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Supporting Information for:

Upgrading Ethanol to 1-Butanol Catalyzed by a Homogeneous Air-Stable Ruthenium Catalyst

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General Considerations

All manipulations were conducted under a nitrogen atmosphere in a glovebox unless otherwise stated. All reagents were purchased from commercial vendors. The 3Å molecular sieves were dried at 250 °C under dynamic vacuum for 24 h. 200 proof anhydrous ethanol (Decon) was sparged with N_2 for 2 h, and then stored over 3Å molecular sieves for 3 days. Sodium ethoxide (Sigma-Aldrich), lithium ethoxide (Sigma-Aldrich), potassium ethoxide (Sigma-Aldrich), and sodium hydroxide (Sigma-Aldrich) were used without further purification. The following compounds were synthesized according to literature methods: Ru(bMepi)(PPh_3)Cl[1], HRu(bMepi)(PPh_3)$_2$[1], Ru(bpi)(PPh_3)$_2$Cl[2], Ru(b4OMepi)Cl(PPh_3)$_2$[2], and Ru(b4Clpi)Cl(PPh_3)$_2$[2]. Diethyl ether (Et_2O), benzene (C_6H_6), dichloromethane (DCM) and pentane were purified using a Glass Contour solvent purification system consisting of a copper catalyst, neutral alumina, and activated molecular sieves then passed through an in-line 2 μm filter immediately before using dispensed.

NMR spectra were recorded on MR400 and Varian vnmrs 500 spectrometers at ambient temperature. ^1H and ^{13}C shifts are reported in parts per million (ppm) relative to TMS, with the residual solvent peak used as an internal reference. The follow abbreviations are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), triplet (t), multiplet (m). ^{13}C NMR resonances were observed as singlets unless otherwise stated. Solid-state IR spectra were collected using a Nicolet iS10 spectrometer equipped with a diamond attenuated total reflectance (ATR) accessory. Elemental analysis was performed by Midwest Microlab, LLC.

General Procedure for GC-FID Analysis

GC-FID analyses were performed using a Shimadzu GC-2014 GC/FID; the GC contains a 15 m long SH-Rxi-5ms column with a 0.25 mm I.D. and utilized H_2 as the carrier gas. GC measurements were conducted using the following method: 50 °C hold for the first 2 min, ramp to 250 °C at 35 °C/min and hold for 2 min. A calibration curve for the Guerbet products was obtained by GC analysis by plotting the ratios of the areas, $A_{sample}/A_{standard}$, against the known the concentrations.

General Procedure for the Catalytic Conversion of EtOH to 1-BuOH under Air

On the benchtop, ethanol (1 mL, 17.1 mmol) was added to a 10 mL Biotage microwave vial (Product No. 351521) containing Ru(bpi)$(PPh_3)_2$Cl (**2-H**) (0.1 mol%, 0.0172 mmol, 16.4 mg), NaOEt (5 mol%, 0.858 mmol, 58.3 mg), and a stir bar. The vial was crimped with a septum, heated to 150 °C using an aluminum-heating block, and stirred at 1500 rpm. After 2 h, the vial was removed from the aluminum-heating block and cooled to room temperature. The solution was diluted with $CHCl_3$ to 25 mL and filtered through celite. The products and yields were analyzed using GC-FID against naphthalene as an internal standard.

General Procedure for the Catalytic Conversion of EtOH to 1-BuOH under N_2

Inside an inert-atmosphere glovebox, ethanol (1 mL, 17.1 mmol) was added to a 10 mL Biotage microwave vial (Product No. 351521) containing catalyst (0.1 mol%, 0.0172 mmol), base (5 mol%, 0.858 mmol), and a stir bar. Unless otherwise stated, Ru(bpi)$(PPh_3)_2$Cl (**2-H**) (16.4 mg, 0.0172 mmol) and NaOEt (58.3 mg, 0.858 mmol) were used. The vial was crimped with a septum, heated to 150 °C using an aluminum-heating block, and stirred at 1500 rpm. After 2 h, the vial was removed from the aluminum-heating block and cooled to room temperature. The solution was diluted with $CHCl_3$ to 25 mL and filtered through celite. The products and yields were analyzed using GC-FID against naphthalene as an internal standard.

