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Complete List of Authors:	P M, Mahitha; Amrita Vishwa Vidyapeetham School of Arts and Sciences Amritapuri, Chemistry S, Nakul; Amrita Vishwa Vidyapeetham School of Arts and Sciences Amritapuri, Chemistry Kulkarni, Naveen; Amrita Vishwa Vidyapeetham School of Arts and Sciences Amritapuri, Chemistry Jagirdar, Balaji; Indian Institute of Science, Department of Inorganic + Physical Chemistry Jones, William; University of Rochester, Department of Chemistry

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Guerbet upgrading of ethanol to n-butanol using Ru(III) catalysts under air†

Mahitha P. M.[a], Nakul S[a]., Naveen V. Kulkarni[a]*, Balaji R. Jagirdar[b]*, William D. Jones[c]*

A series of *in situ* prepared Ru(III) complexes supported by easily accessible N-donor organic pincer ligands were used as catalysts in the Guerbet upgrading reaction of ethanol under aerobic conditions. Tridentate bis(benzimidazole) ligand systems containing amino-dimethyl (L1) and pyridine (L2) backbones were found to make more efficient catalyst systems as compared to the bidentate bis(benzimidazole) ligand systems containing phenyl (L3) and ethene (L4) backbones. Potassium t-butoxide was found to be the most compatible base for this catalyst system. Reaction with 0.1 mol% of the catalyst and 10 mol% of potassium t-butoxide yielded 27% of n-butanol at 71% selectivity (150 °C, 24h). Increase in the catalyst or base loading mostly resulted in increased reactivity but selectivity towards the key product n-butanol was found to decrease. On the other hand, reducing the reaction period to 12h resulted in slightly decreased reactivity but the reaction provides n-butanol in high selectivity (76%). Contrarily, increased reaction period resulted in enhanced conversion of ethanol to higher alcohols. Under moderate and aerobic reaction conditions, the catalytic system was found to efficiently upgrade ethanol to higher alcohols. Decrease in the catalytic activity of the system over time was speculated to be due to the gradual deactivation of the base upon reaction with water (by-product of the Guerbet reaction). Poor solubility of the catalytic system in aqueous solutions makes it unsuitable for direct Guerbet reaction of fermentation broth.

Introduction

In recent years there has been a great altitude shift in the quest for alternative energy sources, especially for the transportation sector. This is mainly due to the diminishing supply of fossil fuels and environmental protection issues. One of the important approaches in this direction is to 'bring in' the economically as well as ecologically viable sustainable biofuels, such as alcohols as substitutes or additives to gasoline. Bioethanol (EtOH) is being probed as a sustainable alternative fuel (or fuel additive) to conventional gasoline[1]. However, there are some concerns with the use of ethanol which should be addressed. Ethanol has only about

a. *Department of Chemistry, Amrita Vishwa Vidyapeetham, Amritapuri 690525, Kerala, India*
b. *Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560012, Karnataka, India*
c. *Department of Chemistry, University of Rochester, Rochester, New York 14450, United States*
E-mail:*naveenvkulkarni@am.amrita.edu (NVK), jagirdar@iisc.ac.in (BRJ), jones@chem.rochester.edu (WDJ)*

