

## Supporting Information

### **Towards the Upgrading of Fermentation Broths to Advanced Biofuels: A Water Tolerant Catalyst for the Conversion of Ethanol to Isobutanol**

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## 1. General Experimental Information

All procedures were carried out under an inert atmosphere of N<sub>2</sub> using standard Schlenk line techniques or in an inert atmosphere glovebox (Ar), unless otherwise specified. All reagents were purchased from commercial suppliers and used without further purification unless otherwise stated. Sodium hydroxide pellets were crushed into a fine powder and dried *in vacuo* overnight before use. Solvents were purified using an anhydrous Engineering Grubbs-type solvent system and then degassed, except anhydrous ethanol and methanol which were purchased from Sigma-Aldrich, degassed and stored under an inert atmosphere over 3Å sieves. Complexes **1**<sup>1</sup> and **2**<sup>2</sup> were prepared according to literature procedures. Complex **3** was purchased from Sigma-Aldrich and used as received. Alcoholic drinks were purchased from local suppliers. Brands of alcoholic drinks used in this study were Yeni-Raki, Plymouth Gin, Asda Own Brand French Brandy VSOP, Cockburn's Special Reserve Port, Harvey's Bristol Cream Sherry, William Hardy Chardonnay (white wine), Hardy's Stamp Cabernet Sauvignon Merlot (red wine), Duvel (lager), Bristol Beer Factory, Gold (ale). NMR spectra were recorded on Jeol ECS 300, Varian 400-MR or Jeol ECS 400 spectrometers. <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H} NMR chemical shifts were referenced relative to the residual solvent resonances. <sup>31</sup>P{<sup>1</sup>H} NMR spectra were referenced relative to 85% H<sub>3</sub>PO<sub>4</sub> external standard. Mass spectra (ESI) were recorded on a Bruker Daltonics microTOF II. Elemental analyses were carried out by the Microanalytical Laboratory of the School of Chemistry, University of Bristol. GC-FID analysis of all catalytic samples was carried out on an Agilent 7820A GC fitted with DB-WAX column 30m x 320µm, I.D. 0.25µm. Method: oven temperature starts at 35 °C for 5 minutes, heat to 250 °C at 50 °C min<sup>-1</sup> then hold at 250 °C for 5 minutes. 1,1-Bis(diphenylphosphino)methane is abbreviated to dppm.

## 2. Catalysis

Catalytic reactions were carried out in a 100 mL Parr stainless steel autoclave with a pre-heated aluminium heating mantle and using magnetic stirring at 500 rpm. A typical procedure is shown below (2. 1.) and results are shown in Tables S1 and S2. Mol% is determined relative to the amount of ethanol used (17.13 mmol).

### 2. 1. Example procedure for the Guerbet coupling of ethanol/methanol to isobutanol

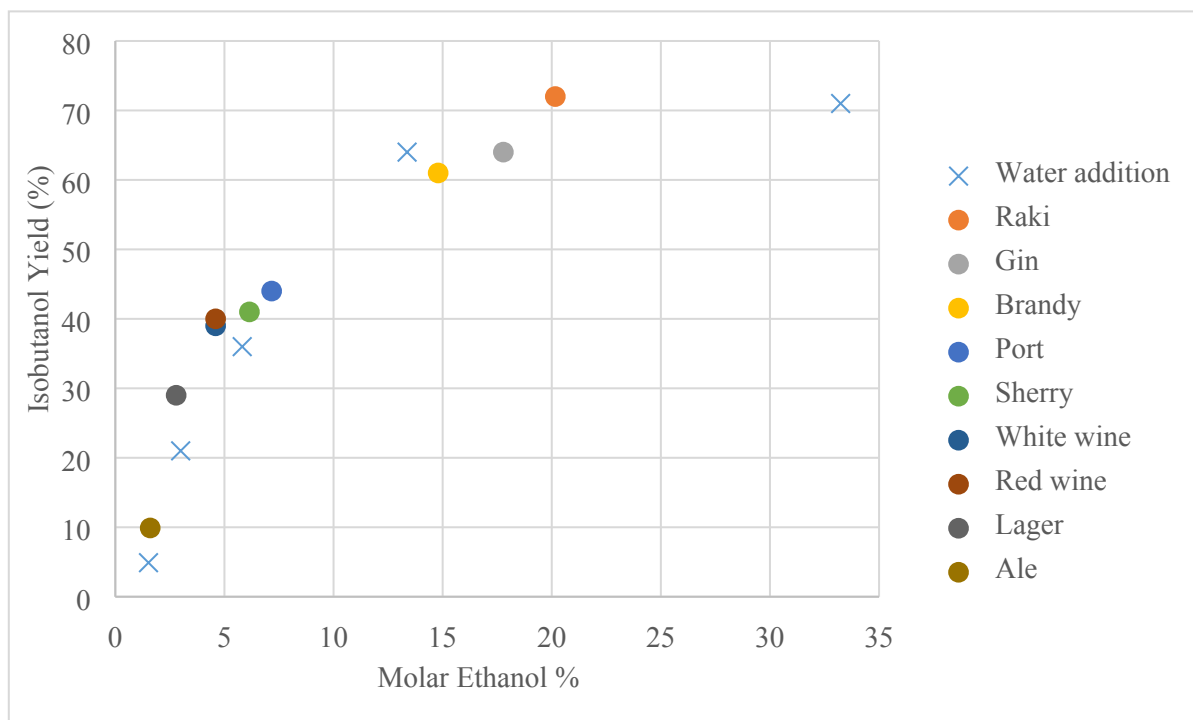
*trans*-[RuCl<sub>2</sub>(dppm)<sub>2</sub>] (**1**) (0.016 g, 0.017 mmol, 0.1 mol %) and NaOH (1.37 g, 34.26 mmol, 200 mol%) were added to a clean, oven dried PTFE sleeve equipped with a stirrer bar in air.\* The PTFE sleeve was then sealed within the autoclave which was evacuated and re-filled with nitrogen three times. Methanol (10 mL, 247.13 mmol) and ethanol (1 mL, 17.13 mmol) were injected into the autoclave through an inlet against a flow of nitrogen. The autoclave was sealed and placed in a pre-heated (180 °C) aluminium heating mantle for 2 h. After 2 h the autoclave was cooled in an ice-water bath. Once at room temperature, any residual pressure was released from the autoclave. A portion of solution was then passed through a 1 cm plug of acidic aluminium oxide and analysed by GC-FID (100 µL sample, 25µL *n*-pentanol standard, 1 mL of methanol). \*Note: Reagents were measured and the autoclave was assembled in the glovebox when catalysts **2** and **3** were used and then sealed, brought out of the glovebox and the same procedure as above followed.

