

Catalytic Conversion of Ethanol to *n*-Butanol Using Ruthenium P–N Ligand Complexes

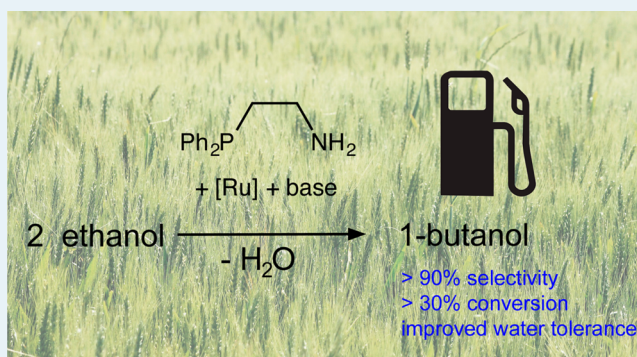
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Supporting Information

ABSTRACT: We report several ruthenium catalysts incorporating mixed donor phosphine-amine ligands for the upgrade of ethanol to the advanced biofuel *n*-butanol, which show high selectivity ($\geq 90\%$) at good (up to 31%) conversion. In situ formation of catalysts from mixtures of $[\text{RuCl}_2(\eta^6\text{-}p\text{-cymene})]_2$ and 2-(diphenylphosphino)ethylamine (**1**) shows enhanced activity at initial water concentrations higher than those of our previously reported diphosphine systems. Preliminary mechanistic studies (electrospray ionization mass spectrometry and nuclear magnetic resonance spectroscopy) suggest the possibility of ligand-assisted proton transfer in some derivatives.

KEYWORDS: biofuels, ethanol upgrading, butanol, ruthenium, Guerbet catalysis



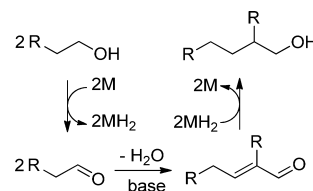
INTRODUCTION

Obtaining liquid fuels from renewable biomass sources remains an important component of future energy provision.¹ Bio ethanol 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 compared to gasoline: it has a lower energy density (70% of that of gasoline), it can be corrosive to current engine technology and fuel infrastructure, and it readily absorbs water leading 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.² 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.³ However, the bulk synthesis of butanol from biosustainable feedstocks remains challenged by low conversion and variable selectivity.⁴

Our approach has been to seek “Guerbet” type catalysts for the conversion of readily available ethanol into this more advanced biofuel.⁵ This methodology is sometimes termed “borrowed hydrogen” chemistry.⁶ In a typical catalytic reaction scheme, an alcohol is dehydrogenated to form an aldehyde, which then undergoes aldol coupling before the resultant product is rehydrogenated to give a longer chain alcohol (Scheme 1).

Unfortunately, ethanol is a specifically difficult substrate for this chemistry,⁷ primarily because base-catalyzed aldol condensation of acetaldehyde is notoriously difficult to control,

Scheme 1. Guerbet Reaction



leading to mixtures of oligomeric and polymeric products.⁸ These factors combine to make achieving good selectivity in ethanol-to-butanol conversion extremely challenging. Some progress has been reported in work by Ishii using a homogeneous iridium catalyst, $[\text{Ir}(\text{COD})(\text{acac})]$, in the presence of a phosphine ligand, the additive 1,7-octadiene, and an alkoxide base to achieve *n*-butanol selectivity of up to 67% at 12% conversion.⁹ As expected, longer chain alcohols are formed as side products of uncontrolled aldol reactions. More recently, heterogeneous catalysts that achieve selectivity of up to 80% at 25% ethanol conversion have been reported.¹⁰ In addition, iridium catalysts that can be used in water and air have been reported.¹¹ We reported a new family of homogeneous ruthenium-based catalysts that demonstrated a step change in performance, achieving the upgrading of ethanol to *n*-butanol at >94% selectivity at good conversion.¹² Key to this high selectivity was the use of small bite angle 1,1-bis-(diphenylphosphino)methane (dppm) ligands, diphosphines with larger bite angles being less effective. As part of our

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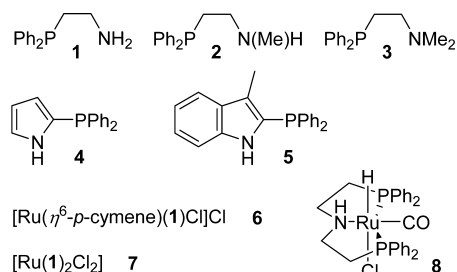
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investigation into a wider variety of ligands, we have discovered that mixed donor P–N ligands are also highly selective.

