Reductive Degradation of Lignin and Model Compounds by Hydrosilanes

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S *Supporting Information*

ABSTRACT: The exploitation of lignin, the second most abundant naturally occurring polymer on earth, has been hampered by its network structure, which makes it difficult to process. Hydrosilanes have previously been shown to convert aryl ethers to hydrolyzable silyl ethers in the presence of $B(C_6F_5)_3$. We demonstrate that the process is general and can be used to convert model lignin compounds to both aryl silyl ethers and alkanes. The relative reactivity of functional groups on model lignin compounds was found to be phenol > primary alcohol > methoxybenzene > alkyl silyl ethers. The process thus leads to cleavage of β-O-4, α-O-4, and methoxybenzene groups with concomitant silylation of phenolic and secondary alcohol groups. At longer time points provided sufficient silane was present, the full reduction of primary and secondary alcohols to alkyl groups was observed. Softwood lignin itself could only be partially solubilized ($\sim$30%) even using excess hydrosilane and high catalyst loadings; the products were not characterized in detail. The lack of further degradation was attributed to its highly branched network structure containing 5-5, β-5, 4-O-5, and other linkages derived from coniferyl alcohol monomers that are not susceptible to reductive silylation. By contrast, over 95% of hardwood lignin was efficiently reduced/degraded into organosoluble products by the monofunctional hydrosilane $HMe_2SiOSiMe_3$ over a few hours at 50 °C. The molecular weight of the silylated products was consistent with oligomeric structures comprised of 3−8 linked aryl groups. This process holds promise to increase the accessibility to value-added products using lignin as a starting material.

KEYWORDS: *Lignin, Renewable resource, Piers−Rubinsztajn reaction, Reductive silylation, Silicone modification, Depolymerization*
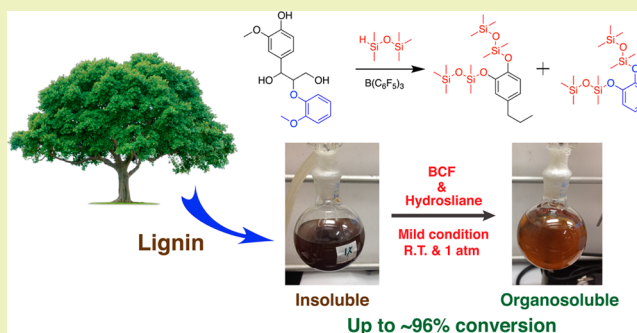
INTRODUCTION

Lignin is a complex polymeric network that works as a glue to bind and integrate the cellulose and hemicelluloses to form cell walls in plants. The biosynthesis of lignin essentially involves the oxidative polymerization of three monomers: p-coumaryl alcohol, coniferyl alcohol (G), and sinapyl alcohol (S) (Figure 1).[1,2] A variety of subtle differences exist between the lignins produced by different organisms. For example, the ratio of these basic building units found in lignin depends on its source.[2] The lignin derived from grass and softwood trees contains larger amounts of coniferyl alcohol units resulting in a more highly branched structure (Figure 1). By contrast, hardwood lignin generally consists of approximately equal amounts of coniferyl and sinapyl alcohol units, resulting in a more linear structure.[2−4]

Although lignin is the second most abundant naturally occurring polymer on the earth, with few exceptions it is not effectively used as a resource in industry. In the natural environment, the majority of lignin is degraded, and then recycled as a resource for carbon.[5] In industry, by contrast, due to the difficulties associated with processing lignin, it is generally used as a comparatively low-value fuel.[6] In spite of significant efforts, lignin is therefore not a feedstock chemical for the "biorefinery", with the exception of vanillin, which may

be obtained by extraction from spent sulfite liquors in Kraft pulping plants.[7−9]

Various methods, including biological, thermochemical, and catalytic reduction/degradation, have been explored to convert lignin into value-added chemicals;[4,10,11] the biodegradation of lignin has been comprehensively reviewed.[12−14] Thermochemical methods for lignin degradation include pyrolysis, hydrogenolysis, hydrolysis, gasification, and thermal oxidation.[10,15] These methods usually are associated with harsh temperature and pressure and rather poor efficiencies.

Catalytic processes would be expected to be able to convert lignin efficiently under mild conditions.[4] Although many catalysts have been developed and proved to efficiently degrade lignin model compounds,[4,16] few of them are able to degrade actual lignin with good conversion. Notable exceptions to this include the work of Yan et al., who achieved 42% conversion of lignin using a platinum catalyst.[17] Higher conversions were reported by using Ni−Mo (49−71%) or Cu−CrO (70% of lignin)[18,19] under rather vigorous thermal conditions. More efficient reduction of alkyl aryl and diaryl ethers could be
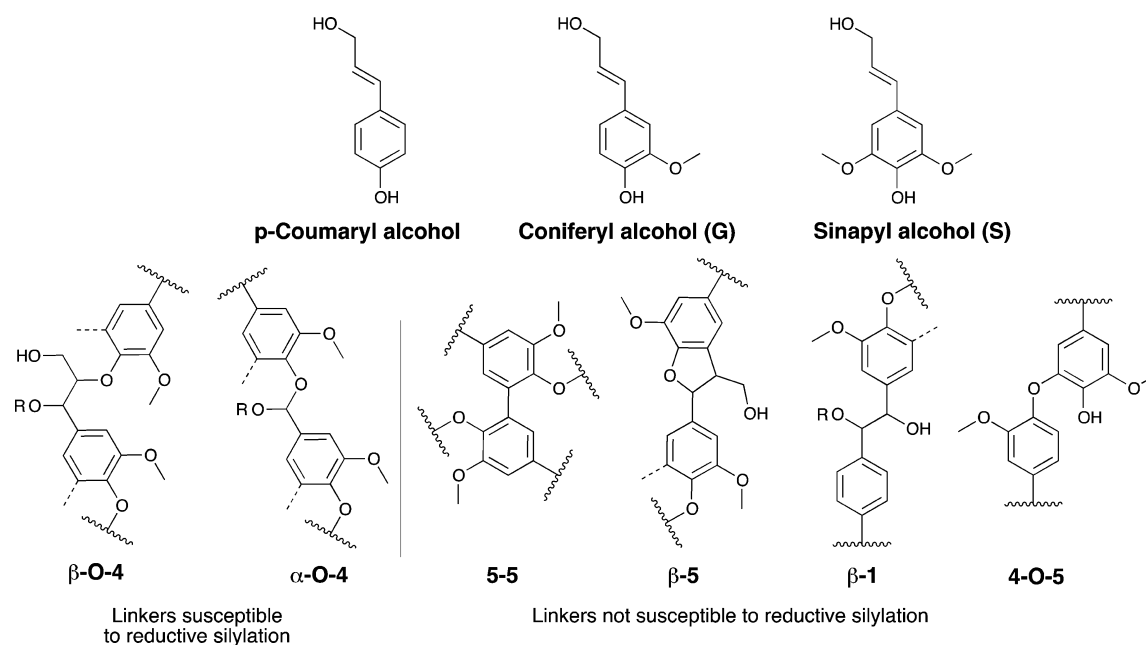
Figure 1. Three basic building units for lignin and some representative linkages found in lignin.

