Heterogeneous & Homogeneous & Bio-
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CATALYSIS

Supporting Information

Trimethylenemethane-Ruthenium(II)-Triphos Complexes as Highly Active Catalysts for Catalytic C–O Bond Cleavage Reactions of Lignin Model Compounds

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cctc_201200215_sm_miscellaneous_information.pdf

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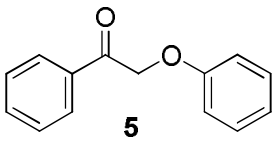
1. General Experimental

If not stated otherwise all reactions and preparations were carried out under argon atmosphere. NMR spectra were recorded on Bruker AV 400 or AV 600 instruments. All NMR chemical shifts are reported as d in ppm relative to the residual solvent signal. Gas chromatographic separations were performed with the following set-up: column: 50 m OV1-IVA; carrier gas: nitrogen; split: 33/1; detector: flame ionization; temperature program: 50 °C iso, 8 °C min^{-1} until 250 °C; *n*-dodecane as internal standard.

2. Substrate Preparation

2-Phenoxy-1-phenylethanol 1 was prepared by etherification of 2-bromoacetophenon with phenol and subsequent reduction with $NaBH_4$ as described by R. G. Bergman, J. A. Ellman, and co-workers.[1]

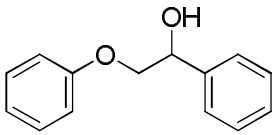
Step 1: A 500 mL three necked flask was loaded with 10.0 g (50.2 mmol) 2-bromoacetophenone, 12.3 g potassium carbonate (89.1 mmol) and 5.9 g (62.7 mmol) phenol. After addition of 250 mL degassed acetone, the resulting suspension was stirred and heated to reflux for 3 h. After filtration through celite and removal of solvent in vacuum, the resulting solid was recrystallized from ethanol to give 6.17 g of 2-phenoxy-1-phenylethanone **5** as colorless crystals (59 %).



5

^{1}H NMR (400 MHz, $CDCl_3$) d 7.95 (d, *J* = 7.7 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.22 (t, *J* = 7.23 Hz, 2H), 6.95-6.84 (m, 3H), 5.21 (s, 2H).

Step 2: 4.0 g (18.9 mmol) 2-phenoxy-1-phenylethanone **5** was dissolved in 56 mL THF and 14 mL water. Sodium borohydride (2.1 g, 56.7 mmol) was added over a period of 5 min to maintain a gentle evolution of gas, after which the reaction mixture was stirred for 3 h at room temperature. The reaction was quenched with saturated aqueous NH_4Cl (100 mL) and then the reaction mixture was diluted with water (100 mL). The aqueous portion was extracted with diethyl ether (3 x 100 mL). The combined organic extracts were washed twice with brine, dried over $MgSO_4$, filtered, and concentrated in vacuum to give 3.24 g of 2-phenoxy-1-phenylethanol **1** as a colorless solid (80%).



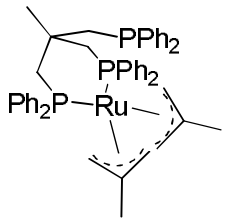
1

^{1}H NMR (400 MHz, $CDCl_3$) d 7.39 (d, *J* = 7.3 Hz, 2H), 7.32 (t, *J* = 7.2 Hz, 2H), 7.27 (d, *J* = 7.2 Hz, 1H), 7.22 (t, *J* = 7.7 Hz, 2H), 6.91 (t, *J* = 7.4 Hz, 2H), 6.85 (d, *J* = 8.2 Hz, 2H), 5.06 (dd, *J* = 8.9, 2.9 Hz, 1H), 4.05 (dd, *J* = 9.7, 3.0 Hz, 1H), 3.94 (t, *J* = 8.9 Hz,1H), 2.70 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$, 25°C): 157.4, 138.5, 128.6, 127.6, 127.2, 125.3, 120.3, 113.6, 72.2, 71.6.

[1] J. M. Nichols, L. M. Bishop, R. B. Bergman, J. A. Ellman, *J. Am. Chem. Soc.* **2010**, *132*, 12554–12555.

