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Palladium-NHC mediated telomerization of aromatic alcohols

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ABSTRACT: The telomerization reaction of dienes with alcohols mediated by organopalladium complexes represents a versatile method to convert butadiene into value-added chemicals. The use of aromatic alcohols in the telomerization is still an under-explored area that has attracted increased interest in recent years. In this contribution, we examine the catalytic behaviour of a series of well-defined palladium *N*-heterocyclic carbene precatalysts (Pd-NHC) in the telomerization of butadiene with aromatic alcohols. The process was optimized by studying the influence of Pd/L ratio, of the base and of the pre-catalyst structure. The versatility of the method was tested employing a series of aromatic alcohols, including lignin-type phenols. In the context of biomass valorisation, an explorative study on the telomerization with lignin was carried out.

1. Introduction

The telomerization reaction refers to the oligomerization of 1,3-dienes with the concomitant addition of a nucleophile (Fig. 1) [1–3]. This process permits to access highly valuable chemicals with applications in pharmaceutical and polymer industry in a complete atom economic way [2,4,5]. During the past decades, telomerization has attracted increasing interest as an environmentally safe and sustainable process and one that possesses several features that align with the principles of Green Chemistry [6]. This reaction can be catalyzed by complexes that contain various transition metals, among these, palladium is by far the most widely deployed [2,3,7]. Various protocols using phosphines and *N*-heterocyclic carbenes as ligands have been developed [1,8–12]. In particular, palladium *N*-heterocyclic carbenes complexes (Pd-NHC) have acquired a leading role in telomerization of aliphatic alcohols and amines [1,12–15] due to their numerous synthetic, catalytic and design advantages [16,17].

Despite the great advancement in telomerization research, the use of aromatic alcohols as telogens is still underexplored [2]. Few examples are reported in the literature, almost all involving Pd-phosphines systems as catalysts [1,11,18–21].

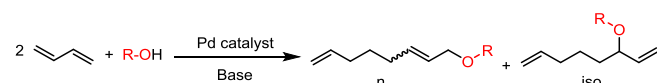


Figure 1. Pd-catalyzed telomerization of butadiene with alcohols.

The telomerization products of butadiene with phenol are involved in organic total synthesis of some pheromones [22,23] and are useful intermediates for organic transformations [24,25]. Nowadays, the telomerization of aromatic alcohols represents an attractive tool for the valorization of biomass-derived molecules. The use of lignin is perhaps the most noteworthy example [20]. Lignin is a natural biopolymer obtained from the pulp and paper industry and represents the most abundant by-product of the cellulose separation process. Chemically, lignin is composed of polyphenolic chains linked with short aliphatic hydroxylated fragments (Fig. 2). There can be small differences in lignin composition depending on the extraction method utilized [11,26]. Its high availability increases the interest in the development of processes that aim at converting it into value-added materials. The telomerization of aromatic alcohols constitutes a useful tool for a study of the telomerization involving lignin [11,20,27].

In this work, we have explored the behaviour of a series of Pd-NHC complexes in the telomerization of aromatic alcohols, firstly optimizing the reaction conditions and subsequently evaluating the reactivity of various substituted phenols. With the achieved results, we conducted an explorative study of the telomerization of butadiene with Kraft lignin employing Pd-NHC complexes as catalysts.

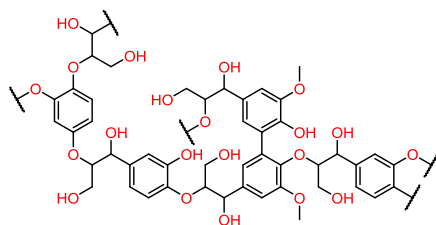


Figure 2. A simplified representation of lignin.

2. Results and Discussion

2.1. Preliminary studies on the telomerization with guaiacol

In our previous work on the telomerization of butadiene with ethanol, we have observed that the Pd-IMes species was the most suitable catalyst, providing the best conversions, telomers yields and n/iso selectivities in the shortest times [12]. A series of well-defined palladium *N*-heterocyclic carbenes bearing the IMes ligand were selected to test their activity in the telomerization reaction of butadiene with aromatic alcohols. Guaiacol was chosen as lignin model substrate since it is a liquid at room temperature allowing the reaction to be performed without solvent and because it showed great reactivity in the Pd/phosphine catalyzed telomerization (Fig. 3) [20].

