

Supporting Information

High-Turnover Supramolecular Catalysis by a Protected Ruthenium(II) Complex in Aqueous Solution

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General. All reagents used were from commercial sources, without further purification unless otherwise noted. The host assembly $K_{12}[Ga_4L_6]$,¹ and the ruthenium complex $[RuCp(PMe_3)(MeCN)_2][PF_6]$ were prepared according to literature procedures.² All NMR spectra were recorded using Bruker AV-500, DRX-500, or AV-400 MHz spectrometers at the indicated frequencies. All 1H NMR chemical shifts are reported in parts per million (δ) relative to residual protic solvent resonances. Multiplicities of 1H NMR resonances are reported as s = singlet, d = doublet, t = triplet, m = multiplet and br = broad).

Preparation of 2, $[RuCp(PMe_3)(MeCN)_2]^+ \subset Ga_4L_6$. $K_{12}Ga_4L_6$ (240 mg, 67 μ mol, 1.05 equiv) was dissolved in MeOH (30 mL) under a nitrogen atmosphere – note that $K_{12}Ga_4L_6$ is slow to dissolve in methanol and this suspension had to be stirred for ~40 minutes to become homogeneous. $RuCpPMe_3(MeCN)_2$ (31 mg, 64 μ mol) was dissolved in ~1 mL MeCN under a glove box atmosphere, yielding a clear, orange solution. The solution of $RuCpPMe_3(MeCN)_2$ was immediately added to the solution of $K_{12}Ga_4L_6$. This mixture was stirred for two minutes, becoming mostly homogeneous and pale green in color. 50 mL anhydrous Et_2O was then added, precipitating a bright yellow powder from solution. This solution was filtered over a second fine frit, and the filter cake was harvested and dried under vacuum, giving **2** as a yellow solid (240 mg, MW~4000, 89.8% yield). 1H NMR (500 MHz, D_2O): δ 8.01 (d, 12H, ArH, J = 8.0 Hz), 7.53 (d, 12H, ArH, J = 9.0 Hz), 7.23 (d, 2H, ArH, J = 7.5 Hz), 6.76 (t, 12H, ArH, J = 8.0 Hz), 6.62 (d, 12H, ArH, J = 8.5 Hz), 6.49 (t, 12H, ArH, J = 7.5 Hz), 6.41 (t, 6H, ArH, J = 7.5 Hz), 2.15 (s, 5H, CpH), 1.63 (d, 3H, MeCN, J = 1.5 Hz), 1.24 (d, 3H, MeCN, J = 1.5 Hz), -1.30 (d, 9H, PMe_3 , J = 9.5 Hz). $^{13}C\{^1H\}$ NMR (125 MHz, D_2O) δ 169.5, 158.7, 154.9, 133.7, 126.5, 125.8, 118.5, 117.7, 115.4, 115.0, 114.96, 114.7, 72.11, 14.8, 14.7. $^{13}P\{^1H\}$ NMR (125 MHz, D_2O) δ 1.03.

Preparation of 1-phenylprop-2-en-1-ol (3c). To a flame-dried 100-mL round bottom flask was added benzaldehyde (1.0 mL, 9.89 mmol) to THF (15 mL). The solution was cooled to 0 °C and a 0.7 M vinyl magnesium bromide solution in THF (21 mL, 14.7 mmol, 1.5 equiv) was added via syringe. The reaction mixture was warmed to 25 °C over two hours. The reaction mixture was then diluted in diethyl ether and quenched with saturated aqueous NH_4Cl . The organic layer was washed twice with water (10 mL) and dried over magnesium sulfate. The solution was filtered and concentrated by rotary evaporation to afford the desired product as a clear oil (1.263 g, 95% yield).

General procedure for allyl alcohol isomerization by encapsulated ruthenium catalyst 2.

