Mild Redox-Neutral Depolymerization of Lignin with a Binuclear Rh Complex in Water

Yuxuan Liu,[†,‡] Changzhi Li,*[,‡,∥] Wang Miao,[†] Weijun Tang,[†] Dong Xue,[†] Chaoqun Li,[†] Bo Zhang,[‡] Jianliang Xiao,[†,§] Aiqin Wang,[‡,∥] Tao Zhang,[‡] and Chao Wang*[,†]

[†]Key Laboratory of Applied Surface and Colloid Chemistry, Ministry of Education, School of Chemistry and Chemical Engineering, Shaanxi Normal University, Xi'an, 710062, China

[‡]Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, 116023, China

[§]Department of Chemistry, University of Liverpool, Liverpool, L69 7ZD, U.K.

[∥]Dalian National Laboratory for Clean Energy, 457 Zhongshan Road, Dalian, 116023, China

Ⓢ *Supporting Information*
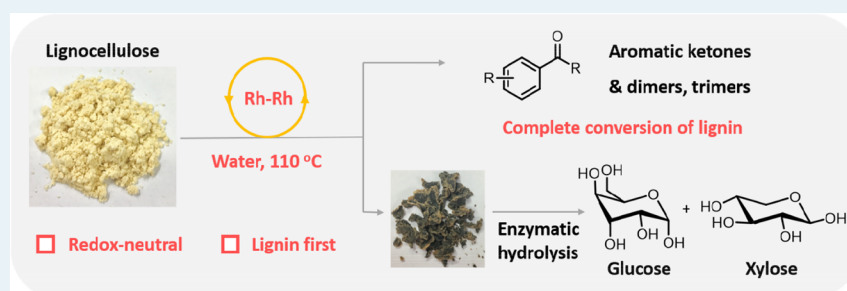
ABSTRACT: A mild redox-neutral lignin depolymerization system featuring a water-soluble binuclear Rh complex has been developed. The catalytic system could be successfully applied to the depolymerization of a lignin-like polymer, alkaline lignin, as well as raw lignocellulose samples to produce aromatic ketones, providing a homogeneous catalytic system for "lignin-first" biorefinery in water. Mechanistic studies on the model substrate suggest that the reaction proceeds via a metal-catalyzed dehydrogenation step to afford a carbonyl intermediate, followed by C−O bond cleavage to afford ketone and phenol products. Deuterium labeling study shows that the hydrogen used for cleavage of the C−O bond originates from the alcohol moiety in the substrate.

KEYWORDS: lignin depolymerization, redox-neutral, rhodium complex, lignin-first biorefinery, aqueous reaction

The development of effective depolymerization methods is pivotal to lignin valorization.[1] The catalytic cleavage of β-O-4 linkages has attracted a great deal of attention because of their high abundance (45−60% of all linkages) in native lignin structure.[2] Both oxidative[3] and reductive[4] catalytic systems for the cleavage of β-O-4 linkages have been extensively studied by several groups including our own.[1b,4a] More recently, a two-step strategy combining oxidation and hydrogenation reactions has also been regarded as an efficient approach to lignin valorization.[3k,5] From the atom-economic and green chemistry viewpoint, the redox-neutral cleavage of β-O-4 linkages would be more ideal, as it avoids the use of extra oxidants or reductants, which are often hazardous and generate waste.

The typical structure of β-O-4 linkage usually contains hydroxyl groups in its side-chain and has the potential to be dehydrogenated to offer hydrogen for the cleavage of bonds in lignin, thus providing a good platform for redox-neutral cleavage. Several heterogeneous catalytic systems have been reported for the redox-neutral cleavage of β-O-4 linkage in lignin.[6] However, structurally well-defined homogeneous catalysts have rarely been reported, although they might offer

mild reaction conditions and provide models for mechanistic studies. In addition, homogeneous catalysts might be superior to heterogeneous catalysts for the depolymerization of native lignin in terms of mass transfer, noting that native lignins are generally insoluble solids. The first homogeneous catalytic system for redox-neutral cleavage of C−O bond of β-O-4 model compounds, as well as a synthetic lignin model polymer, to afford ketone and phenol products, was reported by Bergman and Ellman and their co-workers,[7] which was further studied by James[8] and Li[9] and their co-workers. Klankermayer and co-workers reported a Ru catalyzed redox-neutral cleavage of C−C bond in lignin model substrates.[10] Lancefield, Bruijnincx, and co-workers also reported the cleavage of C−C bond under redox-neutral conditions, which they have applied to the depolymerization of extracted lignin and lignocellulose.[11] Despite this progress, homogeneous catalysts
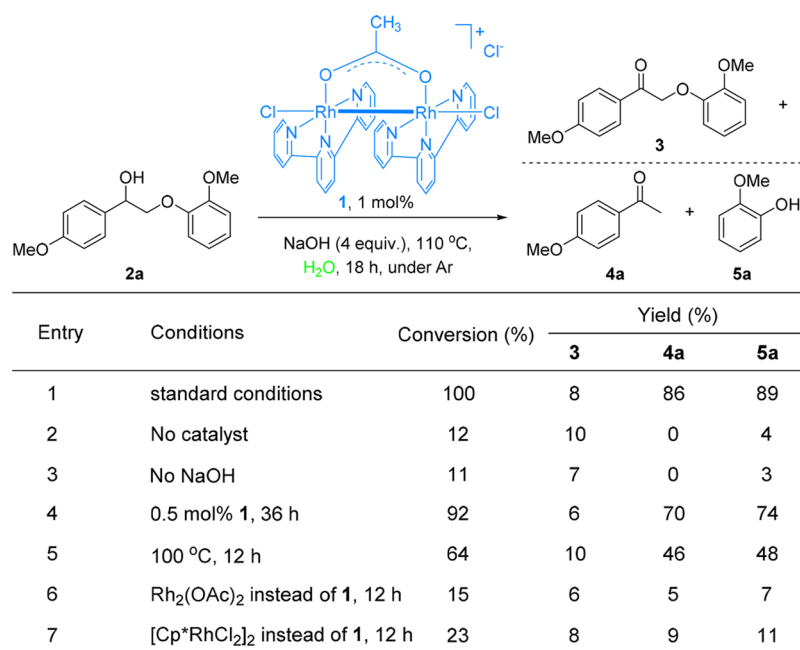
Figure 1. Rh-catalyzed redox-neutral cleavage of a lignin model substrate in water. Reaction conditions: **2a** (0.2 mmol), Catalyst (0.002 mmol), H_2O (1 mL), 110 °C, 12 h, under Ar. Yields were determined by GC-FID with diphenyl as internal standard.