70% of the energy density of gasoline, ethanol absorbs water and forms an azeotropic mixture and over the time, separates from gasoline blends. It is also corrosive to current engine technology and to supply pipelines. Butanol on the other hand, offers a more viable option as it has an energy density closer to that of gasoline (90%) and can be blended with gasoline at higher concentrations. It is immiscible with water, noncorrosive to the engine and provides twice the renewable content compared to ethanol per gallon.[1] Regardless of these clear advantages over ethanol, the broad implementation of butanol in the global transportation sector is still underachieved due to challenges with its production. The methods that are currently employed for the butanol synthesis, the microbial fermentation process or the propylene hydroformylation and hydrogenation process, suffer from low yield, separation and selectivity issues.[2] In such a scenario, the Guerbet reaction appears to be a perfect option as it offers a great opportunity to synthesize butanol from a readily available raw material, ethanol, through a metal catalyzed "borrowed hydrogen" strategy. It involves three important steps: dehydrogenation of ethanol to form acetaldehyde, aldol reaction of acetaldehyde to form crotonaldehyde, and double hydrogenation of crotonaldehyde to obtain butanol (Scheme 1).[3] Although the dehydrogenation of ethanol is thermodynamically uphill and acetaldehyde, an intermediate formed during the reaction, gets involved in various side reactions posing selectivity issues, the Guerbet reaction is gaining attention as it provides a
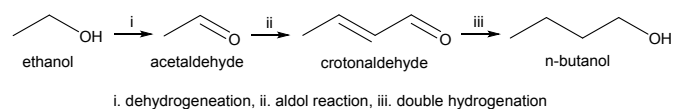
faster route to synthesize butanol and gives an opportunity to use distinct catalysts and vary the reaction conditions at the different steps of reaction.

i. dehydrogeneation, ii. aldol reaction, iii. double hydrogenation

Scheme 1: Steps involved in Guerbet upgrading of ethanol

Several homogeneous catalyst systems have been employed for the Guerbet upgrading of ethanol to n-butanol to date. Most of them contain ruthenium[4] or iridium[5] centers, but lately systems containing manganese[6] centers are also gaining attention. However, most of these catalysts work at elevated temperatures and are sensitive to air and water, leading to catalyst decomposition after a prolonged period. Considering that water is the main by-product of the aldol reaction (second step of the Guerbet reaction, see Scheme 1), water-stability of the catalytic system would greatly benefit the catalyst performance and yield higher conversion. In this regard, phenanthroline-based iridium system developed by Mu et al, which was able to achieve a 52% conversion of ethanol with 26% yield of butanol (with 50% selectivity) under aqueous conditions[7] and the bipyridine supported ruthenium system developed by Jones et al, which could convert the ethanol to n-butanol in up to a 20% yield and 48% selectivity at the composition of fermentation broth (water:ethanol = 90:10, v/v) at 80 °C,[8] are truly remarkable. However, Jones' catalyst still requires air free conditions.

Along the same lines, here in this work, we report a Ru(III) system supported by N-donor pincer type ligands, which is an efficient catalyst system for Guerbet upgrading of ethanol to n-butanol in the presence of air.

Results and Discussion

The ligands L1-L4 used in this work were prepared by following the reported procedures and duly characterized by spectro-analytical techniques (See Supplementary Information).[9]

We started our investigation with the *in situ* catalytic system generated by treating ligand L1 (1.90 mg, 0.1 mol%) and RuCl$_3$.3H$_2$O (1.80 mg, 0.1 mol%) in dry ethanol (0.4 mL, 6.85 mmol, 100 mol%) for 0.5h under air-free conditions in a sealed Schlenk tube. To this mixture a base, potassium t-butoxide (75.60 mg, 10 mol%) was added and the resulting catalytic mixture was heated at 150 °C for 24 h. We observed a good conversion of ethanol (40%), in which the desired n-butanol was obtained in about 28% yield (70% selectivity) and about 12% of other higher alcohols were observed (Entry 1, Table 1) (Catalytic activity data of the reported ruthenium-based catalysts in the Guerbet reaction is provided in ESI). When the same reaction was conducted under air, to our delight, similar conversion was observed (27% n-butanol at 71% selectivity and 11% of other higher alcohols) indicating that the performance of our catalyst is unaffected by the presence of air/O$_2$ (Entry 2, Table 1). This suggested that the active species formed in this catalytic reaction are not decomposed under aerobic conditions. Prompted by this observation, we continued to perform all of our catalytic reactions under aerobic conditions. It should be noted that, air-stable catalyst systems provide several practical advantages over air-sensitive

systems and are beneficial for scaling up of the catalysis process to industrial level.[10]

