Supporting Information for

Efficient hydrogenation of biomass-derived cyclic di-esters to 1,2-diols

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General Experimental

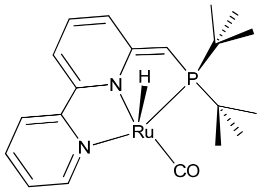
All experiments with metal complexes and phosphine ligands were carried out under an atmosphere of purified nitrogen in a Vacuum Atmospheres glovebox equipped with a MO 40-2 inert gas purifier or using standard Schlenk techniques. All solvents were reagent grade or better. All non-deuterated solvents were refluxed over sodium/ benzophenone ketyl and distilled under argon atmosphere. Deuterated solvents were used as received. All solvents were degassed with argon and kept in the glovebox over 4Å molecular sieves. Most of the cyclic di-esters (glycolide, L-Lactide and rac-lactide) in the catalytic reactions are commercially available and were recrystallized from THF and sublimed twice prior to use.

Thin layer chromatography (TLC) was performed using Merck 1.05554 aluminum sheets precoated with silica gel 60 F254 and the spots were visualized with UV light at 254 nm or under iodine vapor. Column chromatography purifications were performed by flash chromatography using Merck silica gel 60 (0.063-0.200 mm). Specific rotation of the optically pure compounds was recorded using Perkin Elmer Polarimeter 341.

^{1}H, ^{13}C and ^{31}P NMR spectra were recorded using a Bruker AMX-300 NMR spectrometer. NMR chemical shifts are reported in ppm downfield from tetramethylsilane (for $CDCl_3$). ^{1}H NMR chemical shift is referenced to the residual hydrogen signal of the deuterated solvent (7.15 ppm for benzene). ^{31}P NMR chemical shift is reported in ppm downfield from H_3PO_4 and referenced to an external 85%

solution of phosphoric acid in D_2O. Abbreviations used in the NMR follow-up experiments: br, broad; s, singlet; d, doublet; t, triplet; m, multiplet. IR spectra were recorded on a Nicolet FT-IR spectrophotometer. Mass spectra were recorded on Micromass Platform LCZ 4000, using Electro Spray Ionization (ESI) mode. GC–MS was carried out on HP 6890 (flame ionization detector and thermal conductivity detector) and HP 5973 (MS detector) instruments equipped with a 30 m column (Restek 5MS, 0.32 mm internal diameter) with a 5% phenylmethylsilicone coating (0.25 mm) and helium as carrier gas. GC analysis were carried out using a Carboxen 1000 column on a HP 690 series GC system or HP-5 cross linked 5% phenylmethylsilicone column (30m × 0.32mm × 0.25 µm film thickness, FID) on a HP 6890 series GC system using *m*-xylene (1 mmol) as an internal standard.

Synthesis of complex 1



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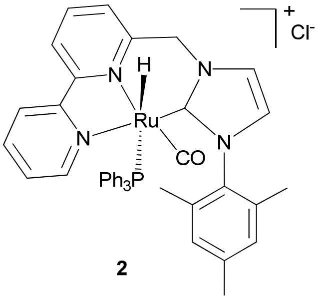
The dearomatized ruthenium-pincer complex **1** was prepared according to previously reported procedure from our group.[1] Complex **1** is stable at low temperature (below -5 °C) under nitrogen/ argon atmosphere for several months (~6 months) and at room temperature after a couple of weeks it started decomposing.

$^{31}P\{^1H\}$NMR (C_6D_6): 92.70 (s). ^1H NMR (C_6D_6): –25.73 (br d, J_{PH} = 23 Hz, 1H, Ru-*H*), 1.31 (d, J_{PH} = 13.8 Hz, 9H, P(C(C*H*$_3$)$_3$), 1.33 (d, J_{PH} = 12.6 Hz, 9H, P(C(C*H*$_3$)$_3$), 3.63 (d, 1H, J_{PH} = 1.8 Hz, PC*H*), 6.06 – 6.11 (m, 1H, *H*-5'), 6.24 – 6.30 (m, 1H, *H*-4'), 6.40 (d, J_{HH} = 9.3 Hz, 1H, *H*-5), 6.55 – 6.60 (m, 1H, *H*-4), 6.72 (d, J_{HH} = 8.1 Hz, 1H, *H*-3), 6.91 – 6.93 (m, 1H, *H*-3'), 8.53 – 8.55 (br m, 1H, *H*-6').