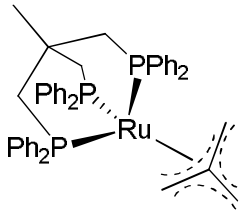
3. Synthesis of Ruthenium-complexes

Complex I-1: Heating a solution of [Ru(cod)(methallyl)$_2$] (3.2 mg, 0.01 mmol) and 1,1,1-tris(diphenylphosphinomethyl)ethane **TRIPHOS-1** (6.3 mg) in 0.5 mL toluene in a sealed NMR tube to 80 °C for 1 h resulted in full conversion to complex **I-1**.



^{1}H NMR (600 MHz, d^8-toluene): d 8.03 (s, 2H), 7.27 (m, 4H), 7.06 (m, 18H), 7.02 (m, 4H), 6.77 (s, 2H), 2.83 (d, *J* = 2.5 Hz, 1H), 2.75 (m, 4H), 2.68 (d, *J* = 2.7 Hz, 4H), 2.40 (dd, *J* = 13.9, 4.2 Hz, 1H), 2.10 (s, 3H), 2.07 (s, 3H), 1.90 (d, *J* = 13.7 Hz, 1H), 1.18 (t, *J* = 7.9 Hz, 3H), 0.96 (d, *J* = 13.7 Hz, 1H), 0.89 (d, *J* = 10.9 Hz, 1H), 0.75 (d, *J* = 10.7 Hz, 1H). ^{31}P-NMR (243 MHz, d^8-toluene): d 40.4 (s, 2 P), -26.2 (s, 1 P).

Complex II-1:



NMR Experiment: Heating a solution of 3.2 mg (0.01 mmol) [Ru(cod)(methallyl)$_2$] and 6.3 mg 1,1,1-tris(diphenylphosphinomethyl)ethane **TRIPHOS-1** in 0.5 mL d^8-toluene in a sealed NMR tube to 110 °C for 2 h resulted in full conversion to complex **II-1**.

^{1}H NMR (600 MHz, d^8-toluene): d 7.20 (bs, 12H, C_{Ar}-H), 6.92 (t, *J* = 7.4 Hz, 6H, C_{Ar}-H), 6.83 (t, *J* = 7.4 Hz, 12H, C_{Ar}-H), 2.27 (bs, 6H, P-CH_2), 2.14 (s, 6H, C-CH_2), 1.28 (s, 3H, CH_3). ^{31}P-NMR (243 MHz, d^8-toluene): d 35.3 (s, 3P).

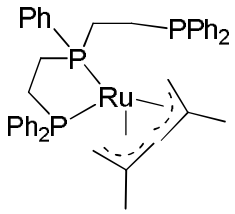
Synthesis of complex II-1: A 35 mL schlenk tube was charged with 159.5 mg (0.5 mmol) [Ru(cod)(methallyl)$_2$] and 312.0 mg 1,1,1-tris(diphenylphosphinomethyl)ethane **TRIPHOS-1** in 25 mL toluene. After heating for 2 h at 110 °C, the resulting solution was concentrated in vacuo and treated with 10 mL of pentane. The precipitating complex was isolated and washed 3 times with 10 mL pentane. After drying complex II-1 was obtained as a bright yellow powder in 76 % yield.

^{1}H NMR (600 MHz, d^2-dichlormethane): d 7.16 - 7.07 (m, 18H, C_{Ar}-H), 6.99 (m, 12H, C_{Ar}-H), 2.28 (bs, 6H, P-CH_2), 1.67 (bs, 6H, C-CH_2), 1.44 (s, 3H, CH_3). ^{13}C NMR (125 MHz, d^2-dichlormethane): d 141.0 (m, C_{Ar}), 132.2 (m, C_{Ar}-H), 127.6 (s, C_{Ar}-H), 127.3 (s, C_{Ar}-H), 106.5 (bs, **C**$(CH_2)_3^{2-}$), 43.2 (m, C(**C**$H_2)_3^{2-}$),

38.9 (q, $J_{C\text{-}P}$ = 9.7 Hz,CH_3), 38.2 (m, $(Ph_2PCH_2)_3$**C**-CH_3), 35.6 (m, P-CH_2) ppm. ^{31}P-NMR (243 MHz, d^8-toluene): d 34.4 (s, 3P).

