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

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Bite angle and electronic effects on the ruthenium-diphosphine catalysed ether bond cleavage of the lignin β-O-4 model compound 2-phenoxy-1-phenethanol were tested. Enhanced conversion of the substrate was observed with increasing σ-donor capacity of the ligands. Kinetic and thermodynamic data suggest oxidative addition of the dehydrogenated model compound to the diphosphine Ru(0) complex to be rate-limiting.

Introduction

The limited availability of fossil reserves and concerns about climate change demand that alternative resources are investigated to meet the future needs of energy and fine chemicals. Most importantly, these alternatives should rank high in renewability and sustainability and not be in direct competition with food production.[1-3] Hence, lignocellulosic biomass is considered as one of the most promising resources for the sustainable production of fuels, chemicals and materials.[4-8]

The estimated annual production of biomass amounts to an impressive 56.8 billion tonnes of elemental carbon. Although only a small part will be available as a feedstock, it will provide a substantial sustainable resource for the chemical industries.[9] Although much research and development is invested in the field of biofuels as an energy source it should be noted that the total energy contents of this produced biomass, which includes food production, is not sufficient to cover the world energy demand. Therefore, biofuels are expected to constitute only part of the future of sustainable energy production, which will be strongly dependent on other sources. However, the harvested biomass can easily cover the volume of chemicals produced today and acquiring chemical feedstocks from biomass conversion therefore seems a promising way forward. A substantial research effort on valorisation of the cellulose component has been carried out successfully over the years producing bio-fuels and chemicals.[10,11] In comparison to this, catalytic lignin valorisation has only more recently been receiving the same attention. Lignin is a highly cross-linked, poly-aromatic macromolecular component that acts as a resin between cellulose and hemicellulose fibres in plant cell walls, giving rigidity to the plant structure[12] and acting as an essential scaffold for the plant nutrient and water transport system.[13,14] The composition of lignocellulosic biomass depends on the plant species and environmental factors, for example. In general, 15-30% of the lignocellulosic biomass is lignin by weight.[15a-b] It is estimated that the annual production of lignin as a non-commercial waste falls in the range of 40-50 million tonnes,[16] which results mainly from paper and pulp industry.[17]

Where (hemi-)cellulose provides ample access to fuels and aliphatic platform chemicals, lignin is anticipated to be a major source for the sustainable production of aromatic compounds in the chemical industry. Lignin is a three-dimensional, amorphous polymer that is derived from methoxylated hydroxycinnamyl alcohol building blocks, the prototypical monolignols. These units are interconnected by various C-O and C-C linkages to give, e.g., the β-O-4, β-β, and β-5 units.[18] About 45-60% of the linkage structures in both softwood and hardwood consists of β-O-4 linkages in the native lignin structure. Cleavage of these linkages in combination with further catalytic upgrading steps could potentially result in an array of value-added, small aromatic molecules.[15a-c] Any method used for lignin valorisation, including thermochemical[19] or mechanochemical degradation,[20] oxidation[21-23] homogeneous or heterogeneous catalysis,[15a-c,24] acid/base-catalysed depolymerisation,[15b,25] solubilisation,[26] liquefaction[27] or enzymatic modifications[28] should preserve the aromatic nature of the end product. In general, homogeneous catalysts can exhibit high reactivity under mild reaction conditions, which provides excellent opportunities to process such a notoriously recalcitrant material as lignin. With respect to the three-dimensional structure of lignin, homogeneous catalysis may be better equipped to reach linkages buried in the macromolecule where heterogeneous catalysis would suffer due to steric hindrance.[8] The non-uniformity and complex structure of lignin poses many challenges when a specific linkage and its cleavage need to be studied in detail. The common practice is to test the catalyst material on a simple chemical compound that mimics the specific linkage of interest. These model compounds are intensively studied to identify efficient catalyst systems and to optimise the reaction conditions.[15a-c,22,29-31]

Bergman, Ellman and co-workers reported the catalytic, redox-neutral cleavage of 2-aryloxy-1-arylethanols as lignin-related β-O-4