Stoichiometry and the nature of the base play an important role in Guerbet chemistry.[5a,6,8] Potassium t-butoxide was the primary choice for our reaction owing to its compatibility and prior success with ruthenium-based catalysts.[6,8] In continuation, when the base loading was increased to 25 mol%, while keeping the catalyst loading the same (0.1 mol%) (Entry 3, Table 1), a slight increase in reactivity was observed, producing 33% of n-butanol. However larger quantities of higher alcohols are also produced (22%) in this reaction which decreased the selectivity towards n-butanol to 60%. On the other hand, lowering the base loading to 5 mol% with 0.1 mol% of catalyst (Entry 4, Table 1) drastically decreased the catalytic activity, yielding only 15% of n-butanol. These observations indicate the necessity of a higher mole percent of base in the current catalytic reaction. Although, 25% loading of base provided us with slightly better conversion, it is accompanied with a decrease in selectivity. Hence, 10 mol% base was considered as a typical loading for further studies. Changing the base to potassium hydroxide (Entry 5, Table 1) was less fruitful, as the reaction yielded only 14% of n-butanol. Sodium ethoxide (Entry 6, Table 1) was found to be equally efficient as potassium t-butoxide, producing 26% of n-butanol. Sodium acetate on the other hand, did not provide any of the expected products (Entry 7, Table 1). A blank reaction carried out without any base (Entry 8, Table 1) also did not produce any of the expected products, indicating the key role of an appropriate base in this catalytic reaction.[6,8]

After optimizing the base loading, we performed several experiments with varying catalyst loadings to find out the optimum catalyst stoichiometry for the current catalytic system. When the catalyst loading was increased to 0.5 mol%, with a base loading of 10 mol% (Entry 9, Table 1), a significant rise in the n-butanol yield was observed (32%), however a slight decrease in selectivity (59%) was also seen due to the formation of slightly larger quantities of higher alcohols (22%). Further increase in the catalyst loading to 1 mol% (Entry 10, Table 1) led to a declined catalytic performance, yielding only 20% of n-butanol. On the other hand, when a lower amount of catalyst (0.05 mol%) was used (Entry 11, Table 1), a reduced activity was observed producing only 12% of n-butanol. From these results, the catalytic mixture containing 0.1 mol% of catalyst and 10 mol% of potassium t-butoxide was established to be the best composition to achieve the higher conversion and selectivity in the Guerbet upgrading of ethanol under our reaction conditions (150 °C, 24 h).

Reaction time also plays an important role in deciding the selectivity of the Guerbet reaction.[4-6] In order to investigate the effect of reaction time on the yield and selectivity, we performed the standard catalytic reaction (0.1 mol% catalyst, 10 mol% base) at different time intervals. We found that extending the reaction time to 48 h (Entry 12, Table 1) resulted in an increase in the formation of higher alcohols (23%), while the amount of n-butanol formed remained mostly the same (28%), thus, decreasing the selectivity of n-butanol formation to 55%. When the reaction time was reduced to 12 h (Entry 13, Table 1), 25% of n-butanol was observed along with relatively lower amounts of higher alcohols (8%), hence providing a higher selectivity towards n-butanol formation (76%).

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Upon further reduction of the reaction time to 6h (Entry 14, Table 1) lower conversion was observed providing only 19% of n-butanol. From these results the significance of the time period on the current Guerbet catalytic reaction was revealed. It is established that providing a longer reaction period can enhance the total Guerbet conversion of ethanol to higher alcohols, but selectivity towards the key product n-butanol is compromised. Considering the better conversion and selectivity balance, 12 h reaction time is accepted to be optimal for this catalyst system.

Since the first stage of the Guerbet reaction (the dehydrogenation step) is thermodynamically uphill, this catalytic reaction is normally conducted at high temperatures, with 120-150 °C being the most common temperature used in the earlier reports.[4-6] Lowering the temperature often led to reduced reactivity, except in the case of the Jones' catalyst[8] which was found to function well even at 80 °C. In the current system, when the reaction temperature was lowered to 100 °C (Entry 15, Table 1), a moderate conversion of ethanol to n-butanol (23%) was observed with a 70% of selectivity after 24h. Although this is a decent conversion, a decrease in the reactivity as compared to the reactions executed at 150 °C was evident.
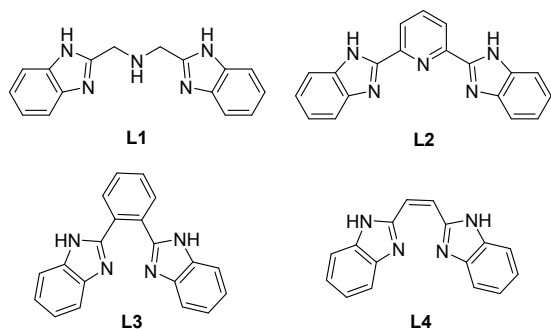

