

Communication

Highly Efficient Process for Production of Biofuel from Ethanol Catalyzed by Ruthenium-Pincer Complexes

Yinjun Xie, Yehoshoa Ben-David, Linda J.W. Shimon, and David Milstein

J. Am. Chem. Soc., **Just Accepted Manuscript** • DOI: 10.1021/jacs.6b05433 • Publication Date (Web): 11 Jul 2016

Downloaded from <http://pubs.acs.org> on July 11, 2016

Just Accepted

“Just Accepted” manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides “Just Accepted” as a free service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. “Just Accepted” manuscripts appear in full in PDF format accompanied by an HTML abstract. “Just Accepted” manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are accessible to all readers and citable by the Digital Object Identifier (DOI®). “Just Accepted” is an optional service offered to authors. Therefore, the “Just Accepted” Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the “Just Accepted” Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these “Just Accepted” manuscripts.

Highly Efficient Process for Production of Biofuel from Ethanol Catalyzed by Ruthenium-Pincer Complexes

Yinjun Xie,[†] Yehoshoa Ben-David,[†] Linda J. W. Shimon,[‡] and David Milstein^{†,*}

Departments of [†]Organic Chemistry and [‡]Chemical Research Support, Weizmann Institute of Science, Rehovot, 76100, Israel

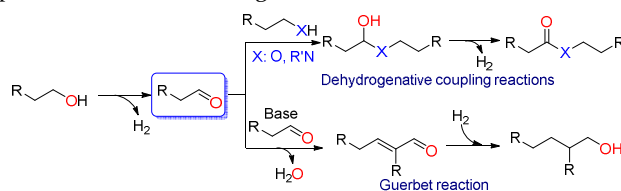
Supporting Information Placeholder

ABSTRACT: A highly efficient pincer-ruthenium catalyzed Guerbet-type process for the production of biofuel from ethanol was developed. It produces the highest conversion of ethanol (73.4%, 0.02mol% catalyst) for a Guerbet-type reaction, including significant amounts of C₄ (35.8% yield), C₆ (28.2% yield) and C₈ (9.4% yield) alcohols. Catalyst loadings as low as 0.001 mol% can be used, leading to a record turnover number of 18209. Mechanistic studies reveal the likely active ruthenium species, and the main deactivation process.

Biofuels generated from renewable biomass are recognized as one of the greenest alternatives to gasoline.¹ In recent years, ethanol, obtained from sugar-containing crops through fermentation, has been used as a renewable replacement of gasoline.² However, ethanol has some drawbacks, as its energy density is only 70% of that of gasoline (See SI), and it can also corrode the engine.³ Moreover, ethanol easily absorbs water, which leads to storage problems. Longer-chain alcohols have larger energy densities than ethanol (1-butanol, 1-hexanol and 1-octanol are 86%, 94% and 99% of that of gasoline, respectively, see SI), and are less miscible with water, thus presenting fewer storage problems. Because of these advantages, long-chain alcohols are termed “advanced biofuels”.⁴ However, large-scale production of these alcohols from renewable biomass is still a great challenge. To date, the best report of bulk synthesis of 1-butanol from feedstocks through the A.B.E. fermentation process (which produces a mixture of acetone, butanol and ethanol) provides only 16% yield of butanol.⁵ The Guerbet reaction also suffers from harsh conditions, poor selectivity, separation issues, and low yield.⁶ Therefore, development of a highly efficient process for these long-chain alcohols from renewable feedstock is highly desirable.

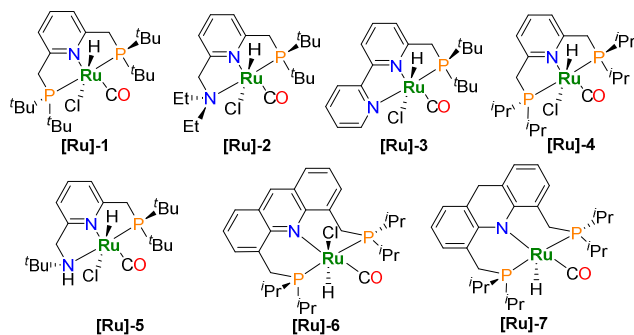
In recent years, significant developments in the catalytic ethanol conversion to butanol were reported. In 2013, Wass and co-workers reported their seminal work on ruthenium catalyzed Guerbet reaction for the synthesis of 1-butanol (45.8% conversion, 35.5% yield, 458 turnover numbers (TON), and 84.6% selectivity) from ethanol.^{7a} More recently, Jones and Baker reported a remarkable tandem catalytic approach for conversion of ethanol to 1-butanol in 34% yield (37% conversion, 186 TON), and >99% selectivity, using an iridium-