Under a nitrogen atmosphere, encapsulated catalyst **2** was dissolved in 0.5 mL degassed D_2O containing 100 mM KDCO_3^- buffer at pH 8.0, containing 5 mM *p*-dioxane as an internal standard. This homogeneous yellow solution was transferred to an NMR tube and sealed with a rubber septum and parafilm. Allyl alcohol substrates were added as a stock solution of 100 mM in the aforementioned D_2O buffer solution, and were added via syringe. The reaction was followed inside an AV-500 NMR spectrometer.

Decomposition of $[\text{RuCp}(\text{PMe}_3)(\text{MeCN})_2]\text{PF}_6$ in aqueous solution. Under a nitrogen atmosphere, crystalline orange solid $[\text{RuCp}(\text{PMe}_3)(\text{MeCN})_2]\text{PF}_6$ (2.1 mg, 4.3 mmol) was suspended in 0.7 mL degassed D_2O containing 100 mM KDCO_3^- buffer at pH 8.0, containing 5 mM *p*-dioxane as an internal standard. This suspension was stirred for 30 minutes, becoming pale yellow in color and remaining heterogeneous. This suspension was then filtered, and 0.6 mL was transferred to an NMR tube and sealed with a rubber septum. This homogeneous yellow solution (containing 1 mM **2** and 2.5-7.3 equiv MeCN) was transferred to an NMR tube and sealed with a rubber septum and parafilm. The conversion of the starting complex to another

unidentified compound was observed over 2 h at 42 °C, with conversion of 68% of the starting complex in that time.

Dependence of catalytic rate on acetonitrile concentration. Under a nitrogen atmosphere, encapsulated catalyst **2** (2.2 mg, 0.6 μmol) was dissolved in 0.5 mL degassed D_2O containing 100 mM KDCO_3^- buffer at pH 8.0, containing 5 mM *p*-dioxane as an internal standard. 30-90 μL of a stock solution of acetonitrile (50 mM) was added, and the mixture was diluted to a total volume of 0.6 mL. This homogeneous yellow solution (containing 1 mM **2** and 2.5-7.3 equiv MeCN) was transferred to an NMR tube and sealed with a rubber septum and parafilm. The 3-buten-2-ol was added as a 100 mM stock solution in the aforementioned D_2O buffer solution, and were added via syringe. The reaction was followed inside an AV-500 NMR spectrometer. The results of these experiments are summarized in Table S1.

Table S1. Effect of acetonitrile buffering on the rate of catalysis by **2** at 42 °C.

[MeCN]	Rate constant ($\times 10^{-5}$)
2.5 mM	12.8
3.2 mM	9.446
4.2 mM	6.955
5.9 mM	5.884
7.3 mM	3.848

Dependence of catalytic rate on substrate concentration. Under a nitrogen atmosphere, encapsulated catalyst **2** (22 mg, 5.5 μmol) was dissolved in 4.4 mL degassed D_2O containing 100 mM KDCO_3^- buffer at pH 8.0, containing 5 mM *p*-dioxane as an internal standard. 400 μL of this solution was transferred to each of ten NMR tubes. This solution was then diluted with buffer according to Table S2. The solutions were then sealed with a rubber septum and parafilm.

Table S2. Preparation of samples for substrate concentration dependence study.

Sample	mL 0.5 M 3-buten-2-ol	mL buffer	[3-buten-2-ol] (mM)	[2] (mM)
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1	5	95	5	1.0
2	10	90	10	1.0
3	15	85	15	1.0
4	20	80	20	1.0
5	25	75	25	1.0
6	30	70	30	1.0
7	40	60	40	1.0
8	50	50	50	1.0
9	75	25	75	1.0
10	100	0	100	1.0

Prior to kinetics measurement, 3-buten-2-ol was added as a stock solution of 0.5 M in the aforementioned D₂O buffer solution via syringe. The reaction was followed inside an AV-500 NMR spectrometer at 42 °C. Pseudo-first-order rate constants were obtained from the first 10% conversion of the substrate. The results of these experiments are summarized in Table S3 and Figure S1.

Table S3. Effect of substrate concentration on the rate of catalysis by **2** at 42 °C.