Fig 1: Ligands used in this work

The electronic and steric factors of the ligand system play an important role in the catalysis.[11] The cooperativity between the metal center and the amino functionality of the ligands has been a key factor in Guerbet catalysis.[4-6] In the current study, the efficacy of the NNN donor pincer-type ligand L1 was compared with other three ligands (L2-L4) of tridentate NNN (L2) and bidentate NN (L3 and L4) ligation pattern and dissimilar backbone structures (Fig. 1). Interestingly, the tridentate NNN donor ligand containing a pyridine backbone (L2) was found to exhibit better reactivity as compared to the lead ligand L1 (which contains the amino-dimethyl backbone), in terms of total conversion of ethanol. However, selectivity of this catalytic system towards the key product n-butanol was inferior (Entry 1, Table 2). In contrast, the other two NN bidentate ligand systems L3 (Entry 2, Table 2) and L4 (Entry 3, Table 2) showed lower conversion efficiencies. Between the two, the system containing a phenyl backbone (L3) performed relatively better than the system containing an ethylene backbone. A blank catalytic reaction performed with RuCl$_3$.3H$_2$O without any supporting ligand (Entry 4, Table 2) produced insignificant amounts of products indicating the requirement of an appropriate ligand in this catalytic reaction. Furthermore, to confirm the homogeneous nature of the catalytic species the standard catalytic reaction was carried out in the presence of a drop of mercury (viz., mercury poisoning test). Since no significant difference in the catalytic activity was observed in this

reaction (Entry 5, Table 2), a contribution from metal nanoparticle mediated heterogeneous pathway is ruled out.[6a,11e]

It was observed that, the catalytic activity of the system slows down after 24h, and ultimately stops after about 48h indicating the deterioration of the active species. Indeed, when we isolated the solid from the catalytic mixture at the end of reaction (after 24h) by applying high vacuum for overnight and used it for a fresh batch of reaction (Entry 16, Table 1), only a trace of butanol was observed suggesting the same.[6a] Consequently, as in the earlier cases,[5,6] we suspected that water, which is a main by-product of the Guerbet reaction, might be playing a vital role in this regard. In order to investigate the influence of water in the current catalytic reaction, we performed a series of catalytic reactions aimed at variation of the water content. Addition of molecular sieves to the reaction mixture was expected to improve the reactivity by absorbing the water produced in the reaction. However, in the present case, we found that addition of activated molecular sieves (3 Å, 1g) to the standard catalytic reaction (Entry 1, Table 3) did not make much difference in the n-butanol yield (28% at 72% selectivity), but led to a higher loss of ethanol during the workup.[6a] When the catalytic reaction was conducted in the presence of an additional 0.123 mL (6.85 mmol, 100 mol%) of water, a sharp drop in reactivity was observed, leading to the formation of only 11% of n-butanol (Entry 2, Table 3). This experiment indicated the detrimental effect of water on catalytic performance.

