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Efficient reductive depolymerization of hardwood and softwood lignins with Brookhart's iridium(III) catalyst and hydrosilanes

Louis Monsigny,^a Elias Feghali,^a Jean-Claude Berthet,^a and Thibault Cantat^{*,a}

Efficient catalytic reduction of lignin model molecules and reductive depolymerization of softwood and hardwood lignins is presented with the iridium based Brookhart's catalyst and hydrosilanes R_3SiH as reductant. This catalyst displays increased stability and selectivity in comparison to the $B(C_6F_5)_3$ /hydrosilane system and it enables a convergent reductive depolymerization of wood lignins to isolable mono-aromatics.

Introduction

Accounting for 15-30 % of organic carbon in the biosphere, lignin is a prominent biopolymer, present in wood, plants, and agricultural residues. Because it derives from aromatic monolignols (Figure 1), this material can be viewed as a large and sustainable source of aromatic chemicals that could advantageously replace petrochemicals in the long run.^{1,2} Whereas lignin is currently burnt to supply energy in the pulp and paper industry, the chemical valorization of this biopolymer requires the selective deconstruction of its polymeric structure into a narrow range of molecules. Such endeavor remains a challenge at present due to the chemical stability and heterogeneity of lignin and the lack of robust and active catalysts as well as reaction conditions of general applicability.³⁻⁸ With a high content of α -O-4 and β -O-4 etheral linkages (up to 70%, Fig. 1),^{9,10} the efficient cleavage of the C–O bonds in lignin is a key step to promote its depolymerization and, at present, two main strategies based on oxidative or reductive conversion are being considered to obtain aromatic chemicals.

The oxidative depolymerization of lignin offers a highly efficient entry to the solubilization of lignin and a difficulty in this approach remains the isolation of pure aromatics.^{11,12} In contrast, mild reductive routes that would converge towards monoaromatics derivatives of the constituting monolignols (Fig. 1), by replacing C–O bonds with C–H bonds, are quite rare.¹³ Recently, Westwood *et al* isolated phenolic monomers of lignin through a two-step procedure involving first selective oxidation of C_α –OH groups and then C–O bond reduction of β -O-4 linkages with stoichiometric amounts of zinc metal.¹⁴ De Vries, Barta *et al.*¹⁵⁻¹⁷ and Luterbacher *et al.*¹⁸ explored over the last years an alternative approach where lignin is first depolymerized *via* acidolysis, in the presence of a diol or formaldehyde to stabilize reactive electrophilic intermediates and avoid re-polymerization through C–C bond formation. Subsequent hydrogenation enabled the formation of a narrow range of monocyclic products. In 2015, our group reported the first catalyst ($B(C_6F_5)_3$) that promotes, in the presence of hydrosilanes, the direct and efficient reductive depolymerization of a variety of *softwood* (resinous trees) and *hardwood* (leaved trees)^{19,20} lignins into isolable monoaromatic products.²¹ Depending on the wood source and the depolymerization conditions a high degree of convergence could be reached, with the formation of 1 to 4 monoaromatics. The stability of the $B(C_6F_5)_3$ catalyst however seemed strongly related to the presence of lignin impurities and the nature of the solvents. More stable catalysts are therefore needed to extend the potential of a direct reductive depolymerization of lignin. Brookhart's cationic iridium(III) pincer complex $[1][B(C_6F_5)_4]$ is a well-known catalyst in the

hydrosilylation of C=O and C–O bonds.²²⁻²⁶ Notably, Brookhart *et al.* have shown that $[1][B(C_6F_5)_4]$ could cleave the $C(sp^3)$ –O bond in alkylethers to yield a silylether and an alkane.²² The similar chemical behavior of the Lewis acids $B(C_6F_5)_3$ and $[1][B(C_6F_5)_4]$ ²⁷⁻²⁹ led us to compare their stabilities and activities in the reduction of α -O-4 and β -O-4 linkages, both in model molecules and lignin matrices. Here, we report the first molecular metal catalyst,