[3-buten-2-ol]	k_{obs}
5	28.07
10	23.77
15	27.88
20	22.67
25	21.06
30	19.15
40	17.33
50	14.82
75	12.32
100	8.443

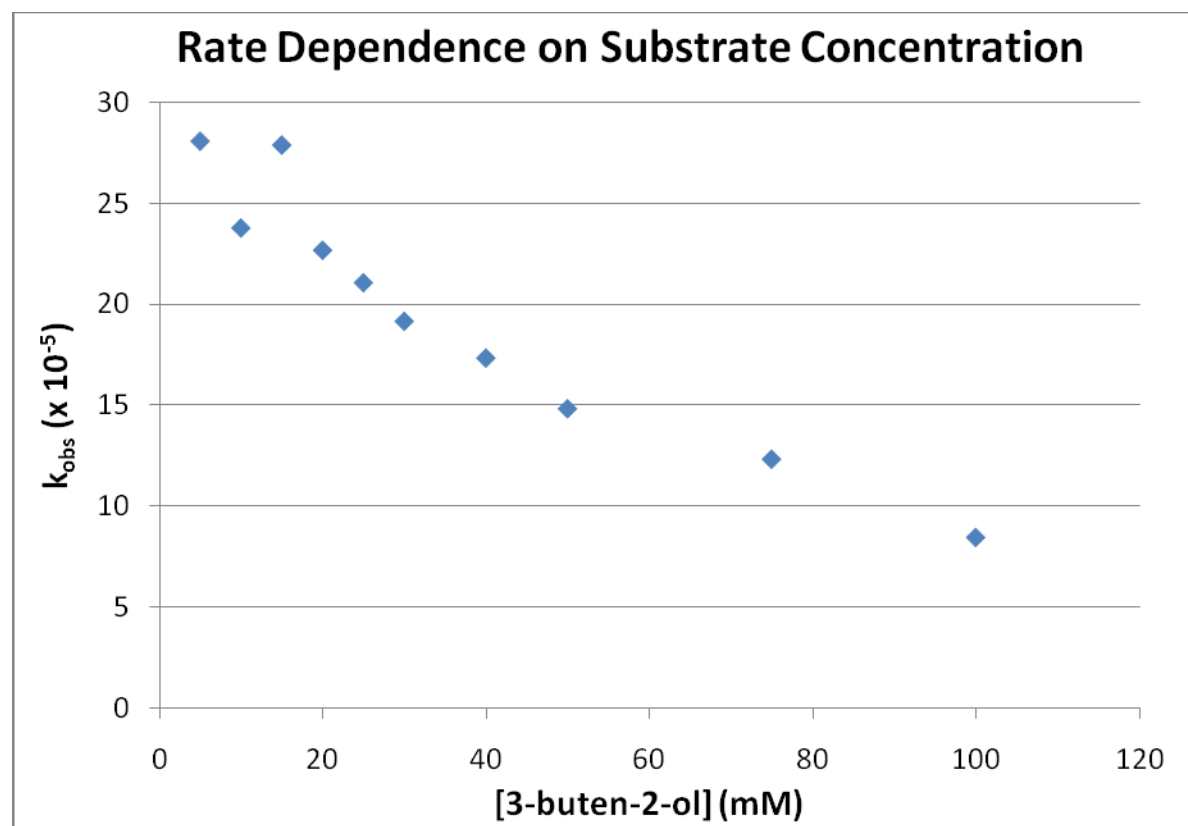
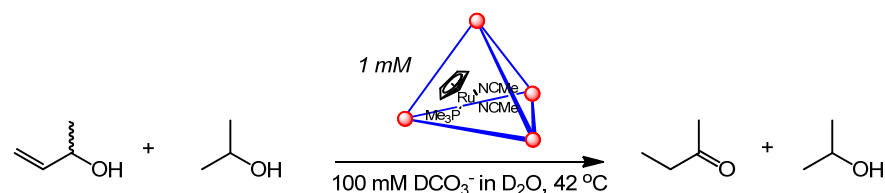


Figure S1. Effect of substrate concentration on the rate of catalysis by **2** at 42 °C.