Table S1. Catalytic Conversion of EtOH to 1-BuOH

Entry	*Conditions*	*Catalyst Amount (mg)*	*1-butanol (%)*	*2-ethyl-1-butanol (%)*	*1-Hexanol (%)*	*2-ethyl-1-hexanol (%)*	*1-Octanol (%)*	*Total Conversion (%)*[a]	*1-BuOH Selectivity (%)*[b]	*TON*[c]	*TOF* (h^{-1})
1	$\mathrm{Ru(bMepi)(PPh_3)Cl}$	12.4	10	0	1	0	0	11	91	118	59
2	$\mathrm{HRu(bMepi)(PPh_3)_2}$	16.4	10	0	0	0	0	10	100	101	51
3[d]	$\mathrm{Ru(bpi)(PPh_3)_2Cl}$	16.4	25	1	3	0	0	30	91	296	148
4	$\mathrm{Ru(bpi)(PPh_3)_2Cl}$ No Stirring	16.4	29	2	4	0	0	35	88	347	174
5[e]	$\mathrm{Ru(bpi)(PPh_3)_2Cl}$ Teflon	16.4	30	3	6	1	1	40	82	397	199
6	0.3 mol% $\mathrm{Ru(bpi)(PPh_3)_2Cl}$	49.5	23	1	3	0	0	27	89	92	46
7	0.05 mol% $\mathrm{Ru(bpi)(PPh_3)_2Cl}$	8.2	20	2	3	0	0	25	81	501	250
8	0.01 mol% $\mathrm{Ru(bpi)(PPh_3)_2Cl}$	1.6	5	0	1	0	0	6	86	625	313
9	0.001 mol% $\mathrm{Ru(bpi)(PPh_3)_2Cl}$	0.2	1	0	0	0	0	1	100	1423	711
10	$\mathrm{Ru(b4OMepi)(PPh_3)_2Cl}$	17.5	24	1	3	0	0	28	89	284	142
11	$\mathrm{Ru(b4Clpi)(PPh_3)_2Cl}$	17.6	21	1	3	0	0	25	89	251	126
12	$\mathrm{Ru(bMepi)(PPh_3)(Cl)CO}$	12.9	16	0	1	0	0	17	95	168	84
13	$\mathrm{Ru(bpi)(CO)_2Cl}$	8.4	3	0	0	0	0	3	100	31	16
14[f]	$\mathrm{Ru(bpi)(PPh_3)_2Cl}$ Set up under air	16.4	27	2	5	0	0	34	83	342	171
15[d]	0.5 h	16.4	3	0	0	0	0	3	100	31	62
16[d]	1 h	16.4	11	0	1	0	0	12	96	116	116
17[d]	4 h	16.4	31	3	6	1	1	45	81	448	112
18[d]	6 h	16.4	32	4	7	2	1	46	80	457	76
19[d]	24 h	16.4	33	4	7	1	1	46	80	460	19
20	10 mol% NaOEt (116.6 mg)	16.4	31	2	6	1	1	42	82	422	211
21	10 mol% NaOEt (116.6 mg) under air	16.4	29	3	6	0	0	38	80	385	192
22	5 mol% LiOEt (44.6 mg)	16.4	4	0	0	0	0	4	100	39	20
23	5 mol% KOEt (72.2 mg)	16.4	19	1	2	0	0	23	89	226	113
24	5 mol% NaOH (34.3 mg)	16.4	26	1	3	0	0	30	90	300	150
25	0.1 mol% $\mathrm{PPh_3}$ (4.5 mg)	16.4	38	3	8	0	0	49	84	489	245
26	0.2 mol% $\mathrm{PPh_3}$ (9.0 mg)	16.4	36	3	8	1	1	49	81	489	245
27	0.4 mol% $\mathrm{PPh_3}$ (18.0 mg)	16.4	37	3	10	1	2	53	78	529	265
28[g]	20% v/v 1-butanol	16.4	23	3	7	1	1	35	85	348	174
29	180 °C	16.4	28	4	6	2	1	41	78	410	205

30	No catalyst	0	0	0	0	0	0	0	0	0	0
31	Ru(bpi)$(PPh_3)_2$Cl – No NaOEt base	0	0	0	0	0	0	0	0	0	0
32[h]	Fisher-Porter tube – 0 psig H_2	16.4	7	0	1	0	0	8	90	78	39
33[h]	Fisher-Porter tube – 45 psig H_2	16.4	28	4	7	2	1	42	76	421	211
34[h]	Fisher-Porter tube – 90 psig H_2	16.4	23	4	5	3	1	36	73	365	182

[a] Conversion of EtOH to Guerbet products. [b] 1-BuOH selectivity calculated with following equation: *mmoles of 1-butanol/mmoles of all products*. [c] TON based on mmol of substrate converted to products per mmol of Ru. [d] Average of 2 runs. [e] The reaction was performed using a 23 mL stainless steel autoclave Parr bomb lined with a Teflon vessel. [f] Average of 3 runs. [g] With 0.2 mL 1-BuOH added (20% by volume). [h] The reaction was performed using a 85 mL Fisher-Porter tube.