Interestingly, when the base loading was increased to 25 mol% (Entry 3, Table 3) we observed a slight increase in the catalytic performance and 16% of n-butanol was obtained. This observation hints that it is perhaps the base which undergoes deactivation upon reaction with water, and loading of higher amount of base can certainly improve the catalytic conversion. We know that potassium t-butoxide, the base used in these reactions, can readily react with water and form t-butanol and potassium hydroxide. Since potassium hydroxide was found to be an unsuitable base for the current catalyst system (Entry 5, Table 1) and a higher percentage of t-butanol was observed in the reaction mixtures with added water in general (Entries 2-7, Table 3), our speculation of a base-deactivation pathway appears to be pertinent. Furthermore, when the base loading was increased to 50 mol% (Entry 4, Table 3) under the same reaction conditions, the n-butanol conversion was increased to 20%, justifying the increase. This higher yield of n-butanol at 50 mol% base loading (Entry 4, Table 3) prompted us to try use this catalyst system at higher water concentrations. But when the reaction was attempted in the presence of 0.246 mL (13.7 mmol, 200 mol%) of water with 50 mol% of base loading (Entry 5, Table 3), the conversion of ethanol to n-butanol dropped to only 7%. Further increase in the amount of added water to 0.492 mL (27.4 mmol, 400 mol%) led to complete loss of reactivity (Entry 6, Table 3). Attempts made to check the catalytic ability of the system to work with a composition of fermentation broth (water:ethanol = 90:10, v/v) with 70 mol% of base loading were also unsuccessful (Entry 7, Table 3). We believe that the insolubility of the catalyst system in the reaction media at higher water percentage is also an important reason for the drop in the activity. Indeed, when a hot ethanolic solution of a catalytic mixture (1.90 mg of L1, 1.80 mg of RuCl$_3$.3H$_2$O and 7.56 mg of potassium t-butoxide in 0.4 mL of

ethanol) was combined with 0.4 mL of water (1:1 v/v), an immediate precipitation of the catalyst-system was observed indicating the lower water solubility of the catalyst.

Formation of higher alcohols was observed in all the high yielding catalytic reactions, since no specific sterically hindering base was used in this study.[5a] From the GC analysis, 2-ethyl butanol, 1-hexanol, 2-ethyl-4-methyl-1-pentanol and 1-octanol were identified in the reaction mixture. The percentage of higher alcohols in all the catalytic reactions was found to follow the trend: percent of C4 alcohol (n-butanol) > C6 alcohols (2-ethyl butanol, 1-hexanol) > C8 alcohols (2-ethyl-4-methyl-1-pentanol and 1-octanol). This trend is in line with the earlier observations and is a result of an uncontrolled Aldol reaction.[4-6] In the case of the catalytic reactions where potassium t-butoxide was used as a base t-butanol was observed in the reaction mixture, owing to the protonation of t-butoxide by water and ethanol. However, in any of the catalytic reactions no ethyl acetate (Tishchenko product) or acetic acid (Cannizzaro product) were detected.

Conclusions

An air stable Ru(III) based catalyst system supported by easily accessible organic N-donor pincer ligands was developed for the efficient Guerbet upgrading of ethanol to n-butanol. A higher yield of n-butanol was achieved at good selectivity under moderate reaction conditions under air. Ligand parameters, catalyst and base stoichiometry, reaction temperature, reaction period and reaction by-product (water) were found to have key influence on the reactivity and selectivity of the catalyst. Gradual deactivation of the base and poor water solubility of the catalyst system are identified to be points of concern, which need to be addressed to improve the efficiency of this catalyst system and its adaptability to aqueous reaction conditions.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

References

1   (a) G. Boyle, Renewable Energy: Power for a Sustainable Future, 3rd ed.; Oxford University Press, 2012; (b) A. Pandey, C. Larroche, S. Ricke, C. -G. Dussap, E. Gnansounou, Eds. Biofuels, Alternative Feedstocks and Conversion Processes, 1st ed.; Academic Press, 2011.

2   (a) C. Jin, M. Yao, H. Liu, C. -F. Lee, J. Ji, Renew. Sustain. Energy Rev. 2011, **15**, 4080; (b) E. M. Green, Curr. Opin. Biotechnol., 2011, **22**, 337.

3   (a) M. C. R. Guerbet, *Acad. Sci. Paris* 1899, **128**, 1002; (b) S. Veibel, J. I. Nielsen, *Tetrahedron,* 1967, **23**, 1723; (c) M. C. R. Guerbet, *Acad. Sci. Paris,* 1909, **149**, 129.