### 2. 2. Example procedure for water stability studies

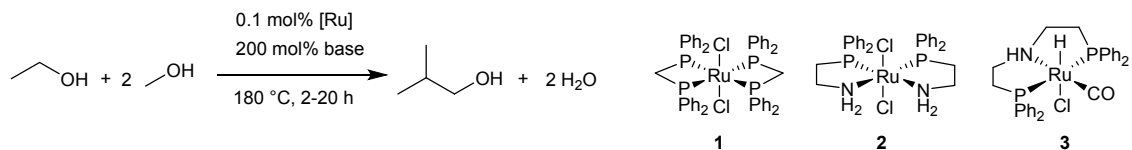
The above procedure (2. 1.) was followed, however the desired volume of degassed water (0.62, 2, 5, 10 or 20 mL) was injected into the autoclave at the same time as methanol and ethanol, against a flow of nitrogen.

### 2. 3. Example procedure using different ethanol sources

The above procedure (2. 1.) was followed, however the desired volume of alcoholic beverage (see Table S2, equivalent to 17.13 mmol of ethanol based on the ABV value) was injected at the same time as the methanol and in place of analytically pure ethanol. The types of alcoholic beverages used and the ABV values are given in the general experimental information and Table S2.



**Figure S1:** Isobutanol yield obtained when adding pure water or alcoholic drink.

**Table S1** Conversion of ethanol/methanol to isobutanol


Entry <sup>a</sup>	Catalyst	Base (mol%) <sup>b</sup>	Water, mL (mmol)	Ethanol Conversion (%) <sup>c</sup>	TON <sup>d</sup> (Yield) [Selectivity] (%) <sup>e</sup>			
					Isobutanol	<i>n</i> -Propanol	<i>n</i> -Butanol	2-methyl-1-butanol
1 <sup>f</sup>	<b>1</b>	NaOMe (200)	-	67	650 (65) [98]	12 (1.2) [1.8]	1 (0.1) [0.2]	7 (0.7) [0.5]
2 <sup>f</sup>	<b>1</b>	NaOH (200)	-	74	710 (71) [96]	28 (2.8) [3.8]	1 (0.1) [0.1]	4 (0.4) [0.2]
3 <sup>f</sup>	<b>1</b>	NaOH (200)	0.62 (34.42)	74	710 (71) [97]	22 (2.2) [3.0]	-	4 (0.4) [0.3]
4	<b>1</b>	NaOH (200)	2 (111.02)	71	640 (64) [92]	53 (5.3) [7.5]	4 (0.4) [0.3]	8 (0.8) [0.5]
5	<b>1</b>	NaOH (200)	5 (277.55)	47	360 (36) [78]	96 (9.6) [21]	3 (0.3) [0.4]	7 (0.7) [0.7]
6	<b>1</b>	NaOH (200)	10 (555.09)	26	210 (21) [81]	48 (4.8) [19]	2 (0.2) [0.3]	-
7	<b>1</b>	NaOH (200)	20 (1110.19)	7.4	49 (4.9) [70]	18 (1.8) [26]	2 (0.2) [1.1]	5 (0.5) [3.1]
8 <sup>g</sup>	<b>1</b>	NaOH (200)	5 (277.55)	33	270 (27) [82]	57 (5.7) [18]	1 (0.1) [0.2]	5 (0.5) [0.8]
9	<b>1</b>	NaOH (150)	-	75	720 (72) [96]	24 (2.4) [3.2]	-	8 (0.8) [0.5]
10	<b>1</b>	NaOH (100)	-	67	590 (59) [90]	53 (5.3) [8.2]	2 (0.2) [0.1]	24 (2.4) [1.9]
11	<b>1</b>	NaOH (50)	-	17	110 (11) [68]	39 (3.9) [25]	4 (0.4) [1.4]	20 (2.0) [6.3]
12 <sup>h</sup>	<b>1</b>	NaOH (200)	5 (277.55)	45	380 (38) [85]	66 (6.6) [15]	1 (0.1) [0.1]	4 (0.4) [0.5]
13	<b>1</b>	NaOC(O)H	-	0.2	1 (0.1) [42]	1 (0.1) [58]	-	-
14	<b>1</b>	Na <sub>2</sub> CO <sub>3</sub> (200)	-	0.2	1 (0.1) [57]	1 (0.1) [43]	-	-
15	<b>1</b>	Na <sub>2</sub> CO <sub>3</sub> (200)	0.62 (34.42)	0.3	1 (0.1) [44]	2 (0.2) [56]	-	-
16	<b>1</b>	Na <sub>2</sub> CO <sub>3</sub> (200)	5 (277.55)	1.8	7 (0.7) [43]	8 (0.8) [48]	-	3 (0.3) [9.4]
17 <sup>f</sup>	<b>2</b>	NaOMe (200)	-	49	390 (39) [86]	31 (3.1) [6.8]	4 (0.4) [0.4]	62 (6.2) [6.8]
18	<b>2</b>	NaOH (200)	-	39	280 (28) [74]	86 (8.6) [23]	6 (0.6) [0.7]	19 (1.9) [2.6]
19	<b>2</b>	NaOH (200)	0.62 (34.42)	19	100 (10) [55]	77 (7.7) [41]	6 (0.6) [1.5]	9 (0.9) [2.4]
20	<b>3</b>	NaOMe (200)	-	48	360 (36) [82]	47 (4.7) [11]	6 (0.6) [0.6]	65 (6.5) [7.3]
21 <sup>i</sup>	<b>3</b>	NaOMe (200)	-	53	440 (44) [89]	24 (2.4) [4.8]	5 (0.5) [0.5]	62 (6.2) [6.2]
22	<b>3</b>	NaOH (200)	-	0.2	-	2 (0.2) [100]	-	-
23	<b>3</b>	NaOH (200)	0.62 (34.42)	1.0	3 (0.3) [48]	2 (0.2) [20]	5 (0.5) [32]	-

