Electronic and bite angle effects in catalytic C-O bond cleavage of a lignin model compound using ruthenium xantphos complexes

Luke Shaw, a D. M. Upulani K. Somisara, a Rebecca C. How, a Nicholas J. Westwood, a Pieter C. A. Bruijnincx, b Bert M. Weckhuysen, b and Paul C. J. Kamer. a *

a. School of Chemistry, University of St. Andrews and EaStCHEM, North Haugh, St. Andrews, Fife, KY16 9ST, United Kingdom.

b. Utrecht University, Faculty of Science, Debye Institute for NanoMaterials Science, Sorbonnelaan 16, Utrecht, The Netherlands.

Corresponding author: PCJK@st-andrews.ac.uk

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General experimental

All reactions were carried out using standard Schlenk techniques under an argon atmosphere or in an inert atmosphere glove-box at ambient temperature. Toluene and TMEDA were distilled from sodium, THF and diethyl ether were distilled from sodium/benzophenone, hexanes from sodium/benzophenone/triglyme and dichloromethane from CaH₂. 2-Phenoxy-1-phenylethanol, 6,7-bis(diphenylphosphino)benzo[k,l]xanthene (14e) and (10,10-di-methyl-10H-dibenzob[1,4]oxasiline-4,6-diyl)bis(diphenyl-phosphane) (14b) were synthesised according to literature procedures. The intermediate (9,9-dimethyl-9H-xanthene-4,5-diyl)bis(dichlorophosphane) (18) was synthesised by modifying literature procedures. All reagents were purchased from commercial suppliers and used as received, unless otherwise noted. NMR spectra were obtained on a Bruker AVANCE III 500 spectrometer. For ¹H and ¹³C NMR the chemical shifts were referenced to the residual solvent signal. All NMR shifts are reported as δ in parts per million (ppm).

Mass spectrometry was carried out at National Mass Spectrometry Facility (NMSF-Swansea). Infrared spectra were measured on a Perkin Elmer 2000 FT-IR system and elemental analysis was carried out in the facility at London Metropolitan University. Gas chromatography was performed on a Thermo Scientific Trace GC Ultra equipment (split/splitless injector, Restek Rtx®-1, 100 % dimethyl polysiloxane column with 30 m × 0.25 mm × 0.25 µm dimensions, carrier gas – He, F.I.D. detector). Data was analysed using Chromeleon data system.

Synthesis of Xantphos-type ligands

4,5-bis(diphenylphosphanyl)phenoxathiine (Thixantphos) – (14c)

At −78 °C, sec-butyllithium (1.4 M in cyclohexane, 10.7 mL, 14.97 mmol) was added drop-wise to a stirred solution of phenoxathiin (1.00 g, 4.99 mmol) and TMEDA (2.25 mL, 14.97 mmol) in dry diethyl ether (50 mL). The reaction mixture was allowed to reach room temperature and stirred for 16 h. Then a solution of chlorodiphenylphosphine (2.92 mL, 14.97 mmol) in hexanes (15 mL) was added drop-wise to the reaction mixture, which was cooled to −78 °C and stirred for 16 h. Solvents were removed in vacuo and the resulting
solid was dissolved in dichloromethane. This solution was washed with water (3 × 10 mL) and the organic fraction was dried with MgSO₄, filtered and the volatiles were removed in vacuo. Resulting solid was crystallised by dichloromethane to give a white crystalline solid. Yield = 2.2 g (77.5%). Mp 244-246 °C. ¹H NMR (500 MHz, CDCl₃): δ 7.24-7.34 (m, 12H), 7.23-7.17 (m, 8H), 7.10 (dd, J = 7.6, 1.5 Hz, 2H), 6.90 (t, J = 7.6 Hz, 2H), 6.50 (dq, J = 7.6, 1.6 Hz, 2H). ³¹P{¹H} NMR (202 MHz, CDCl₃): δ –17.86 (s). ¹³C NMR (126 MHz, CDCl₃): δ 154.2 (t, J = 10.1), 136.9 (t, J = 6.3), 133.9 (t, J = 10.6 Hz), 132.5, 128.3, 128.2 (t, J = 3.4 Hz), 128.0 (t, J = 12.6), 127.2, 124.6, 119.9. IR (KBr, cm⁻¹) 3052 (m), 2851 (w), 1565 (m), 1477 (m), 1433 (s), 1394 (s), 1227 (s), 1204 (m), 1089 (m), 1025 (m). MS: APCI [M+H]+ Calcd.: 569.1252 Found: 569.1242 (%). Anal. Calcd. For C₃₆H₂₆OP₂S: C, 76.04; H, 4.61. Found: C, 75.97; H, 4.52.