4   (a) G. R. M. Dowson, M. F. Haddow, J. Lee, R. L. Wingad, D. F. Wass, *Angew. Chem., Int. Ed.,* 2013, **52**, 9005; (b) R. L. Wingad, P. J. Gates, S. T. G. Street, D. F. Wass, *ACS Catal.,* 2015, **5**, 5822; (c) K. T. Tseng, S. Lin, J. W. Kampf, N. K. Szymczak, *Chem. Commun.,* 2016, **52**, 2901; (d) Y. Xie, Y. Ben-David, L. J. W. Shimon, D. Milstein, *J. Am. Chem. Soc.,* 2016, **138**, 9077.

5   (a) S. Chakraborty, P. E. Piszel, C. E. Hayes, R. T. Baker, W. D. Jones, *J. Am. Chem. Soc.* 2015, **137**, 14264; (b) K. Koda, T. Matsu-ura, Y. Obora, Y. Ishii, *Chem. Lett.* 2009, **38**, 838; (c) M. Wilklow-Marnell, W. W. Brennessel, *Polyhedron,* 2019, **160**, 83.

6   (a) N. V. Kulkarni, W. W. Brennessel, W. D. Jones, *ACS Catalysis* 2018, **8 (2)**, 997; (b) S. Fu, Z. Shao, Y. Wang, Q. Liu, *J. Am. Chem. Soc.,* 2017, **139 (34)**, 11941.

7   G. Xu, T. Lammens, Q. Liu, X. Wang, L. Dong, A. Caiazzo, N. Ashraf, J. Guan, X. Mu, *Green Chem.,* 2014, **16**, 3971.

8   T. A. DiBenedetto, W. D. Jones, *Organometallics*, 2021, **40**, 1884.

9   (a) B. -T. Chen, N. Morlanés, E. Adogla, K. Takanabe, and V. O. Rodionov, *ACS Catalysis,* 2016, **6 (7),** 4647; (b) P. Kopel, D. Wawrzak, V. Langer, K. Cihalova, D. Chudobova, R. Vesely, V. Adam, and R. Kizek, *Molecules,* 2015, **20**, 10360; (c) R. H. Ersan, M. A. Alagoz, T. Ertan-Bolelli, N. Duran, S. Burmaoglu and O. Algul, *Mol. Divers,* 2021, **25**, 2247; (d) E. Polat, O. Turbedaroglu, M. Cakici, *Tetrahedron Lett.,* 2021, **67**, 152871; (e) R. O. Omondi, R. Bellam, S. O. Ojwach, D. Jaganyi, A. A. Fatokund, J. Inorg. Biochem., 2020, **210**, 111156; (f) H. Ali, E. H. G. Alt, *Inorg. Chim. Acta,* 2015, **428**, 100; (f) B. Ülküseven, A. Tavman, G. Ötük, *Met. Based Drugs*, 1999, **6(3)**, 163; (g) B. Dash, E. K. Dora, C. S. Panda, *Indian J. Chem. Sect. B*, 1982, **21B (7)**, 697.