Inhibition of catalysis by isopropanol. Under a nitrogen atmosphere, encapsulated catalyst **2** (2.2 mg, 0.6 μ mol) was dissolved in 0.5 mL degassed D₂O containing 100 mM KDCO₃⁻ buffer at pH 8.0, containing 5 mM *p*-dioxane as an internal standard. 3-buten-2-ol (3 mmol,) was added as a stock solution of 100 mM in the aforementioned D₂O buffer solution, and were added via syringe. The reaction was followed inside an AV-500 NMR spectrometer. The results of these experiments are summarized in Table S4.

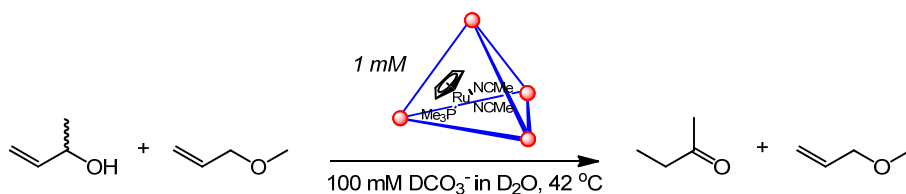
Table S4. Effect of isopropanol concentration on the rate of catalysis by **2** at 35 °C.



Sample	[3-buten-2-ol] (mM)	[isopropanol] (mM)	Initial Rate ($\times 10^{-5} \text{ mM}^{-1}\text{s}^{-1}$)
1	25	0	24.2
2	25	25	24.7
3	25	50	24.2

Inhibition of catalysis by allyl methyl ether. Under a nitrogen atmosphere, encapsulated catalyst **2** (2.2 mg, 0.6 μmol) was dissolved in 0.5 mL degassed D_2O containing 100 mM KDCO_3^- buffer at pH 8.0, containing 5 mM *p*-dioxane as an internal standard. 3-buten-2-ol and allyl methyl ether were added as stock solutions (0.5 M each), and the mixture was diluted to a total volume of 0.6 mL. This homogeneous yellow solution (containing 1 mM **2**) was transferred to an NMR tube and sealed with a rubber septum and parafilm. The reaction was followed inside an AV-500 NMR spectrometer. The results of these experiments are summarized in Table S5.

Table S5. Effect of acetonitrile buffering on the rate of catalysis by **2** at 35 °C.



Sample	[3-buten-2-ol] (mM)	[allyl methyl ether] (mM)	Initial Rate ($\times 10^{-5} \text{ mM}^{-1}\text{s}^{-1}$)
1	25	0	24.7
2	25	25	0.0
3	25	50	0.0
4	50	0	15.1
5	50	2	7.93
6	50	25	0.0
7	50	50	0.0
8	75	0	12.5
9	75	25	0.82

High-turnover catalysis at low catalyst loading. Under a nitrogen atmosphere, encapsulated catalyst **2** (1.3 mg, 0.38 μmol) was dissolved in 0.7 mL degassed D_2O containing 100 mM KDCO_3^- buffer at pH 8.0, containing 5 mM *p*-dioxane as an internal standard. This homogeneous yellow solution (containing 1 mM **2**) was transferred to an NMR tube and sealed with a rubber septum and parafilm. The amount of catalyst added was verified by ^1H NMR integration against the internal standard. 3-buten-2-ol (67 μL , 770 μmol) was added via syringe. The solution was heated at 50 $^\circ\text{C}$ for 15.5 hours, and analyzed by ^1H NMR. High conversion (67 mmol 3-buten-2-ol remaining, 91% conversion) and good yield of methyl ethyl ketone (413 mmol, 54% yield, 1070 turnovers) were obtained. No side products were observed by ^1H NMR.

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- (2) C. Slugovc, E. Ruba, R. Schmid, K. Kirchner, *Organometallics*, **1999**, *18*, 4230-4233.