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Mild Heterogeneous Palladium-Catalyzed Cleavage of β -O-4'-Ether Linkages of Lignin Model Compounds and Native Lignin in Air

Maxim V. Galkin, Supaporn Sawadjoon, Volker Rohde, Monali Dawange, and Joseph S. M. Samec^{*,[a]}

A mild and robust heterogeneous palladium-catalyzed C–O bond cleavage of 2-aryloxy-1-arylethanol using formic acid as reducing agent in air was developed. The cleaved products were isolated in 92–98% yield; and by slightly varying the reaction conditions, a ketone, an alcohol, or an alkane can be generated in near-quantitative yield. This reaction is applicable to cleaving the β -O-4'-ether bond found in lignin polymers of different origin. The reaction was performed on a lignin poly-

mer model to generate either the monomeric aryl ketone or alkane in a quantitative yield. Moderate depolymerization was achieved with native lignin at similar reaction conditions. Mechanistic studies under kinetic control indicate that an initial palladium-catalyzed dehydrogenation of the alcohol is followed by insertion of palladium to an enol equivalent. A palladium–formato complex reductively cleaves the palladium–enolate complex to generate the ketone.

Introduction

Cellulose, hemicellulose, and tall oil are used to produce high-value products^[1] such as pulp, ethanol, and soap, but the lignin part of wood is currently used to recycle process chemicals in the pulping mills and is burnt to generate heat and electricity to a low value.^[2] Taking into account that the lignin polymer constitutes up to 40% of the energy content in lignocellulose, it would be worthwhile to upgrade lignin to more valuable products.^[3] To upgrade lignin into useful substrates for fine and bulk chemicals, sustainable, selective, and preferably catalytic procedures must be developed.^[4] Catalytic processes for both oxidative and reductive lignin depolymerization have been reported.^[2,5]

The lignin polymer is composed of methoxy-substituted phenolic subunits of irregular structural complexity and is not optically active.^[6] The most abundant structural motif in lignin is the β -O-4'-linkage comprising around 50–60% of native lignin (Figure 1). This bond is cleaved in, for example, the Kraft process but not in the sulfite process producing pulp.^[7] In many studies, the β -O-4'-ethanolaryl ethers (marked in blue)

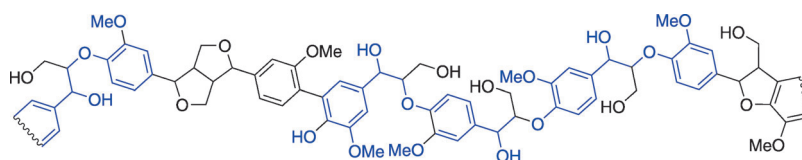


Figure 1. β -O-4'-glycerolaryl ether in lignin and the β -O-4'-ethanolaryl ether in the models (blue).

are used to model the β -O-4'-glycerolaryl ethers and were chosen in this study too.^[2,8]

Here we describe a selective palladium-on-carbon (Pd/C) catalyzed C–O bond cleavage of the β -O-4'-ether bond. The method is notable as a mild and robust procedure in which the catalysis can be performed at 80 °C in air without using specialized equipment. By slightly modifying the reaction conditions, the benzylic ketone, alcohol, or alkane can be selectively generated in above 95% yield even for models having *ortho*-methoxy substitution in both 2- and 6-positions of the aryloxy group. These contributions compare favorably with previously reports concerning the cleavage of the β -O-4'-ether bond of lignin model compounds.^[5]

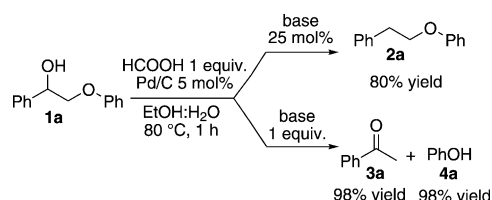
Results and Discussion

We have previously shown that Pd/C is reactive in the transfer hydrogenolysis of benzyl alcohols in which a hydride from formic acid substitutes the hydroxyl group to generate alkyl aryls.^[9] Noteworthy, we found that a catalytic amount of base was required to inhibit a competing disproportionation reaction. Using the same reaction conditions to the β -O-4'-ethanolaryl ether (**1a**) generated the expected phenethoxy benzene

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Scheme 1. Additional base yield cleaved products **3a** and **4a** in favor of **2a**.