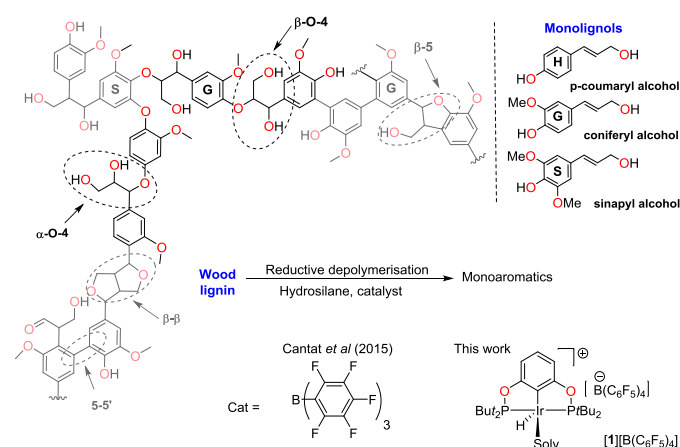


Figure 1 Convergent reductive hydrosilylation procedures for depolymerization of lignin

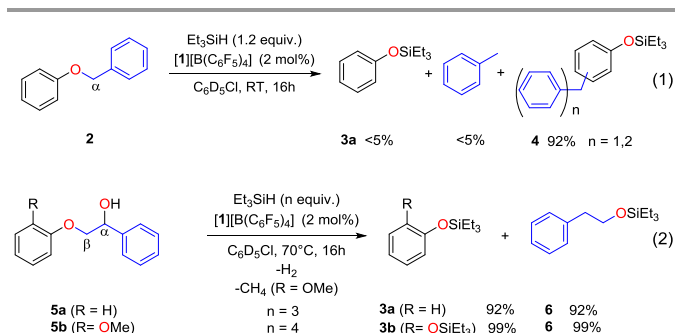
$[1][B(C_6F_5)_4]$, that depolymerizes softwood and hardwood lignins under hydrosilylation conditions and affords the highest yields reported for isolated aromatic products under homogeneous conditions. This reaction also highlights the first successful depolymerization of a natural polymer with the Brookhart catalyst.

Results and discussion

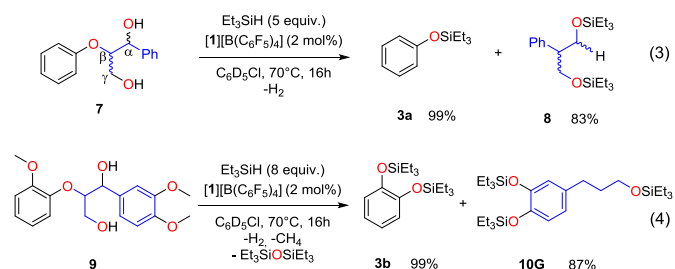
The efficiency of $[1][B(C_6F_5)_4]$ in the catalytic cleavage of α -O-4 and β -O-4 linkages was first evaluated on lignin model compounds. At room temperature (RT), treatment of benzyl phenyl ether **2** in the presence of 1.2 equiv. Et_3SiH and with 2 mol% $[1][B(C_6F_5)_4]$ effectively led, after 16 h in chlorobenzene, to the selective hydrosilylation of the $C(sp^3)$ –O bond with formation of **4** as the major product (92%) and toluene and phenoxysilane **3a** as minor products (<5% yield) (Scheme 1, Eq.1).

Notably, the $C(sp^2)$ –O bond in **2** was left untouched, in line with the previous findings of the Brookhart group.²² Compound **4** is a diaryl product that likely results from a Friedel-Crafts alkylation of **3a** by the transient $PhCH_2^+$ cation (formed by deoxygenation of **2** with a silylium cation). Models **5a** and **5b** exhibit a β -O-4 linkage with a hydroxyl group at the α position for **5a** and **5b** and two hydroxyls at the α and γ positions in the