Entry	Conditions	Conversion (%)	Yield (%) 3	4a	5a
1	standard conditions	100	8	86	89
2	No catalyst	12	10	0	4
3	No NaOH	11	7	0	3
4	0.5 mol% **1**, 36 h	92	6	70	74
5	100 °C, 12 h	64	10	46	48
6	Rh$_2$(OAc)$_2$ instead of **1**, 12 h	15	6	5	7
7	[Cp*RhCl$_2$]$_2$ instead of **1**, 12 h	23	8	9	11

for redox-neutral "lignin-first"[12] depolymerization of lignocellulose are still highly desirable.

Herein, we report a redox-neutral lignin depolymerization system based on a water-soluble binuclear Rh complex. The catalytic system can cleave a series of lignin model compounds into ketones and phenols under mild conditions in water. The water-soluble Rh catalyst could be recycled at least 18 times without a noticeable decrease in activity for the model substrate. Most notably, the catalytic system could be successfully applied to the depolymerization of a lignin-like polymer, alkaline lignin, as well as native lignin samples, providing excellent yield of depolymerized aromatic oil with the monomers mainly consisting of aromatic ketone compounds. In particular, almost complete deconstruction of lignin components from a raw lignocellulose sample has been achieved, providing an example of "lignin-first" catalytic system with a homogeneous catalyst.

In our previous study, we discovered that the binuclear Rh complex **1** (Figure 1) displayed unique activity in dehydrogenation of alcohols, and the hydrogen removed from alcohols could be released as hydrogen gas, intercepted by O_2, or used for the reduction of olefinic bonds.[13] This special property of the binuclear Rh catalyst prompted us to investigate its potential in the dehydrogenative depolymerization of lignin because the alkyl−aryl ether linkage between aromatic rings features different alcohol groups. If the alcohol structure in lignin can be dehydrogenated by the Rh catalyst to afford a ketone intermediate and a Rh hydride complex, the ether C−O bond (bond energy 55.9 kcal/mol) of the ketone intermediate would be weakened compared with that in lignin (bond energy 69.2 kcal/mol),[5b] and consequently, the ether C−O bond in the ketone intermediate might be cleaved by the Rh hydride complex to afford ketone and phenol products. A typical lignin model compound **2a** was chosen as the substrate to verify our hypothesis. After a series of optimization (Figure 1 and Table S1−S2 in SI), compound **2a** was indeed found to be completely cleaved into a ketone **4** (86% yield) and a phenol

5 (89% yield), along with a small amount of the dehydrogenated intermediate **3**, with 1 mol % of **1** as catalyst in the presence of NaOH in water at 110 °C for 18 h under Ar atmosphere (Figure 1, entry 1). Both the catalyst **1** and NaOH are essential for the reaction (Figure 1, entries 2, 3). The reaction could take place at 100 °C or with lower catalyst loading, albeit with lower conversion and yields (Figure 1, entries 4, 5). Other Rh complexes showed much lower activity than **1** (Figure 1, entries 6, 7).

