

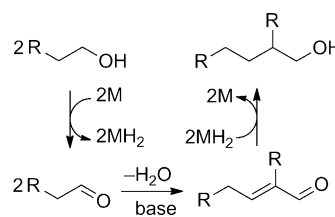
# Catalytic Conversion of Ethanol into an Advanced Biofuel: Unprecedented Selectivity for *n*-Butanol\*\*

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Obtaining liquid fuels for transportation from renewable biomass sources remains an important component of future energy provision, and many aspects of this problem are the subject of intensive research activity, not least the identification of suitable crops which give high yields and allay fears regarding competition for resources with food crops.<sup>[1]</sup> (Bio)-ethanol, obtained by the fermentation of sugar-containing crops, has long been used as a sustainable replacement for conventional gasoline, often in the form of a blend of the two. However, ethanol has a number of significant drawbacks as compared to gasoline: it has a lower energy density (70 % that of gasoline), it is corrosive to current engine technology and fuel infrastructure, and it readily absorbs water, which leads to separation and dilution problems in storage tanks. Higher alcohols, such as butanol, have fuel properties that more closely resemble those of gasoline and can alleviate many of these problems associated with ethanol.<sup>[2]</sup> For example, *n*-butanol is essentially noncorrosive and immiscible with water; the energy density of butanol is also closer to that of gasoline (90 %). This improved performance has led to butanol being termed an “advanced biofuel”, and the commercial availability of this material as a green “drop-in” alternative to gasoline is gathering pace.<sup>[3]</sup> However, the bulk synthesis of butanol from biosustainable feedstocks remains a challenge, with much recent interest focused on revisiting the ABE fermentation process in which mixtures of acetone, butanol, and ethanol are produced by the use of strains of the bacterium *Clostridium acetobutylicum*.<sup>[4]</sup> To date, the best reported selectivity with this process is approximately 60–70 % (by weight) with a yield of about 16 % per kilogram of feedstock.<sup>[5]</sup>

Our approach has been to seek catalysts for the conversion of readily available ethanol into this more advanced biofuel. Catalytic reactions for the conversion of alcoholic substrates are surprisingly rare, but one ideal example exists in the Guerbet reaction,<sup>[6]</sup> a method which enables facile C–C bond formation with normally unreactive alcohols; reactions of this type have more recently been termed “borrowed hydrogen” chemistry.<sup>[7]</sup> In a typical catalytic reaction scheme,

an alcohol is dehydrogenated to form an aldehyde, which then undergoes aldol coupling and rehydrogenation of the product to give a longer-chain alcohol (Scheme 1).



Scheme 1. The Guerbet reaction.

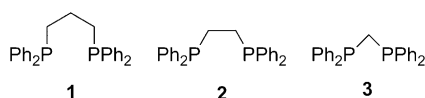
Such Guerbet processes are possible with a wide variety of catalysts<sup>[8]</sup> and are tolerant towards a range of substrates; a recent exciting advance was the synthesis of amines by related reactions.<sup>[9]</sup> Unfortunately, ethanol is a specifically difficult substrate for these transformations. The problems are twofold: first, ethanol is particularly difficult to dehydrogenate; it was even reported that mixtures of methanol and propanol could be selectively dehydrogenated and coupled in ethanol as the solvent.<sup>[10]</sup> Second, the base-catalyzed aldol condensation of acetaldehyde is notoriously difficult to control and usually leads to mixtures of oligomeric and polymeric products.<sup>[11]</sup> These factors combine to make the achievement of any selectivity in the conversion of ethanol into butanol extremely challenging. Some progress was made in pioneering studies by Ishii and co-workers with a homogeneous iridium catalyst, [Ir(cod)(acac)] (acac = acetylacetonate, cod = 1,5-cyclooctadiene), in the presence of a phosphine ligand, the additive 1,7-octadiene, and an alkoxide base. Under these conditions, selectivity for *n*-butanol of up to 67 % at 12 % conversion was reported.<sup>[12]</sup> As expected, longer-chain alcohols were formed as side products of uncontrolled aldol reactions. Recently, heterogeneous catalysts were reported that exhibited selectivity of up to 80 % at 25 % ethanol conversion.<sup>[13]</sup> Herein we report a new family of ruthenium-based catalysts which offer a step change in performance: these catalysts promote the upgrading of ethanol to *n*-butanol with over 94 % selectivity at good conversion.