(9,9-dimethyl-9H-xanthene-4,5-diyl)bis(bis(4-methoxyphenyl)phosphane)–(5a)

At room temperature, a solution of 4-bromoanisole (0.75 mL, 6 mmol) in THF (4 mL) was added drop-wise to a stirred mixture of magnesium turnings (350 mg, 12 mmol) activated with 1,2-dibromoethane (0.05 mL, 0.06 mmol) in THF (3 mL). The reaction mixture was stirred for 3 h, filtered and added dropwise to a stirred solution of (9,9-dimethyl-9H-xanthene-4,5-diyl) bis(dichloro-phosphane) (18) (0.5 g, 1.2 mmol) in THF (10 mL) at 0 °C and allowed to warm to room temperature and stirred for another 3 h. The resulting mixture was hydrolysed with water (5 mL) and the solvents were removed in vacuo. The residue obtained was dissolved in dichloromethane and washed with dilute hydrochloric acid. The organic layer was separated and the aqueous layer was extracted with dichloromethane (3 × 10 mL). Combined organic fractions were dried with MgSO₄, filtered and the dichloromethane removed to give a white crystalline solid. Yield = 0.52 g (62%). Mp 211-212 °C. ¹H NMR (500 MHz, CDCl₃): δ 7.36 (dd, J = 7.7, 1.5 Hz, 2H), 7.05 (dt, J = 8.7, 3.5 Hz, 8H), 6.92 (t, J = 7.6 Hz, 2H), 6.75 – 6.68 (m, 8H), 6.50 (dq, J = 7.6, 1.8 Hz, 2H), 3.76 (s, 12H), 1.61 (s, 6H). ³¹P{¹H} NMR (202 MHz, CDCl₃): δ -20.46 (s). ¹³C NMR (126 MHz, CDCl₃): δ 159.6 (s), 142.6 (s), 135.1 (t, J =11.3 Hz), 131.8 (s), 129.88 (s), 128.5 (t, J = 5.0 Hz), 125.9 (s), 123.2 (s), 113.7 (t, J = 3.8 Hz), 54.9 (s), 31.7 (s). IR (KBr, cm⁻¹) 2961 (m), 2836 (w), 1593 (s), 1565 (m), 1495 (s), 1460 (m), 1459 (s), 1401 (s), 1353 (m), 1282 (s), 1153 (m), 1090 (m), 960 (s), 850 (m), 746 (s).
(9,9-dimethyl-9H-xanthene-4,5-diyl)bis(di-p-tolylphosphane)--(5b)

This compound was synthesised similarly to 5a using 4-bromotoluene (0.75 mL, 6.0 mmol). The white crude product was purified by flash column chromatography (eluent: 10% dichloromethane/hexanes) and crystallised from eluents. White crystalline solid; Yield = 0.45 g (59%). Mp 238-239 °C. ¹H NMR (500 MHz, CDCl₃): δ 7.35 (dd, J = 7.7, 1.5 Hz, 2H), 7.03 (dt, J = 7.4, 3.6 Hz, 8H), 6.98 (d, J = 7.7 Hz, 8H), 6.91 (t, J = 7.6 Hz, 2H), 6.52 (dq, J = 7.6, 1.7 Hz, 2H), 2.29 (s, 12H), 1.61 (s, 6H). ³¹P{¹H} NMR (202 MHz, CDCl₃): δ -19.57 (s).