<sup>a</sup> Conditions: 1 mL (17.13 mmol) ethanol, 10 mL (247.13 mmol) methanol, 0.1 mol% [Ru] (mol% based on ethanol substrate), 180 °C, 2 h. <sup>b</sup> mol% based on ethanol substrate. <sup>c</sup> Conversion of ethanol based on total amount of liquid Guerbet products obtained as determined by GC analysis. <sup>d</sup> TON based on mmol of substrate converted to products per mmol of Ru. <sup>e</sup> Total yield and selectivity of Guerbet products in the liquid fraction as determined by GC analysis. <sup>f</sup> Previously reported by us (modified to account for the production of 2-methyl-1-butanol).<sup>3</sup> <sup>g</sup> Autoclave assembled in air, air saturated solvents used. <sup>h</sup> Addition of *trans*-ferulic acid (0.02 g). <sup>i</sup> 20 h. Note: When using catalyst **3** Et<sub>2</sub>O (1 mL) was used as GC solvent and hexadecane (25 μL) as standard.

**Table S2** Conversion of different ethanol sources to isobutanol using catalyst **1**

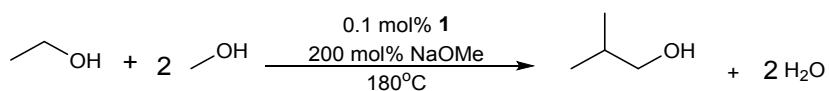
Entry <sup>a</sup>	Ethanol Source	Ethanol Percentage, %	Volume of Ethanol Source (mL)	Ethanol conversion (%) <sup>b</sup>	TON <sup>c</sup> (Yield) [Selectivity] (%) <sup>d</sup>			
					Isobutanol	<i>n</i> -Propanol	<i>n</i> -Butanol	2-methyl-1-butanol
1	Raki	45	2.2	79	720 (72) [93]	42 (4.2) [5.4]	10 (1.0) [0.6]	19 (1.9) [1.2]
2	Gin	41.2	2.4	71	640 (64) [91]	56 (5.6) [7.9]	5 (0.5) [0.3]	8 (0.8) [0.6]
3	Brandy	36	2.8	67	610 (61) [91]	57 (5.7) [8.5]	1 (0.1) [0.1]	6 (0.6) [0.4]
4	Port	20	5.0	51	440 (44) [87]	61 (6.1) [12]	1 (0.1) [0.1]	7 (0.7) [0.7]
5	Sherry	17.5	5.7	48	410 (41) [86]	63 (6.3) [13]	2 (0.2) [0.2]	7 (0.7) [0.7]
6	White wine	13.5	7.4	45	390 (39) [88]	50 (5.0) [11]	2 (0.2) [0.2]	7 (0.7) [0.8]
7	Red wine	13.5	7.4	47	400 (40) [86]	59 (5.9) [13]	1 (0.1) [0.1]	8 (0.8) [0.9]
8	Lager	8.5	11.8	35	290 (29) [85]	48 (4.8) [14]	3 (0.3) [0.5]	8 (0.8) [1.2]
9	Ale	5	20.0	14	99 (9.9) [74]	28 (2.8) [21]	2 (0.2) [0.8]	11 (1.1) [4.0]

<sup>a</sup> Conditions: Ethanol source, volume as stated (17.13 mmol), 10 mL (247.13 mmol) methanol, 0.1 mol% **1**, 200 mol% NaOH (mol% based on ethanol substrate), 180 °C, 2 h. <sup>b</sup> Conversion of ethanol based on total amount of liquid Guerbet products obtained as determined by GC analysis. <sup>c</sup> TON based on mmol of substrate converted to products per mmol of Ru. <sup>d</sup> Total yield and selectivity of Guerbet products in the liquid fraction as determined by GC analysis.

### 3. Kinetic Studies

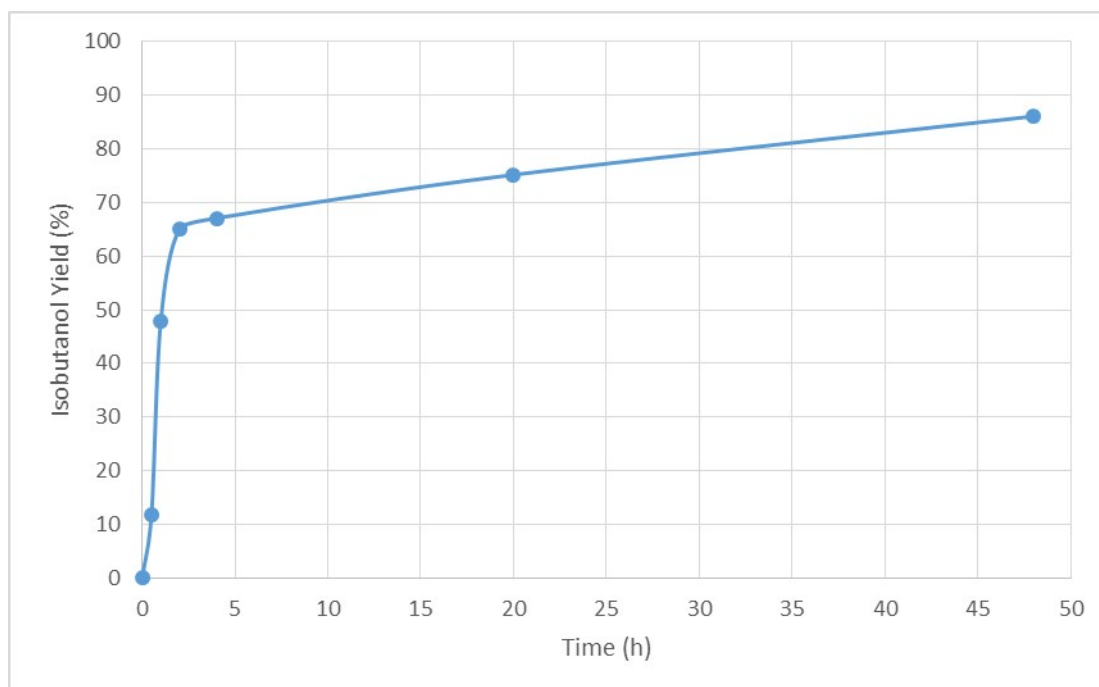
A kinetic plot for complex **1** was generated by performing autoclave runs as for the typical catalytic run above (2.1.) but stopping the reactions at certain times. The results are shown in Table S3 and Figure S2.