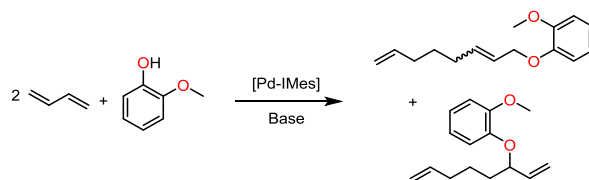


Figure 3. Telomerization of butadiene with guaiacol.

Preliminary results with Pd(OAc)₂/IMes•HCl showed the strong influence of the base, with a 98% conversion with KO^tBu compared to 7% with NaOH. These preliminary tests suggested that the base plays a crucial role in the telomerization reaction and we first evaluated various other bases.

2.1.1. Bases screening

The optimization began using the [Pd(IMes)(cin)Cl] (**Pd-1**, Fig. 4), which proved to be the best pre-catalyst in the telomerization of butadiene with ethanol. The reactions were conducted with 0.01 mol% of [Pd(IMes)(cin)Cl] and 1 mol% of base under an inert atmosphere. KO^tBu was first evaluated and gave the products in 67% yield (entry 1, Table 1). When KO^tBu loading was increased to 5 mol%, a slight drop in performance was noticed (entry 2). When no base is added to the system, the reaction displayed no conversion at all (entry 3). This result confirms the need for a base to achieve the activation of the Pd-NHC pre-catalyst to initiate the process. Switching to NaOH, we observed a drastic decrease in both conversion and yield, respectively 41% and 39%. When the milder base 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) was tested, the conversion stopped at 20% with 11% of the telomers formed (entry 5). The presence of a strong alkoxide base appears to be required to achieve the best performance.

Table 1

Base screening in telomerization of butadiene with guaiacol using **Pd-1**.

Entry	Base	Guaicol Conv. (%)	Telomers Yield (%)	n/iso
1	KO ^t Bu	70	67	19.0
2 ^a	KO ^t Bu	60	55	13.3
3	-	0	-	-
4	NaOH	41	39	8.5
5	DBU	20	11	10.9

Conditions: Butadiene (0.12 mol, 10 mL), guaiacol (0.04 mol, 4.5 mL), [Pd(IMes)(cin)Cl] (0.01 mol%), base (1 mol%), IMes•HCl (0.03 mol%), N₂, 90 °C, t = 16 h. GC conversion and yield values are the average of two runs. ^aReaction performed with 5 mol% of base.

2.1.2. Influence of the palladium/ligand ratio

As the reaction outcome has displayed generally a strong dependence on the metal/ligand ratio [1], we next studied the influence of this Pd/IMes ratio (Table 2).

Table 2

Pd-1/IMes.HCl ratio influence on the reaction outcome.

Entry	Pd-1/ IMes.HCl Ratio	Guaicol Conv. (%)	Telomers Yield (%)	n/iso
1	-	72	70	19
2	1/1	76	75	19
3	1/2	87	85	15.7
4	1/3	100	100	19

Conditions: Butadiene (0.12 mol, 10 mL), guaiacol (0.04 mol, 4.5 mL), **Pd-1** (0.05 mol%), IMes.HCl, KO^tBu (1 mol%), 90 °C, t = 16 h. GC yields are the average of two runs.

The first experiment was carried out with 0.05 mol% of pre-catalyst [Pd(IMes)(cin)Cl] (**Pd-1**, Fig. 4) and led to 72% conversion of guaiacol. A slightly better outcome was achieved when 0.05 mol% of IMes·HCl was added to the reaction mixture, achieving 76% conversion. Doubling the IMes·HCl amount to 0.1 mol% proved beneficial as the conversion was increased to 87%. Finally, complete conversion and a quantitative yield were obtained with 0.15 mol% of imidazolium salt which corresponds to a Pd/IMes ratio of 1:3. This ratio was also found to be the optimal one for the PPh₃ ligand [20]. The linear/branched ratio remained constant throughout these experiments. Remarkably, neither 1,3,7-octatrienes nor 4-vinylcyclohexene were detected in the reaction mixture, revealing the complete selectivity of the process towards the telomers. The role of the added imidazolium salt is believed to increase stability of the catalytic species or to reconvert decomposition species back into active species [1].