Various other lignin model substrates **2b−i** were then tested under the above optimized conditions, and all of them could be fully consumed in 18 or 48 h with moderate to high yields of ketones and phenols (Figure 2). Methoxy groups at ortho-, meta-, and para-positions on both phenyl rings, and a hydroxyl group on the α-phenyl ring (Figure 2, entries 1−6), which are commonly found in natural lignin structure, are all tolerated. Cleaving β-O-4 model compounds containing γ−OH functionality with a redox-neutral homogeneous catalytic system is a challenge,[7−9] and only a few successful examples are reported.[10,11] Delightfully, such kind of substrates can be cleaved in our binuclear Rh catalytic system (Figure 2, entries 7−9). Full conversions were obtained, and two major ketone products were detected for these substrates. We noticed that the yields of the major ketone products and phenols were lower than expected. A detailed analysis of the products/intermediates/byproducts, as well as a plausible mechanism for their formation is given in the Supporting Information (see Section 5 in the SI). The ability to cleave substrates with γ-OH functionality suggests that the catalytic system has the potential for the depolymerization of real lignin (vide infra). One major challenge of the homogeneous catalysts is the recyclability. The binuclear Rh catalyst is water-soluble while the ketone product has very poor solubility in water. Thus, after each reaction, the ketone product was readily extracted with petroleum ether, and the solution containing the catalyst could be reused in the next run.
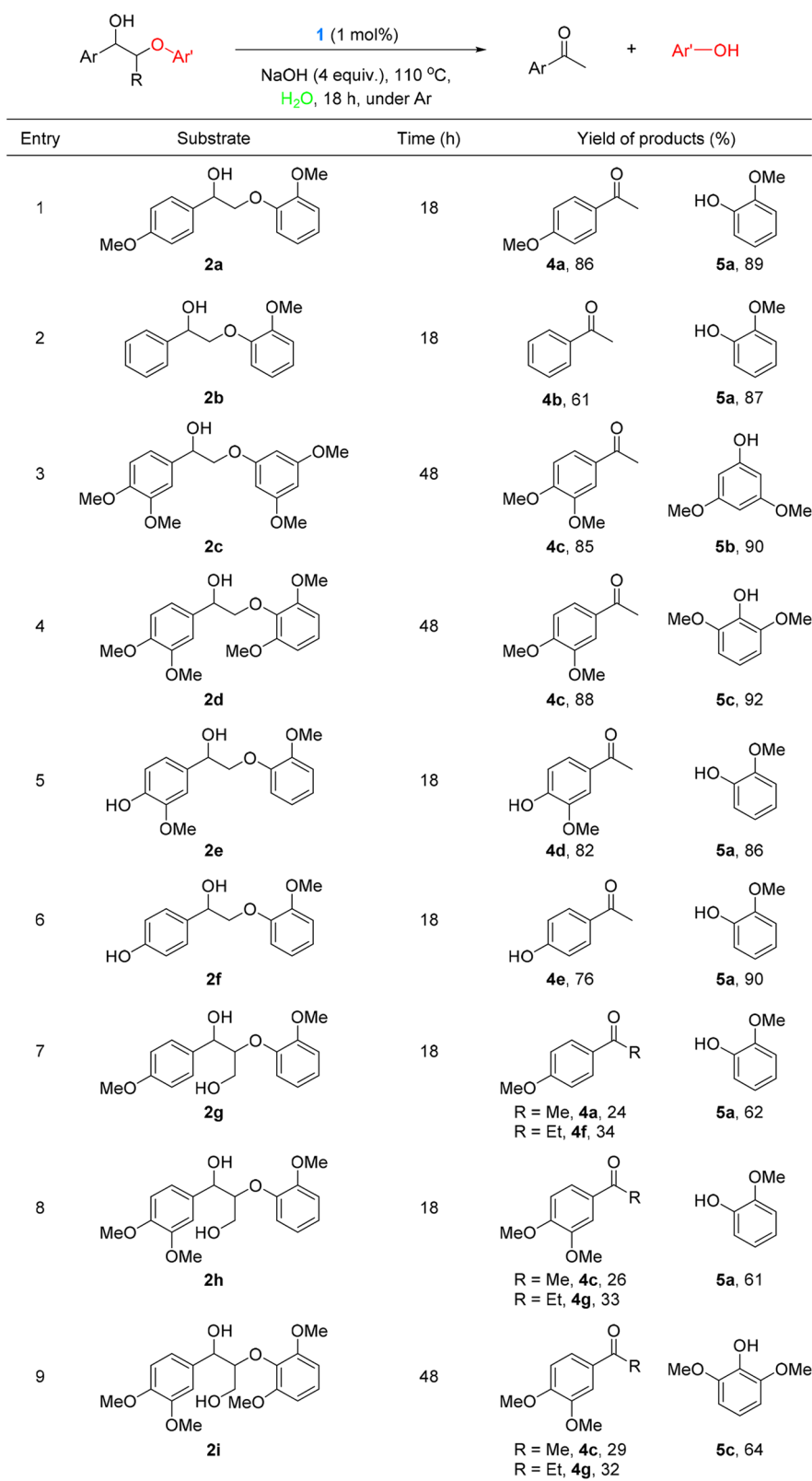
Figure 2. Rh-catalyzed cleavage of different lignin model substrates. See SI for experimental details.

As shown in Scheme S2, the catalyst could be reused in the next run. As shown in Scheme S2, the catalyst could be recycled at least 18 times for the transformation of the model substrate **2a** (see Section 6 in SI for details). The recyclability of the catalytic system is superior to most other homogeneous systems[7−10] and even a certain number of heterogeneous catalytic systems[6a−f] (the number of recycles is normally within 10 for reported heterogeneous catalysts). The versatility of the catalytic system is further demonstrated by a gram-scale reaction with 1.2 g of **2a** as the substrate; full conversion with
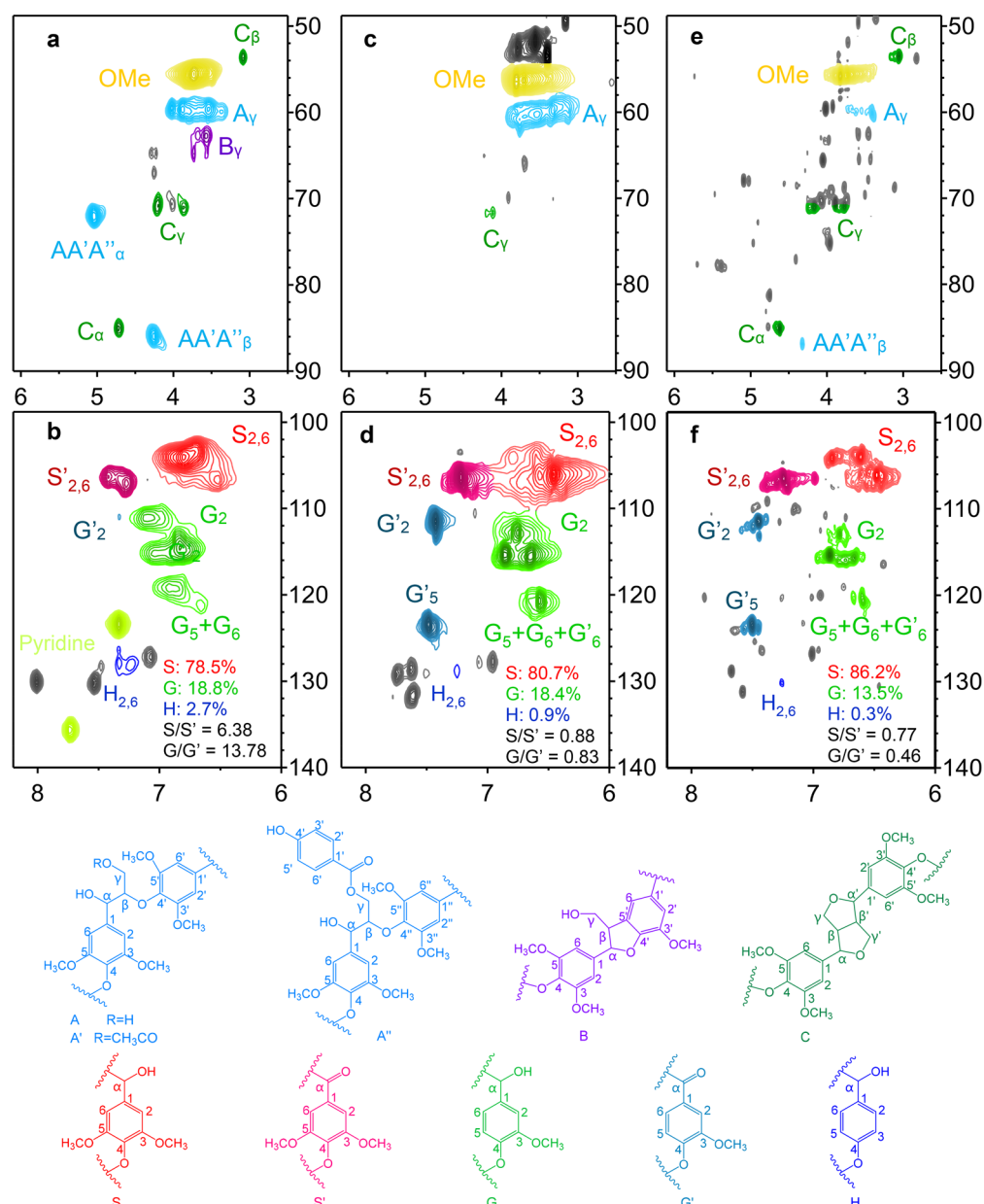
Figure 3. 2D-HSQC-NMR analysis of an alkaline lignin sample and the oil obtained after depolymerization of the alkaline lignin and a native lignocellulose. (a,b) Alkaline lignin sample; (c,d) Oil obtained from the alkaline lignin sample; (e,f) Oil obtained from the native lignocellulose.

