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Hydrogen-Bond-Assisted Activation of Allylic Alcohols for Palladium-Catalyzed Coupling Reactions

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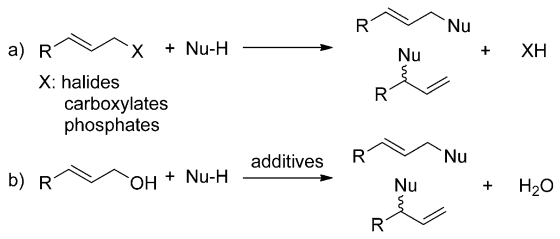
We report direct activation of allylic alcohols using a hydrogen-bond-assisted palladium catalyst and use this for alkylation and amination reactions. The novel catalyst comprises a palladium complex based on a functionalized monodentate phosphoramidite ligand in combination with urea additives and affords linear alkylated and aminated allylic products selectively. Detailed kinetic analysis show that oxidative addition of the allyl alcohol is the rate-determining step, which is facilitated by hydrogen bonds between the alcohol, the ligand functional group, and the additional urea additive.

Introduction

Palladium-catalyzed allylic substitution reactions are efficient and widely used synthetic methods in organic synthesis for C–C and C–X (X: O, N, S) bond formation.[1] Until recently, activated allylic reagents that are substituted with carboxylates,[2] halides,[3] or phosphates[4] have been mainly used as activated allyl alcohol reagents (Scheme 1 a); however, these reagents require an additional synthetic step compared to the use of allylic alcohols and the conversion results in the formation of stoichiometric amounts of waste (salts). In this context, direct conversion of allyl alcohols is an important challenge. In addition, numerous renewable compounds are available that could be converted into interesting intermediates for the fine-chemical and pharmaceutical industry by direct substitution of the allylic alcohol. A commonly used approach is preactivation of allylic alcohols with a stoichiometric or catalytic amount of a Lewis-acid activator such as As_2O_3,[5] B_2O_3,[6] BEt_3,[7] BPh_3,[8] $SnCl_2$,[9] or $Ti(O\text{-}iPr)_4$[10] (Scheme 1 b), but this method is still associated with substantial waste formation in most cases.



Scheme 1. General nucleophilic substitution reactions at allylic reagents (a), and the direct activation of allylic alcohols with the aid of additives (b).

The development of a waste-free direct catalytic transformation of allyl alcohol was initially reported by Ozawa et al. They developed (π-allyl)palladium complexes bearing sp^2-hybridized phosphorus ligands capable of direct conversion of allylic alcohols without any activators, producing water as the only by-product.[11] Afterwards, several Pd catalysts were reported, for various related applications. For example Tamaru and co-workers focused on allylic alkylation reactions with indole derivatives[7] while Beller and co-workers broadened the scope for primary aliphatic amines and electron deficient heterocycles.[12] Notably, the catalytic systems have different methods to activate allylic alcohols. Sarkar reported that Pd complexes with bisphosphine ligands are successful due to the high π-acidity of the phosphorous ligands,[13a] whereas Oshima proposed that hydrogen-bonding between water and allylic alcohols is key in decreasing the activation energy barrier of these processes.[13b] The latter report caught our attention as such supramolecular interactions have recently become a more general tool to control transition-metal-catalyzed reactions. Supramolecular interactions are powerful tools to generate catalysts in situ by self-assembly of functionalized ligand building blocks,[14] preventing intricate ligand synthesis, and utilize H-bond interactions for proper orientation of the substrate via the functional groups to tune the activity and selectivity of the catalyst.[15] The latter strategy was recently also applied in metalloradical carbene transfer reactions using supramolecular H-bond donor appended porphyrin complexes.[16] When functional ligand building blocks are used for the self-assembly of bidentate ligands, these functional groups can also interact with functional groups of the substrate. Breit and co-workers employed bidentate ligands based on self-assembly strategies using phosphine ligands with complementary H-bonding motifs, and they found that these functional groups activate allyl alcohols by hydrogen bonding.[17] We reported simple ligand building blocks that formed heterobidentate ligand complexes through a single hydrogen bond and determined that additional functional groups in the ligand give rise to H-bonding with the substrate, an interaction that appeared crucial in the enantio-