Ruthenium systems have a good track record in borrowed-hydrogen chemistry<sup>[7a]</sup> and related dehydrogenation reactions, such as hydrogen production from alcohols<sup>[7b,c]</sup> and the synthesis of ethyl acetate.<sup>[7d–f]</sup> For our initial catalyst screening, we used [(RuCl<sub>2</sub>(η<sup>6</sup>-*p*-cymene))<sub>2</sub>] as a catalyst precursor with two molar equivalents (Ru/L 1:1) of the inexpensive, commercially available bidentate phosphine ligand 1,3-bis(diphenylphosphanyl)propane (**1**), 1,2-bis(diphenylphosphanyl)ethane (**2**), or bis(diphenylphosphanyl)-

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**Scheme 2.** Ligands used in this study.

**Table 1:** Ruthenium-catalyzed conversion of ethanol into *n*-butanol.

$\text{CH}_3\text{CH}_2\text{OH} \xrightarrow[\text{EtONa (5 mol\%), 150 }^\circ\text{C, 4 h}]{[\text{Ru}] (0.1 \text{ mol\%}), \text{ligand} (0.1 \text{ mol\%})} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH} + \text{H}_2\text{O}$						
Entry	[Ru]	Ligand	Conversion (yield) [%] <sup>[a]</sup>	Selectivity [%] <sup>[b]</sup>	TON <sup>[c]</sup>	TOF <sup>[d]</sup>
1	[{RuCl <sub>2</sub> (η <sup>6</sup> - <i>p</i> -cymene)} <sub>2</sub> ]	<b>1</b>	10.2 (7.8)	88.0	102	26
2	[{RuCl <sub>2</sub> (η <sup>6</sup> - <i>p</i> -cymene)} <sub>2</sub> ]	<b>2</b>	11.8 (10.9)	90.6	118	30
3	[{RuCl <sub>2</sub> (η <sup>6</sup> - <i>p</i> -cymene)} <sub>2</sub> ]	<b>3</b>	20.4 (17.5)	90.0	204	51
4	[RuCl(η <sup>6</sup> - <i>p</i> -cymene)( <b>1</b> )]Cl	–	6.1 (5.0)	86.2	61	15
5	[RuCl(η <sup>6</sup> - <i>p</i> -cymene)( <b>2</b> )]Cl	–	11.0 (9.3)	90.7	110	28
6	[RuCl(η <sup>6</sup> - <i>p</i> -cymene)( <b>3</b> )]Cl	–	22.1 (20.1)	93.6	221	55
7 <sup>[e]</sup>	[RuCl(η <sup>6</sup> - <i>p</i> -cymene)( <b>3</b> )]Cl	–	20.7 (18.0)	90.6	207	10
8	[{RuCl <sub>2</sub> (η <sup>6</sup> - <i>p</i> -cymene)} <sub>2</sub> ]	–	6.9 (5.6)	86.1	69	17
9	[RuCl(η <sup>6</sup> - <i>p</i> -cymene)( <b>3</b> )]Cl	<b>3</b>	13.4 (11.3)	88.9	134	34
10 <sup>[e]</sup>	[RuCl(η <sup>6</sup> - <i>p</i> -cymene)( <b>3</b> )]Cl	<b>3</b>	29.5 (23.3)	84.8	295	15
11	<i>trans</i> -[RuCl <sub>2</sub> ( <b>3</b> ) <sub>2</sub> ]	–	10.5 (9.6)	94.1	105	26
12 <sup>[e]</sup>	<i>trans</i> -[RuCl <sub>2</sub> ( <b>3</b> ) <sub>2</sub> ]	–	41.6 (32.6)	85.1	416	21
13 <sup>[f]</sup>	<i>trans</i> -[RuCl <sub>2</sub> ( <b>3</b> ) <sub>2</sub> ]	–	45.8 (35.5)	84.6	458	19
14 <sup>[e,g]</sup>	<i>trans</i> -[RuCl <sub>2</sub> ( <b>3</b> ) <sub>2</sub> ]	–	13.0 (11.3)	90.6	1300	65
15 <sup>[e]</sup>	<i>cis</i> -[RuCl <sub>2</sub> ( <b>3</b> ) <sub>2</sub> ]	–	39.7 (31.6)	86.0	397	20
16 <sup>[e,h]</sup>	<i>cis</i> -[RuCl <sub>2</sub> ( <b>3</b> ) <sub>2</sub> ]	–	30.5 (25.6)	88.8	610	31
17 <sup>[e]</sup>	<i>cis/trans</i> -[RuH <sub>2</sub> ( <b>3</b> ) <sub>2</sub> ]	–	33.8 (25.4)	81.9	338	17
18 <sup>[e]</sup>	<i>trans</i> -[RuCl <sub>2</sub> ( <b>1</b> ) <sub>2</sub> ]	–	2.3 (1.9)	89.6	23	1
19 <sup>[e]</sup>	<i>trans</i> -[RuCl <sub>2</sub> ( <b>2</b> ) <sub>2</sub> ]	–	2.6 (1.9)	84.4	26	1