catalyst (0.2 mol%) and 10 mol% of a nickel or copper-catalyst.^{8c} Szymczak and co-workers reported Ru-catalyzed high conversion (53%, 530 TON) of ethanol to biofuels.^{7c} The total conversion of ethanol is of major importance for biofuel production. However, the catalytic systems for this transformation in the condensed phase using homogeneous,^{7, 8} and heterogeneous⁹ catalysts exhibit total conversions of ethanol not exceeding 53%. In view of these recent significant developments, an efficient catalytic process for high ethanol conversion to biofuels of longer chain alcohols (including C₄ and the more energetic C₆ and C₈) and high turnover numbers remains challenging. Herein, we present a ruthenium-pincer complex catalyzed process with the highest conversion and turnover numbers (reaching 18209 TON) for a Guerbet-type process of ethanol to long-chain alcohols.



Scheme 1. Catalytic transformation of alcohols

Our group has developed a series of ruthenium pincer complexes which efficiently catalyze acceptorless dehydrogenative coupling of alcohols (generating, for example, esters, acetals, amides, carboxylic acids) as well as various hydrogenation reactions.¹⁰⁻¹² Mechanistic studies indicate that aldehydes are generated as intermediates in these processes, and are subsequently attacked by nucleophiles (Scheme 1). Catalytic amounts of bases were employed to generate the active catalysts when pre-catalysts were employed. Another possible outcome when using a larger amount of catalytic base is deprotonation of the intermediate aldehyde, followed by aldol condensation, to generate an α,β -unsaturated aldehyde, which upon catalytic hydrogenation by the *in situ* generated H₂ can form a longer-chain alcohol, resulting in a Guerbet-type process (Scheme 1). It was of interest to us to explore how our pincer Ru complexes (Scheme 2) would function under these competing types of processes.



Scheme 2. Ruthenium pincer complexes used in this study

Table 1. Optimization of the reaction conditions^a

Entry	[Ru], Base	T (°C) / t (hour)	Conversion (yield) [%]	Selectivity [%]	TON
1	[Ru]-1, EtONa	110/16	7.1 (3.7)	62.6 ^b	355
2	[Ru]-2, EtONa	110/16	8.4 (1.3)	20.9 ^b	420
3	[Ru]-3, EtONa	110/16	4.1 (2.3)	56.8 ^b	205
4	[Ru]-4, EtONa	110/16	7.1 (2.5)	36.2 ^b	355
5	[Ru]-5, EtONa	110/16	5.6 (1.1)	20.1 ^b	280
6	[Ru]-6, EtONa	110/16	23.4 (20.9)	92.5	1171
7	[Ru]-6, EtOK	110/16	20.8 (18.4)	92.0	1042
8	[Ru]-6, NaOH	110/16	16.3 (14.9)	93.9	815
9	[Ru]-6, KOH	110/16	13.0 (12.1)	95.1	650
10	[Ru]-6, LiOH	110/16	1.1 (1.1)	100	56
11	[Ru]-6, EtONa	110/40	25.6 (22.1)	90.6	1280
12	[Ru]-6, EtONa	130/16	36.9 (28.0)	83.2	1844
13	[Ru]-6, EtONa	150/16	62.4 (35.9)	68.1	3122
14	[Ru]-6, EtONa	150/4	48.1 (34.2)	79.4	2407
15 ^c	[Ru]-6, EtONa	150/168	18.2 (14.6)	86.1	18209
16 ^d	[Ru]-6, EtONa	150/168	26.6 (21.1)	85.8	6648
17	[Ru]-7, EtONa	150/16	66.9 (38.4)	68.3	3345

^a Reaction conditions: [Ru] (0.01 mmol, 0.02 mol%), base (2 mmol, 4 mol%), and EtOH (50 mmol), under N₂, for 16 hours. Conversions and yields (in parenthesis) were determined by GC, using 2-pentanol and tetradecane as internal standards; turnover numbers (TON) are based on the amount of EtOH (in mmol) converted to products per mmol [Ru]. ^b Acetal or ethyl acetate were detected as main by-product (see supporting information). ^c [Ru]-6 (0.001 mol%). ^d [Ru]-6 (0.01 mmol, 0.004 mol%), EtONa (2 mmol, 0.8 mol%), and EtOH (250 mmol).