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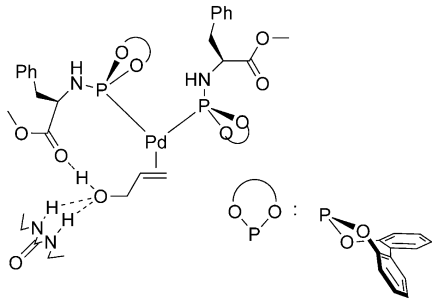


Scheme 2. Activation of allylic alcohols with H-bond donor ligand and 1,3-diethylurea.

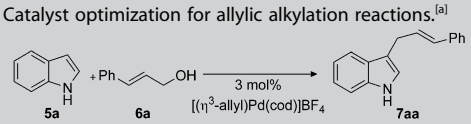
selective hydrogenation of Roche ester precursors.[18] Inspired by these results we decided to study these simple ligand building blocks in the activation of allyl alcohols.

Herein, we report a novel catalyst that operates through cooperative action of the metal and H-bonding interactions between the ligand and the substrate (Scheme 2). We also explored the effect of adding urea moieties as additives to further steer the activity and selectivity of the catalyst. Thus far palladium-catalyzed allylic alkylation reactions with monodentate phosphoramidites have been limited to activated allylic halides or acetates as substrates, where they display high enantio- and regioselectivity.[19] This is the first report wherein phosphoramidite-based palladium complexes are used in the direct conversion of allyl alcohols. We here disclose that a combination of phosphoramidite homocomplexes and urea building blocks provides an efficient and selective catalyst system for direct activation of allylic alcohols towards linear alkylated and aminated products by enabling complementary H-bonding between the catalyst, the substrate, and the urea moiety.

Results and Discussion

To study the concept of allyl alcohol activation with hydrogen bonds the alkylation of cinnamyl alcohol with indole was studied as a model reaction. Simple phosphoramidite and phosphine ligands were explored as ligands to form the palladium based catalyst by in situ mixing with $[(\eta^3\text{-allyl})Pd(cod)]BF_4$ (Scheme 3). The ligands varied in electronic properties (π-accepting and electron-donating abilities), **3** has a hydrogen-bond donor and in ligand **4** both hydrogen-bond-accepting and -donating groups are present. Reactions were carried out in the absence and presence of 3 mol% phenyl urea as a potential additional H-bond donor for activation of the alcohol.

Table 1. Catalyst optimization for allylic alkylation reactions.[a]

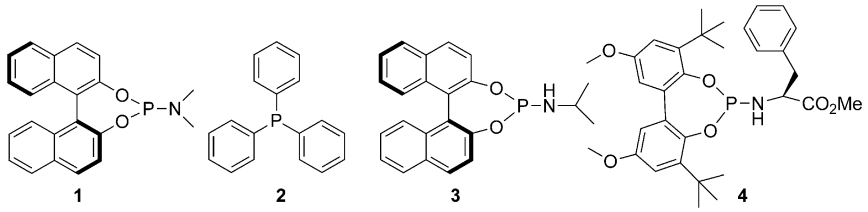


Entry	Ligand	Yield[b] [%]
1	**1**	65(3)[d]
2	**1**/phenyl urea[c]	53(3)[d]
3	**2**	21
4	**2**/phenyl urea[c]	30
5	**3**	trace
6	**3**/phenyl urea[c]	trace
7	**4**	62
8	**4**/phenyl urea[c]	90

[a] Reaction conditions: **5a** (0.128 mmol), **6a** (0.128 mmol), 3 mol% $[(\eta^3\text{-allyl})Pd(cod)]BF_4$, 6 mol% ligand, toluene (0.1 mL), 80 °C, 20 h. [b] Yields are determined via ^1H NMR where mesitylane used as an external standard. [c] 3 mol% phenyl urea. [d] *Bis*-cinnamylether formed as a side product.