(9,9-dimethyl-9H-xanthene-4,5-diyl)bis(bis(4-fluorophenyl)phosphane)-(5c)

This compound was synthesised similarly to 5a using 4-bromofluorobenzene (0.66 mL, 6.0 mmol). The white crude product was purified by flash column chromatography (eluent: 20% ethyl acetate/ petroleum ether 40:60) and crystallised from the eluents. White crystalline solid; Yield = 0.36 g (46%). Mp 196-198 °C. ¹H NMR (500 MHz, CDCl₃): δ 7.46 (dd, J = 7.8, 1.5 Hz, 2H), 7.13 (m, 8H), 7.01 (t, J = 7.7 Hz, 2H), 6.99 – 6.91 (m, 8H), 6.49 (dq, J = 7.6, 1.8 Hz, 2H), 1.68 (s, 6H). ³¹P{¹H} NMR (202 MHz, CDCl₃): δ -19.15 (s). ¹⁹F{¹H} NMR (471 MHz, chloroform-d) δ -112.98 (s). ¹³C NMR (126 MHz, CDCl₃): δ 161.2 (s), 141.9 (s), 133.5 (t, J =11.3 Hz), 130.0 (s), 129.0 (s), 129.0 (s), 128.5 (t, J = 5.0 Hz), 125.99 (s), 122.3 (s), 122.3 (s), 21.3 (s). IR (KBr, cm⁻¹) 3066 (m), 2961 (m), 1896 (w), 1587 (s), 1493 (s), 1402 (s), 1296 (m).
(9,9-dimethyl-9H-xanthene-4,5-diyli)bis(bis(4-(trifluoromethyl)phenyl)phosphane)-
(5d)

This compound was synthesised similarly to 5a using 4-
bromobenzotrifluoride (0.85 mL, 6.0 mmol). The white
(crude product was purified by flash column
chromatography (eluent: 20% dichloromethane/hexanes) and crystallised from the
eluents. White crystalline solid; Yield = 0.53 g (52%). Mp 184-186 °C. ¹H NMR (500
MHz, CDCl₃): δ 7.54 - 7.49 (m, 10H), 7.31 – 7.24 (m, 8H), 7.05 (t, J = 7.7 Hz, 2H), 6.49
(dq, J = 7.6, 1.8 Hz, 2H), 1.56 (s, 6H). ³¹P{¹H} NMR (202 MHz, CDCl₃): δ -17.64 (s).
¹⁹F{¹H} NMR (471 MHz, CDCl₃): δ -62.78 (s). ¹³C NMR (126 MHz, CDCl₃): δ 152.3 (t, J
=10.1 Hz), 141.29 (t, J = 8.8 Hz), 134.3 – 133.6 (m), 131.84 (s), 130.68 (t, J = 37.8 Hz),
127.38 (s), 125.14, 124.13, 123.34 (t, J = 8.8 Hz), 122.89 (s), 120.73 (s), 34.59 (s),
31.61(s). IR (KBr, cm⁻¹) 3066 (m), 2978 (m), 1925 (m), 1607 (m), 1407 (s), 1326 (s),
1238 (s), 1169 (s), 1133 (s), 1060 (s), 1015 (m). APCI [M+H]^⁺ Calcd.: 851.1497 Found:
**GC analysis details**

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**Representative GC chromatogram**

![Representative GC chromatogram](image_url)

**Figure S1.** Representative GC chromatogram.
Kinetic profiles for rate dependence of (1) showing initial rates

Graphs showing conversion (%) vs. time (h) for the C-O cleavage of 2-phenoxy-1-phenylethanol (1) at varying substrate concentrations. Initial TOF (h⁻¹) taken from the gradient of the graphs and plotted in the text (Figure 2) and corrected for the given catalyst loading. The following plots show reactions during the initial rates period and are not full reaction profiles.