**Table S3.** Conversion of ethanol/methanol to isobutanol using catalyst **1** over time



Entry <sup>a</sup>	Time elapsed (h)	Isobutanol Yield (%) <sup>b</sup>	Isobutanol Selectivity (%) <sup>b</sup>
1	0.5	12	90
2	1	48	97
3	2	65	98
4	4	67	99
5	20	75	>99
6	48	86	99

<sup>a</sup> Conditions: 1 mL (17.13 mmol) ethanol, 10 mL (247.13 mmol) methanol, 0.1 mol% **1**, 200 mol% NaOMe (mol% based on ethanol substrate), 180 °C, Run time as stated. <sup>b</sup> Total yield and selectivity of Guerbet products in the liquid fraction as determined by GC analysis.



**Figure S2.** Plot of isobutanol yield vs time for catalyst **1**

## 4. Base Promotion of Sodium Formate and Carbonate Formation

### 4.1. Reaction of *trans*-[RuCl<sub>2</sub>(dppm)<sub>2</sub>] (1) with methanol and sodium hydroxide

*trans*-[RuCl<sub>2</sub>(dppm)<sub>2</sub>] (0.161 g, 1.71 mmol)\* and NaOH (1.370 g, 34.26 mmol) were added to a clean, oven dried PTFE autoclave sleeve equipped with a stirrer bar in air. The PTFE sleeve was sealed within the autoclave which was evacuated and re-filled with nitrogen three times. Methanol (10 mL, 247.13 mmol) was injected into the autoclave through an inlet against a flow of nitrogen. The autoclave was sealed and placed in a pre-heated (180 °C) aluminium heating mantle for 2 h. After 2 h the autoclave was cooled in an ice-water bath. A residual pressure of 10 bar was observed as well as precipitation of white solid from the reaction mixture. The resulting white solid was isolated by filtration and washed as reported in section 6.1 below and analysed by NMR spectroscopy: <sup>13</sup>C{<sup>1</sup>H} NMR (D<sub>2</sub>O, 125.7 MHz) δ 168.47 (CO<sub>3</sub><sup>2-</sup>) ppm; <sup>1</sup>H NMR (D<sub>2</sub>O, 400 MHz) δ 8.40 (1H, s, HCOO<sup>-</sup>) ppm (Only trace amounts of formate produced so unobservable by <sup>13</sup>C{<sup>1</sup>H} NMR spectroscopy). For representative NMR spectra of the solid obtained see Figures S3 and S4. \*Note: ten times the amount of catalyst was used compared to a normal isobutanol forming reaction to observe transition metal species by NMR spectroscopy of the crude post-reaction mixture <sup>31</sup>P{<sup>1</sup>H} NMR (neat, 162 MHz) δ 38.56 (s), 36.03 (s), 30.03 (s), 21.99 (s), 16.42 (s), -3.07 (s) ppm (see Section 5.3. and Figure S7A).

### 4.2. Reaction of *trans*-[RuCl<sub>2</sub>(dppm)<sub>2</sub>] (1) with methanol and sodium methoxide

*trans*-[RuCl<sub>2</sub>(dppm)<sub>2</sub>] (0.161 g, 1.71 mmol) and NaOMe (1.851 g, 34.26 mmol) were added to a clean, oven dried PTFE autoclave sleeve equipped with a stirrer bar in air. The PTFE sleeve was sealed within the autoclave which was evacuated and re-filled with nitrogen three times. Methanol (10 mL, 247.13 mmol) was injected into the autoclave through an inlet against a flow of nitrogen. The autoclave was sealed and placed in a pre-heated (180 °C) aluminium heating mantle for 2 h. After 2 h the autoclave was cooled in an ice-water bath. There was negligible residual pressure and no white solid precipitated from the reaction mixture although undissolved catalyst was observed. The solvent was removed *in vacuo* to give an off-white solid which was washed as reported in section 6.1. below and analysed by NMR spectroscopy: <sup>13</sup>C{<sup>1</sup>H} NMR (D<sub>2</sub>O, 125.7 MHz) δ 171.21 (HCOO<sup>-</sup>), 168.43 (CO<sub>3</sub><sup>2-</sup>), 48.76 (MeO<sup>-</sup>) ppm; <sup>1</sup>H NMR (D<sub>2</sub>O, 400 MHz) δ 8.28 (HCOO<sup>-</sup>), 3.14 (MeO<sup>-</sup>) ppm. For representative NMR spectra of the solid obtained see Figures S3 and S4.

## 5. Catalyst Stability Studies

### 5.1. Reaction of *trans*-[RuCl<sub>2</sub>(dppm)<sub>2</sub>] (1) with methanol/ethanol

*trans*-[RuCl<sub>2</sub>(dppm)<sub>2</sub>] (1) (0.161 g, 0.171 mmol)\* was added to a clean, oven dried PTFE insert equipped with a stirrer bar in air. The PTFE sleeve was then sealed within the autoclave which was evacuated and re-filled with nitrogen three times. Methanol (10 mL, 247.13 mmol) and ethanol (1 mL, 17.13 mmol) were injected into the autoclave through an inlet against a flow of nitrogen. The autoclave was sealed and placed in a pre-heated (180 °C) aluminium heating mantle for 2 h. After 2 h the autoclave was cooled in an ice-water bath. Once at room temperature, any residual pressure was released from the autoclave through a Schlenk line to maintain a nitrogen atmosphere. A portion of solution (0.7 mL) was then taken for analysis by <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy (Figure S5A) under a nitrogen atmosphere and also GC analysis. The remaining solution was then collected in a Schlenk flask, taken to dryness *in vacuo* and analysed by <sup>1</sup>H NMR spectroscopy (Figure S6A), ESI mass spectrometry and IR. GC analysis showed no Guerbet products were formed. <sup>31</sup>P{<sup>1</sup>H} NMR (neat, 162 MHz) δ -0.49 (s, **4**), -12.28 (s, **5**) ppm; <sup>1</sup>H NMR (MeOD, 400 MHz) δ -3.62 (1H, quint, *J* = 20.4 Hz, **4**) ppm; ESI *m/z* 933.1 (**5**), 899.1 (**4**); **4** = *trans*-[RuH(CO)(dppm)<sub>2</sub>]Cl and **5** = *trans*-[RuCl(CO)(dppm)<sub>2</sub>]Cl