(**2a**) in 80% yield (Scheme 1). The remaining 20% corresponded to acetophenone (**3a**) and phenol (**4a**). These findings encouraged us to optimize the reaction conditions towards the cleaved products. We found that the yield of the cleaved products increased with the amount of base.^[10] A stoichiometric amount of base promoted the cleavage of the β -O-4'-linkage to generate **3a** and **4a** in favor of **2a**.

In Table 1, the effects of different sources of metals, hydrogen donors, and bases are summarized for the catalytic cleavage of the β -O-4' bond in 2-phenoxy-1-phenylethanol. Only Pd/C was reactive in the transfer hydrogenolysis using formic

Table 1. Optimization of the β -O-4' bond cleavage in **1a**.

Entry	M/C	H donor	Base	Yield 3a [%] ^[a]
1	Pd/C	HCOOH	NH ₃	> 95
2	Rh/C	HCOOH	NH ₃ /–	0
3	Ir/C	HCOOH	NH ₃ /–	0
4	Re/C	HCOOH	NH ₃ /–	0
5	Ni/C	HCOOH	NH ₃ /–	0
6	Pd/C	2-propanol	NH ₃ /–	0
7	Pd/C	H ₂	<i>p</i> -(allylamine)	0
8	Pd/C	HCOOH	–	0
9	Pd/C	HCOOH	NH ₂ Et	> 95
10	Pd/C	HCOOH	NHEt ₂	> 95
11	Pd/C	HCOOH	<i>p</i> -(allylamine)	> 95
12	Pd/C	–	<i>p</i> -(allylamine)	20
13	Pd/C	HCOOH	<i>p</i> -(allylamine)	40 ^[b]

[a] The reactions were performed on a 0.1 mmol scale under air for 1 h. Yields were determined by ¹H NMR spectroscopy using mesitylene as an internal standard. Phenol **4a** was also isolated in the same yield as **3a** in all reactions. [b] Reaction proceeded under argon atmosphere.

acid as hydrogen donor to generate **3a** and **4a** in high yields (Table 1, entries 1–5).^[11] With Rh/C a disproportionation reaction was observed to generate **2a** in 30% yield if the reaction was performed in the absence of a base (Table 1, entry 2). Ir/C, Re/C, and Ni/C did not exhibit any reactivity in the presence or absence of base (Table 1, entries 3–5). Exchanging the hydrogen donor from formic acid to isopropanol did not give the desired reaction (Table 1, entry 6). Running the reaction in hydrogen gas was unsuccessful (Table 1, entry 7). In the absence of base a disproportionation reaction occurred to generate **2a** and the corresponding ketone. Different bases could be used;

ethylamine, diethylamine, ammonia, and polymer-supported amine all generated **3a** in above 95% yield (Table 1, entries 9–11). Notably, water and a cosolvent are required for the desired reactivity. Green solvents for example, ethyl acetate, *tert*-butyl methyl ether, ethanol, and methanol all work as cosolvents in the transformation. In the absence of formic acid, the reaction of **1a** proceeded in a redox neutral pathway albeit to a lower conversion to afford **3a** (20%) after 1 h (Table 1, entry 12).^[5] The reaction was faster and more selective to generate **3a** under an atmosphere of air than under argon under which only 40% yield of **3a** was obtained (Table 1, entry 13, and Supporting Information).