Initially, we employed 0.02 mol% of RuHCl(^tBuPNP)(CO) (Scheme 2, [Ru]-1)^{10a}, 4 mol% of EtONa and 50 mmol EtOH. After stirring under N₂ in an autoclave at 110 °C for 16 hours, 7.12% conversion (356 TON) of ethanol, resulting in 3.7% yield of 1-butanol (2) (Table 1, entry 1). Other ruthenium-pincer catalysts developed by our group including ([Ru]-2)^{10a}, ([Ru]-3)^{11b}, ([Ru]-4)^{10a}, ([Ru]-5)^{10h}, and ([Ru]-6)^{10c} (Scheme 2) were also examined (Table 1, entries 2-6). To our delight,

with the acridine-based [Ru]-6 as catalyst, 20.9% yield of 1-butanol (92.5 % selectivity) together with longer-chain alcohols (2-ethyl-1-butanol, 1-hexanol, 2-ethyl-1-hexanol, and 1-octanol, see SI) were obtained (Table 1, entry 6), and the total turnover number (TON) reached 1171. Employing the commercial ruthenium complexes [RuCl₂(*p*-cymene)]₂, RuCl₂(DMSO)₄, RuCl₂(*p*-cymene)(CO), [RuCl₂(COD)]_n, [RuCl₂(CO)₃]₂, and RuHCl(CO)(PPh₃)₃ as pre-catalysts gave inferior results compared to [Ru]-6 (see supporting information).

The yield and selectivity depend on the base used. Thus, when EtOK, NaOH, KOH and LiOH were employed, the yields (selectivity) of 1-butanol were 18.4% (92.0%), 14.9% (93.9%), 12.1% (95.1%), and 1.1% (100%), respectively (Table 1, entries 8-10). Hence, we selected [Ru]-6 and EtONa for further experimentation. Extension of the reaction time to 40 hours did not significantly improve the conversion (25.6%) and TON (1280) (Table 1, entry 11). However, increasing the reaction temperature from 110 °C to 130 °C (Table 1, entry 12) and 150 °C (Table 1, entry 13), improved the yields and TONs considerably. When the reaction was carried at 150 °C, 35.9% yield of 1-butanol, 62.4% conversion of ethanol and TON 3122 were obtained (Table 1, entry 13). Reducing the reaction time to 4 hours at 150 °C, a similar yield of 1-butanol (34.2%) and a higher selectivity (79.4%) were observed (Table 1, entry 14). Significantly, decreasing the load of [Ru]-6 from 0.02 to 0.001 mol%, resulted in 18.2% conversion of ethanol, 14.6% yield of 1-butanol, 86.1% selectivity, and a record TON of 18209 after 7 days (Table 1, entry 15). Furthermore, the reaction proceeded very well also at 250 mmol scale, using [Ru]-6 (0.004 mol%) and EtONa (0.8 mol%), giving 1-butanol in higher yield and similar selectivity (Table 1, entry 16). The dearomatized complex [Ru]-7, which is plausibly the actual catalyst in the reaction, functioned very well (38.4% yield of 1-butanol, 3345 TON, Table 1, entry 17). To our knowledge, this represents the most efficient reported process for the production of biofuel from ethanol in the liquid phase, regarding the combined highest conversion, yield, and turnover number.