10   (a) M. Zeng, L. Li, S. B. Herzon, *J. Am. Chem. Soc.* 2014, **136**, 7058; (b) K. Anjali, J. Christopher, A. Sakthivel, *ACS Omega* 2019, **4**, 13454; (c) M. T. Findlay, P. Domingo-Legarda, G. McArthur, A. Yen, I. Larrosa, *Chem. Sci.,* 2022, **13**, 3335. (d) A. Sreenavya, A. Sahu, A. Sakthivel, Ind. Eng. Chem. Res., 2020, **59 (26)**, 11979; (e) R. Sharma, A. Samanta, B. Sardar, M. Roy, D. Srimani, *Org. Biomol. Chem.,* 2022, **20**, 7998; (f) A. Seretis, P. Diamantopoulou, I. Thanou, P. Tzevelekidis, C. Fakas, P. Lilas, G. Papadogianakis, *Front. Chem.,* 2020, **8**, 221; (g) S. Shome, S. P. Singh, *Chem. Rec.,* 2019, **19**, 1935.
(a) P. W. N. M. van Leeuwen, P. C. J. Kamer, J. N. H. Reek, P. Dierkes, *Chem. Rev.*, 2000, **100**, 2741; (b) D. J. Gorin, B. D. Sherry, F. D. Toste, *Chem. Rev.*, 2008, **108**, 3351; (c) B. S. Billow, T. J. McDaniel, A. L. Odom, *Nat. Chem.,* 2017, **9**, 837; (d) G. Reshma, K. Meenu, N. V. Kulkarni, W. D. Jones, Acta Chim. Slov., 2021, **68**, DOI:10.17344/acsi.2021.6920; (e) T. Elkin, N. V. Kulkarni, B. Tumanskii, M. Botoshansky, L. J. W. Shimon, M. S. Eisen, *Organometallics,* 2013, **32**, 6337; (f) N. V. Kulkarni, T. Elkin, B. Tumaniskii, M. Botoshansky, L. J. W. Shimon, M. S. Eisen, *Organometallics*, 2014, **33**, 3119; (g) N. V. Kulkarni, C. Dash, N. B. Jayaratna, S. G. Ridlen, S. K. Khani, A. Das, X. Kou, M. Yousufuddin, T. R. Cundari, H. V. R. Dias, *Inorg. Chem.,* 2015, **54**, 11043; (h) N. V. Kulkarni, A. Das, N. B. Jayaratna, M. Yousufuddin, H. V. R. Dias, Inorg. Chem. 2015, **54**, 5151.

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Table 1: Optimization of Ru(III) catalyzed Guerbet reaction of ethanol. [a]

Entry	Catalyst (mol%)	Base (mol%)	Reaction conditions	n-Butanol formed (%)	2-Ethyl butanol formed (%)	n-Hexanol formed (%)	2-Ethyl-4-methyl-1-penatnol formed (%)	n-Octanol formed (%)	Ethanol remaining (%)	t-Butanol (%)[b]
1[c]	L1 + Ru (0.1)	KO^{t}Bu (10)	24 h, 150 °C	28	5	5	1	1	51	72
2	L1 + Ru (0.1)	KO^{t}Bu (10)	24 h, 150 °C	27	5	4	1	1	53	70
3	L1 + Ru (0.1)	KO^{t}Bu (25)	24 h, 150 °C	33	8	9	3	2	36	90
4	L1 + Ru (0.1)	KO^{t}Bu (5)	24 h, 150 °C	15	2	1	1	-	74	61
5	L1 + Ru (0.1)	KOH (10)	24 h, 150 °C	14	1	1	-	-	78	-
6	L1 + Ru (0.1)	NaOEt (10)	24 h, 150 °C	26	5	4	2	1	53	-
7	L1 + Ru (0.1)	NaOAc(10)	24 h, 150 °C	Traces	-	-	-	-	95	-
8	L1 + Ru (0.1)	No Base	24 h, 150 °C	-	-	-	-	-	94	-
9	L1 + Ru (0.5)	KO^{t}Bu (10)	24 h, 150 °C	32	8	9	3	2	31	93
10	L1 + Ru (1)	KO^{t}Bu (10)	24 h, 150 °C	20	3	2	-	-	67	71
11	L1 + Ru (0.05)	KOtBu (10)	24 h, 150 °C	12	2	1	-	-	75	68
12	L1 + Ru (0.1)	KO^{t}Bu (10)	48 h, 150 °C	28	9	9	3	2	37	92
13	L1 + Ru (0.1)	KO^{t}Bu (10)	12 h, 150 °C	25	3	3	1	1	58	74
14	L1 + Ru (0.1)	KO^{t}Bu (10)	6 h, 150 °C	19	2	2	1	-	67	65
15	L1 + Ru (0.1)	KO^{t}Bu (10)	24 h, 100 °C	23	4	3	2	1	54	87
16	[d]Catalytic mass	-	24 h, 150 °C	Traces	-	-	-	-	95	Traces

[a] Catalysts were generated in situ by reacting the ligand L1 with RuCl$_3$.3H$_2$O; All the catalytic reactions were carried out in a Schlenk bomb tube using 0.4 mL (6.85 mmol, 100 mol%) of dry ethanol at the indicated temperature and duration, under air; conversions and yields are based on GC analysis of at least two reaction samples. [b] Percent of t-butanol resulting from deprotonation of a portion of potassium t-butoxide from water/ethanol. [c] Reaction performed under nitrogen atmosphere. [d] A reaction mixture as that of Entry 1, after the completion of 24 h was evacuated overnight under strong vacuum and the solid isolated was used in this reaction.