more realistic model **7**. In contrast to **2**, no C–O bond scission was observed when **5a/b** and **7** were exposed, at RT, to 2 mol% of **[1]⁺** with excess Et₃SiH (*n* > 5 equiv.) and dehydrogenative silylation of the O–H groups was observed as the sole reaction (see ESI). Nevertheless, at 70 °C, **5a** reacted with 3 equiv. Et₃SiH and 2 mol% **[1][B(C₆F₅)₄]** to yield **3a** and silylether **6** in 92 % yield, without recondensation (Scheme 1, Eq. 2). Similarly, the coniferyl derivative **5b** was converted to **3b** and **6** in 99 % yield, when 4 equiv. Et₃SiH were used, and H₂ and CH₄ by-products were observed by GC. Using analogous conditions, **7** was successfully converted to **3a** and **8** (83–99%), after hydrosilylation of the O–H and C(sp³)–O bonds (Scheme 2, Eq. 3). These reactions also proceeded with other silanes (Et₂SiH₂, PMHS, TMDS...) but, due to the presence of several Si–H functionalities in these reductants, analyses of the products were complicated by the number of silylated compounds (see ESI). Whereas the **[1][B(C₆F₅)₄]/Et₃SiH system is able to reduce the C(sp³)–O bond in the α–O–4 and β–O–4 linkages, no deoxygenation of the primary (γ position) and secondary (α position) alcohols was noted.**



Scheme 1 Reductive cleavage of simple α–O–4 and β–O–4 model **2** (eq. (1)) and **5a** and **5b** (eq. (2)) using Et₃SiH and the catalyst **[1][B(C₆F₅)₄]**.

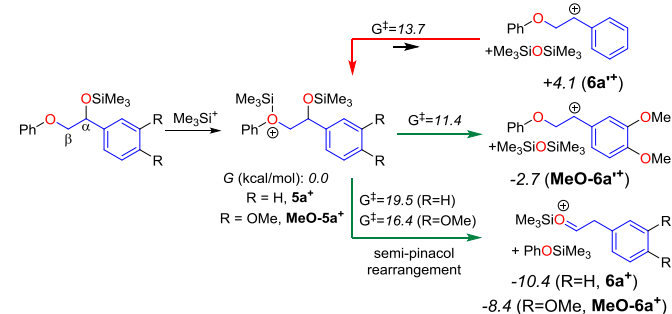


Scheme 2 Reductive cleavage of realistic β–O–4 model **7** (eq. (3)) and **9** (eq. (4)) using Et₃SiH and the catalyst **[1][B(C₆F₅)₄]**.

These observations are consistent with previous results on C–O bond hydrosilylation of ethers²² and the alcoholysis of hydrosilanes by cationic iridium complexes.³⁰ The selective formation of **6** from **5a/b**, instead of the expected silylated 1-phenylethanol (PhCH(OSiEt₃)Me), likely results from a semi pinacol rearrangement with migration of a phenyl group, as observed with the B(C₆F₅)₃–Et₃SiH system.³¹ A similar rearrangement accounts for the formation of **8**. The coniferyl alcohol derivative **9**, which differs from **7** by the presence of additional methoxy substituents on the aromatic rings, is a more realistic structural model of lignin.³² Hydrosilylation of **9** with an excess Et₃SiH (8 equiv.) and 2 mol% **[1][B(C₆F₅)₄]** afforded the tris-silylated primary alcohol **10G** (>80% yield), along with **3b** (Scheme 2, Eq. 4). Further reduction of the C_γ–OSi bond in **10G**, to yield the propyl derivative CH₃–(CH₂)₂–

(C₅H₂{OSiEt₃}₃), only proceeded under harsher conditions (90 °C for 5 days, see ESI). Interestingly, the formation of **10G** shows that the reduction of **9** differs from the reduction of **5** and **7** and occurs without any semi-pinacol rearrangement, thereby exemplifying the importance of the aromatic substituents on the reactivity of lignin model compounds. To better understand this change in reactivity, DFT calculations were performed on model structures of **5** and **9** (see Scheme 3 and ESI). Upon activation of silylated **5** with the R₃Si⁺ cation (generated by the electrophilic activation of the hydrosilane with the Lewis acidic catalyst), the C_α–O bond cleavage in **5a** is kinetically favored. Yet, the formation of the corresponding cation **6a⁺**, bearing a positive charge on C_α, is endergonic (ΔG = +4.1 kcal/mol) and **5a⁺** rather rearranges to the more stable **6a⁺** intermediate by semi-pinacol rearrangement (ΔG = –10.4 kcal/mol). The latter cation then accumulates prior to its reduction to **6** (and **3a**). In contrast, when methoxy substituents are introduced on the phenyl ring (as in **9**), the stability of **MeO-6a⁺** increases and its formation becomes exergonic (ΔG = –2.7 kcal/mol) and kinetically favored, thereby leading to a primary silylether. This behavior directly results from the enhanced stability of a positive charge on the C_α center provided by the electron donating methoxy substituents in G and S units.