RESULTS AND DISCUSSION

Our initial catalyst screening utilized the same procedure we reported for diphosphine ligands: $[\text{RuCl}_2(\eta^6\text{-}p\text{-cymene})]_2$ as a catalyst precursor with a range of P–N donor ligands (Chart 1), sodium ethoxide base, and a run time of 4 h at 150 °C.

Chart 1. Ligands and Complexes Used in This Study



Results are listed in Table 1. Liquid phase selectivities to *n*-butanol are reported in line with previous reports for direct comparison.^{9,11,12}

Comparison of ligand **1** with dppm (compare runs 1 and 2) reveals that **1** has a very similar performance under these conditions. Further investigation under a more varied set of conditions reveals that **1** offers certain advantages in terms of maintaining good conversion and selectivity compared to those of dppm at higher water concentrations (compare runs 3 and 5); this offers distinct technological advantages in industrial application. However, when the concentration of water is increased further, both systems give similar results (compare runs 4 and 6).

Some catalyst decomposition is observed through all runs, so that the reaction solution after 4 h has a black turbid appearance. In our previous paper,¹² we reported that the use of bis-chelate ruthenium complexes such as *trans*- $[\text{RuCl}_2(\text{dppm})_2]$ provided more stable catalysts, albeit at the cost of rate. When 2 equiv of **1** was used in conjunction with $[\text{RuCl}_2(\eta^6\text{-}p\text{-cymene})]_2$, we were pleased to find that the reaction still proceeded with very high selectivity (94.3%) to give an *n*-butanol yield of 20.8% after 4 h (run 7). This compares favorably to our dppm system that gives considerably lower *n*-butanol yields over 4 h.¹² In all runs with 2 equiv of ligand, the final reaction mixture is clear yellow, with little to no evidence of ruthenium metal deposition, suggesting a homogeneous system.

Ligand **1** clearly has the potential to be deprotonated under these reaction conditions and operate via an “outer sphere” mechanism that is common for catalysts of this type in hydrogen transfer reactions.¹³ This is believed to be the case here as will be discussed later, and suggested ligands **2** and **3** with partial and full methylation of the amine may provide insights. The performance of **2** (run 8) is very similar to that of **1**, whereas **3** (run 9) gives reduced conversion and selectivity, albeit not the dramatic switch in performance that may have been expected if an outer sphere mechanism is essential. Given the good performance of dppm, the fact that ligand deprotonation is not critical but may facilitate catalysis seems reasonable. The related ligands **4** and **5** also perform well; **5** (run 11) with a conversion of 31.4% and 92.7% selectivity outperforms even the dppm catalyst. Unfortunately, this

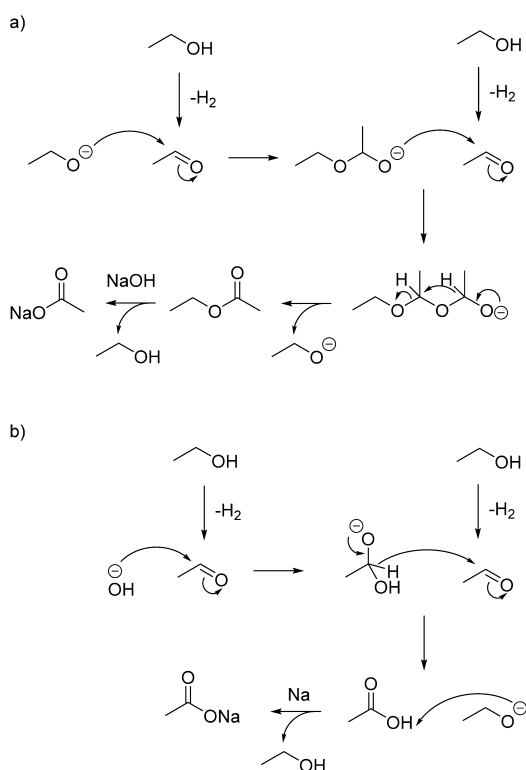
Table 1. Ruthenium-Catalyzed Conversion of Ethanol to *n*-Butanol