2.1.2. Pre-catalyst screening

We next examined a large array of well-defined Pd-IMes pre-catalysts (Fig. 4). We performed the telomerization using guaiacol at 0.01 mol% palladium loading to be able to discern differences in conversions and yields (Table 3). Under these conditions, the [Pd(IMes)(cin)Cl] **Pd-1** gave 70% guaiacol conversion and 67% telomer yield, showing a good activity also at lower catalyst loading. The well-defined [Pd(IMes)(acac)Cl] **Pd-2**, known to be more stable but less easily activated, gave 50% conversion and 44% yield. The newly developed [Pd(IMes)(Mes-cin)Cl] **Pd-3**, presenting a more hindered allyl moiety than the classical **Pd-1**, was found to be much less efficient in the telomerization with guaiacol, giving only a conversion of 15%. The notably reduced activity of this complex may reside in its behaviour in the activation step. For the allylic palladium precursor, the activation by potassium tert-butoxide mechanism is proposed to occur through a nucleophilic substitution of chloride with the ^tBuO⁻ anion [28].

Table 3
Pre-catalysts screening.

Entry	Catalyst	Conv. (%)	Yield (%)	n/iso
1	Pd-1	70	67	19.0
2	Pd-2	50	44	9.9
3	Pd-3	15	10	9.1
4	Pd-4	20	17	11.7
5	Pd-5	40	35	5.3
6	Pd-6	33	31	5.7
7	Pd-7	16	14	9.8
8	Pd-8	23	20	14.7
9	Pd-9	26	22	4.7

Conditions: Butadiene (0.12 mol, 10 mL), guaiacol (0.04 mol, 4.5 mL), [Pd] = 0.01 mol%, IMes·HCl = 0.03 mol%, KO^tBu (1 mol%), 90 °C, 16 h. GC yields are the average of two runs.

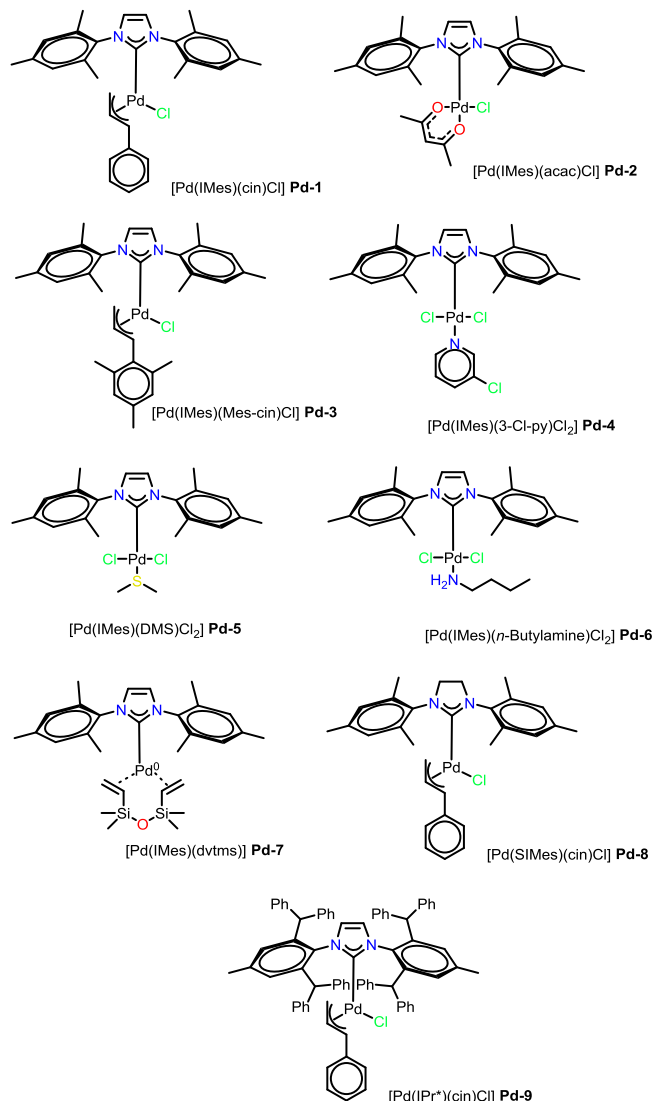


Figure 4. Pd-NHC complexes tested in the telomerization reaction with guaiacol.