achieved with Ni-catalyzed protocols, which are potentially beneficial in the degradation of softwood lignin, but temperatures in excess of 100 °C and longer reaction times are required.[16,20,21]

$B(C_6F_5)_3$ (tris(pentafluorophenyl)borane) has been widely used as a catalyst for the reduction of organic compounds.[22,23] Functional groups including alcohols, aldehydes, ketones, carboxylic acids, and esters are reduced to silyl ethers and then, if sufficient hydrosilane is present, to alkanes, depending the reducing activity of the chosen hydrosilane (Figure 2).[24−27]
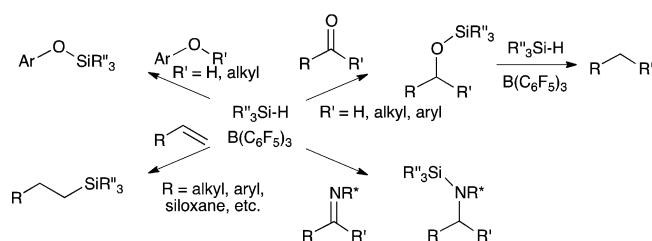

Figure 2. Facile reduction of organofunctional groups using hydrosilanes catalyzed by $B(C_6F_5)_3$.

Alkoxyphenyl and phenol groups are also converted to aryl silyl ethers.[28−30] In light of the structural analogy between these phenolic compounds and the functional aromatic rings and aliphatic alcohols found in lignin, we have examined the ability of this reductive silylation reaction to reduce model compounds of lignin and polymeric samples of hardwood and softwood lignin. A study of the degradation of selected model lignin compounds was recently published,[31] based on previously described silylation studies,[32] which showed that many of the functional groups found on lignin are susceptible to these reducing conditions. We describe the reduction of model compounds, relative reactivity of the functional groups that are found on model lignin compounds, and more importantly, examine the ability of these reducing conditions to convert mostly insoluble hardwood lignin into smaller, silylated, organosoluble oligomers.

EXPERIMENTAL SECTION

Materials. Lignin model compounds: 3-hydroxy-4-methoxybenzyl alcohol, 3-phenyl-1-propanol, 1-phenyl-2-propanol, sinapyl alcohol, 2-phenoxy-1-phenylethanol, guaiacylglycerol-beta-guaiacyl ether, diphenyl ether, and benzyl phenyl ether were purchased from Sigma-Aldrich and used as received. Hydrosilanes: pentamethyldisiloxane (PMDS), dimethylphenylsilane (Me₂PhSiH), methyldiphenylsilane (MePh₂SiH), triethylsilane (Et₃SiH), and poly(hydromethylsiloxane) (Me₃Si(OSiMeH)ₙOSiMe₃, PHMS) were purchased from Gelest. Solvents were purchased from Caledon Laboratories and used after drying over activated alumina. The catalyst, $B(C_6F_5)_3$ (Sigma-Aldrich), was dissolved in dry toluene to prepare a stock solution (40 mg/mL, 78.13 mM). Tetra-n-butylammonium fluoride (TBAF, Sigma-Aldrich) was dissolved in THF containing 1% of methanol (TBAF in THF solution, 0.01 mg/mL). Hardwood lignin (Kraft lignin isolated by FPInnovations Lignoforce Technology)[33] was provided by FPInnovations, Montreal, Canada, and softwood lignin was provided by Weyerhaeuser, Tacoma, Washington, U.S.A. and used after partial drying in a desiccator under vacuum over Dri-rite.

Methods. NMR spectra were recorded on a Bruker Avance 600 MHz nuclear magnetic resonance spectrometer using chloroform-d or DMSO-d_6. The proton impurity of the deuterated solvent was used as a reference for ¹H NMR spectra (for chloroform = 7.24 ppm, for DMSO = 2.50 ppm). For model compounds, 16 scans were sufficient for the ¹H NMR, while for lignin samples, 128 scans were needed for ¹H NMR and 2048 for ¹³C NMR.

Molecular weights were established by gel permeation chromatograph using a Waters 590 HPLC pump with three Waters Styragel columns (HR2, HR3, and HR4) at 40 °C and a Waters 410 differential refractometer operating at 35 °C (Table 1). The eluent, at a flow rate of 0.5 mL/min, was 50 mM LiBr dissolved in N,N-dimethylformamide (DMF), and the system was calibrated with PEG standards (Waters) with molecular weights ranging from 600 to 252,000 g/mol.

The silylated derivatives of lignin model compounds were additionally characterized by molecules that were characterized by GC/MS using an Agilent 6890N GC coupled to an Agilent 5973N mass selective detector (MSD) run in EI mode. The GC flow rate was 1 mL/min through a column (DB17-ht 30 m length × 0.25 mm ID, 0.15 um film thickness, a 50/50 mix of methyl/phenyl silicone phase).

Infrared spectroscopy was used to characterize the functional group change during the degradation of hardwood lignin by running under

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Table 1. Molecular Weight Profile^a of Lignin before and after Reduction

	Mn	Mw
hardwood lignin	3640	30,860
reduced, then desilylated, hardwood lignin fragments^b	440	465

^{a}Solvent: DMF containing 50 mM LiBr determined using poly-(ethylene oxide) standards. ^{b}After reduction, the silyl ethers were removed by treatment with TBAF (Supporting Information). Note, these values are below the lowest calibration standard (600 MW) and are thus estimates.

diffuse reflectance infrared Fourier transform mode (DRIFTS, Thermo Nicolet 6700, scan number = 64, resolution = 4 cm^{-1}).