consistent with literature data.<sup>4</sup> \*Note: ten times the amount of catalyst was used compared to a typical catalytic run to easily observe transition metal species by NMR spectroscopy.

### 5. 2. Reaction of *trans*-[RuCl<sub>2</sub>(dppm)<sub>2</sub>] (**1**) with methanol/ethanol and water

Procedure 5.1. was repeated but with the addition of 0.62 mL of water. (NMR spectra: Figures S5B and S6B). <sup>31</sup>P{<sup>1</sup>H} NMR (neat, 162 MHz) δ 9.59 (t, *J* = 39.5 Hz), -0.62 (s, **4**), -10.99 (t, *J* = 39.5 Hz), -12.39 (s, **5**) ppm; <sup>1</sup>H NMR (MeOD, 400 MHz) δ -3.67 (1H, quint, *J* = 20.4 Hz, **4**) ppm; ESI *m/z* 933.1 (**5**), 899.1 (**4**).

### 5. 3. Reaction of *trans*-[RuCl<sub>2</sub>(dppm)<sub>2</sub>] (**1**) with methanol, sodium hydroxide and water

Procedure 4.1. was repeated but with the addition of water (0.62 mL) at the beginning of the reaction along with the methanol addition. A comparison of the NMR spectra obtained from a water free reaction (4.1.) and water addition reaction (5.3.) is made in section 7 (Figure S7B); <sup>31</sup>P{<sup>1</sup>H} NMR (neat, 162 MHz) δ 36.28 (s), 30.20 (s), 21.99 (s), 16.46 (s), 5.29 (s), -26.36 (s) ppm.

## 6. Solid Analysis

### 6. 1. Typical procedure for analysis of the solid obtained from the post-reaction mixture

The post-reaction mixture was transferred to a flask and the solvents were removed *in vacuo*. The solid was then suspended in toluene (30 mL) and stirred for 1 hour. The solvent was removed by filtration and the solid was washed further with toluene (2 x 20 mL). The solid was then dried *in vacuo*.

### 6. 2. Solid product composition with increased addition of water

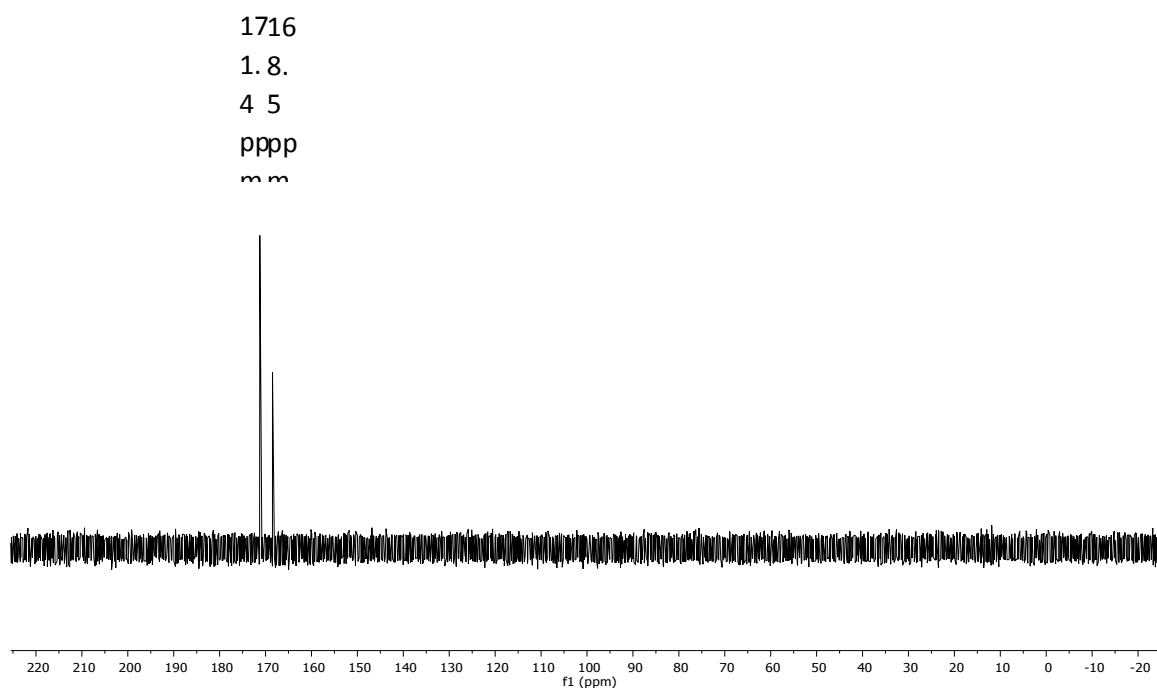
**Table S4** Analysis of solids obtained from post-reaction mixture

Entry <sup>a</sup>	Base	Water	Composition of Solid (wt%)					Total solids (g)
			NaOAc <sup>b</sup>	NaOC(O)H <sup>b</sup>	Na <sub>2</sub> CO <sub>3</sub> <sup>c</sup>	NaOMe <sup>b</sup>	NaOH <sup>d</sup>	
1	NaOMe	-	-	19	37	8	37	1.76
2	NaOH	-	<1	12	35	3	49	1.67
3	NaOH	0.62	<1	10	39	8	43	1.83
4	NaOH	5	1	9	33	<1	57	1.63
5	NaOH	20	1	15	23	<1	60	1.53