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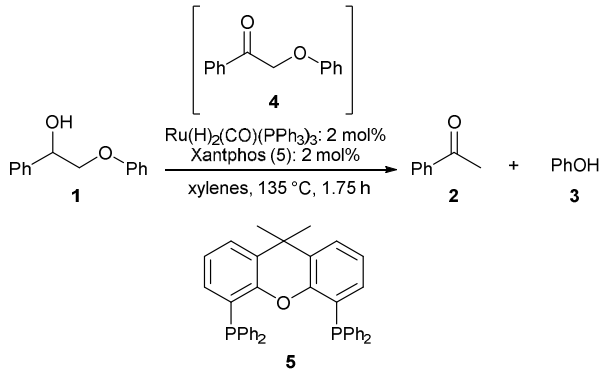
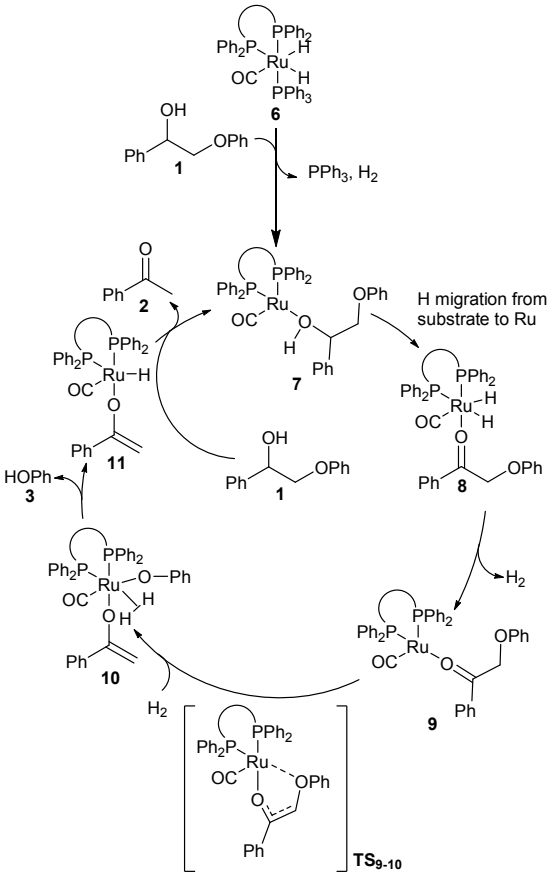


Scheme 1: C-O bond cleavage in 2-phenoxy-1-phenlethanol (**1**) by $(Ru)(H)_2(CO)(PPh_3)_3$-Xantphos catalyst studied by Berman, Ellman and co-workers.[32]

model compounds (Scheme 1).[32] They have tested different catalyst systems and varied reaction conditions to find that $Ru(H)_2(CO)(PPh_3)_3$-Xantphos (in xylenes at 135 °C) performed best and gave 62-98% isolated yields of the cleavage products. The reaction was reported to proceed *via* a tandem catalytic dehydrogenation and C-O ether bond cleavage. Subsequently, Wu *et al*. applied this catalyst to more realistic model compounds and isolated several intermediate complexes confirming the hydrogen transfer mechanism.[33] The reaction mechanisms proposed by both of these studies suggested that the reaction starts with a ruthenium-catalysed dehydrogenation of the benzylic alcohol leading to the corresponding ketone, followed by oxidative addition. Further work by Leitner, Bolm and co-workers showed the [Ru(TMM)triphos] system to be a highly efficient catalyst giving higher yields of phenol and acetophenone than Bergman, Ellman and co-workers reported for $[Ru(methallyl)_2(Xantphos)]$.[34] Details of this work, extended to dilignol model compounds resulting in both C-C and C-O bond cleavage in β-O-4 linkage, was subsequently published in 2015.[35] Concurrently, Bolm and co-workers reported on the base-catalysed cleavage of the β-O-4 linkage in the same dilignol model compound using readily available bases in dimethyl carbonate as solvent.[36] In 2014, Jameel *et al.* suggested that Xantphos can be omitted in Ru-Xantphos catalyst systems when a relatively high concentration of KOH (0.4 M) is applied.[37]