Reduction of Lignin Model Compounds. The reaction conditions for reduction of model lignin compounds are given in Table 2. The general experimental procedure is as follows. The model compound was dissolved in an appropriate solvent (dry toluene, hexane, or chloroform) to which was added the hydrosilane. Then the catalyst solution was added to initiate the reaction. The mixture was sonicated in a 50 °C water bath for 3 h. After reaction, neutral alumina (~1 g) was added to facilitate removal of the catalyst. The resultant solution was filtered, purified by silica chromatography, and the appropriate fractions concentrated under reduced pressure. The products were examined using ^{1}H NMR and GC-MS.

Reduction of Lignins. Softwood and hardwood lignin samples were separately treated using the same protocol. Lignin (low water content <5%, powdered, average particle size = 45 ± 10 μm) was dispersed in dry toluene and then mixed with the appropriate hydrosilane and B(C$_6$F$_5$)$_3$. Extensive experimentation was used to optimize the reduction conditions (Table 3). In particular, this involved the catalyst concentration, concentration of SiH groups in structurally different silanes, and solvents. The suspension was sonicated in a 50 °C water bath for 3 h. The residual undissolved lignin material was washed with toluene and separated by centrifugation (Thermo, Durafuge 100, at 4000 rpm for 20 min). This process was repeated at least three times to completely extract soluble compounds. The supernatants were mixed, and the solvent was removed under reduced pressure. Both the residual and reduced lignin products were examined with ^{1}H NMR, ^{13}C NMR, and GPC for hardwood lignin.

The efficiency of the reduction/degradation of lignin samples was found to strongly depend on catalyst concentration. A separate suite of experiments was used to probe the change in reduction with catalyst concentration. Hardwood lignin was exposed to the reduction conditions with catalyst concentrations starting from 2 wt % B(C$_6$F$_5$)$_3$ (52.5 μL of catalyst containing 2.1 mg of B(C$_6$F$_5$)$_3$) for 105 mg of lignin in 20 mL of toluene with 6 mL of PMDS) up to 10.2 wt % catalyst. Each batch of lignin was allowed to react for a given period of

time, separated from the reaction mixture by centrifugation at 4000 rpm for 20 min (Thermo, Durafuge 100), decanted, and washed with toluene. For some samples, following this reaction sequence, the residue was subjected to a secondary reduction using additional catalyst (B(C$_6$F$_5$)$_3$, 105 μL of catalyst) in toluene (20 mL) and PMDS (6 mL) to first 5.8 wt % and, after an additional wash sequence, a third reduction with 10.2 wt % catalyst (Supporting Information). For each reaction step, reduction was carried out for 3 h sonication in a 50 °C water bath; the suspension was centrifuged, then washed, and recentrifuged (repeated three times). The combined supernatants (from each of the four centrifugations) were combined and purified by removing the solvent by rotary evaporation. Both solid and soluble residues, after evaporation of solvents, were characterized by NMR and FT-IR.

During reduction of hardwood lignin with hydrosilanes, the lignin fragments become partially silylated, typically on phenolic residues. The groups were desilylated by treatment with TBAF solution (dissolved in THF containing 1% methanol) for 48 h. The solvent and siloxane fragments were removed by using a rotary evaporator, and the TBAF was removed by washing the residue with distilled water. After this purification, the sample was dried under vacuum overnight.

■ RESULTS AND DISCUSSION

A suite of model lignin compounds was chosen, as broadly as possible, to match the functional group patterns found in native lignin. The functional groups present included primary, secondary, allylic, and benzylic alcohols; methoxybenzene and other alkoxybenzenes; and a conjugated alkene. As shown in Figure 3, the ability of B(C$_6$F$_5$)$_3$ and Si−H, in the form of PMDS, to reduce these functional groups was explored using a catalyst loading of 0.01−0.3 mol %. Each reaction was optimized to use as little catalyst as possible and still have efficient reactions that would be completed within 0.5 h (Table 2).[4,10,34] A small amount of organic solvent was added to facilitate the reaction. A large molar excess of PMDS was used both to accelerate the process and because a side reaction leading to silicone polymers competes under these conditions (see below).

Hydrosilanes in the presence of B(C$_6$F$_5$)$_3$ efficiently reduced both alcohols and aryl ethers (Figure 3); aliphatic primary, secondary, and allylic alcohols were reduced completely to the corresponding alkanes. For example, 3-phenyl-1-propanol was reduced to *n*-propylbenzene, and ethylbenzene was produced from the reduction of 2-phenoxy-1-phenylethanol (Supporting Information). In the case of 1-phenyl-2-propanol, only partial reduction of the alcohol was initially observed under the conditions used (Supporting Information). Secondary silyl

Table 2. Reaction Conditions and Yields of Model Compounds

	model compound (mmol)	PMDS (mmol)	B(C$_6$F$_5$)$_3$ (μmol)^a	mL^b (solvent)	yield^c (%)
3-phenyl-1-propanol	3.62	11.28	9.77	1 (H)	72^d
1-phenyl-2-propanol	3.79	12.03	9.77	1 (H)	70^e
sinapyl alcohol	0.143	10.0	0.98	3 (T)	NA^f
2-phenoxy-1-phenylethanol	0.08	1.03	2.73	1 (H)	64^e
3-hydroxy-4-methoxybenzyl alcohol	3.23	16.33	9.77	3 (T)	86^e
benzyl phenyl ether	2.72	5.02	15.63	1 (H)	70^e
guaiacylglycerol-beta-guaiacyl ether	0.006	5.0	0.4	3 (T)	>90^g
diphenyl ether	4.25	10.33	11.67	1 (T)	NR^h

^{a}For model compounds, catalyst loadings ranged from about 0.01−0.3 mol %. ^{b}Solvent: (H) = hexane, (T) = toluene. ^{c}Note: Conversion by NMR exceeded 90% in all cases. ^{d}It was not possible to separate the silicone from the propylbenzene products by silica chromatography. The yield is based on mass recovered and the NMR, which showed only two products (Supporting Information). ^{e}Yield of silyl ether; alkylbenzene was lost during evaporation. ^{f}A complex mixture of products was isolated including hydrosilylation of the alkene and partial and complete reduction the alkene. ^{g}Yield estimated from NMR; outcome was limited by the small scale reaction (~2 mg). ^{h}No reaction was observed when diphenyl ether was treated with PMDS and B(C$_6$F$_5$)$_3$.