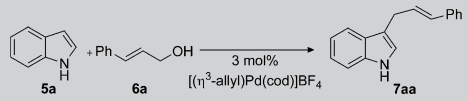
First, we examined commercially available monophos, **1**, and triphenylphosphine, **2**, ligands for catalytic activity. The stronger π-accepting monophos enabled higher conversions than PPh_3 (Table 1, entries 1 and 3). The addition of phenyl urea hardly affected the product yields when using homo-complexes of ligand **1** and **2** (entries 2 and 4). Additionally, we observed formation of bisdicinnamylether as a side product up to 3% when monophos **1** was applied as the ligand. The analogues ligand with the H-bond donor, isophos ligand **3**, did not show any activity, regardless of the presence of urea (entries 5 and 6). Interestingly, the amino-acid-substituted phosphoramidite **4** that has both H-bond-donor and -acceptor groups, resulted in 62% yield of the product without formation of any side products (entry 7). Remarkably, in the presence of phenyl urea as additive the complex based on this ligand (**4**) led to full conversion and 90% yield of the single linear alkylated product (entry 8). Notably, phenyl urea as additive only shows increased conversions if a ligand with functional groups is used. This suggests that the functional groups of the ligand form a more complex hydrogen-bond pattern with the urea and the substrate, which leads to the activation of the allylic alcohol (Scheme 2).

After having established a working protocol based on simple building blocks, we carried out C–C bond formation reactions for a series of indole derivatives with various allylic alcohols (Table 2). For this series of reactions 1,3-diethylurea was used as additive instead of phenyl urea, as 1,3-diethylurea has a better solubility. We have explored several urea derivatives with variable substituents, and it was found that 1,3-diethylurea gave rise to the highest activity (see Supporting Information). With these optimized reaction conditions, the catalyst system (ligand **4** + 1,3-diethylurea) was able to convert a wide variety of



Scheme 3. Phosphoramidite- and phosphine-type of ligands used for catalyst optimization.

Table 2. Allylic alkylation reactions of indole derivatives with various allylic alcohols.[a]

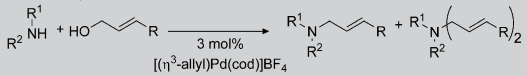


Entry	Nucleophile	Substrate	Product	Yield[b] [%]
1	**5a**	**6a**	**7aa**	42
2	**5b**	**6a**	**7ba**	69
3	**5c**	**6a**	**7ca**	77
4	**5d**	**6a**	**7da**	78
5	**5e**	**6a**	**7ea**	n.r.
6	**5a**	**6b**	**7ab**	97
7	**5a**	**6c**	**7ac** + **7ad**	22
8	**5a**	**6d**	**7ae**	26 (9:3:1)[c]
9	**5a**	**6e**	**7ad–7ae**	19 (9:3:1)[c]
10	**5a**	**6f**	**7af**	21

[a] Reaction conditions: **5a** (0.5 mmol), **6a** (0.75 mmol), 3 mol% $[(\eta^3\text{-allyl})Pd(cod)]BF_4$, 3 mol% 1,3-diethylurea, 6 mol% ligand **4**, toluene (2.5 mL), 80 °C, 20 h. [b] Isolated yields. [c] The ratio of the linear product to the branched and bis-allylated ones.

substrates in high yields and with high selectivity for the linear alkylated products. Primary and secondary aromatic allylic alcohols **6a** and **6b** afforded C3-selective allylated indoles up to 97% yield (entries 1 and 6). The reaction has a high tolerance to functional groups at the indole derivatives. *N*-Methyl, **5b**, C2-methyl, **5c**, and C5-methoxy, **5d**, substituted indole derivatives selectively produced linear alkylated products in high yields (entries 2–4). Notably, C3-methyl substituted indole, **5e**, did not form any allylation product (entry 5), indicating that the reaction is selective for C3-allylation products. The substrate scope was further extended for various aliphatic allylic alcohols that showed moderate isolated yields. Most likely, the

Table 3. Allylic amination reactions of primary and secondary amines with various allylic alcohols.[a]