In 2013, Weickmann and Plietker reported $RuCl_2(PPh_3)_3$ activated by potassium *t*-amylate as an efficient catalyst to cleave the β-O-4 linkage in 2-phenoxy-1-phenylethanol (**1**).[38] Furthermore, they showed that when more electron-donating groups were introduced into the monodentate phosphine ligand in the $RuCl_2(PAr_3)_3$ complex an improved reactivity was observed. Interestingly, the product ketone was prone to efficient α-alkylation using primary alcohols. Recently, a density functional theory (DFT) study on the cleavage of the β-O-4 linkage of lignin using group 8 pincer complexes, carried out by Liu and Wilson, revealed a similar trend. Their study involved the C-O bond cleavage of β-O-4 model compound 2-phenoxy-1-phenylethanol (**1**) by pincer complexes including all possible combinations of three group 8 metals Fe, Ru and Os with five different pincer ligands. They have concluded that C-O bond activation by transition metal catalysis depends on the ability of the metal centre to donate electron density to the C-O bond and, therefore, cleavage of the C-O bond is promoted by electron donating ligands.[39]

A DFT study carried out by Beckham, Paton and co-workers, provided detailed mechanistic insight into the ruthenium-phosphine catalysed C-O bond cleavage of 2-phenoxy-1-phenylethanol (**1**).[40] They proposed that, as in earlier studies, the reaction starts with a catalytic dehydrogenation pathway that involves hydrogen migration from the substrate to the ruthenium centre generating a ruthenium dihydride (**8**). The subsequent C-O bond cleavage proceeds *via* oxidative addition across the ether bond and dihydrogen coordination to the ruthenium centre forming Ru-enolate (**10**), which will then eliminate the products, phenol and acetophenone. Furthermore, they proposed an unusual 5-membered metallacycle as the most likely transition state ($\mathbf{TS_{9\text{-}10}}$) of the oxidative addition step. This kinetically favoured O-bound enolate (**10**), which enables reaction completion, is preferred over a thermodynamically more stable C-bound enolate. This study also indicates a preference for phenol to be released *via* heterolytic dihydrogen activation before acetophenone from the system (Scheme 2).



Scheme 2: Proposed mechanism for the C-O bond cleavage in 2-phenoxy-1-phenylethanol.[32,33,40]

From the previous studies on 2-phenoxy-1-phenylethanol (**1**) as a lignin model compound, we reasoned that the most likely rate determining step for this reaction is the oxidative addition of the C-O bond, which results in the formation of Ru(II) complex (**10**) from Ru(0) complex (**9**) *via* ($\mathbf{TS_{9\text{-}10}}$). This is in line with the electronic effect observed in work carried out by both Weickmann and Plietker,[38] and also by Liu and Wilson.[39] Rates of oxidative addition reactions are dependent on the electronic properties of the ligand

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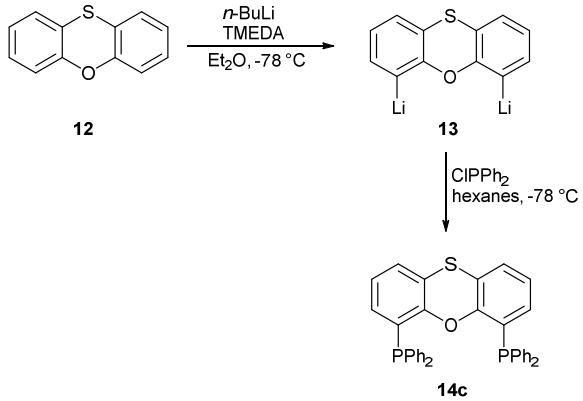
in the catalyst system of interest, which are mainly governed by the σ-donor or π-acceptor ability of the phosphorous moiety. In the case of bidentate ligands, such as Xantphos, steric effects in the form of the ligand bite angle can also have a dramatic effect on catalyst performance.[41-44] In most reactions the individual contribution of these effects is difficult to determine as the overall bite angle effect can influence several steps in a catalytic cycle.[44] Subtle changes in the bite angle of Xantphos-type ligands can be applied by changing the size of the substituent **X** of the xanthene backbone (Table 1 and associated structures, **5**, **14a**-**e**), while electronic properties can be changed by adding electron-donating or electron-withdrawing groups to the phenyl rings of the coordinating phosphine groups (Scheme 4).[45]

Increasing the σ-donor ability and reducing the bite angle in a ligand can increase the reduction potential and stabilise higher oxidation states of the metal centres, promoting oxidative addition in organometallic complexes,[46] although the effect of reducing the bite angle can be obscured by steric factors. Generally, oxidative addition is facilitated by less steric hindrance; hence a ligand with a moderately small bite angle with higher σ-donor ability would be the obvious candidate for an oxidative addition reaction. In order to optimise the catalytic activity and better understand the unique reactivity of Xantphos in the Ru-catalysed ether cleavage we have investigated the influence of small variations in the ligand bite angle on catalyst performance. In addition, we have applied subtle changes in the electron-donating properties to further improve catalyst performance.