Results depicted in Eqs. 1–4 provide interesting trends for comparing the **[1][B(C₆F₅)₄]** and B(C₆F₅)₃ catalysts in the hydrosilylation of lignin models (reaction conditions: 2 mol% catalysts, Et₃SiH as reductant, 16 h). The two catalysts share similar mechanistic schemes, leaving C(sp²)–O bonds untouched



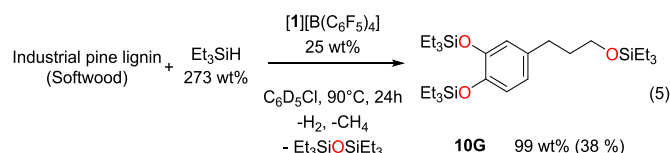
Scheme 3 Influence of methoxy substituents on the potential energy surface for C_α–O bond in lignin model compounds activated with silylium cations, as determined by DFT calculations (see ESI for computational details).

and promoting semi-pinacol rearrangements in **5** and **7**. While B(C₆F₅)₃ is active at RT, heating to 70 °C is required for **[1][B(C₆F₅)₄]**. The latter catalyst overall exhibits an enhanced chemoselectivity and it is able to reduce selectively the C_α–O and C_β–O bonds in **9** with an excess hydrosilane, whereas C_α–O, C_β–O and C_γ–O bond cleavages are competing with the B(C₆F₅)₃/Et₃SiH system, leading to over-reduction.

Having in hand an efficient catalytic system for the reductive cleavage of α–O–4 and β–O–4 linkages, the depolymerization of natural lignin was then attempted, with the aim to overcome the structural diversity and complexity of this biopolymer and access to narrow range of products, in a single step. Lignin, extracted from industrial pine with a Formacell process[†] was exposed to a chlorobenzene solution of **[1][B(C₆F₅)₄]** (25 wt% relative to lignin weight, corresponding to ca. 3.5 mol% per aromatic unit) and a slight

excess of Et₃SiH (273 wt%, ca. 5 Si–H functionalities per aromatic unit). Within 24 h at 90 °C, the complete dissolution of the lignin matrix was observed and **10G** was obtained as the sole monoaromatic product. Compound **10G** was isolated in 99 wt% yield as colorless oil after purification by chromatography (Scheme 4). The expected diaromatic compounds (which would represent a significant amount of the hydrosilylated products ≈ 140 wt% for industrial pine lignin) could not be isolated because they are retained on the chromatographic column. The mass of **10G** corresponds to a molar yield of 38 % in aromatic compounds (see ESI). The formation of **10G** demonstrates the successful transposition of the [1][B(C₆F₅)₄]/Et₃SiH hydrosilylation system to natural lignin and exemplifies the ability of [1*] to convert highly functional substrates.

Optimization of the depolymerization conditions, by extending the reaction time to 48 h in the presence of a low catalyst charge of 10 wt% (ca. 1.3 mol% per aromatic unit)[†] with 300 wt% Et₃SiH at 70 °C (Table 1), enabled the formation of **10G** in 120 wt% yield, corresponding to a molar yield of 46 %.



Scheme 4 Reductive depolymerization of Formacell lignin (derived from industrial pine) to **10G**, using [1][B(C₆F₅)₄]/Et₃SiH.

Table 1 Optimisation of [1][B(C₆F₅)₄]/Et₃SiH system on industrial pine lignin.