HR-MS (EI) $C_{41}H_{45}P_3Ru$: Calc.: 780.177 m/z. Found: 780.178 m/z.

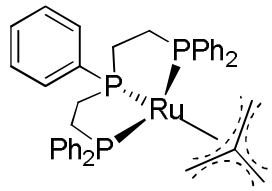
Complex I-2: Heating a solution of 3.2 mg (0.01 mmol) [Ru(cod)(methallyl)$_2$] and 5.3 mg (0.01 mmol) ((phenylphosphinediyl)bis(ethane-2,1-diyl))bis(diphenylphos-phine) **TRIPHOS-2** in 0.5 mL toluene in a sealed NMR tube to 80 °C for 1 h resulted in complex **I-2**.



^{31}P-NMR (243 MHz, d^8-toluene): 85.9 (d, *J* = 7.5 Hz, 1P), 79.8 (d, *J* = 7.5 Hz, 1P) 78.8 (dd, *J* = 26.0, 7.5 Hz, 1P), 68.9 (dd, *J* = 20.1, 7.5 Hz, 1P), -12.7 (d, *J* = 26.0 Hz, 1P), -13.2 (d, *J* = 20.1 Hz, 1P) ppm.

Complex II-2:

NMR Experiment: Heating a solution of 3.2 mg (0.01 mmol) [Ru(cod)(methallyl)$_2$] and 5.3 mg (0.01 mmol) ((phenylphosphinediyl)bis(ethane-2,1-diyl))bis(diphenylphosphine) **TRIPHOS-2** in 0.5 mL toluene in a sealed NMR tube to 110 °C for 2 h resulted in full conversion to complex **II-2**. Layering of this solution with pentane afforded complex **II-2** as yellow crystals.



^{1}H NMR (600 MHz, d^8-toluene):d 7.84 (m, 2H), 7.28 (m, 5H), 7.19 (m, 1H), 7.15 – 7.09 (m, 5H), 7.03 – 7.01 (m, 4H), 6.88 (m, 7H), 2.37 – 2.18 (m, 4H), 2.22 (q, *J* = 3.9 Hz, 2H), 2.10 (q, *J* = 3.9 Hz, 2H) 1.81-1.71 (m, 2H), 1.42 – 1.32 (m, 2H), 0.84 (m, 2H). ^{31}P-NMR (243 MHz, d^8-toluene): d 93.8 (s, 1P), 77.2 (s, 2P). ESI-MS found: 690.1 m/z (solvent THF).

Synthesis of complex II-2: A 35 mL schlenk tube was charged with 16.0 mg (0.05 mmol) [Ru(cod)(methallyl)$_2$] and 26.7 mg (0.05 mmol) ((phenylphosphinediyl)bis(ethane-2,1-diyl))bis(diphenylphosphine) **TRIPHOS-2** in 2.5 mL toluene. After heating for 2 h at 110 °C, the resulting solution was concentrated in vacuo and treated with 2 mL of pentane. The precipitating

complex was isolated and washed 3 times with 2 mL of pentane. After drying complex II-2 was obtained as a yellow powder in 82 % yield.