The optimized reaction conditions were applied to different 2-aryloxy-1-arylethanol with substitution of the two aryl groups in R¹–R⁴-positions (Table 2). This substitution pattern models native lignin from different sources.^[2] Model **1a**, with

Table 2. C–O bond cleavage in various lignin models.

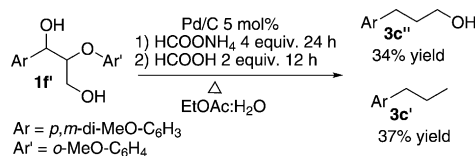
Entry	1	R ¹	R ²	R ³	R ⁴	3	Yield 3 [%] ^[a]
1	1a	H	H	H	H	3a	98
2	1b	MeO	H	MeO	H	3b	97
3	1c	H	H	MeO	MeO	3a	95
4	1d	MeO	H	H	H	3b	98
5	1e	H	H	MeO	H	3a	97
6	1f	MeO	MeO	MeO	H	3c	96
7	1g	HO	H	MeO	H	3d	98 ^[b]
8	1h	HO	MeO	MeO	H	3e	95 ^[b]
9	1i	HO	H	MeO	MeO	3d	92 ^[b]
10	1j	H	H	F	H	3a	96
11	1k	MeO	MeO	F	H	3c	95

[a] Reactions were performed on a 0.5 mmol scale in air for 3 h. Isolated yields of **3** were determined as an average of 2 runs. [b] Yields determined by ¹H NMR spectroscopy.

no methoxy substitution of the aryl is one component in, for example, switch grass.^[2] Substitution of the aryl group by a methoxy group in R³-position (**1b**) corresponds to the substitution pattern found in soft wood, for example, pine and spruce.^[2] Substitution of the aryl group by two methoxy groups in R³ and R⁴-positions (**1c**) corresponds to the substitution pattern in hard wood, for example, birch and eucalyptus.^[2] Gratifyingly, the methoxy substitution in the R³- and R⁴-positions of the aryl group did not affect catalysis negatively (Table 2, entries 2–6). Substrate **1c**, in which the phenol is substituted by two methoxy groups in R³- and R⁴-positions has previously been reported as cumbersome to cleave.^[5] In all cases, the aryl ketones (**3a–d**) were isolated in excellent yields. Using more natural models with hydroxyl groups in R¹-position of the aryl also generated the corresponding ketones in excellent yields (Table 2, entries 7–9). To extend the generality of the reaction to other transformations in organic synthesis and also study the effect of an electron-deficient aryl, substrates **1j** and **1k** were used in the reaction. These substrates generated the

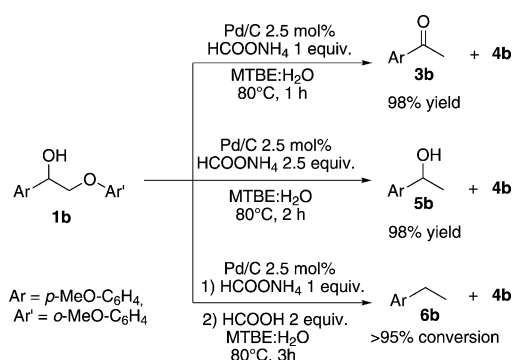
corresponding ketones (**3a**, **c**) in excellent yields (Table 2, entries 10–11).

To expand the methodology, the reaction was performed on model **1f'** having the β -O-4'-glycerolaryl ether. Initial results gave poor conversion and low reproducibility. A major side reaction was the disproportionation without cleavage. After some optimization steps, moderate conversion to the desired products was achieved by using a one-pot two-step procedure. Under the modified reaction conditions, complete consumption of dilignol **1f'** was observed after heating the reaction mixture for 24 h in the presence of Pd/C and ammonium formate. The intermediates formed were reduced by the addition of formic acid to yield the mixture of phenylpropanol **3c''** and propylbenzene **3c'** in an overall yield of 71 % (Scheme 2).