Entry	Nucleophile	Substrate	Product	Yield[b] [%]
1	**8a**	**6a**	**8aa**	78(7)[c]
2	**8b**	**6a**	**8ba**	74(8)[c]
3	**8c**	**6a**	**8ca**	76
4	**8d**	**6a**	**8da**	95
5	**8e**	**6a**	**8ea**	87
6	**8f**	**6a**	**8fa**	55
7	**8g**	**6a**	**8ga** + **8ad**	85
8	**8a**	**6d**	**8ae**	55 (9:1:1)[d]
9	**8a**	**6e**	**8ad–8ae**	64 (9:1:1)[d]
10	**8a**	**6g**	**8ag**	61
11	**8a**	**6h**	**8ag**	54
12	**8a**	**6f**	**8af**	84

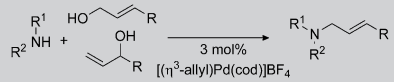
[a] Reaction conditions: **8a** (0.5 mmol), **6a** (0.75 mmol), 3 mol% $[(\eta^3\text{-allyl})Pd(cod)]BF_4$, 3 mol% 1,3-diethylurea, 6 mol% ligand **4**, toluene (2.5 mL), 80 °C, 20 h. [b] Isolated yields. [c] Yield of the disubstituted amines. [d] Ratio of linear products to branched and bis-allylated ones.

low boiling point of these substrates and products led to losses during work-up or during the reaction. Primary unsubstituted allyl alcohol, **6c**, and cyclic secondary aliphatic alcohol, **6f**, afforded single linear products (entries 7 and 10, whereas, methyl substituted linear and branched allylic alcohols, **6d** and **6e**, provided the same allylated products with trace amounts of di-substituted indole as 9:3:1, linear to branched and di-allylated product ratio (entries 8 and 9).

Henceforth, we studied the direct activation of allylic alcohols with primary and secondary amines. The urea assisted Pd catalyst (using ligand **4** + 1,3-diethylurea) afforded high yields and selectivity for linear monosubstituted products with aromatic and aliphatic allyl alcohols (Table 3). Importantly, electron deficient nucleophiles also afforded the desired products in high yields with traces of bis-allylated amines (entries 1–3). Electron-rich secondary amines, which are highly nucleophilic, formed the linear aminated products with excellent yields (entries 4, 5). Primary alkyl amines gave mono-allylated product in moderate yield (entry 6) whereas morpholine, **8g**, produced the desired product in excellent yield (entry 7). The expected products with aliphatic allyllic alcohols obtained with moderate yields. The methyl substituted allylic alcohols, **6d** and **6e**, formed the mixture of linear and branched products together with di-allylated (entries 8, 9). Dimethyl substituted primary and secondary allylic alcohols, **6g** and **6h**, generated only the linear product. No branched or bisallylated products were detected in these reactions (entries 10, 11). Also, secondary cyclic aliphatic alcohol afforded the monosubstituted product with excellent yields (entry 12).

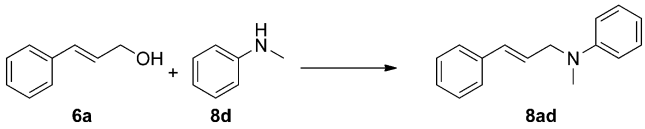
The application of this novel catalyst system was further studied in the direct activation of terpenols (Table 4). These are long-chain hydrocarbons with OH substituents that are essential oils found in nature. Terpenols are important building blocks for the preparation of the terpenes and intermediates for natural product synthesis. Functionalization of these valuable alcohols with amine derivatives leads to intermediates relevant for the synthesis of biologically active compounds. Excellent yields were obtained when these alcohols were reacted using the combined Pd/Ligand **4**/1,3-diethylurea catalytic system. Linear and branched isomeric alcohols, geraniol and linalool, **6k** and **6l**, showed full conversions with primary aromatic and secondary aliphatic amines, with high selectivity for the monoallylated linear products (entries 1–2 and 5–6). Additionally, longer chain alcohols, farnesol and neralidol, **6m** and **6n**, showed similar activity and regioselectivity (entries 3–4 and 7–8). Interestingly, the linear and the branched isomeric alcohols result in formation of the same linear products. This result suggests that these reactions go through the same intermediate for the corresponding allylic alcohols. Indeed, analysis of the reaction mixtures with ESI-MS show the formation of the same π-allylic intermediate during the conversion of either the linear or branched alcohols (see Supporting Information).