Table 3. Reaction Conditions for Degradation of Hardwood and Softwood Lignin

type of lignin	starting mass of lignin (mg)	isolated/residual products[a] (mg)	solubilization efficiency[b] (%)	hydrosilane (mL)	$B(C_6F_5)_3$ vol (μL)	$B(C_6F_5)_3$ wt %[d]	toluene (mL)
softwood	87.1	91.4	$-^c$	PMDS (6)	108	5	20
	99.3	109.0	$-^c$	PMDS (6)	248	10	20
	108	88.6	18.0	Me_2PhSiH (6)	264	10	20
	49.6	56.7	$-^c$	$MePh_2SiH$ (3)	132	10	10
	50.2	97.2	$-^c$	PHMS (3)	132	10	10
	53.7	37.8	29.6	Et_3SiH (3)	132	10	10
hardwood	122.9	90.2	26.6	PMDS (8)	30.7	1	50
	163.0	92.4	43.3	PMDS (10)	200	5	70
	41.1	2.8	93.2	PMDS (3)	60	6	15
	157.4	6.9	95.5	PMDS (10)	394	10	70

[a]Decrease in weight of isolated product compared to starting lignin reflects the formation of organosoluble materials. [b](1 − Final insoluble weight/ starting insoluble weight) × 100. [c]Data could not obtained because the mass of silylated isolated product was higher than the mass of starting lignin. [d]Catalyst concentrations (wt %, weight of catalyst/weight of lignin ×100) ranged from 1% to 10%. Additional experimentation (data not shown) demonstrated there was a large change in efficiency of reduction starting at about 6 wt % catalyst.
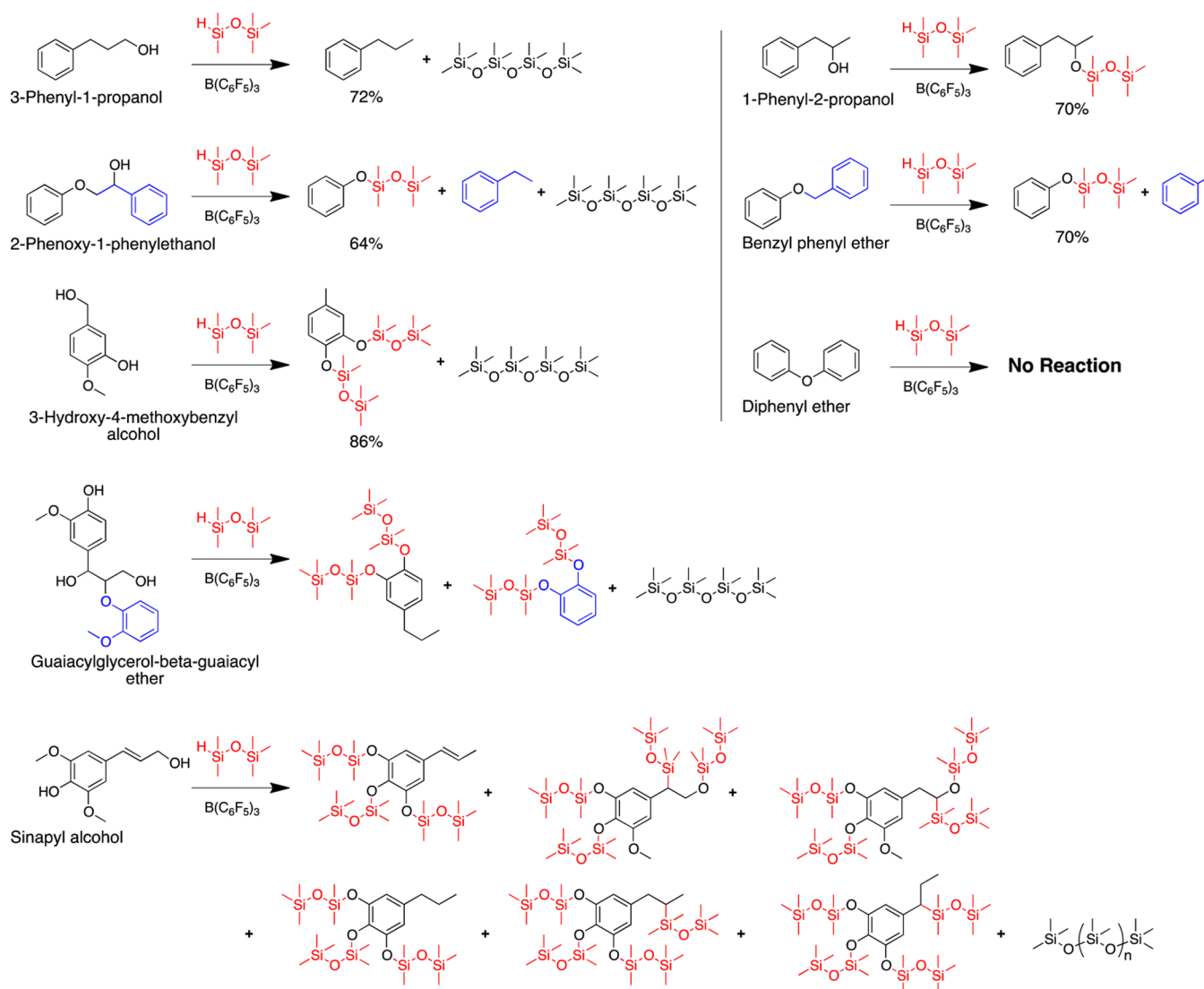

Figure 3. Reaction of model lignin compounds with PMDS in the presence of $B(C_6F_5)_3$.