run	catalyst	conversion (%) [yield (%)] ^a	selectivity (%) ^b	TON ^c
1	1 + $[\text{RuCl}_2(\eta^6\text{-}p\text{-cymene})]_2$	25.1 (21.9)	91.1	251
2 ^d	dppm + $[\text{RuCl}_2(\eta^6\text{-}p\text{-cymene})]_2$	20.4 (17.5)	90.0	204
3 ^e	1 + $[\text{RuCl}_2(\eta^6\text{-}p\text{-cymene})]_2$	9.8 (9.8)	>99	98
4 ^f	1 + $[\text{RuCl}_2(\eta^6\text{-}p\text{-cymene})]_2$	4.9 (4.9)	>99	49
5 ^e	dppm + $[\text{RuCl}_2(\eta^6\text{-}p\text{-cymene})]_2$	5.7 (5.3)	95.1	57
6 ^f	dppm + $[\text{RuCl}_2(\eta^6\text{-}p\text{-cymene})]_2$	4.3 (4.0)	95.2	43
7	2 equiv of 1 + $[\text{RuCl}_2(\eta^6\text{-}p\text{-cymene})]_2$	22.7 (20.8)	94.3	227
8	2 + $[\text{RuCl}_2(\eta^6\text{-}p\text{-cymene})]_2$	23.8 (18.8)	84.9	238
9	3 + $[\text{RuCl}_2(\eta^6\text{-}p\text{-cymene})]_2$	16.7 (12.1)	79.6	167
10	4 + $[\text{RuCl}_2(\eta^6\text{-}p\text{-cymene})]_2$	19.7 (17.5)	92.4	197
11	5 + $[\text{RuCl}_2(\eta^6\text{-}p\text{-cymene})]_2$	31.4 (28.1)	92.7	314
12	6	23.6 (20.5)	90.8	236
13	7	18.8 (17.1)	93.5	188
14 ^g	1 + $[\text{RuCl}_2(\eta^6\text{-}p\text{-cymene})]_2$	20.5 (18.0)	91.7	205
15	8	13.3 (1.6)	12.4 ^h	133
16	10	21.1 (19.5)	95.1	211

^aTotal conversion of ethanol to Guerbet products (see the Supporting Information), with the yield of *n*-butanol in parentheses. ^bTotal selectivity to *n*-butanol in the liquid fraction determined by gas chromatography. ^cTurnover number (TON) based on millimoles of substrate converted to products per millimole of Ru. ^dData taken from ref 12. dppm = 1,1-bis(diphenylphosphino)methane. ^eWith 1.84 mL of water added (5% by volume). ^fWith 3.89 mL of water added (10% by volume). ^gWith 10 g of 3 Å molecular sieves added. ^hThe major product is ethyl acetate (see the Supporting Information).

particular ligand decomposes during the run to yield traces of foul-smelling 3-methylindole, making it an unattractive derivative for further development. The ruthenium complexes $[\text{RuCl}(\eta^6\text{-}p\text{-cymene})(\mathbf{1})\text{Cl}]$ **6**¹⁴ and $[\text{RuCl}_2(\mathbf{1})_2]$ **7**¹⁵ (Chart 1) may be preformed by known methods before the catalysis is conducted. Under our standard catalytic conditions, identical results within error compared to those of in situ-formed catalysts are obtained (compare runs 1 and 12 and runs 7 and 13).

Perhaps the most surprising feature of these catalysts is that they yield *n*-butanol as the major product and yet are similar to reported ruthenium catalysts based on tridentate P–N–P ligands that produce only ethyl acetate in excellent selectivity.¹⁶ A closer examination of the full mass balance for our catalysts reveals that some acetate products are formed as solid sodium acetate byproducts; for example, run 1 results in 1.16 g or 14.1 mmol of sodium acetate in addition to liquid products.¹⁷ This result is consistent with the hydrogen also produced during the reaction¹⁸ and implies parallel Cannizzaro¹⁹ or Tishchenko type²⁰ pathways (Scheme 2) in addition to Guerbet chemistry.