Synthesis of complex 2

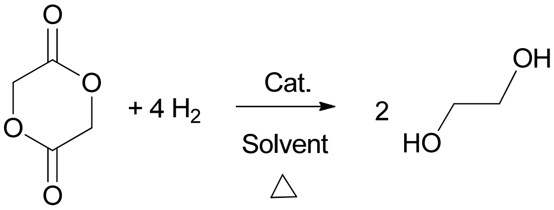


2

The CNN Ru(II) pincer complex **2** was prepared according to previously reported procedure from our group.[2] Complex **2** is stable at -35 °C for about 3 months (under atmosphere of N_2), stable at room temperature for about 4 days under open air without decomposition, and stable to air in dichloromethane solution in the dark for 2 h.

General procedure for catalytic hydrogenation

1. Catalytic hydrogenation of glycolide to ethylene glycol

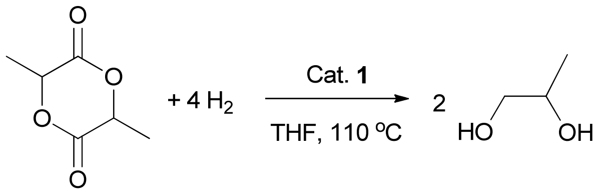


(a) Substrate/catalyst 100/1: A solution of catalyst **1** (4.5 mg, 0.01 mmol) in THF or 1,4-dioxane (1.0 mL) was transferred into a 100 mL Fischer-Porter tube followed by addition of the glycolide (116 mg, 1.0 mmol) in THF or 1,4-dioxane (2.0 mL) under an atmosphere of purified nitrogen in a glovebox. The pressure tube was taken out of the glovebox, followed by three successive cycles of pressurization/ venting with H_2 (2 atm), then pressurized with H_2 (6 or 10 atm) and tightly-closed. The tube was placed behind a protective shield and the reaction mixture was heated in an oil bath at 110 °C with constant stirring for the specified required time (see Table 1). After cooling to room temperature, excess H_2 gas was vented carefully and the products were determined by GC with *m*-xylene (1.0 mmol) as an internal standard, using a HP-5 cross linked 5% phenylmethylsilicone column (30m × 0.32mm × 0.25 μm film thickness) on a HP 6890 series GC system.

(b) A solution of KO^{t}Bu (0.01 mmol) in THF (1.0 mL) was transferred into a Fischer-Porter tube (100 mL) containing 0.01 mmol of complex **2**, followed by addition of the glycolide (1.0 mmol) in THF (2.0 mL) in a nitrogen glovebox. The Fischer-Porter tube was flushed with dihydrogen (thrice with 2 atm) and filled with H_2 (10 atm). The solution was heated at 110 °C (bath temperature; actual temperature is ~80 °C) with stirring for 2 h. After cooling to ~5 °C (with a cold water bath), excess H_2 gas was vented carefully, and the products were determined by GC analysis.

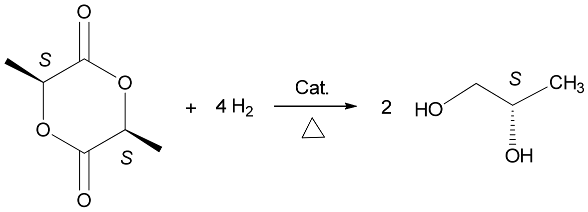
(b) Substrate/catalyst 500/1: In a nitrogen glovebox, a solution of catalyst **1** (9 mg, 0.02 mmol) in THF (5 mL) was added to a stainless-steel high pressure reactor (30 mL) equipped with a magnetic stirring bar containing 10.0 mmol (1.16 g) of the solid glycolide. The high pressure reactor was taken out of the glovebox and the nitrogen present in the pressure reactor was flushed with hydrogen by three successive cycles of pressurization/ venting with H_2 (5 atm), then pressurized with H_2 (50 atm) and tightly closed. The tube was covered by a protective shield and the reaction mixture was heated in an oil bath at 110 °C with constant stirring for 12 h. After cooling to room temperature, excess H_2 gas was vented carefully and the products were determined by GC with *m*-xylene (1.0 mmol) as an internal standard.