ethers are much more resistant to reduction to the alcohol than primary ethers.[26,35] However, the secondary silyl ether could be further reduced to the alkane if a larger excess of hydrosilane and/or a longer reaction time was used (Supporting Information). The allylic alcohol of sinapyl alcohol was also cleanly reduced to the alkane, a process that was accompanied by partial hydrosilylation of the alkene leading to an inseparable mixture of regioisomeric products (Supporting Information).
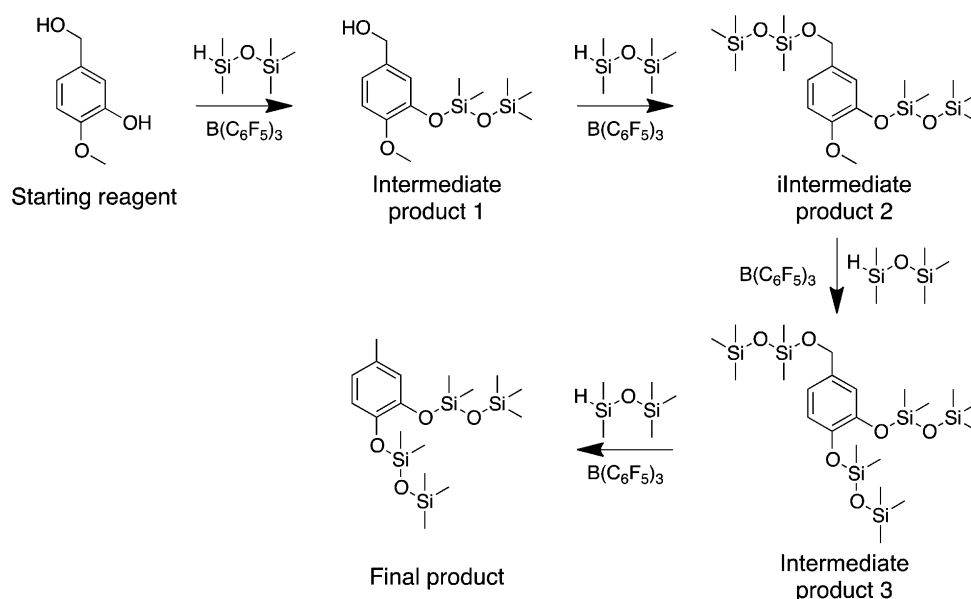
Figure 4. Staged reduction of 3-hydroxy-4-methoxybenzyl alcohol. The relative reactivity order is phenol > primary alcohol > methoxybenzene > aliphatic silyl ether ≫ aromatic silyl ether.

The ether bond between two aromatic rings (corresponding to the 4-O-5 linkage in lignin, Figure 1) was not reduced under these conditions. When diphenyl ether was treated with PMDS and $B(C_6F_5)_3$, there was no change in the ^1H NMR and ^{13}C NMR spectra (Supporting Information). However, aryl alkyl ethers and phenols were cleanly converted into phenyl silyl ethers under the reaction conditions forming hydrogen or methane byproducts, respectively. This was clearly observed in the reduction of 3-hydroxy-4-methoxybenzyl alcohol (Supporting Information). Most important when developing processes to degrade lignin is the ability to cleave the phenyl/alkyl ethers that bridge aromatic residues. The reduction of benzyl phenyl ether demonstrated that α-O-4 linkages (Figure 1) could be easily cleaved, and the β-O-4 linkage in 2-phenoxy-1-phenyl-ethanol was cleaved even though there was no functional group in the γ position, as previously reported.[31]

The relative reactivity of the different groups present in lignin was determined using the model multifunctional compound 3-hydroxy-4-methoxybenzyl alcohol. Staged reductions were achieved by sequentially adding molar equivalents of the hydrosilane. The phenolic alcohol was found to be more reactive than the other functional groups (Figure 4, Supporting Information). Additional hydrosilane then led to the stepwise loss of the benzylic alcohol and then the methoxy–benzene group. While the aliphatic ether was finally reduced to the alkane, the aryl silyl ether was stable under these conditions, as previously reported.[26]

Guaiacylglycerol-beta-guaiacyl ether is a model compound with a structure that is particularly closely related to lignin polymers and is therefore widely used as a representative model compound.[4,34] Compared to guaiacylglycerol-beta-guaiacyl ether, a huge molar excess of PMDS (Table 2) was used in order to mimic the conditions that were necessary for actual lignin degradation (see below). The β-O-4 linkage, which is an important primary linkage in lignin, was cleaved efficiently using PMDS in the presence of $B(C_6F_5)_3$. In addition, the methoxybenzene and phenolic groups were converted to aryl silyl ethers, and both the primary aliphatic and benzylic alcohols were reduced to alkanes via the silyl ether (vide infra).

Figure 5 shows the ^1H NMR spectra of guaiacylglycerol-beta-guaiacyl ether before and after degradation. The methoxy groups in the starting compound were found at 3.85 ppm, and the peaks for α, β, and γ protons (with respect to the aryl ring) were found at 5.57, 4.96, and 3.64 ppm, respectively. After degradation, the methoxy groups had completely disappeared (via methane formation), while the peaks of α, β, and γ protons shifted to 2.45, 1.6, and 0.9 ppm, respectively. The two products shown were also identified by GC/MS (Supporting Information). These findings suggested that lignin itself could be reduced into much smaller oligomeric structures under these conditions. To test this hypothesis, we examined the reaction with both softwood and hardwood lignin.