Scheme 2. Tishchenko (a) and Cannizzaro (b) Type Pathways for the Formation of Sodium Acetate


As expected, the generation of free water facilitates these side reactions, and conducting a standard run in the presence of 3 Å molecular sieves considerably reduces acetate make (0.53 g, 6.4 mmol) while retaining excellent conversion and selectivity within the liquid fraction to *n*-butanol (run 14). We remained

surprised that no *n*-butanol product was reported with tridentate ligand complexes given our observations and further speculated that the different reaction conditions employed in this ethanol to ethyl acetate catalysis (typically lower temperature and an open vessel to allow hydrogen to escape) might be influential. We therefore tested the tridentate ligand complex **8** (Chart 1) under our conditions (run 15). Even under these conditions, ethyl acetate is produced in a yield higher than that of *n*-butanol (5.4% yield, 40.6% selective) in stark contrast to runs with our catalysts. This implies a genuine ligand effect on selectivity, and defining the origin of this effect is an ongoing objective.

In Situ Monitoring of Catalyst. To gain mechanistic insight, particularly into the active form of the catalyst and the origin of the excellent selectivity observed, a series of ongoing catalytic runs were studied using a combination of ^1H and $^{31}\text{P}\{^1\text{H}\}$ nuclear magnetic resonance (NMR) spectroscopy and electrospray ionization mass spectrometry (Figure 1). Reaction conditions were changed slightly to simplify this study and allow the use of low-pressure vessels, so that a reaction temperature of 78 °C was used. Under these conditions, the catalyst still converts ethanol to *n*-butanol with good selectivity (96.7%), albeit at much lower conversion after 4 h (see the Supporting Information); nevertheless, the products obtained, being very similar to those from a standard run, lead us to believe the same catalytically active organometallic species are present. The precatalyst **6** is observed before addition of base with a distinct $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy resonance at 61.4 ppm; mass spectrometry reveals a parent ion peak at m/z 500.08 due to $[\text{RuCl}(\eta^6\text{-}p\text{-cymene})(\mathbf{1})]^+$. Upon addition of NaOEt at room temperature, the ethoxide complex $[\text{Ru}(\eta^6\text{-}p\text{-cymene})(\mathbf{1})(\text{OEt})]^+$ is not observed, and the only species visible in the NMR spectrum is a hydride [$\delta_{\text{p}} = 74.0$ ppm; $\delta_{\text{H}} = -9.01$ ppm (d, $^2J_{\text{PH}} = 45$ Hz)], the mass spectrum of which

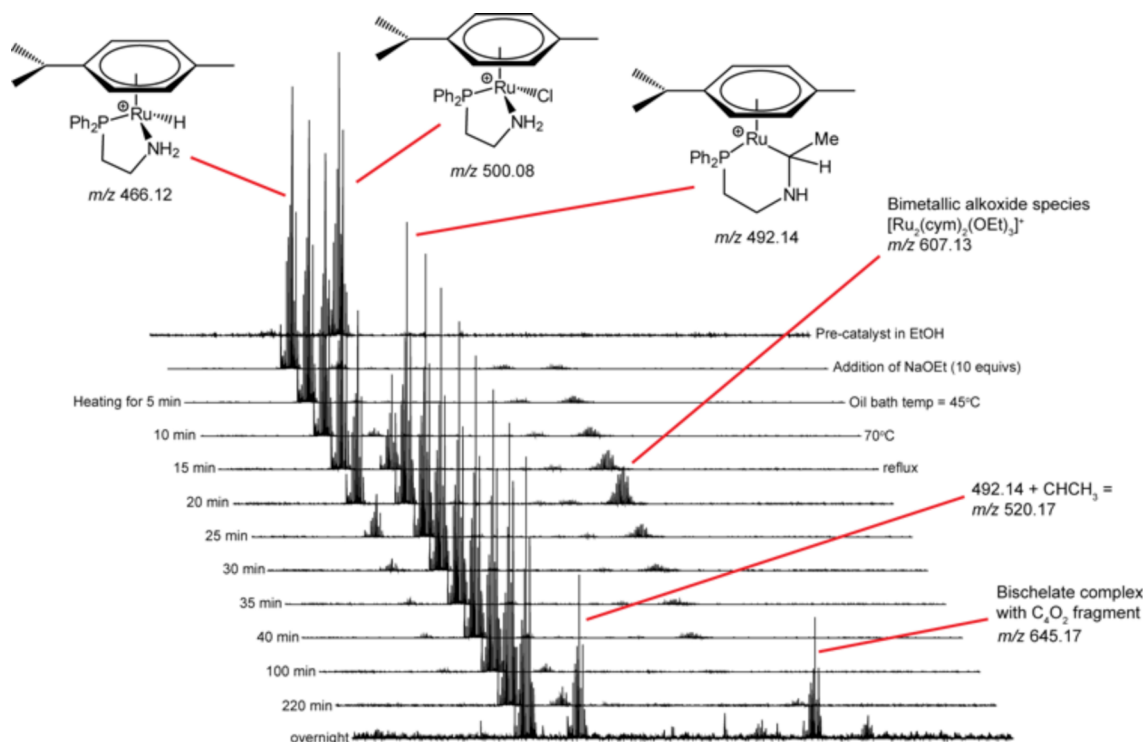
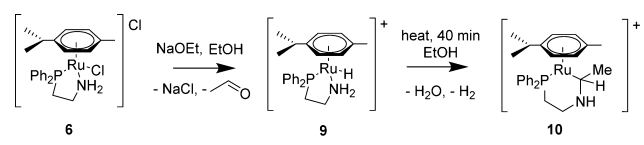