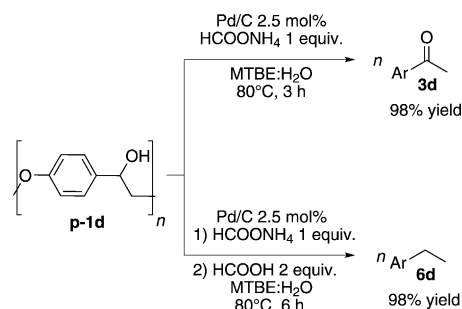
Scheme 2. One-pot procedure to generate **3c'** and **3c''** from **1f'**.

With slightly modified reaction conditions, the reaction can selectively be directed to ketone (**3b**), alcohol (**5b**), or alkane (**6b**, Scheme 3). Using an equimolar amount of formate, the reaction proceeded to afford **3b** in 98 % yield. Using 2.5 equivalents of formate, the reaction proceeded to generate **5b** in 98 % yield. The second equivalent of formate reduces the ketone to the alcohol.^[12] Addition of formic acid in a second step generated the transfer-hydrogenolysis product **6b** in above 95 % conversion.^[9]



Scheme 3. Substrate **1b** can selectively be transformed to products **3b**, **5b**, and **6b**.

Owing to the heterogeneous nature of the catalyst, we were curious whether the catalytic system would be applicable to a model polymer (**p-1d**). Gratifyingly, the catalytic system was efficient and depolymerized the polymer (5 kDa) of similar molecular weight to native lignin to generate **3d** in a quantitative yield (Scheme 4). Noteworthy, the reaction parameters did not need to be modified for efficient depolymerization of the



Scheme 4. Transformation of model polymer (**p-1d**) to generate either **3d** or **6d**.

poorly soluble polymer. With the addition of formic acid after 3 h, **6d** could be generated in high yield.

Encouraged by the results on the artificial lignin model polymer, we next performed the reaction on organosolv lignin from *Pinus sylvestris*. To achieve an efficient transformation, the reaction was performed by a two-step one-pot procedure. Organosolv lignin, Pd/C, and ammonium formate were heated in ethyl acetate and water for 24 h, after which formic acid was added to the reaction mixture and the reaction was continued for 12 h. A control experiment, in which Pd/C was absent, was also performed. The reaction mixture was analyzed by gel permeation chromatography (GPC) (Figure 2), 2D NMR spectroscopy (Figure 3), and GC–MS (Supporting Information). The GPC

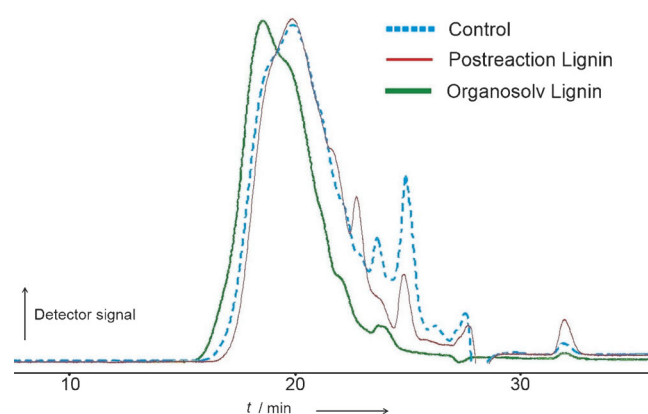


Figure 2. GPC chromatograms depicting the molecular weight distribution of organosolv lignin, that of the corresponding control experiment (THF soluble part), and the postreaction product mixtures.

analysis revealed a moderate change towards lower molecular weight fragments. The NMR data showed that 73 % of the β -O-4'-glycerolaryl ether bonds were degraded by the present methodology. In addition, resinol and aryl coumaran ether linkages were also cleaved. GC–MS spectra identified monomeric compounds including coniferyl dihydroalcohol, coumaryl dihydroalcohol, and derivatives thereof. Interestingly, in the control reaction, without Pd/C, GC–MC analysis revealed only the presence of oxidation products such as vanilic acid. None of the compounds detected in the catalyzed reaction were observed in the control reaction. The experiment without Pd/C displayed