General Procedure for Poisoning Experiments

Following the general procedure of the Guerbet reaction, the experiment was conducted by allowing the reaction to proceed for 30 min. The reaction was removed from the aluminum-heating block and cooled for 15 min at room temperature. Then PBu_3 or Hg(0) was added to the reaction. The reaction was crimped and reheated to 150 °C for 1.5 h.

For the water poisoning experiments, water was added concomitantly with ethanol. The volume of the reaction remained constant. For example, entry 3 below indicates that 5% and 95% of the reaction volume is water and ethanol respectively (50 μL of water and 950 μL of ethanol).

Table S2. Catalytic Conversion of EtOH to 1-BuOH with Poisoning Additives

Entry	*Conditions*	*Amount (uL)*	*1-butanol (%)*	*2-ethyl-1-butanol (%)*	*1-Hexanol (%)*	*2-ethyl-1-hexanol (%)*	*1-Octanol (%)*	*Total Conversion (%)*[a]	*1-BuOH Selectivity (%)*[b]	*TON*[c]	*TOF (h^{-1})*
1	Control: cool for 15 min after 0.5 h at 150 °C, then reheated for 1.5 h at 150 °C	—	29	2	4	0	0	35	89	348	179
2	0.025 mol% P(*n*-Bu)$_3$	1.1	25	1	3	0	0	30	88	299	150
3	0.1 mol% P(*n*-Bu)$_3$	4.3	25	2	4	0	0	30	86	298	149
4	0.2 mol% P(*n*-Bu)$_3$	8.6	3	0	0	0	0	3	100	31	16
5[d]	~20 mol% Hg(0)	1 drop (~50 μL)	26	2	4	0	0	31	87	312	156
6	5% v/v Water	50	24	1	2	0	0	28	90	279	140
7	10% v/v Water	100	4	0	0	0	0	4	100	40	20
8	20% v/v Water	200	8	0	0	0	0	8	100	81	41

[a] Conversion of EtOH to Guerbet products. [b] 1-BuOH selectivity calculated with following equation: *mmoles of 1-butanol/mmoles of all products*. [c] TON based on mmol of substrate converted to products per mmol of Ru. [d] Average of 2 runs.

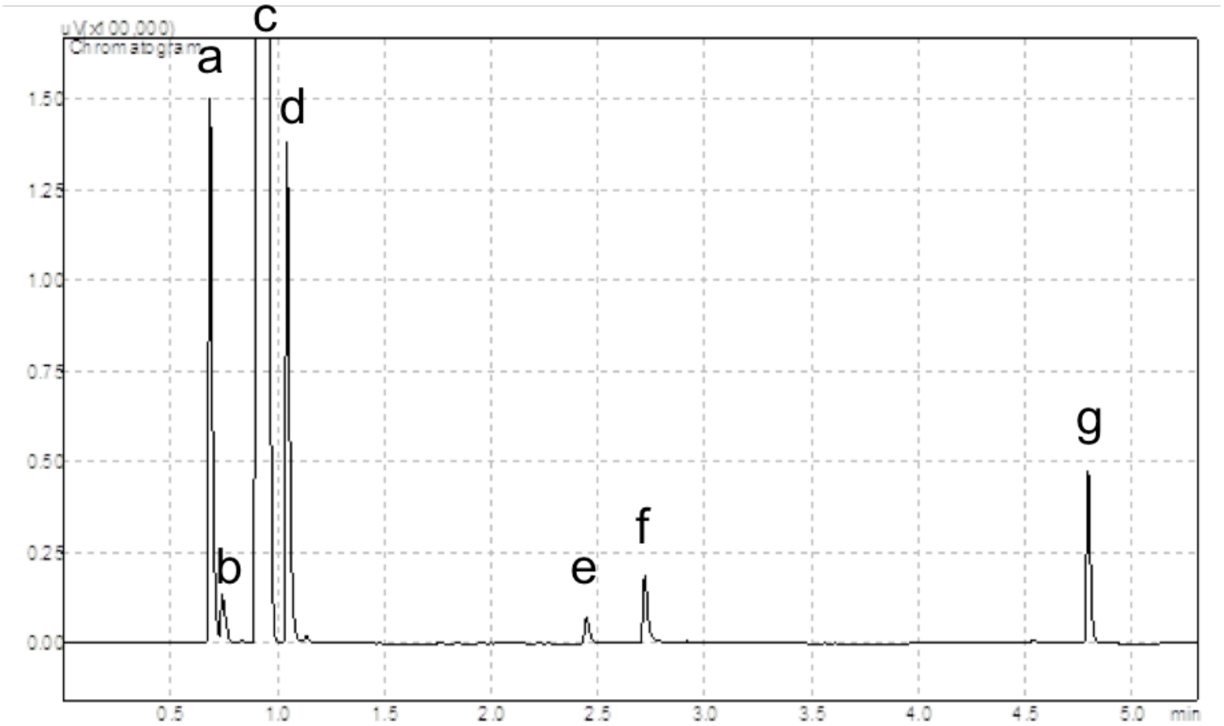

Figure S1. Representative GC Chromatogram of Conversion of EtOH to 1-BuOH Catalyzed by **2-H**.