Figure 1. In situ monitoring of ruthenium complex **6** by electrospray ionization mass spectrometry.

corresponds to that of $[\text{Ru}(\eta^6\text{-}p\text{-cymene})(\text{I})(\text{H})]^+$ (**9**; m/z 466.12). After a 15 min heating, other species are also observed in the mass spectrum, specifically a signal at m/z 492.14. Initially, we proposed the formation of the amido carbonyl complex, $[\text{Ru}(\eta^6\text{-}p\text{-cymene})(\text{Ph}_2\text{P}(\text{CH}_2)_2\text{NH})(\text{CO})]^+$ (exact mass of m/z 492.10), in which the phosphinoamine ligand is deprotonated at nitrogen; the decarbonylation of alcohols by related ruthenium species is known, and we presumed a similar process was operating here.²¹ However, upon isolation of this species and further analysis [infrared, $^{13}\text{C}\{^1\text{H}\}$, and two-dimensional NMR spectroscopy (see the [Supporting Information](#))], the balance of evidence suggests this species may be a metalated alkyl amine complex ([Scheme 3](#)) in which a CHCH_3

Scheme 3. Evolution of the Ruthenium Precatalyst



group has inserted into the Ru–N bond, $[\text{Ru}(\eta^6\text{-}p\text{-cymene})(\text{Ph}_2\text{P}(\text{CH}_2)_2\text{NHCHCH}_3)]^+$ **10**, which is also consistent with the MS data (exact mass of m/z 492.14). Complex **10** is catalytically active, giving a yield and a selectivity similar to those of complex **6** (run 16), and our working hypothesis is that **10** is an off-cycle catalyst resting state. After 40 min, virtually all of the hydride is converted to **10**, which is persistent throughout the reaction time (22 h). After 22 h, a multitude of species is observed: species **10** as well as compounds consistent with bis-chelate complexes (m/z 617.16, 645.17, and 673.20) formed via ligand redistribution reactions. As shown previously, bis-chelate complexes are catalytically active for this process ([Table 1](#), run 13). Of particular interest is the observation of mass spectrum data consistent with a bis-chelate complex containing a bound C_4 dioxygenated fragment (m/z 645.17); this opens the tantalizing possibility of a metal-templated aldol condensation, something we have previously suggested might be a reason for the excellent selectivity of these systems. Attempts to isolate and further study such species are underway.

CONCLUSION

We have explored the use of mixed donor phosphine-amine ligands in the ruthenium-catalyzed upgrading of ethanol to the advanced biofuel *n*-butanol; these systems achieve performance that matches that of our previously reported ruthenium–1,1-bis(diphenylphosphino)methane catalysts, as well as giving certain advantages in terms of water tolerance. Preliminary mechanistic studies suggest the possibility of ligand-assisted proton transfer in some derivatives. The reasons for the excellent selectivity of such catalysts on the production of *n*-butanol as opposed to ethyl acetate, observed in very similar systems, are an area of continuing study.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acscatal.5b01327](https://doi.org/10.1021/acscatal.5b01327).