Extensive attempts were made to render softwood lignin organosoluble by reducing/degrading it with hydrosilanes in the presence of $B(C_6F_5)_3$ using the conditions optimized for model compounds. However, after reaction in a 50 °C water bath for 3 h, with sonication to facilitate both reagent ingress and lignin particle degradation, suspensions of softwood lignin in neat disiloxane PMDS containing $B(C_6F_5)_3$ (up to 10 wt %) exhibited no visible changes (Supporting Information). Less than 10% by weight of the lignin was converted to organosoluble materials, as determined by collection and evaporation of the supernatant after centrifugation. Attempts were therefore made to degrade the softwood lignin using hydrosilanes with different chemical structures, such as monomeric $MePh_2SiH$ and Me_2PhSiH (both aromatic, similar to lignin monomers), Et_3SiH (different steric hindrance), and polymeric PHMS (high density of reducing functional groups). Although all the silanes (PMDS, $MePh_2SiH$, and PHMS) led to some reduction (Table 3, Supporting Information), there was only a modest increase in the fraction of organosoluble products. The small organosilanes Me_2PhSiH (~13% converted to soluble products) and Et_3SiH (~30% converted to soluble products) were only marginally better at breaking down the lignin into organosoluble products than PMDS. This might be associated with improved solubility of these hydrosilanes in lignin. The impact of catalyst concentration on silylation efficiency with the silanes was also studied. However, increasing
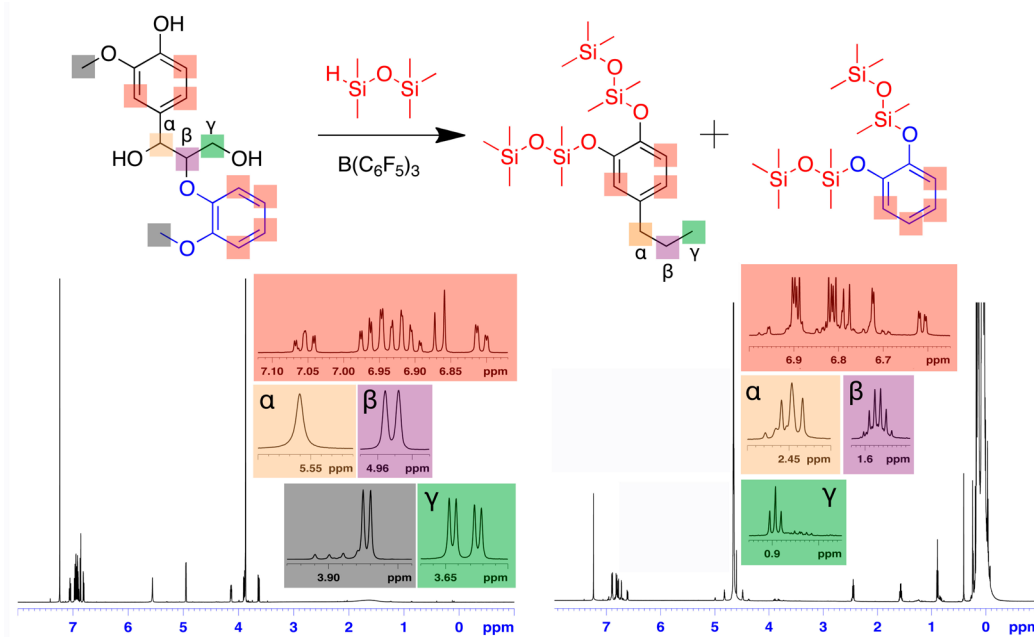
Figure 5. ^{1}H NMR of guaiacylglycerol-beta-guaiacyl ether and its silylated products (solvent CDCl$_3$).

the catalyst concentration up to 10 wt % did not lead to further improvements in conversion (Table 2).

The insoluble fraction of all the softwood lignin reduction reactions often exhibited weight gain, consistent with silylation of the surface functional groups but not the required removal of cross-links. Silylation was also qualitatively observed through the enhanced water repellency of the modified surface; the insoluble product would float on, but not disperse in, water.

Given that the desired efficient degradation of softwood lignin was not observed, the product characterization was limited to ensuring that reduction had actually taken place. For the most efficient degradation, performed with Et$_3$SiH, the organosoluble product mixture was further characterized with ^{1}H NMR and ^{13}C NMR (Supporting Information). The chemical shifts for oxygenated aliphatic protons (near 4 ppm) in the ^{1}H NMR of softwood lignin disappeared, while new peaks associated with aliphatic protons ranging from 0 to 2 ppm were observed. Also, new signals for the reduced carbon were found ranging from 10 to 30 ppm in ^{13}C NMR.

Thus, reductive silylation and degradation of softwood lignin are occurring but not nearly as efficiently as would be expected from the model compound studies. The challenge of efficiently degrading softwood lignin by reduction may be attributed to its chemical structure. G units are more abundant than S units in softwood lignin.[1] Many linkages associated with G units exhibit direct carbon chain connectivity or a single oxygen between aryl groups, neither of which is susceptible to reductive silylation. Linkages such as 5-5, β-5, β-1, and 4-O-5 (Figure 1) that are not expected to react under these relatively mild conditions (as shown by the model study with diphenyl ether) will also impede fragmentation and simultaneously the ingress of reagents.[2,4] In light of the inability to encourage efficient degradation of softwood lignin, the objective of this work, we turned to hardwood lignin.

Hardwood lignin was much more easily reduced/degraded than softwood lignin by hydrosilanes in the presence of B(C$_6$F$_5$)$_3$. The process was found to be dependent on the chemical structure of the hydrosilane and the catalyst and

hydrosilane concentrations. Using the protocol described above for model compounds, PMDS, a monofunctional low viscosity Si−H bearing disiloxane, was found to be suitable for hardwood reduction/degradation. Unlike the model compounds, a large excess of the reagent was necessary to reduce raw lignin. The reaction productivity was highly dependent on catalyst concentration. When the catalyst was present below 5 wt % (weight ratio B(C$_6$F$_5$)$_3$ to mass of raw lignin), up to about 43% of the lignin could be reduced/degraded to soluble materials, while at higher catalyst concentrations, starting at 6%, over 90% of the lignin could be converted into organic solvent-soluble materials. These experiments were repeated several times and always showed this dependence of reactivity near 6 wt % B(C$_6$F$_5$)$_3$. The behavior may be ascribed to a variety of factors. Any Lewis bases present in the medium, including water, competitively complexed with B(C$_6$F$_5$)$_3$. Any such complexation reduces the effective concentration of active catalyst. The moisture content of the lignin is near 5 wt %, which on a molar basis is a large excess compared the concentration of B(C$_6$F$_5$)$_3$. In addition, a secondary reaction catalyzed by B(C$_6$F$_5$)$_3$ that occurs with the silanes will reduce the available catalyst for the desired reaction. Growth of linear silicone chains, with concomitant formation of volatile Me$_2$SiH$_2$, occurs under these conditions (2 Me$_3$SiOSiMe$_2$H → Me$_2$SiH$_2$ + Me$_3$SiOSiMe$_2$OSiMe$_3$ → longer polymers. For GC/MS, see sinapyl alcohol reduction in the Supporting Information).[36]

At the higher catalyst concentrations, the turbid black suspension typical of the lignin starting materials gave way to a clear light amber-colored solution (Supporting Information). The reaction was also much faster than with softwood lignin. For example, a hardwood lignin suspension containing 6% catalyst changed from brown opaque to yellow translucent after only 10 to 20 min of sonication at room temperature, whereas no obvious change in turbidity was observed with up to 6 h of treatment of the softwood lignin (Supporting Information).