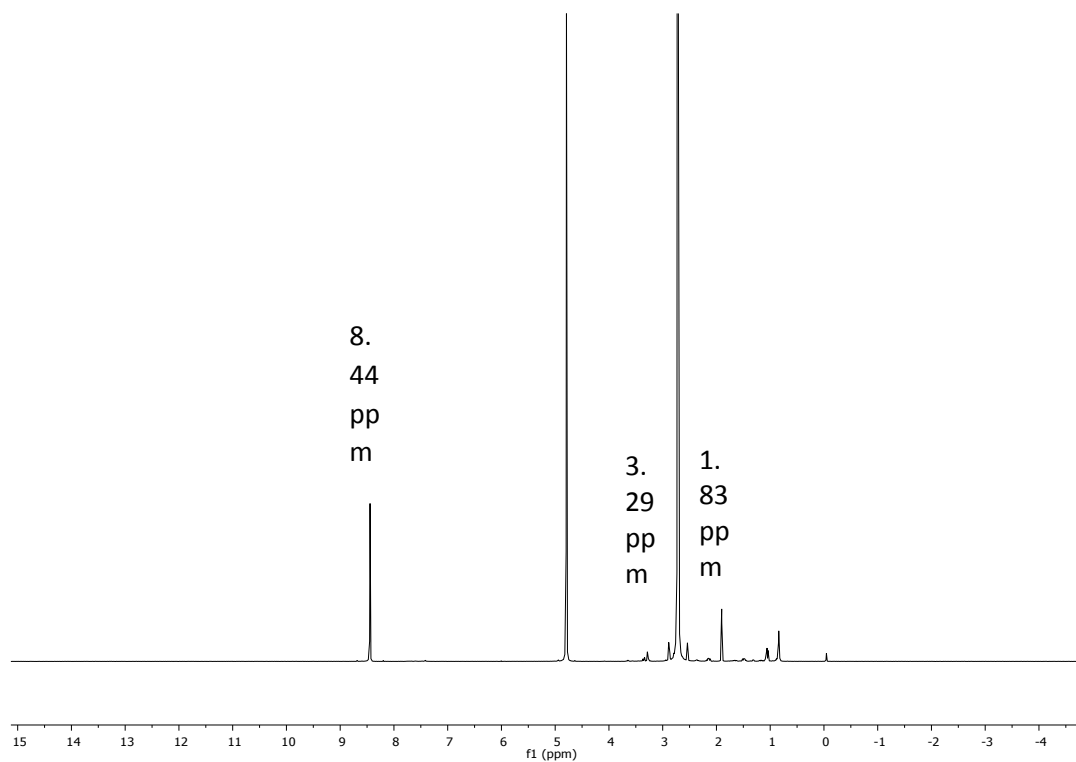
<sup>a</sup> Analysis of solid collected from the post reaction mixture using catalyst **1**. Conditions: 1 mL (17.13 mmol) ethanol, 10 mL (247.13 mmol) methanol, 0.1 mol% **1**, 200 mol% base, water as stated, 180 °C (mol% based on ethanol substrate). <sup>b</sup> Amount of sodium acetate, formate and methoxide obtained from <sup>1</sup>H NMR spectroscopic analysis in D<sub>2</sub>O with DMSO as a standard. <sup>c</sup> Amount of sodium carbonate formed obtained from microanalysis for inorganic carbon. <sup>d</sup> The remaining solids are presumed to be sodium hydroxide.