Experimental details of catalysis, kinetic plots, monitoring experiments, and spectra ([PDF](#))

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Notes

The authors declare no competing financial interest.

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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) (a) Many examples, including: Atsumi, S.; Cann, A. F.; Connor, M. R.; Shen, C. R.; Smith, K. M.; Brynildsen, M. P.; Chou, K. J. Y.; Hanai, T.; Liao, J. C. *Metab. Eng.* **2008**, *10*, 305–311. (b) Harvey, B. G.; Meylemans, H. A. J. *Chem. Technol. Biotechnol.* **2011**, *86*, 2–9.
- (3) (a) Ramey, D. E. U.S. 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. U.S. National Agricultural Biotechnology Council: Ithaca, NY, 2007; Vol. 19, pp 136–147. (b) Szulczyk, K. R. *Int. J. Energy Environ.* **2010**, *1*, 501–512. (c) Verma, R. P. Butanol: A Possible Alternative Energy Source, International Symposium on Biofuels, September 25–26, New Delhi, India, 2007.
- (4) (a) Green, E. M. *Curr. Opin. Biotechnol.* **2011**, *22*, 337–343. (b) Jin, C.; Yao, M.; Liu, H.; Lee, C.-F.; Ji, J. *Renewable Sustainable Energy Rev.* **2011**, *15*, 4080–4106.
- (5) (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) Gabriëls, D.; Hernández, W. Y.; Sels, B.; Van Der Voort, P.; Verberckmoes, A. *Catal. Sci. Technol.* **2015**, *5*, 3876–3902.
- (6) Review of borrowed hydrogen activation of alcohols: (a) Haniti, M.; Hamid, S. A.; Slatford, P. A.; Williams, J. M. J. *Adv. Synth. Catal.* **2007**, *349*, 1555–1575. For related ruthenium dehydrogenation-based chemistry, see: (b) Morton, D.; Cole-Hamilton, D. J.; Utuk, I. D.; Paneque-Sosa, M.; Lopez-Poveda, M. J. *Chem. Soc., Dalton Trans.* **1989**, 489–495. (c) Edwards, M. G.; Jazzar, R. F. R.; Paine, B. M.; Shermer, D. J.; Whittlesey, M. K.; Williams, J. M. J.; Edney, D. D. *Chem. Commun.* **2004**, *1*, 90–91. (d) Black, P. J.; Edwards, M. G.; Williams, J. M. J. *Eur. J. Org. Chem.* **2006**, *2006*, 4367–4378.
- (7) Carlini, C.; Di Girolamo, M.; Macinai, A.; Marchionna, M.; Novello, M.; Raspolti Galletti, A. M.; Sbrana, G. *J. Mol. Catal. A: Chem.* **2003**, *200*, 137–146.
- (8) (a) Furukawa, J.; Saegusa, T.; Tsuruta, T.; Fujii, H.; Tatano, T. *J. Polym. Sci.* **1959**, *36*, 546. (b) Degering, E. F.; Stoudt, T. *J. Polym. Sci.* **1951**, *7*, 653–656.
- (9) Koda, K.; Matsu-ura, T.; Obora, Y.; Ishii, Y. *Chem. Lett.* **2009**, *38*, 838–839.
- (10) Riitonen, T.; Toukonitty, E.; Madnani, D. K.; Leino, A.-R.; Kordas, K.; Szabo, M.; Sapi, A.; Arve, K.; Warna, J.; Mikkola, J.-P. *Catalysts* **2012**, *2*, 68–84. For a recent review, see: Galadima, A.; Muraza, O. *Ind. Eng. Chem. Res.* **2015**, *54*, 7181–7194.
- (11) Xu, G.; Lammens, T.; Liu, Q.; Wang, X.; Dong, L.; Caiazza, A.; Ashraf, N.; Guan, J.; Mu, X. *Green Chem.* **2014**, *16*, 3971–3977.
- (12) Dowson, G. R. M.; Haddow, M. F.; Lee, J.; Wingad, R. L.; Wass, D. F. *Angew. Chem., Int. Ed.* **2013**, *52*, 9005–9008; *Angew. Chem.* **2013**, *125*, 9175–9178.

