-C32.
- [29] J.-S. Song, D. J. Szalda, R. M. Bullock, Organometallics 2001, 20, 3337–3346.
- [30] C. P. Casey, T. E. Vos, G. A. Bikzhanova, Organometallics 2003, 22, 901–903.
- [31] P. J. Fagan, W. S. Mahoney, J. C. Calabrese, I. D. Williams, Organometallics 1990, 9, 1843–1852.
- [32] A. Stasunik, W. Malisch, J. Organomet. Chem. 1984, 270, C56-C62.