high yields of **4a** and **5a** (88% and 90%, respectively) were obtained in 40 h (Scheme S3). Moreover, a lignin-like polymer was also synthesized[14] and tested in the catalytic system, which gave complete conversion with a good monomer yield of 80% (Scheme S4).

The results obtained with the model compounds encouraged us to apply the methodology to the conversion of authentic lignin feedstock. One typical alkaline lignin extracted from basswood was chosen as the substrate to be depolymerized by **1**. Pleasingly, the alkaline lignin was effectively converted into liquid oil with a high yield of 88 wt %. MALDI-TOF characterization of the oil (Scheme S7) showed that the obtained aromatic products are exclusively in the $m/z = 0-400$ range, indicating monomers and dimers as the major products. The quantified monomers in the oil were about 11 wt % as measured by GC-FID (Table S5), with aromatic ketones as the major products. To gain some insight into the cleavage

mechanism for real lignin, 2D-HSQC-NMR spectra of the alkaline lignin and the oil products were compared (Figure 3). Figure 3a,c illustrate the side chain region of the lignin and its oil product. It was found that cross signals of methoxy groups and β-O-4 aryl ether were the dominant linkages in basswood lignin. In addition, a small amount of β-S/α-O-4 linkages (resinol structure B 22.8%) and phenylcoumaran ($\beta-\beta$, Structure C 2.1%) were observed. After the reaction, most of the A, B, C linkages of the lignin disappeared in the side-chain region of the oil (Figure 3, panel a vs c), indicating that the three major linkages of A, B, and C are effectively cleaved by the catalyst.

Typically, basswood lignin belongs to G-S lignin, which comprises a mixture of S and G units along with a trace amount of the H unit.[15] Hence, the aromatic region of both the lignin material and the resulting bio-oil showed similar S:G:H molar ratios (78.5%, 18.8% and 2.7% vs 80.7%, 18.4%
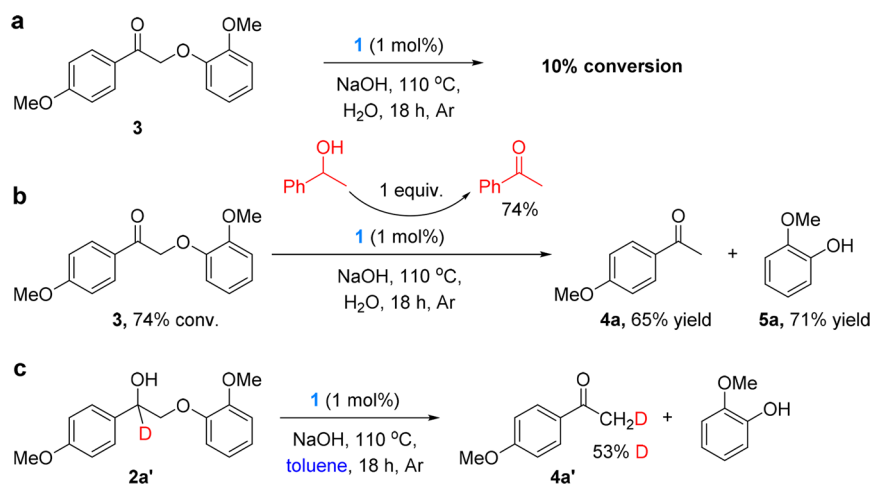
Figure 4. Mechanistic studies. (a,b) Verification of intermediate. (c) Deuterium labeling experiment.