DFT calculations [29] have supported that the active $\text{Pd}^0\text{-L}$ catalyst is formed through a transition state shown in Fig. 5. This step may be disfavoured by the major steric hindrance of the mesityl groups resulting in a greater decomposition rate of the pre-catalyst at high reaction temperature.

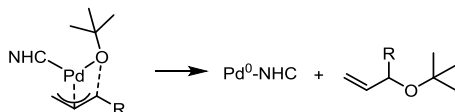


Figure 5. Transition state leading to the formation of the $\text{Pd}^0\text{-L}$ species from the R-allyl-based complexes.

The well-defined $[\text{Pd}(\text{IMes})(3\text{-Cl-py})\text{Cl}_2]$ **Pd-4** exhibited a notably inferior activity, converting 20% of the guaiacol leading to a 17% yield of the products.

Subsequently, the newly designed $[\text{Pd}(\text{IMes})(\text{DMS})\text{Cl}_2]$ **Pd-5** complex was tested. This pre-catalyst family bears a dimethyl sulfide as a leaving group and was found to be extremely active in C-C and C-N couplings [30]. The complex led to 40% conversion of guaiacol and 35% yield of telomers, revealing an inferior activity to the cinnamyl-based analogue. The $[\text{Pd}(\text{IMes})(n\text{-butylamine})\text{Cl}_2]$ **Pd-6** complex exhibited a slightly inferior activity to the DMS congener resulting in a conversion of 33% and a yield of 31%. Both the DMS and the amino-based well-defined complexes are reported to be easily activated at room temperature [30,31]. The facile activation of these structures may be the cause of their reduced activity in the telomerization due to the high temperature of the process that can cause faster decomposition of the pre-catalysts. The $[\text{Pd}(\text{IMes})(\text{dvtms})]$ **Pd-7** complex was finally tested. Unlike all other pre-catalysts, this species presents a Pd^0 oxida-

tion state and was designed and tested by Beller *et al.* in the telomerization with methanol exhibiting incredible activity [15]. In our case, this complex is one of the least active, achieving only 16% conversion of the starting material. The Pd⁰ increased sensitivity and susceptibility to oxidation may be the reason for its reduced activity. Since the experiments were conducted using the raw materials without any further purification, a more robust Pd^{II} pre-catalyst appears more suitable for this process.

An additional test with the pre-catalyst **Pd-8**, bearing the SIMes carbene was performed to observe the influence of the saturation of the backbone of the NHC ligand. The obtained values of conversion and yield, amounting respectively to 23 and 20%, showed a considerable decrease in the catalytic performance. Finally, a test with the [Pd(IPr*)(cin)Cl] **Pd-9** complex was conducted to explore the use of a sterically hindered carbene. The experiment ended with a conversion of 26% and a telomers yield of 22% showed that modest catalytic activity is achieved when IMes is replaced with IPr*. These experiments inarguably showed that the [Pd(IMes)(cin)Cl] **Pd-1** is by far the best pre-catalyst for the telomerization with guaiacol. Its combination of robustness and easy activation provided by the cinnamyl leaving group merged with the apparent advantageous steric and electronic properties of the IMes ligand led to the best pre-catalyst composition for this process.

2.1.3. Optimization of the catalytic conditions

The optimization of the palladium catalytic charge was next investigated. Keeping the Pd/IMes·HCl ratio constant at 1/3, we screened various catalyst loadings (Table 4).

Table 4
Screening of various catalyst loadings using **Pd-1**/IMes·HCl ratio of 1:3.

Entry	Pd-1 (mol%)	Conv. (%)	Yield (%)
1	0.05	> 99	> 99
2	0.01	70	67
3	0.03	> 99	> 99
4	0.02	> 99	> 99
5 ^a	0.02	95	93

Conditions: Butadiene (0.12 mol, 10 mL), guaiacol (0.04 mol, 4.5 mL), **Pd-1** (x mol%), IMes·HCl (3x mol%), KO^tBu (1 mol%), 90 °C, t = 16 h. GC yields are the average of two runs. ^aReaction performed under air.