^{1}H NMR (400 MHz, d^{2}-dichloromethane):d 7.67 (t, *J* = 8.5 Hz, 2H, C_{Ar}-H), 7.35 (q, *J* = 7.3 Hz, 3H, C_{Ar}-H), 7.19 (t, *J* = 8.5, 4H, C_{Ar}-H), 7.07 (t, *J* = 7.3 Hz, 2H, C_{Ar}-H), 7.00 – 6.94 (m, 6H, C_{Ar}-H), 6.94 - 6.84 (m, 8H, C_{Ar}-H), 2.63 – 2.38 (m, 4H, CH_2-PPh_2), 1.84 – 1.54 (m, 4H, CH_2PPh), 1.59 (q, *J* = 4.1 Hz, 2H, C-CH_2), 1.48 (q, *J* = 4.1 Hz, 2H, C-CH_2), 0.18 – 0.10 (m, 2H, C-CH_2). ^{13}C-NMR (151 MHz, d^{2}-dichloromethane): 143.5 (m, C_{Ar}), 138.8 (m, C_{Ar}), 132.1 (d, J_{CP}= 11.9 Hz, C_{Ar}-H), 131.2 (d, J_{CP}= 10.9 Hz, C_{Ar}-H), 130.8 (d, J_{CP}= 10.9 Hz, C_{Ar}-H), 128.1 (m, C_{Ar}-H), 127.5 (d, J_{CP}= 8.9 Hz, C_{Ar}-H), 127.1 (d, J_{CP}= 8.9 Hz C_{Ar}-H), 107.3 (bs, **C**$(CH_2)_3^{2-}$), 45.5 (d, J_{CP}= 30.4 Hz, C(**C**$H_2)_3^{2-}$), 36.3 (d, J_{CP}= 30.4 Hz, C(**C**$H_2)_3^{2-}$), 32.3 (m, CH2-P), 31.2 (m, CH2-P). ^{31}P-NMR (243 MHz, d^{2}-dichloromethane): d 94.4 (s, 1P), 75.8 (s, 2P).

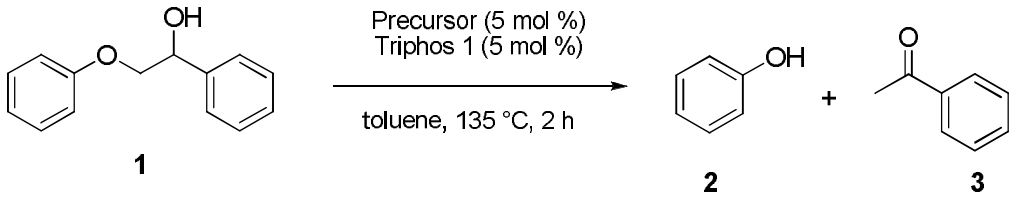
HR-MS(EI) $C_{38}H_{39}P_3Ru$: Calc.: 690.130 m/z, found: 690.130 m/z.

4. Procedure for catalytic transformation

Representative procedure: In a typical experiment a 10 mL vial was charged with 3.18 mg (0.01 mmol) [Ru(cod)(methallyl)$_2$] and 5.35 mg (0.01 mmol) ((phenylphosphinediyl)bis(ethane-2,1-diyl))bis(diphenylphos-phine) **TRIPHOS-2** in 0.5 mL toluene. After addition of 42.8 mg (0.2 mmol) 2-phenoxy-1-phenylethanol, the reaction was heated for 2 h at 135 °C. After the desired reaction time, the reaction was quenched in an ice bath and subjected to GC analysis.

5. Variation of reaction parameters for catalytic cleavage of 2-phenoxy-1-phenethanol 1

Table S1[a] Variation of reaction parameters for catalytic cleavage of **1**.



1 **2** **3**

Entry	Precursor	Yield **1** [%]	Yield **2** [%]
1[b]	$H_2Ru(PPh_3)_3CO$	35 - 60	37 - 55
2[c]	$HRu(PPh_3)_3Cl$	75	78
3	$Ru(PPh_3)_2Cl_2$	0	0
4	$Ru(cymen)_2Cl_2$	0	0
5	$Ru(acac)_3$	0	0
6	$Ru(methallyl)_2COD$	77	79
7	$RuCl_3$	0	0
8	$RuCl_2COD$ polymer	0	0

[a] Reaction conditions: 0.2 mmol substrate, 5 mol % $Ru(methallyl)_2COD$, 5 mol% **Triphos-1**, 0.5 mL toluene, 135 °C performed in microwave at 300 W, 2 h. [b] results varied and could not be reproduced satisfyingly [c] in 0.5 mL dioxane.