2. Catalytic hydrogenation of *meso*-lactide to propylene glycol



A 100 mL Fischer-Porter tube was charged under nitrogen with catalyst **1** (4.5 mg, 0.01 mmol), *meso*-lactide (144 mg, 1.0 mmol) and THF (3 mL). The Fischer-Porter tube was purged by three successive cycles of pressurization/venting with H_2 (2 atm), then pressurized with H_2 (10 atm). The solution was heated at 110 ºC (bath temperature) with stirring for 48 h. After cooling to ~5 ºC (ice/water), the H_2 was vented carefully and the products were determined by GC.

3. Catalytic hydrogenation of L-lactide to *S*-(+)-1,2-propanediol



(a) Substrate/catalyst 100/1: A 100 mL Fischer-Porter tube was charged under nitrogen with catalyst **1** (4.5 mg, 0.01 mmol), L-lactide (144 mg, 1.0 mmol) and THF (3 mL). The Fischer-Porter tube was purged by three successive cycles of pressurization/venting with H_2 (2 atm), then pressurized with H_2 (10 atm). The solution was heated at 110 °C (bath temperature) with stirring for 48 h. After cooling to ~5 °C (with a cold water bath), excess H_2 gas was vented carefully and the products were determined by GC with *m*-xylene (1.0 mmol) as an internal standard. After careful removal of the solvent under reduced pressure, the reaction mixture was passed through short silica gel bed and the 1,2-diol was eluted with CH_2Cl_2:MeOH (10:1) and concentrated under vacuum to yield 69% of the optically pure (*S*)-(+)-1,2-propanediol ($[\alpha]_D^{22}$ = +27.5° (c = 1, $CHCl_3$); lit.[3] $[\alpha]_D^{22}$ = +26.9° (c = 2.26, $CHCl_3$)).

In the case complex **2** (+ 1 equivalent of base; procedure similar to 1(b)), the isolated yield was 57%. The optical rotation of the pure isolated (*S*)-(+)-1,2-propanediol is ($[\alpha]_D^{22}$ = +27° (c = 1, $CHCl_3$) essentially the same as reported in the literature.[3]

(b) Substrate/catalyst 500/1: In a nitrogen glovebox, a solution of catalyst **1** (9 mg, 0.02 mmol) in THF (5 mL) was added to a stainless-steel high pressure reactor (30 mL) equipped with a magnetic stirring bar containing 10.0 mmol (1.44 g) of the L-lactide. The high pressure reactor was taken out of the glovebox and the nitrogen present in the pressure reactor was flushed with hydrogen by three successive cycles of pressurization/ venting with H_2 (5 atm), then pressurized with H_2 (50 atm) and well-closed. The tube was placed behind a protective shield and the reaction mixture was heated in an oil bath at 110 °C with constant stirring for 12 h. After cooling to ~5 °C (with a cold water bath), excess H_2 gas was vented carefully and the products were determined by GC with *m*-xylene (1.0 mmol) as an internal standard. After careful

removal of the solvent under reduced pressure, the reaction mixture was passed through short silica gel bed and the product was eluted with CH_2Cl_2:MeOH (10:1) and concentrated under vacuum to yield 73% of the optically pure (*S*)-(+)-1,2-propanediol ($[\alpha]_D^{22} = +26.7^\circ$ (c = 1, $CHCl_3$)).

Under the same conditions, the conversion of the L-lactide after 2 h was only 31%. In order to confirm that it did not undergo any racemization, the solvent was concentrated (to ~0.5 mL) under reduced pressure, followed by addition of hexane (2 mL) resulted the formation of precipitate. The white solid was filtered off and dried under vacuum for about 3 h to yield 60% of unreacted L-lactide. The optical rotation of the recovered L-lactide is $[\alpha]_D^{22} = -284.2^\circ$ (c = 1, toluene); lit.[4] $[\alpha]_D^{22} = -285^\circ$.

References

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2. E. Fogler, E. Balaraman, Y. Ben-David, G. Leitus, L. J. W. Shimon and D. Milstein, *Organometallics,* 2011, **30**, 3826-3833.
3. M. Poterała and J. Plenkiewicz, *Tetrahedron: Asymmetry,* 2011, **22**, 294-299.
4. A. Garcés, L. F. Sánchez-Barba, C. Alonso-Moreno, M. Fajardo, J. Fernández-Baeza, A. Otero, A. Lara-Sánchez, I. López-Solera and A. M. Rodríguez, *Inorg. Chem.,* 2010, **49**, 2859-2871.