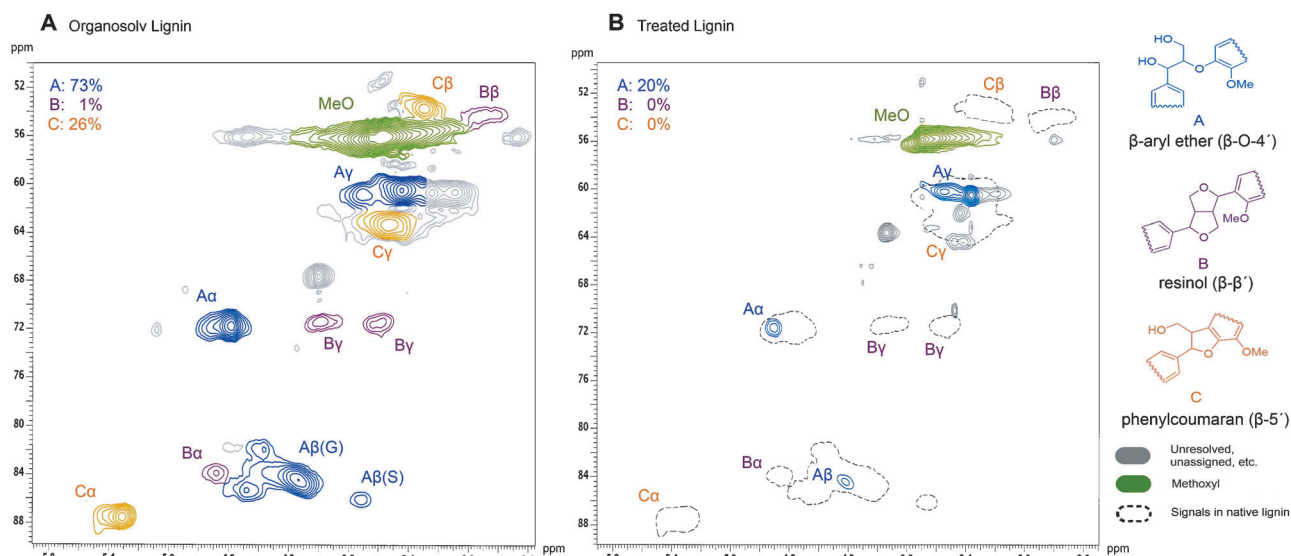


Figure 3. 2D HSQC NMR spectra of an isolated *Pinus sylvestris* lignin before and after reaction.

seemingly similar GPC chromatograms. However, in the chromatogram only the soluble part of the material is shown and the THF-insoluble residue formed in the control experiment was not suitable for analysis.

Size distribution data of the catalyst obtained by TEM (Figure 4) revealed that a fraction of 2–3 nm sized particles dominated in the sample (Supporting Information). The surface area determined by BET quantification methods was $813 \text{ m}^2 \text{ g}^{-1}$ with a total pore volume of $0.635 \text{ m}^3 \text{ g}^{-1}$.

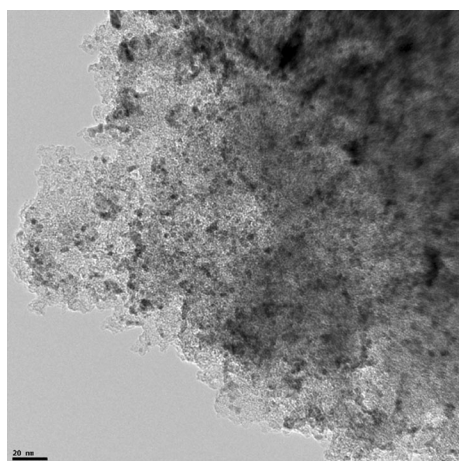


Figure 4. TEM image of Pd/C. Scale bar = 20 nm.