As previously shown, 0.01 mol% of **Pd-1** ([Pd(IMes)(cin)Cl]) gave telomer in 67% yield and converted 70% of the guaiacol, while using 0.05 mol%, complete conversion and quantitative yield were achieved (Table 4, entries 1 and 2). The same catalytic activity was preserved when the **Pd-1** loading was decreased initially to 0.03 and finally to 0.02 mol% (Table 4, entries 3 and 4). To our delight, an additional test performing the reaction under ambient atmosphere resulted in 93% and 95% values respectively for yield and conversion (Table 4, entry 5). Therefore, the system was shown to be marginally affected by oxygen and water confirming the robustness of the **Pd-1** pre-catalyst. The conditions utilized in entry 4 were selected for further experiments.

2.2. Scope of aromatic alcohols

A scope of aromatic alcohols was then examined, focusing on lignin-type phenols to investigate the efficacy of our system (Fig. 6). We carried out the experiments using the optimized conditions of [Pd(IMes)(cin)Cl] (0.02 mol%), IMes·HCl (0.06 mol%) and KO^tBu (1 mol%) (Table 5). As mentioned, the reaction with guaiacol (**1**) proceeded smoothly to completion, giving the telomers in quantitative yield in a n/iso ratio of 19.

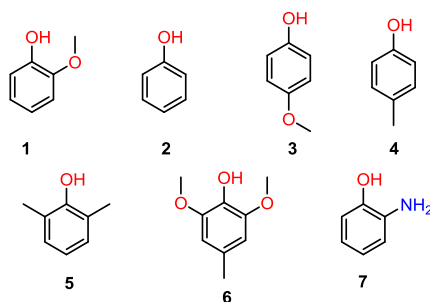
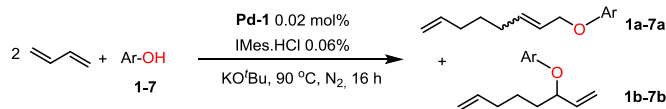


Figure 6. Scope of aromatic alcohols ArOH.

Table 5
Telomerization of butadiene with phenol derivatives.



Entry	ArOH	m.p. [°C]	THF	Conv. (%)	Yield (%)	n/iso
1	1	28-32	-	> 99	> 99	19.0
2	2	40-42	-	59	30	7.2
3	2	40-42	yes	58	55	9.8
4	3	55-57	-	86	80	10.6
5	3	55-57	yes	> 99	> 99	21.8
6	4	31-35	-	79	71	7.1
7	5	43-45	-	95	91	6.8
8	6	37-42	-	-	-	-
9	6	37-42	yes	29	21	9.0
10	7	174-177	yes	87	44	13.2

Conditions: Butadiene (0.12 mol, 10 mL), ArOH (0.04 mol), **Pd-1** (0.02 mol%), IMes·HCl (0.06 mol%), KOtBu (1 mol%), 90 °C, t = 16 h. GC yields are the average of two runs.

The telomerization of butadiene with the other phenols (**2-7**) are more challenging since they are solid at room temperature. We decided to perform a first screening without any solvent addition since most of them have a melting point under 90 °C. The telomerization with phenol occurred with a 59% conversion and 30% yield with a n/iso ratio of 7.2. Another unidentified product was detected by GC analysis. One possible by-product is one of the isomers **2c**, **2d** or **2e** after the Claisen rearrangement (Fig. 7), that is reported to form for this type of molecules [20].

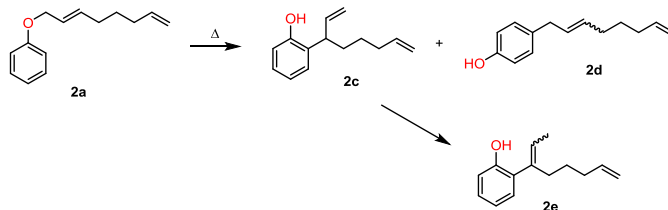


Figure 7. Claisen rearrangement, possible products of reaction.