Entry	[1][B(C ₆ F ₅) ₄] (wt%) ^(a)	Et ₃ SiH (wt%) ^(a)	Time (h)	10G (wt%) ^(a)	Yield ^(b)
1	50	273	16	65 ^(c)	25
2	20	273	24	110	42
3	20	300	24	120	46
4	10	300	48	120	46
5	5	300	72	0	0

^(a) wt% = wt / wt of lignin ^(b) The molar yield is defined as being the ratio between the isolated molar number of **10G** (mol) and the molar number of monoaromatic units in lignin (mol) (see ESI) ^(c) Traces of over-reduction of **10G** to the corresponding alkane are recorded. All reactions at 70 °C.

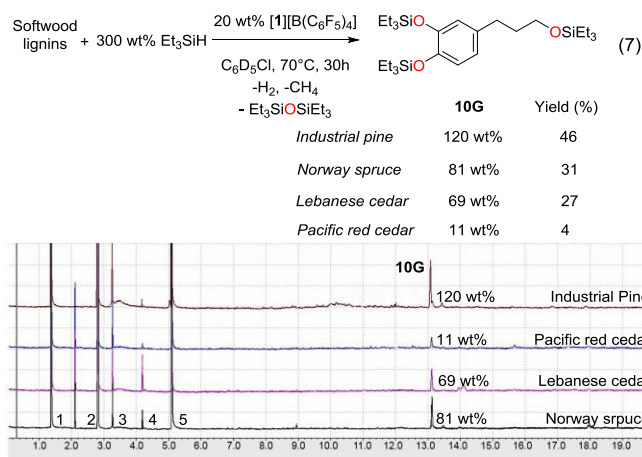
Interestingly, in presence of 5 wt% [1][B(C₆F₅)₄], no depolymerization products could be identified by GC-MS and NMR spectroscopies, although the lignin matrix was completely solubilized, from the hydrosilylation of the hydroxyl groups (Entry 5, Table 1).

This would suggest that a minimum quantity of catalyst is required because common impurities in lignin, such as residual carbohydrates and lipids, are known to deactivate and poison catalyst systems.³²

Replacing industrial pine with other softwood varieties, namely Pacific red cedar, Lebanese cedar and Norway spruce, Formacell lignins were deconstructed to **10G**, in 11, 69 and 81 wt% yield,

respectively, with molar yields ranging 4 to 31 % (Scheme 5, Eq. 7).

As depicted in Scheme 5, the reactions are highly selective leading to **10G** as the major monoaromatic product. The other diaromatic compounds were not detected in GC-MS because of their excessive weights. The depolymerization of hardwood lignins was carried out next. In addition to contain a greater proportion of β-O-4 cleavable linkages than softwood², these lignins present both sinapyl (**S**) and coniferyl (**G**) residues.



Scheme 5 Depolymerization of softwood lignins with [1][B(C₆F₅)₄]/Et₃SiH to **10G** (Eq. 7). GC-MS chromatograms of the crude reaction mixture for a variety of softwood lignins. 1) CH₂Cl₂ (solvent added for GM-MS analyses), 2) C₆H₅Cl, 3) Et₃SiOH, 4) Et₃SiH, 5) Et₃SiOSiEt₃

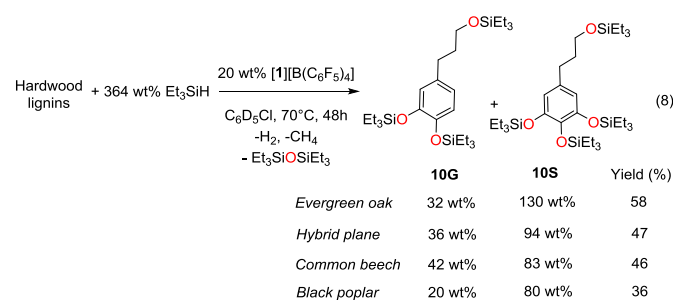
They are thus more oxidized and require forcing conditions with a larger charge of hydrosilane. As a consequence, the hydrosilylation of lignin samples obtained from black poplar, evergreen oak, hybrid plane and common beech was achieved at 70 °C in chlorobenzene, with 20 wt% catalyst and 364 wt% Et₃SiH (i.e. ca. 6.3 molar equivalents per aromatic unit) (Scheme 6, Eq. 8).