![Graph showing conversion (%) vs. time (h) for C-O bond cleavage of 2-phenoxy-1-phenylethanol by Ru(H)(CO)(PPh₃)₃ and Xantphos (ligand 5). Conditions: 2-phenoxy-1-phenylethanol with a 0.02 mmol catalyst loading and 0.125 mmol of 1,2,4,5-tetramethylbenzene as the internal standard in anhydrous xylenes at 135 °C. Samples withdrawn at regular intervals and were analysed by gas chromatography. Results from duplicates of experiments.](image-url)

Figure S2. C-O cleavage rate dependence on the concentration of 1 (0.5 mmol). Conversion (%) vs. Time (h) for C-O bond cleavage of 2-phenoxy-1-phenylethanol by Ru(H)(CO)(PPh₃)₃ and Xantphos (ligand 5). Conditions: 2-phenoxy-1-phenylethanol with a 0.02 mmol catalyst loading and 0.125 mmol of 1,2,4,5-tetramethylbenzene as the internal standard in anhydrous xylenes at 135 °C. Samples withdrawn at regular intervals and were analysed by gas chromatography. Results from duplicates of experiments.
Figure S3. C-O cleavage rate dependence on the concentration of 1 (0.75 mmol). Conversion (%) vs. Time (h) for C-O bond cleavage of 2-phenoxy-1-phenylethanol by Ru(H)2(CO)(PPh3)3 and Xantphos (ligand 5). Conditions: 2-phenoxy-1-phenylethanol with a 0.02 mmol catalyst loading and 0.125 mmol of 1,2,4,5-tetramethylbenzene as the internal standard in anhydrous xylenes at 135 °C. Samples withdrawn at regular intervals and were analysed by gas chromatography. Results from duplicates of experiments.

Figure S4. C-O cleavage rate dependence on the concentration of 1 (1.0 mmol). Conversion (%) vs. Time (h) for C-O bond cleavage of 2-phenoxy-1-phenylethanol by Ru(H)2(CO)(PPh3)3 and Xantphos (ligand 5). Conditions: 2-phenoxy-1-phenylethanol with a 0.02 mmol catalyst loading and 0.125 mmol of 1,2,4,5-tetramethylbenzene as the internal standard in anhydrous xylenes at 135 °C. Samples withdrawn at regular intervals and were analysed by gas chromatography. Results from duplicates of experiments.
**Figure S5.** C-O cleavage rate dependence on the concentration of 1 (1.5 mmol). Conversion (%) vs. Time (h) for C-O bond cleavage of 2-phenoxy-1-phenylethanol by Ru(H)$_2$(CO)(PPh$_3$)$_3$ and Xantphos (ligand 5). Conditions: 2-phenoxy-1-phenylethanol with a 0.02 mmol catalyst loading and 0.125 mmol of 1,2,4,5-tetramethylbenzene as the internal standard in anhydrous xylenes at 135 °C. Samples withdrawn at regular intervals and were analysed by gas chromatography. Results from duplicates of experiments.

**Figure S6.** C-O cleavage rate dependence on the concentration of 1 (2.0 mmol). Conversion (%) vs. Time (h) for C-O bond cleavage of 2-phenoxy-1-phenylethanol by Ru(H)$_2$(CO)(PPh$_3$)$_3$ and Xantphos (ligand 5). Conditions: 2-phenoxy-1-phenylethanol with a 0.02 mmol catalyst loading and 0.125 mmol of 1,2,4,5-tetramethylbenzene as the internal standard in anhydrous xylenes at 135 °C. Samples withdrawn at regular intervals and were analysed by gas chromatography. Results from duplicates of experiments.
Kinetic profiles for rate dependence of catalyst loading showing initial rates

Graphs showing conversion (%) vs. time (h) for the C-O cleavage of 2-phenoxy-1-phenylethanol (1) at varying substrate concentrations. Initial TOF (h⁻¹) taken from the gradient of the graphs and plotted in the text (Figure 3.) and corrected for the given catalyst loadings. The following plots show reactions during the initial rates period and are not full reaction profiles.