The same reaction performed with the addition of dry THF as solvent occurred with a phenol conversion of 58% but resulted to be considerably cleaner giving the telomers **2a** and **2b** as almost exclusive products in 55% yield and a linear/iso ratio of 9.8. The telomerization with mequinol **3** in the absence of solvent occurred with 86% conversion and produced the telomers in 80% yield with a n/iso of 10.6. To our delight, the reaction performed in dry THF led to a complete conversion of the starting material and quantitative yield with a 21.8 n/iso ratio. Next, we tested the telomerization with *p*-cresol **4** without solvent. The experiment concluded with a conversion of 79% and gave the telomers in 71% yield with n/iso of 7.1. The telomerization with 2,6-xylenol **5** occurred smoothly in the absence of THF, giving 91% of the products in 6.8 n/iso ratio with a total conversion of 95%. The 2,6-dimethoxy-4-methylphenol **6** revealed to be the most challenging substrate for the telomerization. The reaction without THF did not lead to the products formation. When THF was added, the products formed in 21% yield with a conversion of the aromatic alcohol of 29%. Lastly, we tested the telomerization of the 2-aminophenol **7**. The peculiarity of this substrate is the presence of both hydroxy and amine functions, both reactive in the telomerization process. The existing examples of telomerization with amines mediated by Pd-NHCs reported that a cationic Pd-allyl species is needed to achieve the reaction, but there is no report of telomerization with aromatic amines in the scope [13]. The reaction was carried out with THF since the melting range of **7** is 174-177 °C. The telomerization occurred with 87% conversion of **7**. The crude is a mixture of the expected linear telomer **7a** and the disubstituted product **7c** bearing a C8 chain linked to the oxygen atom and one linked to the amino function (Fig. 8). The ratio between these two species is 51/49 with a global yield of 44%. This result reveals that the alcohol function is more reactive towards the telomerization than the amino group and showed the possibility to achieve the telomerization on the aromatic amines with a Pd-IMes catalytic system.

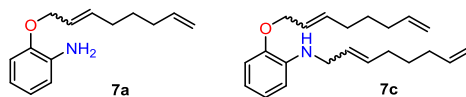


Figure 8. Products obtained from the telomerization of 2-aminophenol **7**.

2.3. Preliminary studies on the telomerization with lignin

The final part of this study addresses the application of the system in the telomerization of butadiene with lignin (Fig. 9). As observed from the structure in Fig. 2, the lignin composition presents a large density of hydroxyl functions, predominantly aromatic. In addition, there is a lower concentration of carboxylic acid functions that can also undergo telomerization [32,33]. Depending on the method of separation, the final product can present additional functionalization. Kraft lignin extracted using the namesake method presents also -SH groups due to the use of Na₂S in the process.

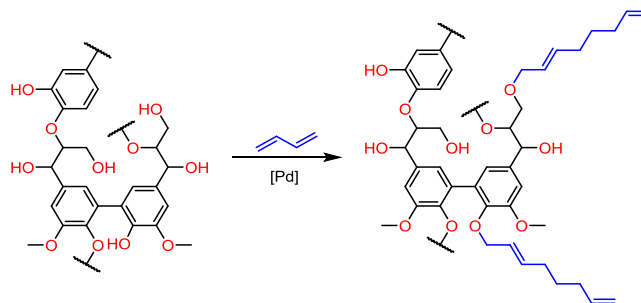


Figure 9. Simplified representation of the telomerization of butadiene with lignin.

We performed our experiments involving mostly Kraft lignin, since it accounts for about 85% of the global lignin production [34]. The OH amount in the Kraft lignin used was first evaluated in our laboratory by titration with a phosphitylation agent [35] giving 2.04 mmol/g for aliphatic OH, 4.99 mmol/g for aromatic OH and 0.64 mmol/g for COOH. The first challenge is related to the base influence on the reaction. The **Pd-1** pre-catalyst, as all the Pd-NHCs, needs the presence of a strong base to be activated for the telomerization [10]. Unfortunately, lignin can precipitate in organic solvent under alkaline conditions, and may cause issues along the reaction progress. A first test was carried out on 250 mg of lignin with 2 mL of butadiene in 5 mL of THF in the presence of 1 mol% of **Pd-1**, 3 mol% of IMes·HCl and 2 mol% of KO^tBu. Analysis by ¹H NMR of the final product showed no modification of lignin. To explore the influence of the amount of base, we conducted a base-free experiment. The final lignin did not offer any desired functionalization. Therefore, the next step was to increase the amount of base to 1 equivalent with respect to the total OH amount. To our delight, the ¹H NMR analysis showed peaks relative to the modified lignin (one example is shown in Fig. 10).