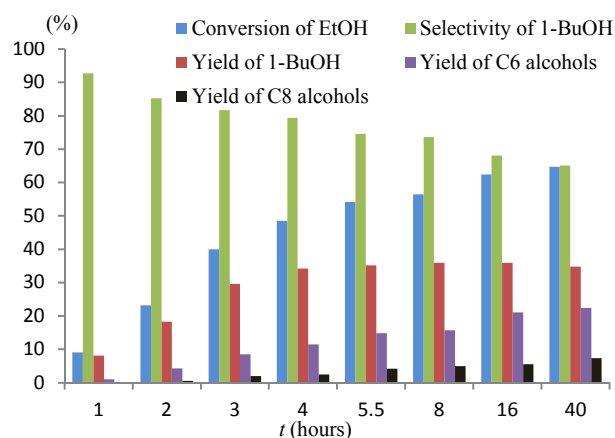


Figure 1. Reaction profile of the ruthenium-catalyzed Guerbet-type process for biofuel production. Conditions: [Ru]-6 (0.01 mmol), EtONa (2 mmol), and EtOH (50 mmol), 150 °C.

Further, we investigated the relationship between the reaction time, the conversion of ethanol, and the yield and selec-

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

tivity of 1-butanol. As shown in Figure 1, after 4 hours at 150 °C the yield of 1-butanol reached 34.2% (79.4% selectivity), and it didn't increase significantly upon prolonging the reaction time. In contrast to the unchanged yield of 1-butanol between 4 and 40 hours, the conversion of ethanol increased from 48.5 to 64.7% (Figure 1). This result indicates that with reaction progress, the generating rate of 1-butanol and its consumption rate (being converted to C₆ and C₈ alcohols via cross-coupling and homo-coupling) became similar. Naturally, along with increasing yields of C₆ and C₈ alcohols, the selectivity of 1-butanol decreased from 79.4 to 65.1%, because of the base catalyzed aldol condensation.

Compared with results of 16 and 40 hours, the conversion of ethanol, and the yield and selectivity of 1-butanol changed very slowly. Careful analysis of the reaction mixtures after 16 hours and 40 hours revealed by ¹H NMR 74% and 98% yield (respectively) of sodium acetate (yield of NaOAc based on the amount of EtONa). This is likely a result of the reaction of ethanol with water and base, liberating H₂^{10f}. NaOAc was also formed in Wass's work, probably via Cannizzaro or Tishchenko-type pathways.^{7b} Upon replacing EtONa by NaOAc, no desired product was observed after reacting at 150 °C for 16 hours. This indicates that as the consumption of strong base continues, due to water generation, the reaction becomes slower, and when all EtONa is converted to NaOAc, the reaction stops. To remove the formed H₂O, molecular sieves, or Na₂SO₄ were added to the reactions; however, it didn't improve the products yields (see SI). We also tried employing a Dean-Stark apparatus for water removal, using an ethanol-toluene solution, but only 0.9% yield of 1-butanol was detected after 80 hours, perhaps due to the low azeotropic temperature.

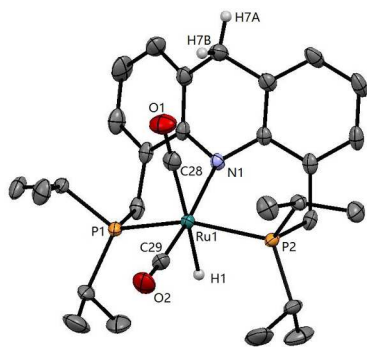


Figure 2. Molecular structure of [Ru]-8 with ellipsoids set at 50% probability. Selected bond lengths (Å): Ru1-N1 2.260(2), Ru1-P1 2.3376(7), Ru1-P2 2.3416(7), Ru1-C28 1.951(3), Ru1-C29 1.848(3), Ru1-H1 1.74(5), see SI for details.

Significantly, a crystal of the dearomatized hydrido dicarbonyl complex [Ru]-8 was obtained from the reaction solution after 5 days at 130 °C (Figure 2).¹⁰ⁱ We believe that the coordinatively unsaturated [Ru]-7¹⁰ⁱ is the actual catalyst, and [Ru]-8 is generated from it by decarbonylation of an intermediate aldehyde.

Based on mechanism studies (details see SI) and DFT calculations^{10i,13}, a plausible mechanism for aldehyde formation in this system (Figure 3) involves ethanol coordination cis to the hydride in the unsaturated 7 followed by coupling of the

hydride with the OH proton of I to generate H₂ and the unsaturated alkoxide intermediate II. The latter undergoes β-H elimination to form the complexed aldehyde intermediate III, followed by dissociation of the aldehyde product, which undergoes the base-catalyzed Guerbet process (Scheme 1). We believe that a mechanism involving O-H activation by metal-ligand cooperation based on the Ru-amido bond is less likely, due to the low basicity of the amido ligand in this case.