Results and Discussion

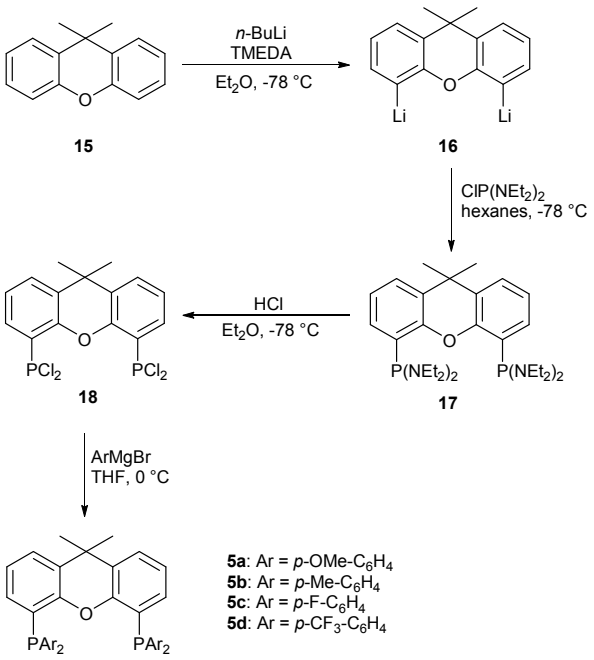
Synthesis of Xantphos-type ligands

4,6-Bis(diphenylphosphanyl)phenoxathiine (Scheme 3 (**14c**) Thixantphos) was prepared by selective dilithiation of phenoxathiin (**12**) followed by reaction with chlorodiphenyl-phosphine.[42]



Scheme 3: Synthesis of Thixantphos.

The electronically modified Xantphos ligands (**5a**-**d**) were synthesised by reacting (9,9-dimethyl-9H-xanthene-4,5-diyl)bis(dichlorophosphane) (**18**) with the freshly prepared Grignard reagent of the corresponding *p*-substituted aryl bromide (Scheme 4).[47]



Scheme 4: Synthesis of a series of Xantphos-type ligands with electron-donating or electron-withdrawing *p*-substituents.

Ligand bite angle effect on C-O bond cleavage of 2-phenoxy-1-phenylethanol (1)

The rate of oxidative addition is affected by the ligand bite angle but the effects are not always straightforward and sometimes difficult to predict.[45,48] Therefore, the bite angle was changed from 102° (Homoxantphos, **14a**) to 121° (Benzoxantphos, **14e**) (Table 1).

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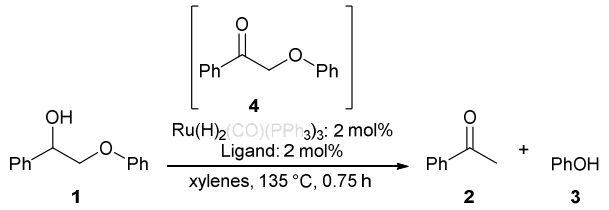
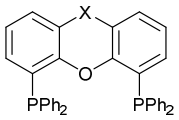
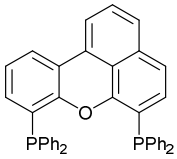
Table 1: Bite angle effect on C-O bond cleavage of 2-phenoxy-1-phenylethanol.[a]



	X	β_n (°)[b]	Conversion (%)[c] 1	Yield (%)[c] 2	3[d]	4
14a	C_2H_4	102°	20.3	-[e]	-[e]	5.0
14b	$Si(CH_3)_2$	109°	28.5	15.8	10.6	11.8
14c	S	110°	27.7	14.8	10.9	12.2
5	$C(CH_3)_2$	111°	44.6	29.4	25.3	13.5
14d	NH	114°	26.6	24.8	19.0	1.8
14e	-	121°	8.4	4.1	1.4	4.2