a = Ethanol (0.66 min). b = stabilizer in $CHCl_3$ (0.75 min). c = Chloroform (solvent, 0.93 min).
d = 1-butanol (1.054 min). e = 2-ethyl-1-butanol (2.46 min). f = 1-hexanol (2.73 min)
g = naphthalene (internal standard, 4.81 min)

Preparation of Ru(bMepi)(PPh$_3$)(Cl)CO (3). DCM (5 mL) was added to a Fisher-porter tube containing Ru(bMepi)(PPh$_3$)Cl (101.1 mg, 0.139 mmol) and a stir bar. The reaction vessel was charged with CO (30 psig) and allowed to stir at room temperature for 15 h. The DCM solution was layered with pentane (15 mL). After 24 h at room temperature, the precipitates were collected and washed with pentane (4 × 10 mL). Evaporation of the volatiles under vacuum afforded the product as a dark orange solid. Crystals were obtained from vapor diffusion of pentane into a C_6H_6 solution at room temperature. Yield: 79 mg (75%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.76 (dd, J_{HH} = 5.6, 2.4 Hz, 2H), 7.52 (dd, J_{HH} = 5.6, 2.4 Hz, 2H), 7.49 (t, J_{HH} = 7.8 Hz, 2H), 7.16 (t, J_{HH} = 7.6 Hz, 3H), 7.09 (d, J_{HH} = 7.2 Hz, 2H), 7.03 (d, J_{HH} = 7.8 Hz, 2H), 6.93-6.89 (m, 6H), 6.55-6.50 (m, 6H). ^{13}C{^{1}H} (126 MHz, CD_2Cl_2): δ 206.03 (d, J_{CP} = 19.2 Hz), 165.45, 160.55, 155.63, 141.08, 136.91, 133.24 (d, J_{CP} = 9.6 Hz), 130.78, 130.41, 130.27 (t, J_{CP} = 3.3 Hz), 128.28 (d, J_{CP} = 9.6 Hz), 125.92, 121.72 (d, J_{CP} = 8.6 Hz), 31.71. ^{31}P{^{1}H} (162 MHz, CD_2Cl_2): δ 43.5 (s). IR (ATR, cm^{-1}): 3066, 3015, 1929, 1639, 1604, 1577, 1545, 1519, 1474, 1432, 1393, 1371, 1318, 1286, 1236, 1187, 1156, 1117, 1094, 992, 903, 882, 800, 782, 750, 735, 714, 688. Anal. Calculated (found): C, 62.19 (62.15); H, 4.15 (4.14); N, 9.30 (9.12).

Preparation and Characterization of Ru(bpi)(CO)$_2$Cl (4b). C_6H_6 (8 mL) was added to a Fisher-porter tube containing **2-H** (81.5 mg, 0.0849 mmol) and a stir bar. The reaction vessel was charged with CO (30 psig) and allowed to stir at room temperature for 24 h. The precipitate was collected on a frit and washed with Et_2O (5 mL) and pentane (4 ×10 mL). The product was dried under vacuum to afford a yellow solid. Crystals were obtained from vapor diffusion of Et_2O into a DCM solution at 5 °C. Yield: 33 mg (79%). ^{1}H NMR (500 MHz, CD_2Cl_2): δ 8.76 (d, J_{HH} = 6.0 Hz, 2H), 8.07 (dd, J_{HH} = 5.2, 3.2 Hz, 2H), 7.86 (t, J_{HH} = 7.6 Hz, 2H), 7.69-7.65 (m, 4H), 7.04 (t, J_{HH} = 6.0 Hz, 2H). ^{13}C{^{1}H} (126 MHz, CD_2Cl_2): δ 196.27, 192.31, 157.49, 156.84, 156.78, 138.94, 138.89, 131.19, 128.75, 122.00, 120.07. IR (ATR, cm^{-1}): 3091, 3069, 2046, 1977, 1647, 1603, 1577, 1528, 1459, 1428, 1381, 1321, 1307, 1287, 1201, 1184, 1150, 1121, 1101, 1011, 910, 875, 869, 846, 771, 745, 702. Anal. Calculated (found): C, 48.94 (48.73); H, 2.46 (2.45); N, 14.27 (13.71).

References

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2. Tseng, K.-N. T.; Kampf, J. W.; Szymczak, N. K. *ACS Catal*. **2015**, *5*, 5468.