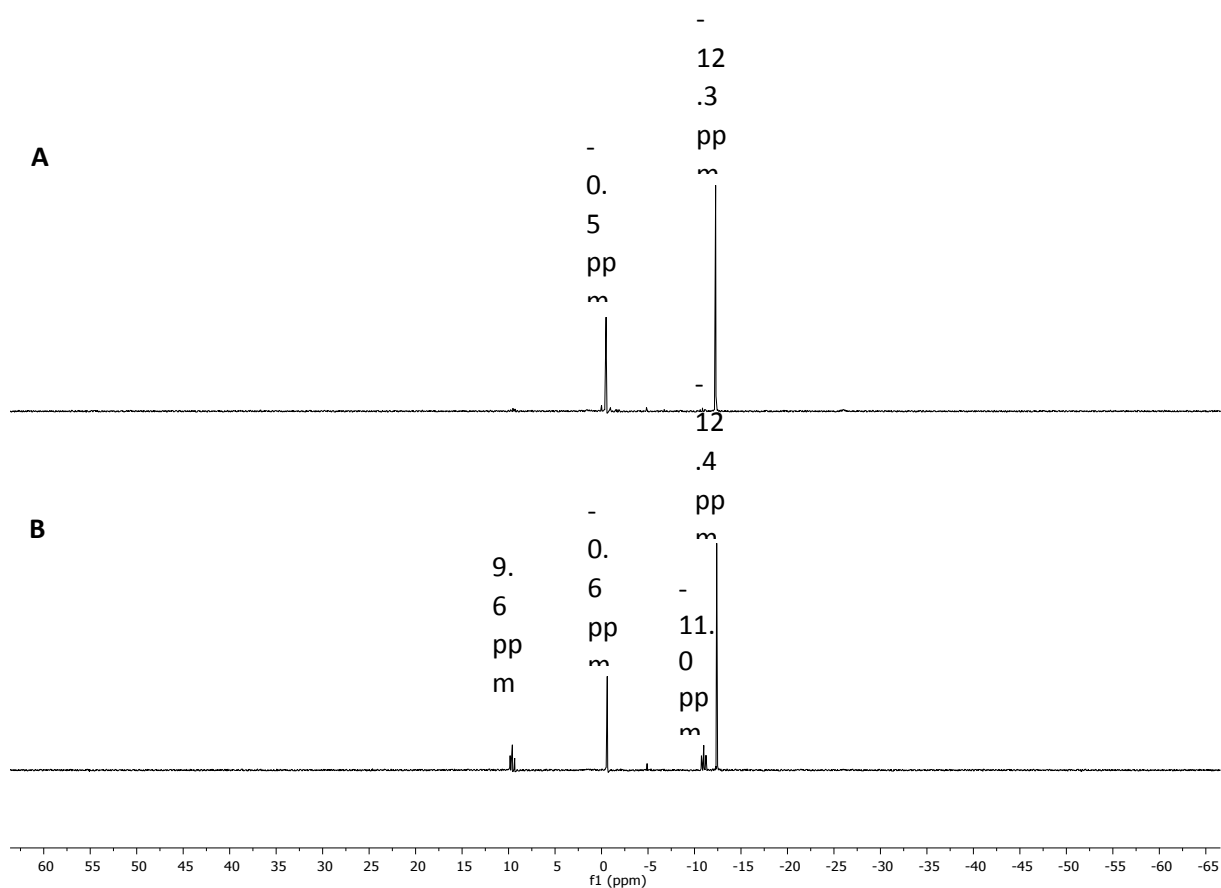
## 7. NMR Spectra



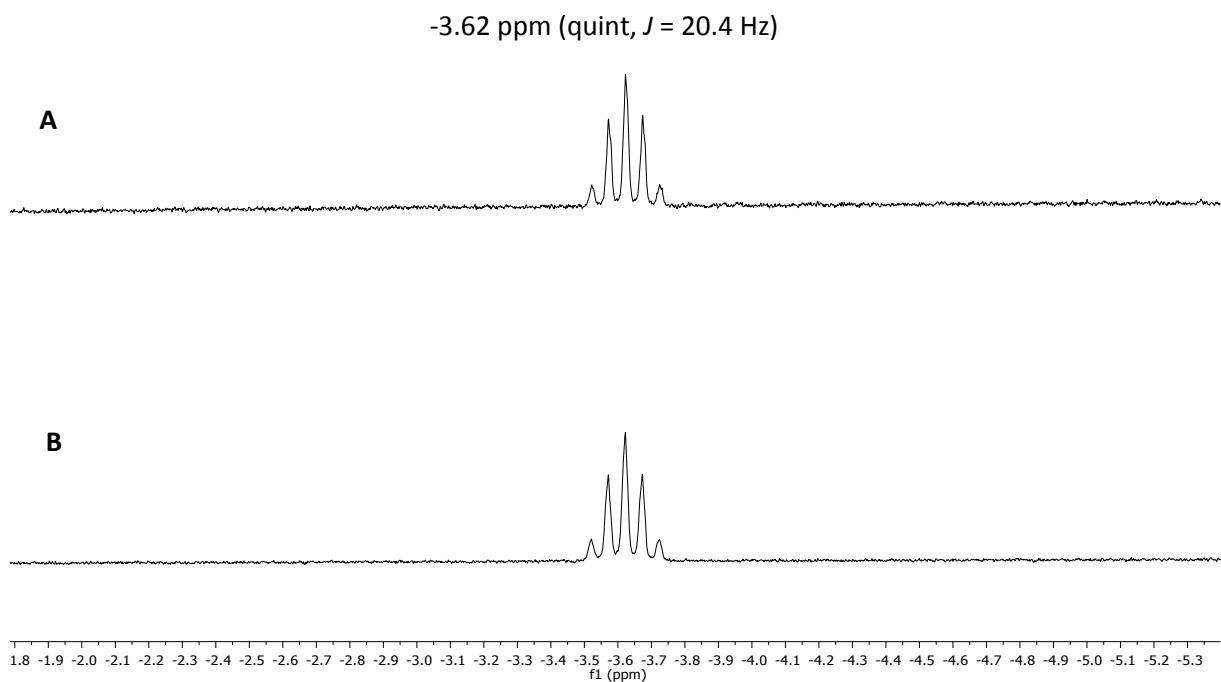
**Figure S3.** A typical  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of the solid obtained from the post reaction mixture (101 MHz,  $\text{D}_2\text{O}$ )  $\delta$  171.38 (formate), 168.49 (carbonate).



**Figure S4.** A typical  $^1\text{H}$  NMR spectrum of the solid obtained from the post reaction mixture (400 MHz,  $\text{D}_2\text{O}$ )  $\delta$  8.44 ppm (s,  $\text{NaOC(O)H}$ ), 3.29 (s,  $\text{NaOMe}$ ), 1.83 (s,  $\text{NaOAc}$ ) ppm. (2.72 ppm is DMSO standard for quantitative analysis).