Figure S7. C-O cleavage rate dependence on the concentration of Ru(H)₂(CO)(PPh₃)₃/Xantphos catalyst (1 mol%). Conversion (%) vs. Time (h) for C-O bond cleavage of 2-phenoxy-1-phenylethanol. Conditions: 1 mmol of 2-phenoxy-1-phenylethanol with 0.01 mmol catalyst loading, 0.125 mmol of 1,2,4,5-tetramethylbenzene as the internal standard in anhydrous xylenes at 135 °C. Samples withdrawn at regular intervals and were analysed by gas chromatography. Results from duplicates of experiments.
Figure S8. C-O cleavage rate dependence on the concentration of Ru(H)_2(CO)(PPh_3)_3/Xantphos catalyst (1.5 mol%). Conversion (%) vs. Time (h) for C-O bond cleavage of 2-phenoxy-1-phenylethanol. Conditions: 1 mmol of 2-phenoxy-1-phenylethanol with a 0.015 mmol catalyst loading, 0.125 mmol of 1,2,4,5-tetramethylbenzene as the internal standard in anhydrous xylenes at 135 °C. Samples withdrawn at regular intervals and were analysed by gas chromatography. Results from duplicates of experiments.

Figure S9. C-O cleavage rate dependence on the concentration of Ru(H)_2(CO)(PPh_3)_3/Xantphos catalyst (2 mol%) Conversion (%) vs. catalyst loading for C-O bond cleavage of 2-phenoxy-1-phenylethanol. Conditions: 1 mmol of 2-phenoxy-1-phenylethanol with a 0.02 mmol catalyst loading, 0.125 mmol of 1,2,4,5-tetramethylbenzene as the internal standard in anhydrous xylenes at 135 °C. Samples withdrawn at regular intervals and were analysed by gas chromatography. Results from duplicates of experiments.
Figure S10. C-O cleavage rate dependence on the concentration of Ru(H)₂(CO)(PPh₃)₃/Xantphos catalyst (3 mol%). Conversion (%) vs. catalyst loading for C-O bond cleavage of 2-phenoxy-1-phenylethanol. Conditions: 1 mmol of 2-phenoxy-1-phenylethanol with a 0.03 mmol catalyst loading, 0.125 mmol of 1,2,4,5-tetramethylbenzene as the internal standard in anhydrous xylenes at 135 °C. Samples withdrawn at regular intervals and were analysed by gas chromatography. Results from duplicates of experiments.

Figure S11. C-O cleavage rate dependence on the concentration of Ru(H)₂(CO)(PPh₃)₃/Xantphos catalyst (4 mol%). Conversion (%) vs. catalyst loading for C-O bond cleavage of 2-phenoxy-1-phenylethanol. Conditions: 1 mmol of 2-phenoxy-1-phenylethanol with a 0.04 mmol catalyst loading, 0.125 mmol of 1,2,4,5-tetramethylbenzene as the internal standard in anhydrous xylenes at 135 °C. Samples withdrawn at regular intervals and were analysed by gas chromatography. Results from duplicates of experiments.
**Figure S12.** C-O cleavage of 2-phenoxy-phenylethanol with 2% 2-phenoxyacetophenone (4) by Ru(H₂)(CO)(PPh₃)₃ and Xantphos (ligand 5). Conversion (%) vs. time (h) for C-O bond cleavage of 2-phenoxy-1-phenylethanol. Conditions: 1 mmol of 2-phenoxy-1-phenylethanol with a 0.02 mmol catalyst loading 0.125 mmol of 1,2,4,5-tetramethylbenzene as the internal standard in anhydrous xylenes at 135 °C. Samples withdrawn at regular intervals and were analysed by gas chromatography. Results from duplicates of experiments.