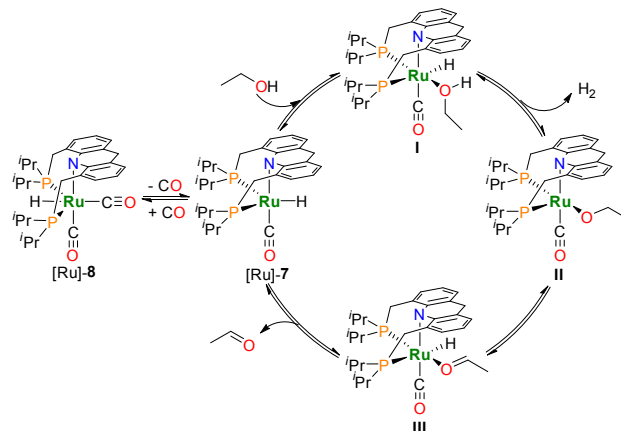


Figure 3. Plausible mechanism of dehydrogenation

The isolated [Ru]-8 was quantitatively independently synthesized by reaction of [Ru]-7 with CO (see SI). Indeed, when [Ru]-7 (Table 1, entry 17) and [Ru]-8 were used as catalysts, 38.4% and 37.4% yields (68.3% and 68.7% selectivity) of 1-butanol were obtained after 16 hrs (respectively), slightly better than when [Ru]-6 was used (Table 1, entry 13). Isolation of [Ru]-8 after 5 days, and the catalytic testing of [Ru]-8 as pre-catalyst indicate that the Ru-catalyst [Ru]-7 is not deactivated after this period. Therefore, these results suggest that the reason for termination of the reaction is lack of a strong base to catalyze the aldol condensation.

Table 2. Exploration of reactions for producing more longer-chain alcohols^a

CCO $\xrightarrow[150\text{ }^\circ\text{C, 40 h}]{[\text{Ru}]\text{-6 (0.02 mol\%)} \text{ EtONa (x mol\%)}}$ CCCCO + CCCCCO + CCCCCO

Entry	EtONa [mol%]	Conversion [%] (TON)	Yield (Selectivity) [%]		
			C ₄ H ₉ OH	C ₆ H ₁₃ OH	C ₈ H ₁₇ OH
1	4	64.7 (3234)	34.8 (65.1)	22.4 (28.0)	7.4 (6.9)
2	10	67.8 (3391)	35.3 (63.3)	24.7 (29.6)	7.9 (7.1)
3	15	69.3 (3464)	34.2 (60.9)	26.9 (31.9)	8.2 (7.2)
4	20	73.4 (3671)	35.8 (60.3)	28.2 (31.8)	9.4 (7.9)

^a Reaction conditions: [Ru]-6 (0.01 mmol, 0.02 mol%), EtONa, and EtOH (50 mmol), under N₂, for 40 hours. Conversions, TONs and yields of products, based on the amount of EtOH converted to products per mmol [Ru], were determined by GC, using 2-pentanol and tetradecane as internal standards.

As is well known, longer-chain alcohols like 1-hexanol and 1-octanol are more similar to gasoline than 1-butanol, and have higher energy densities (see SI). To obtain higher conversion to longer-chain alcohols, more EtONa was used, with results shown in Table 2. Obviously, more EtONa helps increasing the conversions of ethanol and the yields of hexanols and octanols. Thus, using 20 mol% of EtONa, 28.2 % yield of hexanol (C₆) and 9.4 % yield of octanol (C₈) were obtained, together with 35.8% yield of 1-butanol (Table 2). With these results, this reaction system can be counted as the most efficient process for making hexanol and octanol directly from ethanol through a Guerbet-type reaction.