After reduction/degradation, the hardwood lignin was converted into organosoluble fragments. The starting hardwood lignin, which showed molecular weights ranging up to
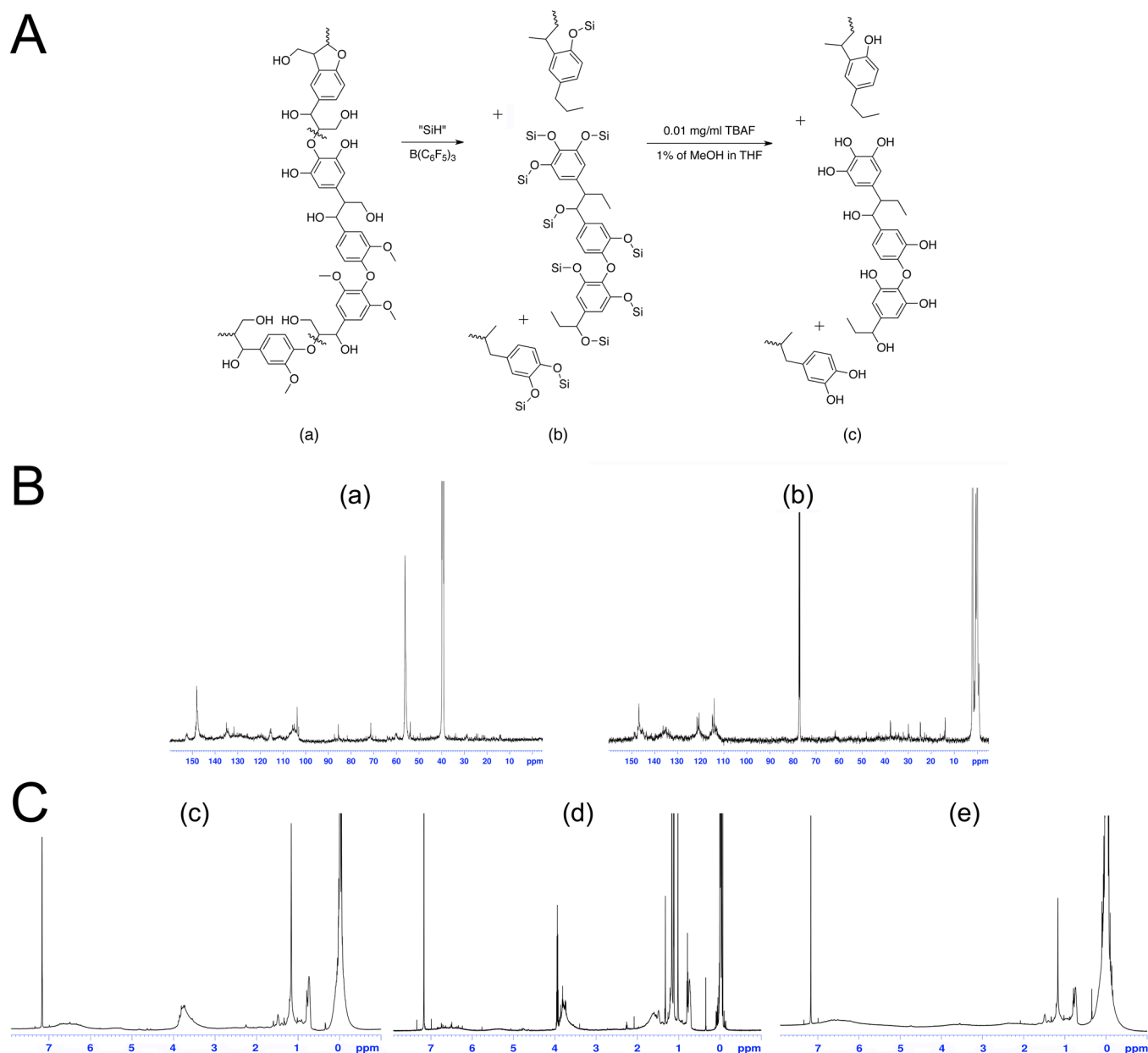
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Figure 6. (A) Schematic illustration of possible structural changes to lignin during reduction and desilylation. (B) ^{13}C NMR of (a) hardwood lignin and (b) reduced and silylated hardwood lignin fragments (in DMSO d_6 and CDCl$_3$, respectively). (C) Reduction with three different catalyst concentrations showing increasing reduction/silylation: (c) 2.0% B(C$_6$F$_5$)$_3$, (d) 5.8%, and (e) 10.2%. Samples were run in CDCl$_3$.

3600 g mol^{-1}, was converted, after reduction and then desilylation using TBAF (tetrabutylammonium fluoride),[37] to fragments of less than 600 g mol^{-1} (DMF with LiBr was used as solvent, Supporting Information). Figure 6A shows a model of structural changes of lignin that can occur during the degradation. In the ^{13}C NMR, as shown in Figure 6B(a), signals for the α/β carbons of β-O-4 and methyl carbons of phenyl methyl ethers in the starting lignin could be found in the ranges from 70 to 90 and 50 to 60 ppm.[38,39] However, after reduction by PMDS (Figure 6B(b)), the intensity of these signals was reduced with the concomitant formation of signals ranging from 10 to 40 ppm (alkyl groups) and near 0 ppm (silyl groups). Thus, the cleavage of β-O-4 linkers, reduction/silylation of α/γ alcohol, and silylation of phenyl methyl ethers occurred.