The heterogeneous nature of the catalyst was determined by different techniques.^[13] The effect of agitation on the initial reaction rate was studied. At stirring speeds below 500 rpm, diffusion control and not kinetic control was operating and, therefore, the kinetic experiments were performed by using stirring speeds above 500 rpm (Figure 5). High reproducibility in the kinetic runs, together with the absence of an observed

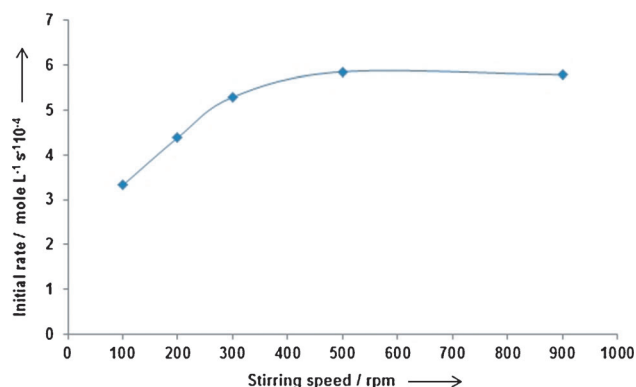


Figure 5. Effect of the stirring rate on the initial reaction rate.

sigmoidal shape of the initial rate, supported that the Pd/C is responsible for the catalysis.

Different inhibition experiments were performed (Figure 6). Addition of mercury (25 equiv. to palladium) to the reaction mixture inhibited the reaction and only traces of the product were observed. Addition of one equivalent of triphenylphosphine to palladium also inhibited the catalysis and only trace

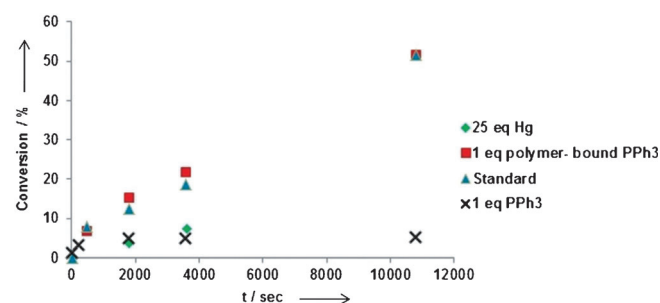
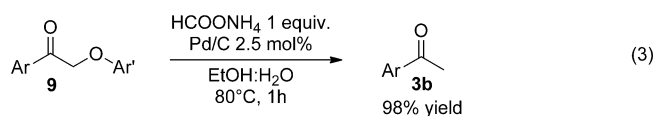
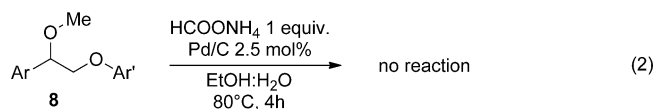
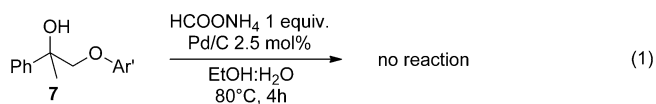


Figure 6. Effect of inhibitors on the reaction.

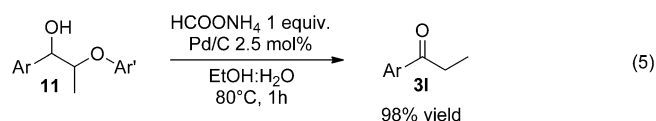
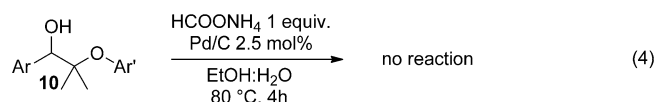
amounts of product were observed. However, if one equivalent of polymer-bound triphenylphosphine was added to the reaction mixture, no effect on the reaction outcome was observed as compared to the blank reaction. These findings supported that heterogeneous Pd/C is the active catalyst in the cleavage of the β -O-4'-ethanolaryl ether bond.