In conclusion, we have developed a very efficient pincer-ruthenium catalyzed Guerbet-type process for production of biofuel from ethanol with the highest TON (18209; 86.1% selectivity to 1-butanol) of a Guerbet-type reaction. By increasing the amount of catalytic base, the amount of C₆ and C₈ alcohols increases substantially, reaching a record total conversion of 73.4% (37.6% selectivity to C₆+C₈ alcohols). Our mechanistic studies, including complex isolation from the catalytic reaction, show that the likely actual catalyst is the dearomatized [Ru]-7, and indicate that the major deactivation pathway is consumption of the strong base by catalytic reaction of the formed water with ethanol and EtONa to form inactive NaOAc.

We believe that our findings contribute significantly to the development of superior biofuel, based on long-chain alcohols, from ethanol. Experiments are underway aimed at further mechanistic insight and improvements.

ASSOCIATED CONTENT

Supporting Information Available:

Experimental details –catalysts, kinetic plots, monitoring experiments, spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

david.milstein@weizmann.ac.il

Author Contributions

The manuscript was written through contributions of all authors. / All authors have given approval to the final version of the manuscript.

ACKNOWLEDGMENT

This work was supported by the Israel Science Foundation and by the Bernice and Peter Cohn Catalysis Research Fund. D. M. holds the Israel Matz Professorial Chair of Organic Chemistry. Y.X. thanks the Alternative Sustainable Energy Research Initiative (AERI) of the Weizmann Institute for a postdoctoral fellowship.

REFERENCES

(1) Ragauskas, A. J.; Williams, C. K.; Davison, B. H.; Britovsek, G.; Cairney, J.; Eckert, C. A.; Frederick, W. J., Jr.; Hallett, J. P.; Leak, D. J.;

Liotta, C. L.; Mielenz, J. R.; Murphy, R.; Templer, R.; Tschaplinski, T. *Science* **2006**, *311*, 484–489.

(2) Sheehan, J.; Aden, A.; Paustian, K.; Killian, K.; Brenner, J.; Walsh, M.; Nelson, R. *J. Ind. Ecol.* **2003**, *7*, 117–146.

(3) (a) Harvey, B. G.; Meylemans, H. A. *J. Chem. Technol. Biotechnol.* **2011**, *86*, 2–9.

(4) (a) Ramey, D. E. US National Agricultural Biotechnology Council (NABC) Reports, Agricultural Biofuels: Technology, Sustainability and Profitability, Part III: Technology: Biomass, Fuels and Co-Products: Butanol: The Other Alternative Fuel **2007**, *19*, 136–147; (b) Szulczyk, K. R. *Int. J. Energy Environ.* **2010**, *1*, 501–512; (c) Runge, W. *Technology Entrepreneurship: A Treatise on Entrepreneurs and Entrepreneurship for and in Technology Ventures*; KIT Scientific Publishing, Mannheim, Vol. 2, P 1057.

(5) (a) Weizmann, C. GB 191504845 A, 1919 (b) Jin, C.; Yao, M.; Liu, H.; Lee, C.-F.; Ji, J. *Renewable Sustainable Energy Rev.* **2011**, *15*, 4080–4106.

(6) (a) Guerbet, M. C. R. *Acad. Sci. Paris* **1899**, *128*, 1002–1004; (b) Guerbet, M. M. C. R. *Acad. Sci. Paris* **1909**, *149*, 129–132; (c) Veibel, S.; Nielsen, J. I. *Tetrahedron* **1967**, *23*, 1723–1733. (d) O'Lenick, A. J., Jr. *J. Surfactants Deterg.* **2001**, *4*, 311–315; (e) Sushkevich, V. L.; Ivanova, I. I.; Taarning, E. *ChemCatChem* **2013**, *5*, 2367–2373; (f) Ghaziaskarab, H. S.; Xu, C. *RSC Adv.* **2013**, *3*, 4271–4280; (g) Hanspal, S.; Young, Z. D.; Shou, H.; Davis, R. J. *ACS Catal.* **2015**, *5*, 1737–1746; (h) Gabriels, D.; Hernandez, W. Y.; Sels, B.; Van Der Voort, P.; Verberckmoes, A. *Catal. Sci. Technol.* **2015**, *5*, 3876–3902.