5, 14a-d

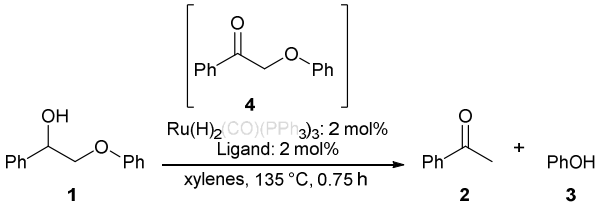


14e

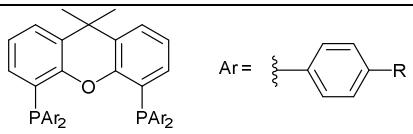
a) Conditions: 0.25 mmol of 2-phenoxy-1-phenylethanol with 2 mol% catalyst loading (0.005 mmol of $Ru(H)_2(CO)(PPh_3)_3$, 0.005 mmol of ligand (**5**, **14a-e**)) and 0.125 mmol of 1,2,4,5-tetramethylbenzene as the internal standard in anhydrous xylenes in a closed CEM microwave vial, 135 °C, 45 min. b) Calculated natural bite angle of the ligand. [42] c) Determined by gas chromatography. Results from 3 sets of experiments. d) Lower phenol yield due to degradation in GC inlet. e) Not observed in GC.

The bite angle effect on the efficiency of catalytic ether bond cleavage showed a clear optimum in the conversion of 2-phenoxy-1-phenylethanol (**1**) to phenol and acetophenone. The highest activity was obtained using Xantphos (**5**) as the ligand, and both smaller and larger bite angles resulted in lower activities. Additionally, in terms of selectivity to the desired ether cleavage products, Nixantphos (**14d**) showed promising results. Obtaining a clear optimum for Xantphos with varying bite angles does not provide decisive information about whether the oxidative addition step or the hydrogen transfer is the rate-determining step. However, when subtle changes in electronic properties of the ligands were made, by increasing the σ-donor ability of the ligand, a clear trend between electron-donating capacity of the ligand and catalyst activity was observed. The most electron-donating 4-methoxyphenyl derivative **5a** shows higher activity than the parent Xantphos ligand (Table 2, entries **5a** and **5**). These results are in accordance with the expected trend that stronger σ-donor character in the ligands stabilises higher oxidation states of metal centres, promoting oxidative addition, as also observed by Weickmann and Plietker using monodentate ligands[38] and Liu, Wilson and co-workers using group 8 pincer ligands.[39] These results are in line with a rate-determining oxidative-addition step.

Table 2: Electronic effect on C-O bond cleavage of 2-phenoxy-1-phenylethanol.[a]



	R	σ_p[b]	χ_i,[c] (cm^{-1})	Conversion (%)[d] 1	Yield (%)[d] 2	3	4
5a	OCH_3	-0.27	3.4	47.6	35.7	31.6	11.1
5b	CH_3	-0.17	3.5	46.5	32.0	27.6	13.9
5	H	0.00	4.3	44.6	29.4	25.3	13.5
5c	F	0.06	5.0	26.2	13.2	9.8	11.5
5d	CF_3	0.54	6.6	5.1	2.2	1.0	2.6



5, 5a-d

a) Conditions: 0.25 mmol of 2-phenoxy-1-phenylethanol (**1**) with 2 mol% catalyst loading (0.005 mmol of $Ru(H)_2(CO)(PPh_3)_3$, 0.005 mmol of ligand (**5**, **5a-d**)) and 0.125 mmol of 1,2,4,5-tetramethylbenzene as the internal standard in anhydrous xylenes in a closed microwave vial, 135 °C, 45 min. b) Hammett σ_p values.[49] c) Tolman χ_i values.[50] d) Determined by gas chromatography. Results from 3 sets of experiments.

The electronic effect on the conversion of the substrate can be a result of either improved catalyst activity or catalyst stability, as both will lead to higher conversions. To acquire a better understanding of the activity and stability of the catalyst complexes containing the ligands **5** and **5a**, reaction profiles were obtained by monitoring separate reactions as a function of time for a period of 4 hours. The complete kinetic profiles of the two catalysts obtained using ligands **5** and **5a** is consistent with a change in activity and not stability of the catalyst (Figure 1). As demonstrated in Figure 1, an increase in the initial rate of reaction for ligand **5a** relative to **5** is observed, which could indicate a rate limiting oxidative addition step within the catalytic cycle.