If the reaction of **1** was carefully monitored by taking aliquots from the reaction mixture at a low conversion, the monomeric ketone and phenol (**3** and **4**) were the only products observed in the presence of formate. The reaction may proceed either by an initial dehydrogenation step to generate the 2-phenoxy-1-phenylethanone **9** followed by an ether bond cleavage^[5a] or by the ether bond cleavage preceding the dehydrogenation step. A possibility to distinguish between these two different pathways would be to use substrates in which the dehydrogenation to generate the ketone is not possible. If 1-phenoxy-2-phenylpropan-2-ol (**7**) was used as the substrate, no reaction occurred [Eq. (1)]. Likewise, no reaction occurred if (1-methoxy-2-phenoxyethyl)benzene (**8**) was used as the substrate [Eq. (2)]. If dehydrogenation product **9** was used as the substrate, a fast ether bond cleavage generating the monomeric ketone was observed [Eq. (3)].



Ar = *p*-MeO-C₆H₄, Ar' = *o*-MeO-C₆H₄

These experiments supported a pathway proceeding through an initial palladium-catalyzed dehydrogenation, followed by C–O ether bond cleavage. The observation that the transformation is more efficient in air than in argon atmosphere is also supportive of this hypothesis (Supporting Information). The second step in the reaction mechanism may be generation of an enol equivalent followed by insertion of palladium.^[14] A possible way to evaluate this hypothesis is to selectively block the β -position by substituting the hydrogen atoms with alkyl groups. If 2-methyl-2-phenoxy-1-phenylpropan-1-ol (**10**) was used as the substrate, no reaction occurred [Eq. (4)]. To exclude that this was caused by steric hindrance, 2-phenoxy-1-phenylpropan-1-ol (**11**) was used as the substrate [Eq. (5)]. This substrate generated the expected propiophenone (**3l**) in 1 h exhibiting similar reactivity to substrate **1a**. These results are in agreement with that the reaction proceeds through a palladium–enolate intermediate.



Ar = *p*-MeO-C₆H₄, Ar' = *o*-MeO-C₆H₄

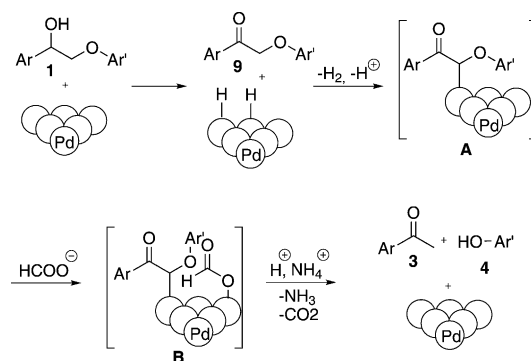
Kinetic isotope effects of the C–O bond cleavage of **1b** were investigated by selective deuteration of the α - and β -positions of **1b** as well as by using formic acid deuterated in the hydride position (Table 3).^[15] A primary kinetic isotope effect

Table 3. Kinetic deuterium isotope effect on the cleavage of substrates **1b**, **1b- α D**, and **1b- β D2**.

Entry	Run	Kinetic isotope effect
1	$k_{1b}/k_{1b-\alpha D}$	1.65 ± 0.07
2	$k_{1b}/k_{1b-\beta D2}$	1.11 ± 0.01
3	k_{HCOOH}/k_{DCOOH}	1.72 ± 0.13

(1.65) was observed if **1b- α D** deuterated in the α -position was used, in agreement with a slow dehydrogenation step. A secondary kinetic isotope effect (1.11) was observed if substrate **1b- β D2** deuterated in the β -position was used in agreement with a fast keto–enol tautomerization step.^[16] A primary kinetic isotope effect (1.72) was observed if formic acid, deuterated in the hydride position, was used in agreement with a slow hydrogen transfer from formate to Pd/C.