^{1}H NMR spectra of reduced hardwood lignin exhibited new chemical shifts between 0.8 and 1.5 ppm alkyl groups and near 0.0 ppm for methyl siloxane protons (including the isolated/ residual products) reflecting, as demonstrated with the lignin model compounds, cleavage of linkages (β-O-4 linkage, alcohol, and alkoxybenzene, etc.), and silylation of alcohols by hydrosilane PMDS. The changes are most easily observed from the three spectra showing increasing degrees of reduction/silylation produced with increasing catalyst concentrations (Figure 6C). The NMR spectral signals attributed to oxygenated aliphatic protons in the range of 3−4 ppm diminished in intensity or disappeared with increased catalyst loading, while the aliphatic (deoxygenated) signals in the range of 0.6−2 ppm increased concomitantly. As with softwood lignin, the 5-5, β-5, β-1, and 4-O-5 linkages in hardwood lignin were not expected to react. However, they have low abundance

in this polymer, and therefore, it is possible to break the material into lower molecular weight organosoluble fragments.

FT-IR spectra of soluble products collected from the first, second, and third reductions were also used to track the structural changes of lignin. As shown in Figure 7, the exhibited
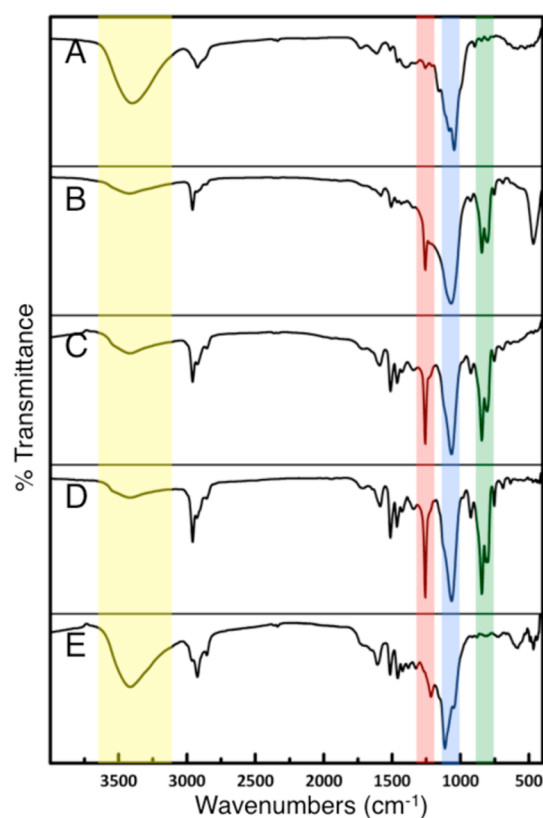

Figure 7. FT-IR spectra of hardwood lignin and its reduced/degraded products: (A) residual/isolated product. Soluble products collected from the (B) third, (C) second, and (D) first reduction processes. (E) unmodified hardwood lignin (yellow, OH groups; red, Si—O; blue, Ph—O/C—O; green, Si—O and Si—CH$_3$).

bands of increasing intensity at 1258, 1040, and 790 cm^{-1} (highlighted by red, blue, and green boxes) are consistent with the presence of Si—O—Si, Si—CH$_3$, O—Si—CH$_3$, and Si(CH$_3$)$_2$ functional groups, respectively, while the bands at 1214, 1324, 1378, and 2850 cm^{-1} due to the C—O and O—CH$_3$ groups etc., either weakened or disappeared with increasing catalyst loading. A dramatic drop in the intensity of the −OH peaks above 3000 cm^{-1} was observed in the IR spectra of soluble products. Note that the Si—O—Si linkages can originate both from silyl ethers (Ar-OSiMe$_2$OSiMe$_3$) and the silicone polymers produced in the reaction.

Lignin is an underexploited resource primarily due to the difficulties in breaking down aromatic network polymer chains. Reactions with model compounds demonstrate that the combination of hydrosilanes and B(C$_6$F$_5$)$_3$ efficiently silylate aryl alkyl ethers and phenols and, in addition, reduce aliphatic alcohols to alkyl groups. Softwood lignin contains a significant fraction of coniferyl alcohol (G) units that are not susceptible to the reductive conditions presented here. As a consequence, while it is possible to surface modify the lignin particles, it is difficult to reduce the network polymer to low molecular weight soluble fragments. Hardwood lignin with low concentrations of coniferyl alcohol (G) units, by contrast, underwent

reductive silylation giving over 90 wt % of organosoluble products under rather mild conditions. This provides a convenient route to take a readily available thermoset polymer and convert it into low molecular weight materials that are much more amenable for further processing.

CONCLUSIONS

Lignin is a network polymer comprised of linked aromatic rings. Many of the functional groups, including alcohols, phenols, and aryl alkyl ethers, are susceptible to reductive silylation by hydrosilanes in the presence of B(C$_6$F$_5$)$_3$. Methoxybenzene groups and β-O-4 and α-O-4 linkages in model compounds were cleaved to give phenyl silyl ethers and the corresponding hydrocarbons. Alcohols and phenols were silylated and, in the case of alkyl silyl ethers, reduced to corresponding hydrocarbons. The relative reactivity was found to follow the order of phenol > primary alcohol > methoxy > silyl ether. Softwood lignin was surface modified with silyl groups, but solubilization was limited to about 30 wt % because many of the linkages derived from coniferyl alcohol units are not susceptible to the reaction. By contrast, hardwood lignin, which has a much lower fraction of such groups, was reduced/degraded very efficiently by monofunctional hydrosilanes. The efficiency of the reduction process depended on B(C$_6$F$_5$)$_3$ concentration. At higher concentrations, up to 10%, over 95% of hardwood lignin could be rendered soluble in organic solvents.

ASSOCIATED CONTENT

ⓈSupporting Information

^{1}H NMR of reduction products of 2-phenoxy-1-phenylethanol, 1-phenyl-2-propanol, 3-phenyl-1-propanol, benzyl phenyl ether, 3-hydroxy-4-methoxybenzyl alcohol (including staged reductions), diphenyl ether, sinapyl alcohol, and guaiacylglycerol-beta-guaiacyl ether; GC/MS of sinapyl alchol and guaiacylglycerol-beta-guaiacyl ether; general processes for reduction; ^{1}H NMR of softwood lignin soluble fractions; reaction outcomes with hardwood lignin and different catalyst loadings; changes in turbidity with reductive silylation; and GPC data for the hardwood lignin before and after reductive silylation (and after desilylation). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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