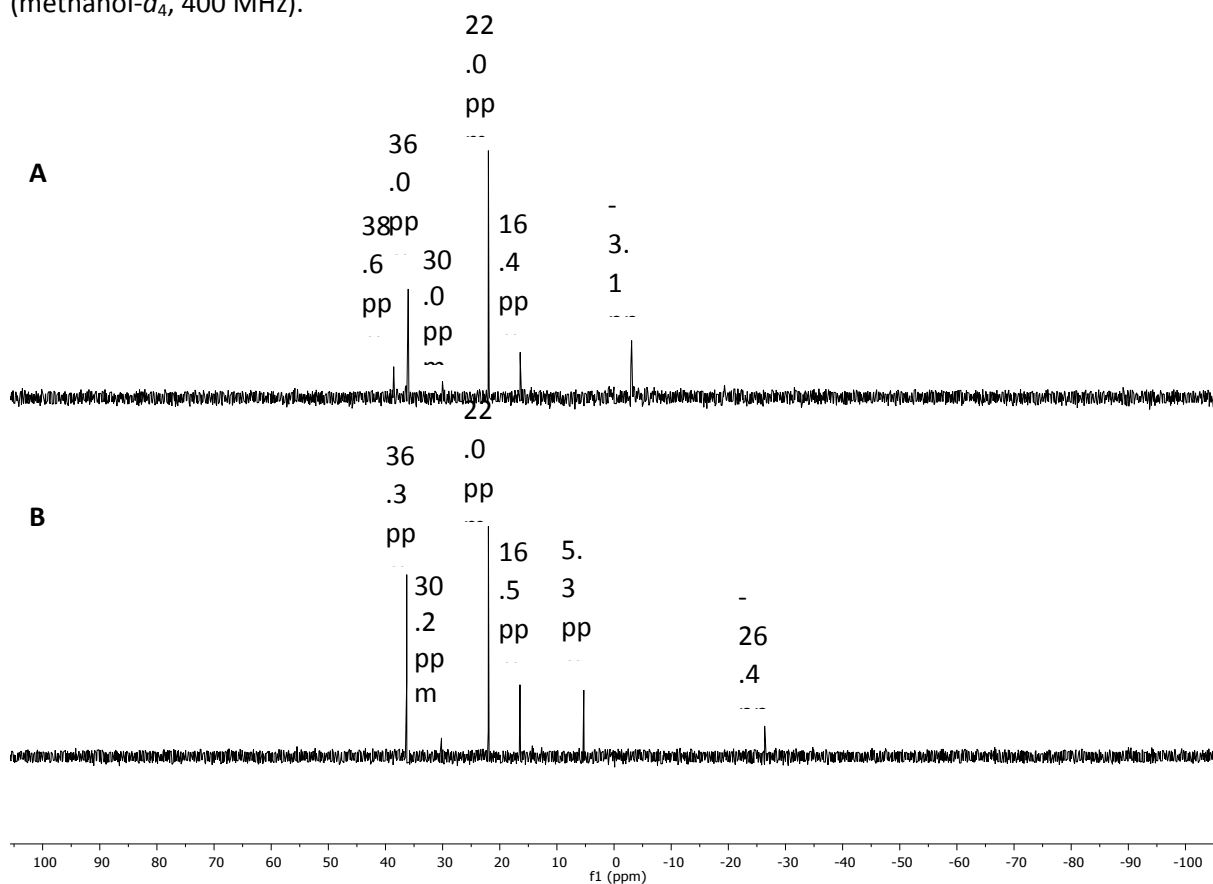


**Figure S5.** A)  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum obtained after reaction of *trans*- $[\text{RuCl}_2(\text{dppm})_2]$  (**1**) with methanol/ethanol (neat, 162 MHz). B)  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum obtained after reaction of *trans*- $[\text{RuCl}_2(\text{dppm})_2]$  (**1**) with methanol/ethanol in the presence of water (neat, 162 MHz).

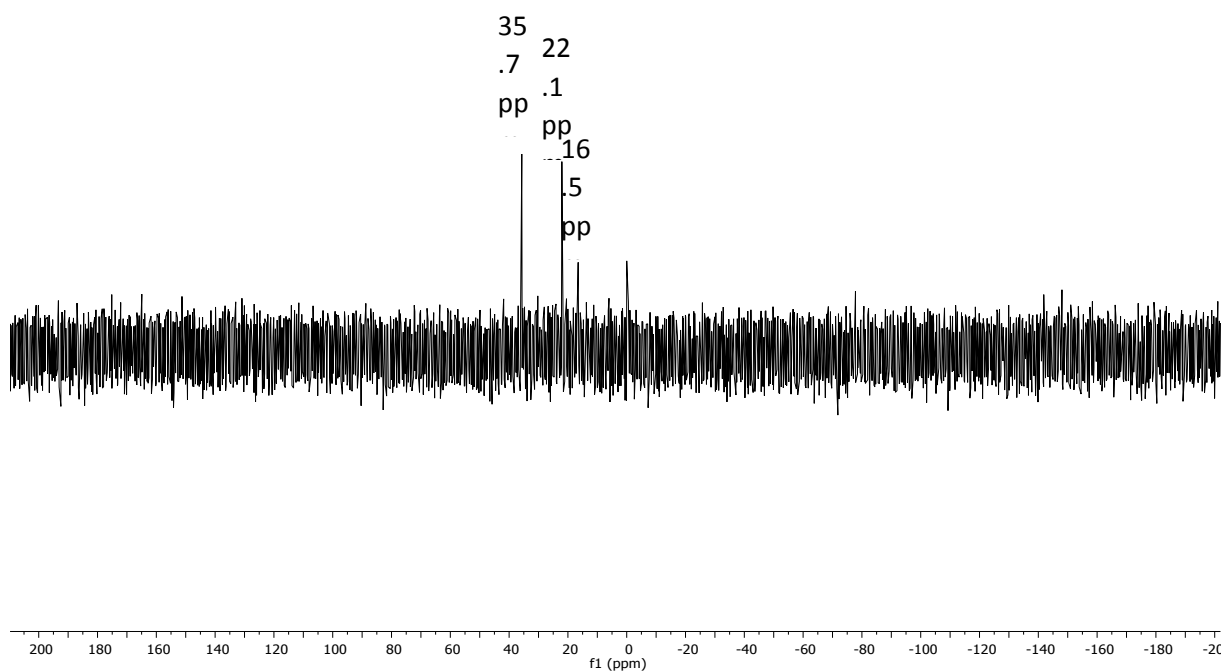


**Figure S6.** A)  $^1\text{H}$  NMR spectrum (hydride region) obtained after reaction of *trans*- $[\text{RuCl}_2(\text{dppm})_2]$  (**1**) with methanol/ethanol (methanol- $d_4$ , 400 MHz). B)  $^1\text{H}$  NMR spectrum (hydride region) obtained

after reaction of *trans*-[RuCl<sub>2</sub>(dppm)<sub>2</sub>] (**1**) with methanol/ethanol in the presence of water (methanol-*d*<sub>4</sub>, 400 MHz).



**Figure S7.** A) <sup>31</sup>P{<sup>1</sup>H} NMR spectrum obtained after reaction of *trans*-[RuCl<sub>2</sub>(dppm)<sub>2</sub>] (**1**) with methanol and sodium hydroxide (neat, 162 MHz). B) <sup>31</sup>P{<sup>1</sup>H} NMR spectrum obtained after reaction of *trans*-[RuCl<sub>2</sub>(dppm)<sub>2</sub>] (**1**) with methanol and sodium hydroxide in the presence of water (neat, 162 MHz).



**Figure S8.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of the post reaction mixture from Table S2, Entry 2 (162 MHz, No solvent)  $\delta$  35.69 (s), 22.06 (s), 16.51 (s) ppm.

## 8. References

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