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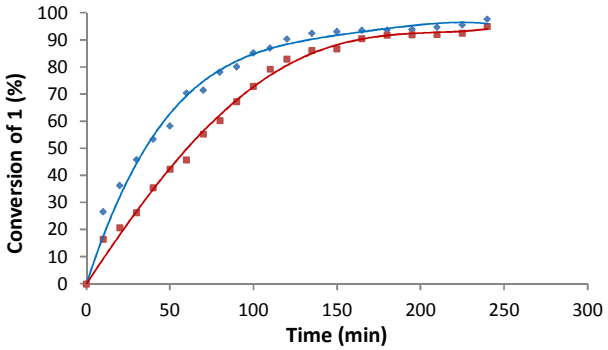

Figure 1: Conversion of substrate **1** with xantphos-type ligands. Blue – reaction with **5a** as ligand. Red – reaction with **5** as ligand. Conditions: 1 mmol of 2-phenoxy-1-phenylethanol (**1**) with 2 mol% catalyst loading (0.02 mmol of $Ru(H)_2(CO)(PPh_3)_3$, 0.02 mmol of ligand (**5** or **5a**)) and 0.125 mmol of 1,2,4,5,-tetramethylbenzene as the internal standard in anhydrous xylenes, 135 °C, samples were analysed by gas chromatography. Results from duplicates of experiments.

Kinetic studies on the reaction of 2-phenoxy-1-phenylethanol (**1**) with $Ru(H)_2(CO)(PPh_3)_3$ and Xantphos (**5**) were carried out with varying substrate concentrations and catalyst loadings (Figures 2 and 3). An induction period was observed during the course of the reactions, which is due to the required build-up of the intermediate ketone prior to ether bond cleavage (ESI, Figures S2 – S11). This was confirmed by the addition of 2 mol% intermediate ketone, which saw a reduction in the observed induction period (ESI, Figure S12). A reaction using substrate **1** in the presence of hydrogen saw an increase in the induction period (ESI, Figure S13) as the alcohol-ketone equilibrium would be pushed towards the alcohol, confirming that the required build-up of ketone is the cause of the induction period. A plot of initial TOF vs substrate concentration (Figure 2) shows a first-order rate dependency on substrate (**1**), as expected from the proposed catalytic cycle in which the only starting material is the substrate (**1**).

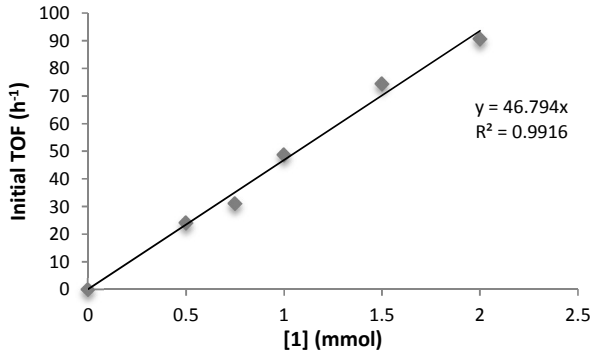

Figure 2: Initial Turnover Frequency (TOF) vs Substrate concentration for C-O bond cleavage of 2-phenoxy-1-phenylethanol (**1**) by $Ru(H)_2(CO)(PPh_3)_3$ and Xantphos (ligand **5**). Conditions: 2-phenoxy-1-phenylethanol (**1**) with a 0.02 mmol catalyst loading (with a ruthenium:ligand ratio of 1:1) 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.

The effect of catalyst loading on initial TOF was also investigated (Figure 3) and a clear first-order rate dependency was observed, which is in line with expectations for a monometallic catalytic system.