6. Single Crystal X-Ray Diffraction of Ru(trimethylenmethane)(TRIPHOS-2)

Intensity data were collected with a Bruker SMART APEX CCD detector on a D8 goniometer equipped with an Incoatec microsource (Mo-K_a radiation, $l = 0.71073$ Å).[2] Temperature was controlled using an Oxford Cryostream 700 instrument. Data were processed with SAINT+.[3]

The structure was solved by direct methods in the space groups *Pn* and *P*21/*c* and refined using F^2 with SHELXL-97.[4] Non hydrogen atoms were refined with anisotropic displacement parameters, carbon atoms in space *P*21/*c* have assigned isotropic displacement parameters. Hydrogen atoms were placed in idealized positions (C – H = 0.93 Å for phenyl rings and C – H = 0.97 Å for others) and included as rigid with U_{iso}(H) = 1.2 $U_{eq.}$(non-H). Some geometrical parameter restraints (SADI, FLAT, DFIX) were used to fix disordered fragments to be chemically reasonable. Multiscan-absorption corrections were applied.[5]

There are two possible space groups: *Pn* or *P*21/*c*. The structure was solved in the non centrosymmetric space group *Pn* containing two symmetrically independent molecules. The two molecules are related by pseudo-symmetry. A Flack parameter of 0.46 indicates the pseudo-symmetric relation between the two molecules. The plotting of the two molecules results in the following picture. The inner part of the molecules fits well but the outer part, consisting of the phenyl rings, is arranged differently.

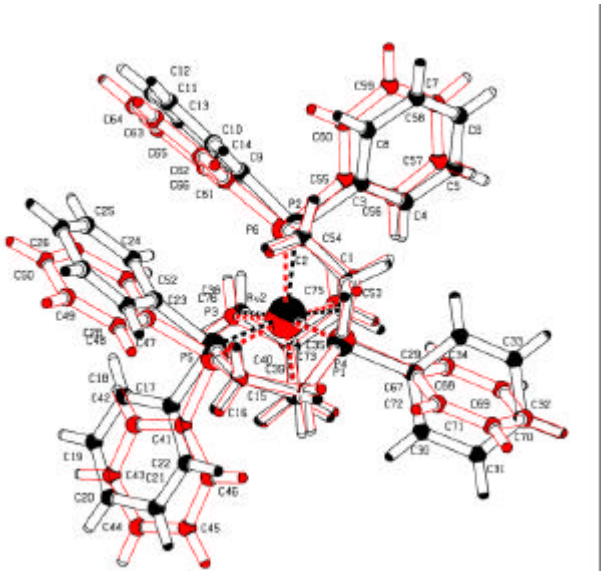


Figure S-1 Structure of Ru(trimethylenmethane)(TRIPHOS-2)

[2] Bruker AXS Inc., Madison, Wisconsin, USA. SMART (version 5.624). Program for Bruker CCD X-ray diffractometer control, **2000**.
[3] Bruker AXS Inc., Madison, Wisconsin, USA. SAINT+ (version 6.02). Program for reduction of data collected on Bruker CCD area detector diffractometer, **1999**.
[4] G. M. Sheldrick, *Acta Crystallogr. Sect.A* **2008**, *64*, 112.
[5] G.M. Sheldrick, SADABS, version 2.03, program for empirical absorption correction of area detector data, University of Göttingen, 1996.

85% of the electron density fit to the transformation into the space group *P*21/*c*. The transformation into *P*21/*c* results in disorder of one phenyl ring. The results for both structure calculations are summarized in table. The extinction conditions for the presence of a 2_1-screw axis are violated.

Parameter	***P*n**	***P*21/*c***
a/Å	8.9874(14)	8.9874(14)
b/Å	17.045(3)	17.045(3)
c/Å	21.380(3)	21.522(3)
ß/°	101.209(2)	102.973(5)
V/Å^3	3212.8(9)	3212.8(9)
Variables refined	758	211
Restraints	8	93
R_{int}	0.0392	0.0835
wR_2(all reflections)	0.0976	0.2498
R_1(all/obs)	0.0411/0.0413	0.1252/0.1148
GOF	1.043	3.194

The refinement results for the non-centrosymmetric space group *Pn* are much better than for the centrosymmetric space group *P*21/*c*.