(13) (a) Bacchi, A.; Balordi, M.; Cammi, R.; Elviri, L.; Pelizzi, C.; Picchioni, F.; Verdolino, V.; Goubitz, K.; Peschar, R.; Pelagatti, P. *Eur. J. Inorg. Chem.* **2008**, 2008, 4462–4473. (b) Hounjet, L. J.; Bierenstiel, M.; Ferguson, M. J.; McDonald, R.; Cowie, M. *Inorg. Chem.* **2010**, 49, 4288–4300. (c) Hounjet, L. J.; Ferguson, M. J.; Cowie, M. *Organometallics* **2011**, 30, 4108–4114.

(14) Abdur-Rashid, K.; Guo, R.; Chen, X.; Jia, W. Canadian Patent Application CA2636947 A1 20090106, 2009.

(15) Saudan, L.; Dupau, P.; Riedhauser, J. J.; Wyss, P. U.S. Patent Application US20100280273 A1 20101104, 2010.

(16) (a) Nielsen, M.; Kammer, A.; Cozzula, D.; Junge, H.; Gladiali, S.; Beller, M. *Angew. Chem., Int. Ed.* **2011**, 50, 9593–9597. (b) Nielsen, M.; Junge, H.; Kammer, A.; Beller, M. *Angew. Chem., Int. Ed.* **2012**, 51, 5711–5713. For related ethanol to ethyl acetate catalysts, see: (c) Spasyuk, D.; Smith, S.; Gusev, D. G. *Angew. Chem., Int. Ed.* **2013**, 52, 2538–2542. (d) Kossoy, E.; Diskin-Posner, Y.; Leitius, G.; Milstein, D. *Adv. Synth. Catal.* **2012**, 354, 497–504.

(17) A total of 2.04 g of solid is obtained at the end of run 1. ^1H NMR spectroscopy of a weighed amount of this solid with a known amount of dimethyl sulfoxide added as a standard in methanol- d_4 (see the [Supporting Information](#)) shows the solid to contain sodium acetate (1.16 g, 14.1 mmol), sodium formate (0.01 g, 0.1 mmol), and sodium butanoate (0.08 g, 0.7 mmol). The remaining solid is presumably sodium hydroxide, formed from the hydrolysis of sodium ethoxide either during the reaction or during workup of the postreaction mixture. The maximal amount of sodium hydroxide should therefore be 0.60 g, assuming the remaining sodium equivalents are in this form; 0.19 g of solid remains unidentified. In line with previous reports and to allow comparisons to be made with other literature catalysts, we have reported selectivity in the liquid fraction in [Table 1](#); including solid products in the selectivity calculation gives an overall selectivity to *n*-butanol of 75.6%

(18) During the reactions, a pressure buildup is noted; for example, for run 1, the internal reactor pressure reaches approximately 10 bar. After cooling, approximately 4 bar of pressure remains. Gas chromatography analysis shows the gas to be a combination of hydrogen and methane (ratio of 1250:1).

(19) (a) Cannizzaro, S. *Justus Liebigs Ann. Chem.* **1853**, 88, 129–130.

(b) Cook, J.; Hamlin, J. E.; Nutton, A.; Maitlis, P. M. J. *J. Chem. Soc., Dalton Trans.* **1981**, 2342–2352.

(20) (a) Claisen, L. *Ber. Dtsch. Chem. Ges.* **1887**, 20, 646–650.

(b) Tischtschenko, W. *J. Russ. Phys. Chem.* **1906**, 38, 355–418.

(c) Tischtschenko, W. *Chem. Zentralbl.* **1906**, 77, 1309. (d) Seki, T.; Nakajo, T.; Onaka, M. *Chem. Lett.* **2006**, 35, 824–829.

(21) (a) Sieffert, N.; Réocreux, R.; Loursusso, P.; Cole-Hamilton, D. J.; Bühl, M. *Chem.—Eur. J.* **2014**, 20, 4141–4155. (b) Lau, C. P.; Ng, S. M.; Jia, G.; Lin, Z. *Coord. Chem. Rev.* **2007**, 251, 2223–2237. (c) Chen, Y.-Z.; Chan, W.; Lau, C.; Chu, H.; Lee, H.; Jia, G. *Organometallics* **1997**, 16, 1241–1246.