and 0.9%) in 2D-HSQC-NMR spectra (Figure 3b,d). However, it is interesting to note that the S/S′ and G/G′ molar ratio of the oil products (Figure 3d, 0.88, 0.83) was significantly lower than that of lignin (Figure 3b, 6.38, 13.78). The increased molar ratio of S′ in the oil products indicates the dehydrogenation of the C_α−OH group. Similarly, certain amounts of G_2′, G_5′, and G_6′ appeared in the oil products (Figure 3, panel b vs d), indicating the dehydrogenation of C_α−OH group in the neighboring G-type units. These results suggest that the C_α−OH groups in the lignin materials have been transformed into ketone groups and accordingly, the cleavage of C−O bonds in real lignin likely follows the same reaction pathway as that proposed in Figure 5 (vide infra). Further, *raw basswood powder (40−60 mesh, 1000 mg) without pretreatment* was also submitted to deconstruction catalyzed by **1**. Impressively, 26.6 wt % aromatic oil was obtained in water at 110 °C for 24 h. The total yield of the monomers is 2.3 wt % based on the starting raw basswood powder. HPLC-MS analysis showed that the crude product did not contain any sugar derivatives, such as glucose, xylose, 5-hydroxylmethyl-furfural, and polyols, and the distribution of aromatic monomers in the oil was similar to that obtained from isolated lignin. 2D-HSQC-NMR characterization showed that the S:G:H molar ratio of the oil was in agreement with that of the alkaline lignin, and the S/S′, G/G′ molar ratio was 0.77, 0.46, respectively (Figure 3e,f). Noting that the lignin content in this basswood powder is determined to be 28 wt % in our previous work,[15] it is clear that most of the lignin has been selectively deconstructed to the aromatic oil with the molecular weight in the range of 0−500 (Scheme S9), leaving the other two components (cellulose and hemicellulose) almost intact as a solid residue (see Section 11 in SI for details). Enzymatic hydrolysis experiment confirms that the solid residue is mainly consist of cellulose and hemicellulose because glucose and xylose are the main hydrolysis products. The rate of enzymatic hydrolysis of the solid residue is much faster than that of raw basswood powder (Scheme S11), showcasing the advantage of this lignin first system.[12]

GC-FID analysis of the monomers obtained from both the extracted lignin and raw basswood powder also showed that similar products were obtained, and aromatic ketones were the dominant monomer products (see Schemes S8 and S10, SI). These results suggest that the catalytic system operates via the same mechanism as that of the model substrates and is highly

selective even for real lignin material. Aromatic ketone products are valuable fine chemicals.

The mechanism of the catalytic system was then investigated with model substrates. As there is no external hydrogen source added and the binuclear Rh complex has been shown to catalyze the dehydrogenation of alcohols to ketones,[13b] we reasoned that the hydroxyl group of **2a** would be first dehydrogenated to form a ketone intermediate **3**, whose ether C−O bond would then be cleaved by a Rh hydride intermediate. As shown in Figure 1, compound **3** was observed in the reaction. **3** was then synthesized, and it was almost inactive under the standard catalytic condition for 18 h in the absence of a hydrogen source (Figure 4a). Interestingly, when 1 equiv of 1-phenylethan-1-ol was added, 74% of **3** was converted to 65% of **4a** and 71% of **5a** under the standard conditions for 18 h (Figure 4b); meanwhile, 1-phenylethan-1-ol was completely consumed and 74% acetophenone was detected, suggesting that the ether C−O bond of **3** could be selectively cleaved to afford the ketone and phenol product with an external hydrogen source. These results suggest that **3** is an intermediate during the reaction,[6,7] and the same process may be happening for real lignin cleavage.

Deuterium labeling study with deuterium labeled **2a′** as substrate and toluene as solvent further confirmed the hydrogen transfer process for the redox-neutral cleavage reaction (Figure 4c). It clearly showed that the deuterium atom on the carbon adjacent to the hydroxyl group could be transferred to the methyl group of the ketone product, implying that the removed hydrogens from the alcohol group participate in the subsequent cleavage of the ether C−O bond. Further, KIE experiments indicated that the dehydrogenation of **2a** to form **3** is the rate-limiting step (Scheme S13).

On the basis of these mechanistic studies, a catalytic mechanism for the lignin cleavage is tentatively proposed (Figure 5). Under basic conditions, the chloride in the Rh catalyst might first be replaced by a hydroxide to form complex **I**, which might be the real catalyst. Complex **I** could then deprotonate the lignin substrate **II** to form an intermediate **III**, which would undergo β-hydride elimination to produce a ketone intermediate **IV** and a Rh hydride **V**. **IV** could then be cleaved by **V** with the aid of H_2O to afford the cleaved products and regenerate **I** (Figure 5). As 2D-HSQC-NMR has revealed that the C_α−OH groups in the lignin materials were transformed into ketone groups and the depolymerization of
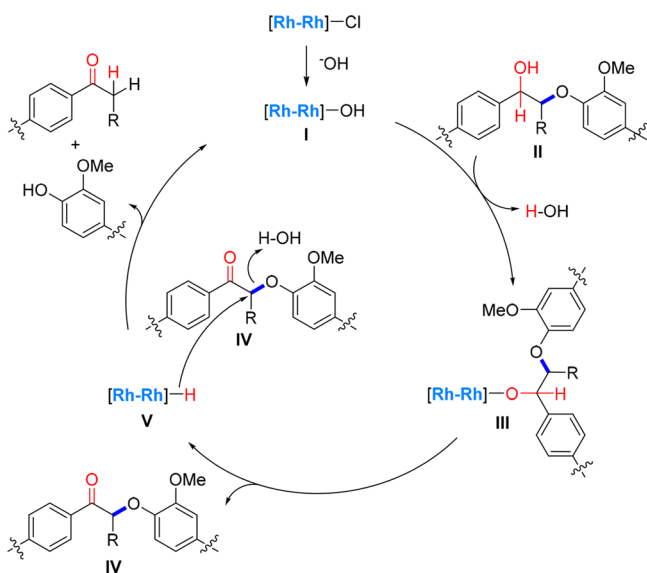
Figure 5. Proposed mechanism for the cleavage of lignin.