[a] Total conversion of ethanol into Guerbet products (see Table S1 in the Supporting Information). The yield of *n*-butanol is given in parenthesis. [b] Total selectivity for *n*-butanol in the liquid fraction, as determined by GC. [c] Turnover number (TON) based on the amount of substrate (in mmol) converted into products per mmol of Ru. [d] Turnover frequency (TOF) based on the amount of substrate (in mmol) converted into products per mmol of Ru per hour. [e] Reaction time: 20 h. [f] Reaction time: 24 h. [g] The reaction was carried out with 0.01 mol % of [Ru]. [h] The reaction was carried out with 0.05 mol % of [Ru].

methane (**3**; Scheme 2) and sodium ethoxide as the base (Table 1).

Ligands **1** and **2** gave modest conversion of around 10 % (Table 1, entries 1 and 2); however, the small-bite-angle diphosphine **3** gave an excellent result, with 20.4 % conversion after 4 h (entry 3). Crucially, this family of ruthenium catalysts exhibited unprecedented selectivity for the formation of *n*-butanol: 90.0 % with ligand **3**. Moreover, 1,7-octadiene and the 2 h catalyst-preactivation period reported by Ishii and co-workers were unnecessary with these catalysts. Careful analysis of the reaction products showed the exclusive production of *n*-butanol in the C<sub>4</sub> fraction and small amounts (typically less than 10 %) of higher alcohols (2-ethylbutanol, *n*-hexanol, and 2-ethylhexanol; see Table S1 in the Supporting Information) as side products, consistent with Guerbet coupling of the *n*-butanol product with the ethanol substrate. Analysis of the headspace gases at the end of a typical reaction (Table 1, entry 3) also showed the presence of hydrogen (8.1 %) and methane (0.2 %). Whereas the former is clearly consistent with the Guerbet mechanism, the latter

requires decarbonylation of the intermediate acetaldehyde: a reaction which is known for similar systems.<sup>[14]</sup> Surprisingly, preformed ruthenium complexes of ligands **1** and **2** gave inferior results in terms of productivity (Table 1, entries 4 and 5). However, a positive effect was observed when the

preformed complex of ligand **3** was used (Table 1, entry 6): a higher yield and even higher (93.6 %) selectivity were observed for the formation of *n*-butanol. Running the reaction for extended periods did not produce an increase in conversion (Table 1, entry 7). In the absence of the diphosphine ligand (Table 1, entry 8), low baseline catalytic activity (6.9 % conversion in 4 h) was observed, albeit with slightly lower selectivity.

In many of these reactions, the catalyst solution appeared to be unstable, with the formation of a black precipitate reminiscent of nanoparticulate metal over the course of the reaction; this precipitate was catalytically inactive. By contrast, when an extra equivalent of the ligand was added to the preformed complex [RuCl(η<sup>6</sup>-*p*-cymene)(**3**)]Cl, the reaction mixture remained homogenous throughout (Table 1, entries 9 and 10). A decrease in productivity over 4 h can be overcome by carrying out the reactions for an extended period (20 h), but at the cost of selectivity: an artifact of these batch experiments and the increased concentration of *n*-butanol relative to that of ethanol at higher conversion.

The ruthenium complexes [RuCl<sub>2</sub>(**L**)<sub>2</sub>] may be preformed before executing the catalysis.<sup>[15]</sup> Under our standard catalytic conditions, *trans*-[RuCl<sub>2</sub>(**3**)<sub>2</sub>] exhibited lower conversion than [RuCl(η<sup>6</sup>-*p*-cymene)(**3**)]Cl alone (compare entries 6 and 11 in Table 1) but gave very similar results to [RuCl(η<sup>6</sup>-*p*-cymene)(**3**)]Cl in the presence of an excess of the ligand (Table 1, entry 9) and similarly remained homogeneous throughout the catalysis. Again, longer reaction times resulted in higher conversion, up to 45.8 % (Table 1, entries 12 and 13). Such complexes can be obtained in either the *cis* or *trans* geometry depending on the reaction conditions used during their formation.<sup>[15]</sup> Both geometries of precursor [RuCl<sub>2</sub>(**3**)<sub>2</sub>] gave identical catalytic results within experimental error (compare entries 12 and 15 in Table 1), which suggests that the same active species is formed. It is possible that complexes of the type [RuX<sub>n</sub>(**3**)<sub>2</sub>] are in fact the true catalytic species in these reactions regardless of the amount of the starting ligand used; when the M/L ratio is 1:1, ligand-redistribution reactions may occur and result in lower concentrations of such complexes together with heterogeneous ruthenium systems. Indeed,