The proposed reaction mechanism is shown in Scheme 5.^[17] Substrate **1** is dissociatively chemisorbed to palladium to produce **9** and hydrogen adsorbed to palladium.^[18] According to the kinetic isotope effect ($k_{1b}/k_{1b-\alpha D} = 1.65$), this occurs in a slow reaction step.



Scheme 5. Proposed mechanism for the transformation of **1** to **3** and **4**.

The observation that no C–O bond cleavage occurred in hydrogen gas supports this hypothesis. Hydrogen desorption from palladium is facilitated by molecular oxygen in air, to generate water (see the Supporting Information).^[19] Ketone **9** is in fast equilibrium with its enol tautomer, which adsorbs to palladium to generate intermediate **A**. The observation that substrate **10** was unreactive in the transformation is supportive of this hypothesis. A formate ion adsorbs to palladium to generate intermediate **B** that may decompose to generate a palladium hydride. Either the formate complex or a generated palladium hydride promotes the C–O bond cleavage of the ether in a slow reaction step according to the kinetic isotope effect ($k_{\text{HCOOH}}/k_{\text{DCOOH}} = 1.72$) to generate **3**, which desorbs from palladium. For further reduction, the role of the second equivalent of formate is to reduce the ketone to the alcohol.^[12] The mechanism for the transfer hydrogenolysis has previously been reported.^[9]

Conclusions

A robust, mild, and efficient palladium-catalyzed cleavage of the β -O-4'-ether bond of model lignin compounds has been developed. Dimer models of lignin sources were efficiently transformed to the corresponding aryl ketones and phenols in excellent yield. By slightly modifying the reaction conditions, a ketone, alcohol, or alkane can selectively be generated in excellent yield. Also polymers with the β -O-4'-ether linkage were efficiently cleaved to generate either the aryl ketone or alkane in excellent yield. Degradation experiments with organosolv lignin revealed a moderate shift toward lower molecular weight species upon catalytic treatment. Initial mechanistic studies indicate an initial dehydrogenation step of the substrate followed by Pd insertion to give a palladium-enolate complex.

Experimental Section

General procedure for cleavage of lignin model compound (**1b**): Pd/C (5 wt %) (0.027 g, 2.5 mol %), NH_4HCO_2 (0.032 g, 0.5 mmol), and compound **1b** (0.137 g, 0.5 mmol) were added to a 5 mL vial. The vial was sealed and 2.4 mL of methyl *tert*-butyl ether and 0.6 mL of water were added by a syringe. Another needle was inserted through a septum to release pressure during the solvent addition. The needle was removed and the vial was placed in a preheated oil bath at 80 °C and stirred with a stirring speed of 1000 rpm for 3 h. The vial was uncapped and left in the bath for additional 30 min. The vial was cooled to RT and the reaction mixture was filtrated through a celite pad, using diethyl ether (10 mL) as eluent. Diethyl ether (50 mL) and 10% K_2CO_3 solution (10 mL) were added to the filtrate. The mixture was extracted with diethyl ether (2 \times 30 mL). Organic fractions were combined and dried over anhydrous MgSO_4 . Solvent was removed in vacuo to give compound **3b** as a white solid (0.073 g, 0.49 mmol) in 97% yield. To isolate the guaiacol, the aqueous layer was acidified with 6 M HCl solution (pH 2–3) and extracted with diethyl ether (2 \times 50 mL). Organic fractions were combined and dried over anhydrous MgSO_4 . The solvent was removed in vacuo, to give compound **4b** as a transparent oil (0.059 g, 0.48 mmol) in 95% yield.

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Keywords: heterogeneous catalysis • cleavage reactions • green chemistry • palladium • polymers • lignin

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