extracted lignin and lignocellulose mainly produced aromatic ketone products, we thus propose that the cleavage of aryl C–O bonds in real lignin follows the same mechanism as that for the model substrates (Figure 5). It is therefore very interesting to note that hydrogenolysis of real lignin does not involve an external hydrogen source over the binuclear Rh complex under such mild conditions (110 °C, 1 atm Ar) in water, a green and readily available solvent. Hence, our catalytic system holds great promise for the redox-neutral production of aromatic compounds from lignin, which has been identified as a key challenge in the biorefinery area.

In conclusion, a redox-neutral lignin depolymerization system featuring a water-soluble binuclear Rh complex is reported. The catalytic system can cleave a series of lignin model compounds, lignin-like polymer, alkaline lignin, as well as raw lignocellulose samples, into ketones and phenols under mild conditions in water. Mechanistic studies suggest that benzyl-hydroxyl units in the side-chain between the aromatic units are the hydrogen source for the cleavage of the ether C–O bonds, and an intramolecular dehydrogenation-hydrogenolysis cascade pathway is coupled to afford excellent yield of aromatics. In particular, almost complete deconstruction of lignin component from a raw lignocellulose sample was achieved, providing an example of H$_2$ self-sufficient "lignin-first" system with a homogeneous catalyst. The advantages of mild conditions, low catalyst loading, green and cheap water solvent, and no need of extra-hydrogen source are of great significance for the cost-efficient production of aromatic chemicals from biomass.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.9b00669.

    Experimental procedures and characterization data for cleaved products (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: licz@dicp.ac.cn (C.Z.L.).

*E-mail: c.wang@snnu.edu.cn (C.W.).

ORCID Ⓘ

Changzhi Li: 0000-0001-6748-2575

Dong Xue: 0000-0002-7269-6356

Aiqin Wang: 0000-0003-4552-0360

Tao Zhang: 0000-0001-9470-7215

Chao Wang: 0000-0003-4812-6000

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

■ REFERENCES

(1) (a) Ragauskas, A. J.; Beckham, G. T.; Biddy, M. J.; Chandra, R.; Chen, F.; Davis, M. F.; Davison, B. H.; Dixon, R. A.; Gilna, P.; Keller, M.; Langan, P.; Naskar, A. K.; Saddler, J. N.; Tschaplinski, T. J.; Tuskan, G. A.; Wyman, C. E. Lignin Valorization: Improving Lignin Processing in the Biorefinery. *Science* **2014**, *344*, 1246843. (b) Li, C.; Zhao, X.; Wang, A.; Huber, G. W.; Zhang, T. Catalytic Transformation of Lignin for the Production of Chemicals and Fuels. *Chem. Rev.* **2015**, *115*, 11559−11624. (c) Gillet, S.; Aguedo, M.; Petitjean, L.; Morais, A. R. C.; Da Costa Lopes, A. M.; Łukasik, R. M.; Anastas, P. T. Lignin Transformations for High Value Applications: Towards Targeted Modifications Using Green Chemistry. *Green Chem.* **2017**, *19*, 4200−4233. (d) Schutyser, W.; Renders, T.; Van Den Bosch, S.; Koelewijn, S. F.; Beckham, G. T.; Sels, B. F. Chemicals From Lignin: An Interplay of Lignocellulose Fractionation, Depolymerisation, and Upgrading. *Chem. Soc. Rev.* **2018**, *47*, 852−908. (e) Sun, Z.; Fridrich, B.; De Santi, A.; Elangovan, S.; Barta, K. Bright Side of Lignin Depolymerization: toward New Platform Chemicals. *Chem. Rev.* **2018**, *118*, 614−678.

(2) Chakar, F. S.; Ragauskas, A. J. Review of Current and Future Softwood Kraft Lignin Process Chemistry. *Ind. Crops Prod.* **2004**, *20*, 131−141.

(3) (a) Crestini, C.; Pro, P.; Neri, V.; Saladino, R. Methyltrioxorhenium: A New Catalyst for the Activation of Hydrogen Peroxide to the Oxidation of Lignin and Lignin Model Compounds. *Bioorg. Med. Chem.* **2005**, *13*, 2569−2578. (b) Son, S.; Toste, F. D. Non-Oxidative Vanadium-Catalyzed C-O Bond Cleavage: Application to Degradation of Lignin Model Compounds. *Angew. Chem., Int. Ed.* **2010**, *49*, 3791−3794. (c) Badamali, S. K.; Luque, R.; Clark, J. H.; Breeden, S. W. Co(Salen)/SBA-15 Catalysed Oxidation of A β-O-4 Phenolic Dimer Under Microwave Irradiation. *Catal. Commun.* **2011**, *12*, 993−995. (d) Sedai, B.; Díaz-Urrutia, C.; Baker, R. T.; Wu, R.; Silks, L. A. P.; Hanson, S. K. Comparison of Copper and Vanadium Homogeneous Catalysts for Aerobic Oxidation of Lignin Models. *ACS Catal.* **2011**, *1*, 794−804. (e) Zakzeski, J.; Bruijnincx, P. C. A.; Weckhuysen, B. M. In Situ Spectroscopic Investigation of the Cobalt-Catalyzed Oxidation of Lignin Model Compounds in Ionic Liquids. *Green Chem.* **2011**, *13*, 671−680. (f) Hanson, S. K.; Wu, R.; Silks, L. A. CC or CO Bond Cleavage in A Phenolic Lignin Model Compound: Selectivity Depends on Vanadium Catalyst. *Angew. Chem., Int. Ed.* **2012**, *51*, 3410−3413. (g) Zhang, G.; Scott, B. L.; Wu,