Table 2: Guerbet reaction of ethanol catalyzed by Ru(III) complexes supported by different ligands (L1-L4).[a]

Entry	Catalyst (mol%)	Base (mol%)	n-Butanol formed (%)	2-Ethyl butanol formed (%)	n-Hexanol formed (%)	2-Ethyl-4-methyl-1-penatnol formed (%)	n-Octanol formed (%)	Ethanol remaining (%)	t-Butanol (%)[b]
1	L2 + Ru (0.1)	KO^{t}Bu (10)	29	6	4	1	1	51	74
2	L3 + Ru (0.1)	KO^{t}Bu (10)	20	3	4	1	-	64	70
3	L4 + Ru (0.1)	KO^{t}Bu (10)	14	1	1	-	-	79	72
4	RuCl$_3$.3H$_2$O (0.1)	KO^{t}Bu (10)	Traces	-	-	-	-	96	62
5[c]	L1 + Ru (0.1)	KO^{t}Bu (10)	26	5	4	1	1	52	69

[a] Catalysts were generated in situ by reacting the ligands L1-L4 with RuCl$_3$.3H$_2$O; All the catalytic reactions were carried out in a Schlenk bomb tube using 0.4 mL (6.85 mmol, 100 mol%) of dry ethanol at 150 °C for 24 h, under air; conversions and yields are based on GC analysis of at least two reaction samples. [b] Percent of t-butanol resulting from deprotonation of a portion of potassium t-butoxide from water/ethanol. [c] A drop of metallic mercury (~ 50 mg) was added to the reaction.

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Table 3: Investigation of influence of water on Guerbet reaction of ethanol catalyzed by Ru(III) system supported by ligand L1. [a]

Entry	Catalyst (mol%)	Base (mol%)	Reaction conditions	n-Butanol formed (%)	2-Ethyl butanol formed (%)	n-Hexanol formed (%)	2-Ethyl-4-methyl-1-penatnol formed (%)	n-Octanol formed (%)	Ethanol remaining (%)	t-Butanol (%)[b]
1	L1 + Ru (0.1)	KO^{t}Bu (10)	24 h, 150 °C, 1 g of 3Å mol. sieves	28	4	5	1	1	44	74
2	L1 + Ru (0.1)	KO^{t}Bu (10)	24h, 150 °C, 0.123 mL of water	11	1	-	-	-	82	91
3	L1 + Ru (0.1)	KO^{t}Bu (25)	24h, 150 °C, 0.123 mL of water	16	2	1	-	-	77	96
4	L1 + Ru (0.1)	KO^{t}Bu (50)	24h, 150 °C, 0.123 mL of water	20	3	2	1	-	69	92
5	L1 + Ru (0.1)	KO^{t}Bu (50)	24h, 150 °C, 0.246 mL of water	7	-	-	-	-	89	93
6	L1 + Ru (0.1)	KO^{t}Bu (50)	24h, 150 °C, 0.492 mL of water	-	-	-	-	-	94	94
7	L1 + Ru (0.1)	KO^{t}Bu (70)	24h, 150 °C, 3.80 mL of water	-	-	-	-	-	95	95

[a] Catalysts were generated in situ by reacting the ligand L1 with $RuCl_3.3H_2O$; All the catalytic reactions were carried out in a Schlenk bomb tube using 0.4 mL (6.85 mmol, 100 mol%) of dry ethanol at the indicated temperature and duration, under air; conversions and yields are based on GC analysis of at least two reaction samples. [b] Percent of t-butanol resulting from deprotonation of portion of potassium t-butoxide from water/ethanol.