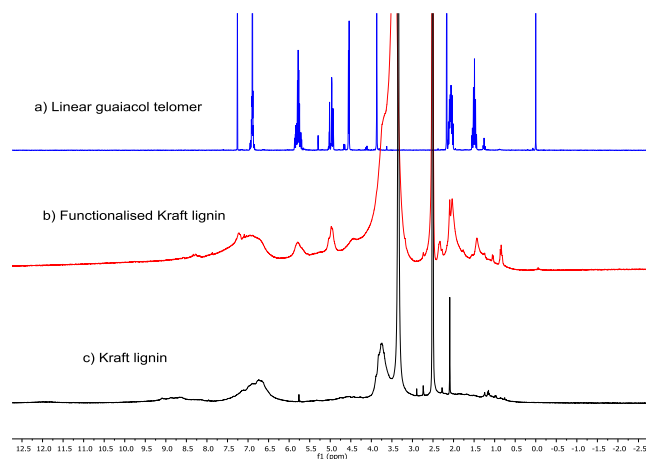


Figure 10. Comparison of the ¹H NMR spectra of the linear guaiacol telomer (blue spectrum) with those of the modified lignin (red) and of the Kraft lignin (black).

For a first evaluation of the lignin conversion, we performed an analysis ¹H NMR with pentafluorobenzaldehyde (PFB) as internal standard. The conversion of the OH groups reached 11%. We then investigated the reaction exploring different amounts of base. A remarkable improvement was obtained with 0.5 equivalent of KO^tBu leading to the modified lignin with 38% conversion of the total OH functions (entry 3, Table 6). When 0.25 equivalent was employed, the conversion dropped to 17% (entry 4). Therefore, we continued the experiments with 0.5 equivalent of base. The reaction without additional IMes·HCl salt ended with 25% conversion, confirming the positive influence of the imidazolium salt (entry 5). By increasing the butadiene amount to 8 mL, we did not notice any further improvement (entry 6).

Table 6
Conditions for the optimization of lignin telomerization.

Entry	Pd-1 mol% (eq. per OH)	IMes·HCl mol%	Buta- diene (mL)	Eq. KO'Bu	Conv. OH _{total} (%)
1	1	3	2	-	-
2	1	3	2	1	11
3	1	3	2	0.5	38
4	1	3	2	0.25	17
5	1	-	2	0.5	25
6	1	3	8	0.5	18

General conditions: **Pd-1**, lignin (250 mg), THF (5 mL), N₂, 90 °C, 16 h.
Conversion determined by ¹H NMR analysis with PFB as internal standard.

In order to better understand the catalytic performance of our Pd-NHC system, we analysed the best sample (entry 3) with ³¹P NMR analysis of phosphorylated lignin to determine the overall distribution of hydroxyl groups present in a lignin sample [36]. The conditions shown in Table 7 are the best found for Pd-NHC system, but are still not as good as the ones achieved with Pd/phosphines systems [11].

Table 7
Lignin conversion calculated with ³¹P NMR analysis.

Entry	Conv. OH _{total} (%)	Conv. OH _{aliph} (%)	Conv. OH _{arom} (%)	Conv. COOH (%)
1	38	15	37	36

Conditions: **Pd-1** 1 mol% eq. per OH, IMes·HCl 3 mol%, KO'Bu 0.5 eq., 90 °C.
General conditions: lignin: 250 mg, butadiene: 2 mL, N₂, 16 h.