R.; Silks, L. A. P.; Hanson, S. K. Aerobic Oxidation Reactions Catalyzed by Vanadium Complexes of Bis(Phenolate) Ligands. *Inorg. Chem.* **2012**, *51*, 7354−7361. (h) Chan, J. M. W.; Bauer, S.; Sorek, H.; Sreekumar, S.; Wang, K.; Toste, F. D. Studies on the Vanadium-Catalyzed Nonoxidative Depolymerization of Miscanthus giganteus-Derived Lignin. *ACS Catal.* **2013**, *3*, 1369−1377. (i) Biannic, B.; Bozell, J. J. Efficient Cobalt-Catalyzed Oxidative Conversion of Lignin Models to Benzoquinones. *Org. Lett.* **2013**, *15*, 2730−2733. (j) Zhang, J.; Liu, Y.; Chiba, S.; Loh, T.-P. Chemical Conversion Of *β*-O-4 Lignin Linkage Models through Cu-Catalyzed Aerobic Amide Bond Formation. *Chem. Commun.* **2013**, *49*, 11439−11441. (k) Lancefield, C. S.; Ojo, O. S.; Tran, F.; Westwood, N. J. Isolation of Functionalized Phenolic Monomers through Selective Oxidation and C-O Bond Cleavage of the *β*-O-4 Linkages in Lignin. *Angew. Chem., Int. Ed.* **2015**, *54*, 258−262. (l) Hanson, S. K.; Baker, R. T. Knocking on Wood: Base Metal Complexes as Catalysts for Selective Oxidation of Lignin Models and Extracts. *Acc. Chem. Res.* **2015**, *48*, 2037−2048.

(4) (a) Li, C.; Zheng, M.; Wang, A.; Zhang, T. One-Pot Catalytic Hydrocracking of Raw Woody Biomass into Chemicals over Supported Carbide Catalysts: Simultaneous Conversion of Cellulose, Hemicellulose and Lignin. *Energy Environ. Sci.* **2012**, *5*, 6383−6390. (b) Kleine, T.; Buendia, J.; Bolm, C. Mechanochemical Degradation of Lignin and Wood by Solvent-Free Grinding in A Reactive Medium. *Green Chem.* **2013**, *15*, 160−166. (c) Shuai, L.; Amiri, M. T.; Questell-Santiago, Y. M.; Héroguel, F.; Li, Y.; Kim, H.; Meilan, R.; Chapple, C.; Ralph, J.; Luterbacher, J. S. Formaldehyde Stabilization Facilitates Lignin Monomer Production During Biomass Depolymerization. *Science* **2016**, *354*, 329−333. (d) Zhai, Y.; Li, C.; Xu, G.; Ma, Y.; Liu, X.; Zhang, Y. Depolymerization of Lignin via A Non-Precious Ni−Fe Alloy Catalyst Supported on Activated Carbon. *Green Chem.* **2017**, *19*, 1895−1903. (e) Sun, Z.; Bottari, G.; Afanasenko, A.; Stuart, M. C. A.; Deuss, P. J.; Fridrich, B.; Barta, K. Complete Lignocellulose Conversion with Integrated Catalyst Recycling Yielding Valuable Aromatics and Fuels. *Nat. Catal.* **2018**, *1*, 82−92. (f) Shao, Y.; Xia, Q.; Dong, L.; Liu, X.; Han, X.; Parker, S. F.; Cheng, Y.; Daemen, L. L.; Ramirez-Cuesta, A. J.; Yang, S.; Wang, Y. Selective Production of Arenes via Direct Lignin Upgrading over A Niobium-Based Catalyst. *Nat. Commun.* **2017**, *8*, 16104.

(5) (a) Rahimi, A.; Azarpira, A.; Kim, H.; Ralph, J.; Stahl, S. S. Chemoselective Metal-Free Aerobic Alcohol Oxidation in Lignin. *J. Am. Chem. Soc.* **2013**, *135*, 6415−6418. (b) Nguyen, J. D.; Matsuura, B. S.; Stephenson, C. R. J. A Photochemical Strategy for Lignin Degradation at Room Temperature. *J. Am. Chem. Soc.* **2014**, *136*, 1218−1221. (c) Rahimi, A.; Ulbrich, A.; Coon, J. J.; Stahl, S. S. Formic-Acid-Induced Depolymerization of Oxidized Lignin to Aromatics. *Nature* **2014**, *515*, 249. (d) Zhu, R.; Wang, B.; Cui, M.; Deng, J.; Li, X.; Ma, Y.; Fu, Y. Chemoselective Oxidant-Free Dehydrogenation of Alcohols in Lignin Using Cp*Ir Catalysts. *Green Chem.* **2016**, *18*, 2029−2036.