heating an ethanolic solution of  $[\text{RuCl}(\eta^6\text{-}p\text{-cymene})(\mathbf{3})]\text{Cl}$  in the autoclave at  $150^\circ\text{C}$  resulted in the formation of *trans*- $[\text{RuCl}_2(\mathbf{3})]$ . The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum (unlocked) of the product solution of a typical catalytic run (Table 1, entry 11) exhibited a set of mutually coupled triplets at 15.4 and 1.9 ppm ( $^2J_{\text{PP}} = 29.2$  Hz) and a singlet at 10.3 ppm, which we attribute to *cis* and *trans* isomers of  $[\text{RuH}_2(\mathbf{3})]$ . We synthesized this dihydride complex according to a previously reported method<sup>[16]</sup> and found it to be catalytically active (Table 1, entry 17).  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopic analysis of catalytic solutions after longer reaction times (e.g. Table 1, entry 12) also showed several unknown species at 40.9 (s), 33.4 (s), and 21.1 ppm (s); their presence suggests some catalyst decomposition. The importance of the small bite angle of the diphosphine is apparent by comparison of the results obtained with *trans*- $[\text{RuCl}_2(\mathbf{L})]$  complexes of **1** and **2** (Table 1, entries 18 and 19).

Preliminary mechanistic studies, as well as the observed higher-alcohol side products, support a Guerbet-type mechanism. Treatment of  $[\text{RuCl}(\eta^6\text{-}p\text{-cymene})(\mathbf{3})]\text{Cl}$  with NaOEt under catalysis-like conditions led rapidly to the formation of a species with a triplet signal in the  $^1\text{H}$  NMR spectrum at  $-9.47$  ppm (triplet,  $^2J_{\text{PH}} = 33$  Hz), consistent with a ruthenium hydride. Addition of the ethanol substrate to this preactivated catalyst led to butanol formation. This result suggests that after initial formation of a ruthenium ethoxide,  $\beta$  elimination leads to the formation of the active hydride and the aldehyde. The addition of ethanol results in metathesis with the hydride, loss of hydrogen, and the formation once again of the ruthenium ethoxide to close the dehydrogenation cycle.

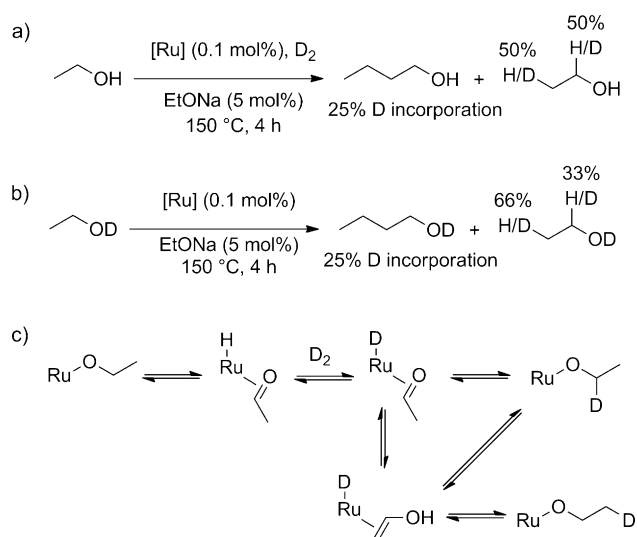
To investigate whether the hydrogen remains bound to the metal center during the catalytic cycle prior to delivery for later hydrogenation, we performed a catalytic reaction in the presence of  $\text{D}_2$  (2.5 bar; Scheme 3a). Significant D incorporation (25% across all sites) in the butanol product was observed, which suggests the presence of free hydrogen, or at

least rapid exchange between free and bound hydrogen/hydrides. Similar results were obtained when EtOD was used as the substrate (Scheme 3b). Indeed, deuterium incorporation into C–H/D bonds of “unreacted” ethanol was also observed in this experiment; moreover, the labeling pattern was very distinctive, with a 2:1 preference for monodeuteration at the ethanol 2-position over the 1-position. A simple ethoxide  $\beta$ -elimination/reinsertion mechanism would seem to favor incorporation at the 1-position (Scheme 3c), and this result suggests the intermediacy of an enolate  $\pi$ -bound to the ruthenium center through the C=C bond.