3. Conclusion

We have explored the reactivity of a series of well-defined palladium *N*-heterocyclic carbenes in the telomerization of aromatic alcohols. The best performing pre-catalyst is [Pd(IMes)(cin)Cl], confirming the IMes carbene as the most suitable for telomerization. The system showed to be notably robust, leading to excellent results under ambient air atmosphere compared with conventional phosphine-based catalysts. The use of dry THF as reaction solvent generally resulted in an increase in performance when the alcohol is a solid. Initial tests showed a moderate activity of our system in the telomerization with lignin. Further experiments are needed to optimize the process.

4. Experimental section

4.1 General procedure for aromatic phenol telomerization reaction

Alcohol (if solid), palladium pre-catalyst, IMes·HCl and base (1 mol%) were weighed and introduced into a 100 mL stainless steel pressure reactor equipped with a magnetic stirring bar. The reactor was closed and three vacuum/N₂ cycles were performed. The reactor was connected to a cryostat and the system was cooled to -20 °C. Alcohol (1 eq., 0.04 mol), if liquid, was added with a syringe through a septum under nitrogen counterflow. Butadiene (3 eq., 10 mL, 0.12 mol) was condensed in a Schlenk tube cooled to -40 °C in a liquid nitrogen/acetone bath and added into the reactor via cannula through a septum under nitrogen counterflow. The cryostat was removed, and the system was connected to a pre-heated water bath. The reaction was conducted for 16 h. The pressure decrease was monitored during the experiment as a gauge of butadiene consumption. At the end, the reactor was cooled to room temperature and butadiene excess was removed by opening a reactor valve.

4.2. General procedure for telomerization reaction with lignin

Lignin (250 mg), palladium pre-catalyst, IMes·HCl and base were weighed and added to a 100 mL stainless steel pressure reactor equipped with a magnetic stirring bar. The reactor was closed and three vacuum/N₂ cycles were performed carefully to prevent lignin spreading. Dry and degassed THF (5 mL) was added in the reactor with a syringe through a septum under nitrogen counterflow. The reactor was connected to a cryostat and the system was cooled to -20 °C. Butadiene was condensed in a 5 or 10 mL graduated Schlenk tube cooled to -40 °C in a liquid nitrogen/acetone bath and added to the reactor via cannula through a septum under nitrogen counterflow. The cryostat was removed and the system was connected to a pre-heated water bath. The reaction was carried out for 16 h. The pressure decrease was monitored during the experiment as a gauge of butadiene consumption. At the end, the reactor was cooled to room temperature and butadiene excess was removed by opening a reactor valve. The reaction crude was transferred in a flask and THF was evaporated with a rotavapor. The crude was dissolved in a minimum quantity of THF and pentane was added to precipitate the product as a dark brown/black powder. The modified lignin was dried and analyzed to evaluate the functionalization rate.

4.3. General procedure for the lignin conversion calculation with ³¹P NMR.

³¹P NMR experiments were carried out following the following method : lignin (30 mg) was dissolved in a CDCl₃/pyridine mixture (1:1.6 v/v, 0.5 mL). The phosphorylation reagent, 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (150 μL) and the internal standard *N*-hydroxy-6-norbornene-2,3-dicarboximide (100 μL of 0.1 M solution in 1:1.6 v/v CDCl₃/pyridine mixture) were successively added. Chromium(III) acetylacetonate (100 μL of 0.014 M solution) in the same CDCl₃/pyridine mixture was added to the solution in order to homogenize and accelerate phosphorus relaxation. Spectra were recorded with a 15 sec relaxation time and an average number of 512 scans. Chemical shifts are relative to the signal of the phospholane hydrolysis product at 132.2 ppm. The integrated value of the internal standard was used for calculation of the absolute amount of each functional group. A comparison with the amounts of functional groups in technical lignins leads to the characterization of modified lignins [11,36].

4.4. General considerations

Kraft lignin (UPM BioPiva 100 - Softwood) was provided by UPM Biochemicals. Lignin was dried under reduced pressure at 60 °C for 48 h before use. Chemicals were purchased from Sigma-Aldrich, Alfa Aesar, Acros Organics and Strem Chemicals. 1,3-butadiene was purchased from Linde Gas France.

Data availability

All data supporting the findings of this contribution can be found in the ESI.

Declaration of competing interest

The authors declare no conflict of interest.

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Appendix A. Supplementary material

Supplementary material can be found online at. (doi of the paper).

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