(6) (a) Harms, R. G.; Markovits, I. I. E.; Drees, M.; Herrmann, H. C. M. W. A.; Cokoja, M.; Kühn, F. E. Cleavage of C-O Bonds in Lignin Model Compounds Catalyzed by Methyldioxorhenium in Homogeneous Phase. *ChemSusChem* **2014**, *7*, 429−434. (b) Galkin, M. V.; Samec, J. S. M. Selective Route to 2-Propenyl Aryls Directly from Wood by A Tandem Organosolv and Palladium-Catalysed Transfer Hydrogenolysis. *ChemSusChem* **2014**, *7*, 2154−2158. (c) Zhang, B.; Li, C.; Dai, T.; Huber, G. W.; Wang, A.; Zhang, T. Microwave-Assisted Fast Conversion of Lignin Model Compounds and Organosolv Lignin over Methyltrioxorhenium in Ionic Liquids. *RSC Adv.* **2015**, *5*, 84967−84973. (d) Galkin, M. V.; Smit, A. T.; Subbotina, E.; Artemenko, K. A.; Bergquist, J.; Huijgen, W. J. J.; Samec, J. S. M. Hydrogen-Free Catalytic Fractionation of Woody Biomass. *ChemSusChem* **2016**, *9*, 3280−3287. (e) Luo, N.; Wang, M.; Li, H.; Zhang, J.; Hou, T.; Chen, H.; Zhang, X.; Lu, J.; Wang, F. Visible-Light-Driven Self-Hydrogen Transfer Hydrogenolysis of Lignin Models and Extracts into Phenolic Products. *ACS Catal.* **2017**, *7*, 4571−4580. (f) Zhang, J.-W.; Lu, G.-P.; Cai, C. Self-Hydrogen Transfer Hydrogenolysis of *β*-O-4 Linkages in Lignin

Catalyzed by MIL-100(Fe) Supported Pd-Ni Bmnps. *Green Chem.* **2017**, *19*, 4538−4543. (g) Wu, X.; Fan, X.; Xie, S.; Lin, J.; Cheng, J.; Zhang, Q.; Chen, L.; Wang, Y. Solar Energy-Driven Lignin-First Approach to Full Utilization of Lignocellulosic Biomass under Mild Conditions. *Nat. Catal.* **2018**, *1*, 772−780.

(7) Nichols, J. M.; Bishop, L. M.; Bergman, R. G.; Ellman, J. A. Catalytic C-O Bond Cleavage of 2-Aryloxy-1-Arylethanols and Its Application to the Depolymerization of Lignin-Related Polymers. *J. Am. Chem. Soc.* **2010**, *132*, 12554−12555.

(8) Wu, A.; Patrick, B. O.; Chung, E.; James, B. R. Hydrogenolysis of *β*-O-4 Lignin Model Dimers by A Ruthenium-Xantphos Catalyst. *Dalton Trans* **2012**, *41*, 11093−11106.

(9) Huo, W.; Li, W.; Zhang, M.; Fan, W.; Chang, H.-M.; Jameel, H. Effective C-O Bond Cleavage of Lignin *β*-O-4 Model Compounds: A New RuHCl(CO)(PPh$_3$)$_3$/KOH Catalytic System. *Catal. Lett.* **2014**, *144*, 1159−1163.

(10) Vom Stein, T.; Den Hartog, T.; Buendia, J.; Stoychev, S.; Mottweiler, J.; Bolm, C.; Klankermayer, J.; Leitner, W. Ruthenium-Catalyzed C-C Bond Cleavage in Lignin Model Substrates. *Angew. Chem., Int. Ed.* **2015**, *54*, 5859−5863.

(11) (a) Jastrzebski, R.; Constant, S.; Lancefield, C. S.; Westwood, N. J.; Weckhuysen, B. M.; Bruijnincx, P. C. A. Tandem Catalytic Depolymerization of Lignin by Water-Tolerant Lewis Acids and Rhodium Complexes. *ChemSusChem* **2016**, *9*, 2074−2079. (b) Lancefield, C. S.; Teunissen, L. W.; Weckhuysen, B. M.; Bruijnincx, P. C. A. Iridium-Catalysed Primary Alcohol Oxidation and Hydrogen Shuttling for the Depolymerisation of Lignin. *Green Chem.* **2018**, *20*, 3214−3221.

(12) (a) Renders, T.; Van Den Bosch, S.; Koelewijn, S. F.; Schutyser, W.; Sels, B. F. Lignin-First Biomass Fractionation: the Advent of Active Stabilisation Strategies. *Energy Environ. Sci.* **2017**, *10*, 1551−1557. (b) Rinaldi, R. A Tandem for Lignin-First Biorefinery. *Joule* **2017**, *1*, 427−428. (c) Cao, Z.; Dierks, M.; Clough, M. T.; Daltro De Castro, I. B.; Rinaldi, R. A Convergent Approach for A Deep Converting Lignin-First Biorefinery Rendering High-Energy-Density Drop-In Fuels. *Joule* **2018**, *2*, 1118−1133.

(13) (a) Cheng, J.; Zhu, M.; Wang, C.; Li, J.; Jiang, X.; Wei, Y.; Tang, W.; Xue, D.; Xiao, J. Chemoselective Dehydrogenative Esterification of Aldehydes and Alcohols with A Dimeric Rhodium-(II) Catalyst. *Chem. Sci.* **2016**, *7*, 4428−4434. (b) Wang, X.; Wang, C.; Liu, Y.; Xiao, J. Acceptorless Dehydrogenation and Aerobic Oxidation of Alcohols with A Reusable Binuclear Rhodium(II) Catalyst in Water. *Green Chem.* **2016**, *18*, 4605−4610. (c) Li, J.; Liu, Y.; Tang, W.; Xue, D.; Li, C.; Xiao, J.; Wang, C. Atmosphere-Controlled Chemoselectivity: Rhodium-Catalyzed Alkylation and Olefination of Alkylnitriles with Alcohols. *Chem. - Eur. J.* **2017**, *23*, 14445−14449.

(14) Kishimoto, T.; Uraki, Y.; Ubukata, M. Easy Synthesis of *β*-O-4 Type Lignin Related Polymers. *Org. Biomol. Chem.* **2005**, *3*, 1067−1073.

(15) Guo, H.; Zhang, B.; Qi, Z.; Li, C.; Ji, J.; Dai, T.; Wang, A.; Zhang, T. Valorization of Lignin to Simple Phenolic Compounds over Tungsten Carbide: Impact of Lignin Structure. *ChemSusChem* **2017**, *10*, 523−532.