GC chromatograms recorded after 48 h showed **10S** and **10G** to be the main monoaromatic products. In contrast to the resinous counterparts, they also evidenced a number of minor and undetermined side products (see ESI). For the hardwood lignins, the quantities of **10S** are larger than that of **10G**, with yields varying within 80-130 wt% and 20-42 wt%, respectively, in line with their relative proportions in the lignin matrices (e.g. ratio **10S**/**10G**: 70/30, see ESI). Here again, the mean molar yields depend on the wood type and are quite high ranging 36 % for black poplar to 58 % for evergreen oak (Eq. 8).

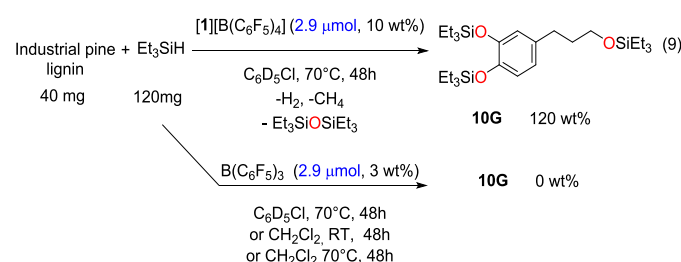
While the reductive depolymerization of lignin could be achieved within hours at RT when catalysed with B(C₆F₅)₃, Brookhart's catalyst appears less reactive requiring heating to 70 °C. To compare precisely the two catalytic systems, depolymerization experiments of pine lignin were thus carried out with the same molar quantities (2.9 μmol) of catalyst, namely 10 wt% [1][B(C₆F₅)₄] and 3 wt% B(C₆F₅)₃.

Under these conditions, as summarized in Scheme 7, the boron catalyst proved inefficient at RT or 70 °C, both in dichloromethane and chlorobenzene, and no trace of **10G** could be detected by GC-MS. The lack of activity of B(C₆F₅)₃ certainly results from its degradation or poisoning. This also reveals the enhanced robustness of the iridium catalyst which displays a

TON of **28** considering the molar yield of monoaromatic products with respect to the catalyst loading (see ESI).⁵



Scheme 6 Reductive depolymerization of Formacell lignin (derived from hardwood) to **10G** and **10S**, using **[1][B(C₆F₅)₄]/Et₃SiH.**



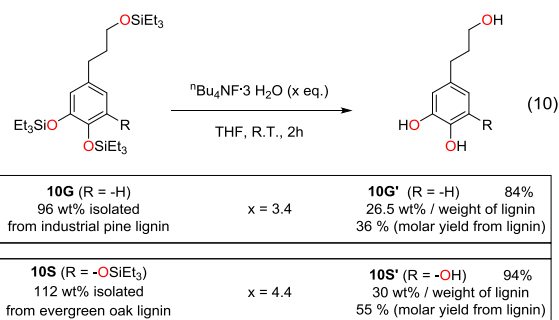
Scheme 7 Reductive depolymerization of industrial pine (softwood lignin) to **10G** using 2.9 μmol of **[1][B(C₆F₅)₄]** (top) and 2.9 μmol of **B(C₆F₅)₃** (down) with Et₃SiH.

Another key difference between the two catalysts **[1]⁺** and **B(C₆F₅)₃** lies on their distinct chemoselectivity. While **10G** and **10S** are obtained selectively from the treatment of softwood and hardwood lignins with **[1]⁺** and an excess hydrosilane, respectively, over-reduced derivative with the propyl chain was only obtained with the use of **B(C₆F₅)₃**.¹⁹

The efficiency of lignin depolymerization with **[1][B(C₆F₅)₄]** was quantified as the ratio of the experimental yield in monoaromatic products on the theoretical yield (see ESI). It is different from the molar yield because not all the interunit linkages in lignin can be reduced. This calculation required the knowledge of the mean molecular weight of Formacell lignin (determined by SEC analyses) and the content in cleavable linkages (e.g. β-O-4 content).²¹ The amount of β-O-4 linkages was evaluated from the HSQC NMR spectra of the lignin samples by two classical approaches, i) when quantified with

respect to aromatics units or ii) when expressed as a percentage of the total side chain linkages (See details in ESI). The β-O-4 contents vary in the range of 42–48 per 100 aromatics and 65–70% of the interunit linkages in hardwood lignin (Table 2). While the former approach (i) fails and provides aberrant results (see ESI), the second approach was used, affording efficiencies in the range of 42 to 100 % (Table 2). Overall, softwood and hardwood lignins exhibit similar efficiencies.