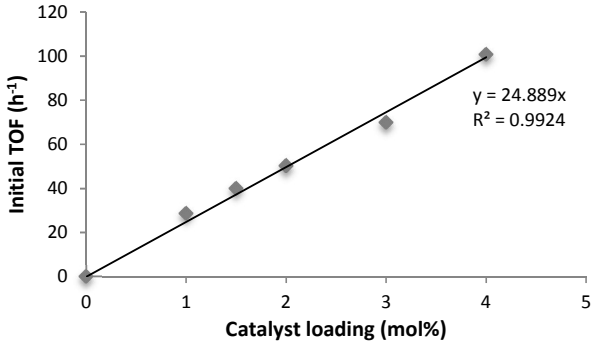

Figure 3: Initial Turnover Frequency (TOF) vs. catalyst loading for C-O bond cleavage of 2-phenoxy-1-phenylethanol (**1**) by $Ru(H)_2(CO)(PPh_3)_3$ and Xantphos (ligand **5**). Conditions: 1 mmol of 2-phenoxy-1-phenylethanol (**1**) with a given catalyst loading (With a ruthenium:ligand ratio of 1:1) 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.

In order to provide additional evidence to support our proposal of a rate limiting oxidative addition step, we investigated the temperature dependence of the reaction. An Eyring plot for the ether cleavage of substrate **1** was produced (ESI, Figure S14), and a value of 156 KJ mol^{-1} was obtained for the $\Delta G^{\ddagger}$. Attempts were made to produce an Eyring plot for the initial dehydrogenation step; however, due to a high initial rate this was unfortunately not possible. Lowering the temperature below 25 °C in order to moderate the high rate for the initial dehydrogenation led to substrate precipitation. The concentration was also lowered in order to moderate the initial rate, which led to issues of large scatter in the analysis due to GC detection limits. Therefore we calculated the initial TOF for the formation of ketone **4** at the lowest possible temperature, 25 °C. An estimated value of 62.6 h^{-1} was obtained. However, we believe this to be an underestimate of the true initial rate as our first data points were already outside the pseudo first order initial rates regime (ESI Figure S15) and the substrate already contained a small amount of residual ketone, i.e. 0.2 mol %. Even at concentrations approaching equilibrium a value of 4.1 h^{-1} was obtained (ESI Figure S15). This is already higher than the initial TOF obtained for the lowest temperature at which ether cleavage is observed (105 °C), a value of 0.8 h^{-1} (ESI Figure S16). It is clear that the initial dehydrogenation has a much higher rate than the corresponding ether cleavage. This again is indicative of a rate limiting oxidative addition step in the catalytic cycle.

Conclusions

Profound effects of the ligand bite angles and electronic properties on the catalytic ether bond cleavage of the lignin model compound 2-phenoxy-1-phenylethanol (**1**) have been observed. Newly synthesised ligands (9,9-dimethyl-9H-xanthene-4,5-diyl)bis(bis(4-methoxyphenyl)phosphane) (**5a**) and (9,9-dimethyl-9H-xanthene-4,5-diyl)bis(di-p-tolylphosphane) (**5b**) with stronger σ-donor capacity, gave higher conversions compared to Xantphos (**5**). The kinetic profile for **5a** showed that the improved conversion was a result of an intrinsically higher initial rate and not caused by

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increasing catalyst stability. Furthermore, kinetic studies showed first order kinetics with respect to the substrate and catalyst loading. A higher initial TOF was observed for the dehydrogenation at low temperature compared to the initial TOF for the ether cleavage at a higher temperature. This, along with increased conversion for electron-donating ligands indicate a likely rate limiting oxidative addition step. Further in-depth mechanistic studies are currently underway.

Experimental

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 CaH_2. 2-Phenoxy-1-phenylethanol (**1**),[32] 6,7-bis(diphenyl-phosphino) benzo[k,l]xanthene (**14e**)[46] and (10,10-di-methyl-10H-dibenzo[b,e][1,4]oxasiline-4,6-diyl)bis(diphenyl-phosphane) (**14b**)[42] were synthesised according to literature procedures. The intermediate (9,9-dimethyl-9H-xanthene-4,5-diyl)bis(dichlorophosphane) (**18**) was synthesised by modifying literature proceedures.[51-55] 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 ^{1}H and ^{13}C 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 30m×0.25mm×0.25µm dimensions, carrier gas – He, F.I.D. detector). Data was analysed using Chromeleon data system.