The remarkable feature of these catalysts is their extremely high selectivity as compared to that of all previous systems. Assuming a Guerbet-type mechanism, a key facet of this selectivity must be the exertion by the catalysts of extremely high levels of control over the base-catalyzed acetaldehyde aldol reaction, so that only dimeric products are obtained, rather than the usual mixtures of higher oligomers.

To study this hypothesis, we performed a series of aldol condensation reactions for both acetaldehyde and butylaldehyde in the presence and absence of the ruthenium catalyst (see Table S2 in the Supporting Information for a summary of these experiments). Under analogous conditions to those of the catalytic reactions but in the absence of ruthenium, acetaldehyde was oligomerized with 100% conversion in 4 h by NaOMe with little or no control, and the expected dimerization product crotylaldehyde accounted for only 14.6% of the total product mixture; the rest of the products were higher oligomers. By contrast, when the analogous reaction was performed in the presence of  $[\text{RuCl}(\eta^6\text{-}p\text{-cymene})(\mathbf{3})]\text{Cl}$  (0.1 mol %), 56.9% of the product was crotylaldehyde, with 100% conversion. The same experiment with butylaldehyde was also revealing: in the absence of ruthenium, 85% selectivity for a mixture of higher oligomers ( $\text{C}_{8+}$ ) was observed in 4 h, whereas in the presence of  $[\text{RuCl}(\eta^6\text{-}p\text{-cymene})(\mathbf{3})]\text{Cl}$  (0.1 mol %), only 24% selectivity was observed for oligomers in the same reaction time, and  $\text{C}_4$  species made up 76% of the product, including *n*-butanol (19%). These results suggest that the ruthenium catalyst biases the aldol condensation to give the desired  $\text{C}_4$  products by increasing the rate of acetaldehyde coupling but reducing the rate of aldol reaction with  $\text{C}_4$  or higher alcohols.

Aldehyde-hydrogenation experiments also revealed why such high selectivity is observed. Under catalysis-like conditions with  $[\text{RuCl}(\eta^6\text{-}p\text{-cymene})(\mathbf{3})]\text{Cl}$  and  $\text{H}_2$  (2.5 bar), no conversion of acetaldehyde into ethanol was observed within 4 h; indeed, only coupling products were observed ( $\text{C}_4$ ,  $\text{C}_6$ , and  $\text{C}_8$ ), including *n*-butanol (31.8%). By contrast, butylaldehyde was hydrogenated to *n*-butanol with 48.9% conversion in 4 h, and higher oligomers ( $\text{C}_{8+}$ ) made up only 19.4% of the product. These results suggest a regime during catalysis in which the aldol condensation of ethanol is favored over that of  $\text{C}_4$  or higher aldehydes, but the hydrogenation of  $\text{C}_4$  or higher aldehydes is favored over that of acetaldehyde. The low, steady concentration of acetaldehyde that results allows the reaction to proceed in a selective manner. It is tempting to also propose an “on-metal” aldol condensation to account for the unusually high selectivity of this step, especially since the intermediacy of the required enolates is implied by our



**Scheme 3.** a,b) Deuterium incorporation into the *n*-butanol product and ethanol substrate in the presence of  $\text{D}_2$  gas (a) and EtOD (b) under catalytic conditions ( $[\text{Ru}] = [\text{RuCl}(\eta^6\text{-}p\text{-cymene})(\mathbf{3})]\text{Cl}$ ). c) Ethoxide-elimination/reinsertion mechanism.

labeling studies (Scheme 3). Investigations in this regard are continuing.

The superior performance of small-bite-angle diphosphine ligands over that of analogues with wider bite angles is intriguing. A structural study of ruthenium precatalysts of ligand **3** was revealing. Depending on the solvent used for crystallization, either bidendate (methanol) or monodendate (acetone) complexes with one or two coordinated chloride ligands were formed (see the Supporting Information). This facile change in coordination mode implies that the potential hemilability of **3** may be important; in contrast, ligands **1** and **2** are more strongly chelating.

In conclusion, we have discovered a new ruthenium-bis(diphenylphosphanyl)methane catalyst for the upgrading of ethanol to the advanced biofuel *n*-butanol with 94% selectivity at over 20% conversion. To our knowledge, this catalyst is by some margin the most efficient yet reported for this transformation. Preliminary mechanistic studies suggest a range of factors for the excellent performance of these systems; these factors center on the ability of the catalyst to tame the notoriously uncontrolled base-catalyzed aldol condensation of acetaldehyde.

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