(7) For ruthenium catalyzed upgrading of ethanol see: (a) Dowson, G. R. M.; Haddow, M. F.; Lee, J.; Wingad, R. L.; Wass, D. F. *Angew. Chem., Int. Ed.* **2013**, *52*, 9005–9008; (b) Wingad, R. L.; Gates, P. J.; Street, S. T. G. Wass, D. F. *ACS Catal.* **2015**, *5*, 5822–5826; (c) Tseng, K. T.; Lin, S.; Kampf, J. W.; Szymczak, N. K. *Chem. Commun.* **2016**, *52*, 2901–2904; (d) Wingad, R. L.; Bergstrom, E. J. E.; Everett, M.; Pellow, K. J.; Wass, D. F. *Chem. Commun.* **2016**, *52*, 5202–5204.

(8) For iridium catalyzed upgrading of ethanol see: (a) Koda, K.; Matsu-ura, T.; Obora, Y.; Ishii, Y. *Chem. Lett.* **2009**, *38*, 838–839; (b) Xu, G.; Lammens, T.; Liu, Q.; Wang, X. Dong, L.; Caiazzo, A.; Ashraf, N.; Guan, J.; Mu, X. *Green Chem.* **2014**, *16*, 3971–3977; (c) Chakraborty, S.; Piszal, P. E.; Hayes, C. E.; Baker, R. T.; Jones, W. D. *J. Am. Chem. Soc.* **2015**, *137*, 14264–14267.

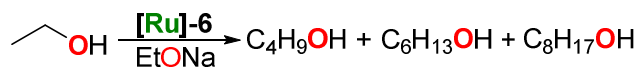
(9) A review of heterogeneously catalyzed upgrading of ethanol: Galadima, A.; Muraza, O. *Ind. Eng. Chem. Res.* **2015**, *54*, 7181–7194.

(10) (a) Zhang, J.; Leitius, G.; Ben-David, Y.; Milstein, D. *J. Am. Chem. Soc.* **2005**, *127*, 10840–10841; (b) Gunanathan, C.; Ben-David, Y.; Milstein, D. *Science* **2007**, *317*, 790–792; (c) Gunanathan, C.; Shimon, L. J. W.; Milstein, D. *Angew. Chem. Int. Ed.* **2008**, *47*, 8861–8864; (d) Gunanathan, C.; Shimon, L. J. W.; Milstein, D. *J. Am. Chem. Soc.* **2009**, *131*, 3146–3147; (e) Gnanaprakasam, B.; Balaraman, E.; Ben-David, Y.; Milstein, D. *Angew. Chem. Int. Ed.* **2011**, *50*, 12240–12244; (f) Balaraman, E.; Khaskin, E.; Leitius, G.; Milstein, D. *Nat. Chem.* **2013**, *5*, 122–125; (g) Khusnutdinova, J. R.; Ben-David, Y.; Milstein, D. *J. Am. Chem. Soc.* **2014**, *136*, 2998–3001; (h) Fogler, E.; Garg, J.; Hu, P.; Leitius, G.; Shimon, L. J. W.; Milstein, D. *Chem. Eur. J.* **2014**, *20*, 15727–15731. (i) Gellrich, U.; Khusnutdinova, J. R.; Leitius, G. M.; Milstein, D. *J. Am. Chem. Soc.* **2015**, *137*, 4851–4859.

(11) (a) Zhang, J.; Leitius, G.; Ben-David, Y.; Milstein, D. *Angew. Chem., Int. Ed.* **2006**, *45*, 113–115; (b) Balaraman, E.; Gnanaprakasam, B.; Shimon, L. J. W.; Milstein, D. *J. Am. Chem. Soc.* **2010**, *132*, 16756–16758; (c) Balaraman, E.; Ben-David, Y.; Milstein, D. *Angew. Chem., Int. Ed.* **2011**, *50*, 11702–11705.

(12) For selected reviews see: Gunanathan, C.; Milstein, D. *Science* **2013**, *341*, 1229712; (b) Gunanathan, C.; Milstein, D. *Chem. Rev.* **2014**, *114*, 12024–12087.

(13) For DFT calculations for the mechanism of aldehyde formation, see: Ye, X.; Plessow, P. N.; Brinks, M. K.; Schelwies, M.; Schaub, T.; Rominger, F.; Paciello, R.; Limbach, M.; Hofmann, P. *J. Am. Chem. Soc.* **2014**, *136*, 5923–5929.



Highly efficient biofuel production

Up to 18209 TON.

Up to 73.4 % conversion.