Isolation of phenolic compounds instead of the silylated species was important as the former are valuable synthons in chemical synthesis and industry. Hydrolysis of compounds **10S** and **10G** with hydrated tetrabutyl ammonium fluoride afforded the corresponding propylhydroxycathecols **10S'** and **10G'** in 94 and 84 % yield, respectively. **10S'** and **10G'** were thus isolated, respectively, in 55 % molar yield from evergreen oak lignin (30 wt%/wt lignin) and 36 % molar yield from industrial pine lignin (26.5 wt%/wt lignin) (scheme 8). These are the highest yields in isolated mono-aromatic compounds ever obtained from lignin under homogeneous conditions.^{7,8} The cost of the catalysts as well as the release of wastes (siloxanes, fluorosilanes) are however drawbacks of the present method. Current efforts are being devoted to improve the sustainability of hydrosilylation chemistry, for example through the use of silylformates.³³ In addition, formic acid would be an attractive reductant in lignin depolymerization.



Scheme 8 Hydrolysis of the silyl ethers products with ⁿBu₄NF·3H₂O from softwood and hardwood lignins

Table 2 Abundance of β-O-4 content in lignin samples and calculations of efficiencies of the depolymerisation within the experimental conditions:

70 °C in chlorobenzene, 30–48h, **[1][B(C₆F₅)₄]** (10–20 wt%), 300–364 wt% Et₃SiH.

Lignin source	β-O-4' content	Molar yield in 10G or 10G + 10S (%)	Theoretical yield (%)	Eff ^(c)	Yield in phenolic compounds (10G' or 10S')
			Based on relative abundance of β-O-4 in lignin side chains		
Industrial Pine	63 % ^(a) (35.1) ^(b)	46 %	46 %	100 %	38 %
Norway Spruce	46 % (20.2)	31 %	35 %	89 %	n.d.
Lebanese Cedar	59 % (38.9)	27 %	46 %	58 %	n.d.
Pacific Red Cedar	20 % (21)	4 %	10 %	42 %	n.d.
Evergreen Oak	70 % (48.1)	58 %	60 %	96 %	55 %
Hybrid Plane	65 % (42.5)	47 %	60 %	79 %	n.d.
Common Beech	65 % (43.7)	46 %	60 %	77 %	n.d.
Black Poplar	76 % (47.2)	36 %	60 %	60 %	n.d.

Conclusions

In summary, we have reported herein the first use of the Brookhart's iridium complex as a catalyst in the reductive cleavage of lignin model molecules and softwood and hardwood lignins.

Combined with hydrosilanes, **[1][B(C₆F₅)₄]** favors selective splitting of the C(sp³)-O bonds in alkyl ethers and secondary silyl ether to provide silylated monoaromatic chemicals, with coniferyl **G** and sinapyl **S** residues, that can be isolated with high yields in a pure form. Although **[1][B(C₆F₅)₄]** displays a lower catalytic activity than B(C₆F₅)₃, this complex exhibits a greater stability and selectivity and represent a rare example of a catalyst able to depolymerize lignin to isolable monoaromatics.

Acknowledgements

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Notes and references

[†] We have previously reported from steric exclusion chromatography (ref. 19) that lignin obtained from the formacell organosolv process consisted in oligomers featuring a mean sequence of 5 aromatic units, with mainly **S** and **G** aromatic units (Scheme 1) for hardwood and essentially **G** units for softwood.

^{*} 1.3 mol% is found with **[1][B(C₆F₅)₄]** (1351 g.mol⁻¹) and a mean molecular weight for industrial pine lignin of 1099 g.mol⁻¹.

[§] If one considers that the production of **10G** from softwood lignin requires 6 C–O and O–H bond silylation events, then the TON is 170 per aromatic units (see ESI).

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