**Figure S13.** Conversion (%) vs. time (h) for C-O bond cleavage of 2-phenoxy-1-phenylethanol by Ru(H₂)(CO)(PPh₃)₃ and Xantphos (ligand 5) under H₂. Conditions: 1 mmol of 2-phenoxy-1-phenylethanol with a 0.02 mmol catalyst loading of 2 mol% 0.125 mmol of 1,2,4,5-tetramethylbenzene as the internal standard in anhydrous xylenes at 135 °C under a H₂ atmosphere. Samples withdrawn at regular intervals and were analysed by gas chromatography. Results from duplicates of experiments.
Eyring plot for the formation of acetophenone (2)

\[ -17.148x + 19.712 \]
\[ R^2 = 0.976 \]

\[ \Delta H^\ddagger = 142 \text{ KJ mol}^{-1} \]
\[ \Delta S^\ddagger = -33 \text{ J K}^{-1} \text{ mol}^{-1} \]
\[ \Delta G^\ddagger = 156 \text{ KJ mol}^{-1} \]

**Figure S14.** Eyring plot for the formation of acetophenone (2) by Ru(H)₂(CO)(PPh₃)₃ and Xantphos. Conditions: 1 mmol of 2-phenoxy-1-phenylethanol with 0.02 mmol catalyst loading and 0.125 mmol of 1,2,4,5-tetramethylbenzene as the internal standard in anhydrous xylenes. Samples were analysed by gas chromatography, results from duplicate experiments. Error bars were calculated by standard deviation based on quadruple measurements on T = 130 °C.
Kinetic profile for the formation of 2-phenoxyacetophenone (4) at 25 °C and acetophenone (2) at 105 °C

![Graph](image)

**Figure S15.** Conversion (%) vs. time (h) for dehydrogenation of 2-phenoxy-1-phenylethanol by Ru(H)_2(CO)(PPh_3)_3 and Xantphos (ligand 5). Conditions: 1 mmol of 2-phenoxy-1-phenylethanol with a 0.02 mmol catalyst loading 0.125 mmol of 1,2,4,5-tetramethylbenzene as the internal standard in anhydrous xylenes at 25 °C. Samples withdrawn at regular intervals and were analysed by gas chromatography. Results from duplicates of experiments.

![Graph](image)

**Figure S16.** Conversion (%) vs. time for ether cleavage of 2-phenoxy-1-phenylethanol by Ru(H)_2(CO)(PPh_3)_3 and Xantphos (ligand 5). Conditions: 1 mmol of 2-phenoxy-1-phenylethanol with a 0.02 mmol catalyst loading 0.125 mmol of 1,2,4,5-tetramethylbenzene as the internal standard in anhydrous xylenes at 105 °C. Samples withdrawn at regular intervals and were analysed by gas chromatography. Results from duplicates of experiments.
NMR data for ligands 5a – c and 14c

Figure S17. $^1$H NMR spectra of 5a

Figure S18. $^{13}$C DEPTQ NMR spectra of 5a
Figure S19. $^{31}$P($^1$H) NMR spectra of 5a
Figure S20. $^1$H NMR spectra of 5b

Figure S21. $^{13}$C DEPTQ NMR spectra of 5b
Figure S22. $^{31}\text{P}^{(1\text{H})}$ NMR spectra of 5b
Figure S23. $^1$H NMR spectra of 5c

Figure S24. $^{13}$C DEPTQ NMR spectra of 5c
Figure S25. $^{31}$P($^1$H) NMR spectra of 5c

Figure S26. $^{19}$F($^1$H) NMR spectra of 5c
Figure S27. $^1$H NMR spectra of 5d

Figure S28. $^{13}$C DEPTQ NMR spectra of 5d
Figure S29. $^{31}$P($^1$H) NMR spectra of 5d

Figure S30. $^{19}$F($^1$H) NMR spectra of 5d
Figure S31. $^1$H NMR spectra of 14c

Figure S32. $^{13}$C DEPTQ NMR spectra of 14c
Figure S33. $^{31}$P($^1$H) NMR spectra of 14c
References