Synthesis of Xantphos-type ligands

4,6-bis(diphenylphosphanyl)phenoxathiine (Thixantphos) – (14c)

At −78 °C, *sec*-butyllithium (1.4 M in cyclohexane, 10.7 mL, 14.97 mmol) was added dropwise 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 dropwise 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 $MgSO_4$, filtered and the volatiles were removed *in vacuo*. The resulting solid was crystallised from dichloromethane to give a white crystalline solid. Yield = 2.2 g (77.5%). Mp 244-246 °C. ^{1}H NMR (500 MHz, $CDCl_3$): 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). $^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$): δ – 17.86 (s). ^{13}C NMR (126 MHz, $CDCl_3$) 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 $C_{36}H_{26}OP_2S$: C, 76.04; H, 4.61. Found: C, 75.97; H, 4.52.

Representative procedure for the synthesis of electronic xantphos-type ligands

At room temperature, a solution of the corresponding aryl bromide (6 mmol) in THF (4 mL) was added dropwise 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 obtained residue 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). The combined organic fractions were dried over $MgSO_4$, filtered and the dichloromethane was removed *in vacuo* to give the corresponding solid.

Catalytic reactions

Representative procedure for testing the ligand effect

Reaction mixture preparations were carried out in a glove box. 2-phenoxy-1-phenylethanol (53.6 mg, 0.25 mmol), $Ru(H)_2(CO)(PPh_3)_3$ (4.59 mg, 0.005 mmol), desired ligand (0.005 mmol) and 1,2,4,5-tetramethylbenzene (16.8 mg, 0.125 mmol) were diluted in anhydrous xylenes (2 mL), in a 10 mL CEM microwave vial. The reaction mixture was sealed and heated to 135 °C for 45 min, after which the reaction mixture was cooled to room temperature, filtered through silica and analysed by gas chromatography (stock solutions for each of the reagents were prepared prior to the reactions).

Representative procedure for obtaining kinetic profiles

2-phenoxy-1-phenethanol (214.25 mg, 1 mmol), $Ru(H)_2(CO)(PPh_3)_3$ (18.39 mg, 0.02 mmol), Xantphos (11.57 mg, 0.02 mmol) or **5a** (13.97 mg, 0.02 mmol) and 1,2,4,5-tetramethylbenzene (0.125 mmol from stock solution) were diluted in anhydrous xylenes (20 mL), in a 100 mL three necked round bottom flask fitted with a reflux condenser and connected to Schlenk. The reaction mixtures were heated to 135 °C. 0.1 mL Aliquots were taken from the reaction mixture every 10 min for 2 h and every 15 min thereafter for 2 h more. Each sample taken was diluted with acetone (0.5 mL), filtered through silica and analysed by gas chromatography. For the Eyring plots the same above procedure was used, but at varying temperatures (see ESI for further details).

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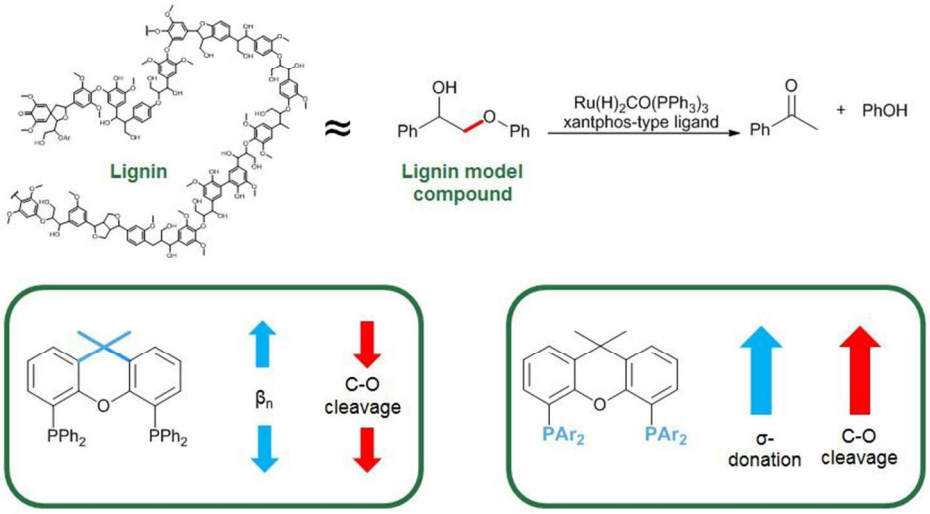

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