Table 4. Allylic amination reactions of primary and secondary amines with various allylic alcohols[a]



Entry	Nucleophile	Substrate	Product (*E/Z*)[b]	Yield[c] [%]
1	**8a**	**6k**	**8ak** 1:1.6	74
2	**8a**	**6l**	**8ak** 1:1.6	57
3	**8a**	**6m**	**8am** 1:1.6:1.7:2.5	90
4	**8a**	**6n**	**8am** 1:1.4:1.6:2.4	96
5	**8g**	**6k**	**8gk** 1:1.9	81
6	**8g**	**6l**	**8gk** 1:1.8	93
7	**8g**	**6m**	**8gm** 1: 3.3.2.5	57
8	**8g**	**6n**	**8gm** 1: 6.7: 5.0	57

[a] Reaction conditions: **8a** (0.5 mmol), **6a** (0.75 mmol), 3 mol% [(η3-allyl)Pd(cod)]BF_4, 3 mol% 1,3-diethylurea, 6 mol% ligand **4**, toluene (2.5 mL), 80 °C, 20 h. [b] The *E/Z* isomeric ratio of the products were determined by GC. [c] Isolated yields.



Scheme 4. The model allylic amination reaction of the kinetic studies.

Next, we studied the mechanism of the urea-assisted nucleophilic substitution of allylic alcohols. For the kinetic studies we chose the *N*-methylaniline, **8d**, as a nucleophile in combination with cinnamyl alcohol, **6a**, as the catalyst system produces a single product with full conversion and 95% isolated yield (Table 3, entry 4)—(Scheme 4). We studied the effect of the concentration of the alcohol substrate, the nucleophile, the Pd catalyst and urea additive by monitoring the reaction in time and analyzing the data with reaction progress kinetics.[20]

The reaction progress was monitored by GC and initial rates were calculated from the slope of curve taken at the beginning of the reaction. These data were utilized to determine the order of the each reactant (Figure 1). We observed first order kinetics in alcohol and zero order kinetics in nucleophile concentration (Figure 1a). These results are consistent with literature data where it was suggested that the oxidative addition is the rate determining step for the allylic substitution of allyl alcohol substrates.[21] As expected, the kinetic data reveal a first order kinetics in Pd catalyst. At high Pd concentrations we ob-

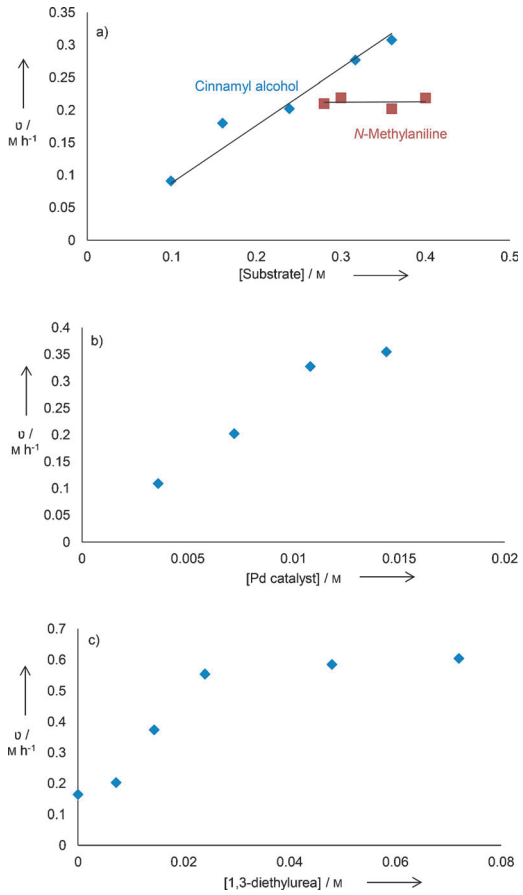


Figure 1. Kinetic analysis of amination reaction (Scheme 3) a) Rate versus substrate concentration of cinnamyl alcohol, **6a**, and *N*-Methylaniline, **8d**. b) Rate versus Pd catalyst concentration. c) Rate versus 1,3-diethylurea concentration.

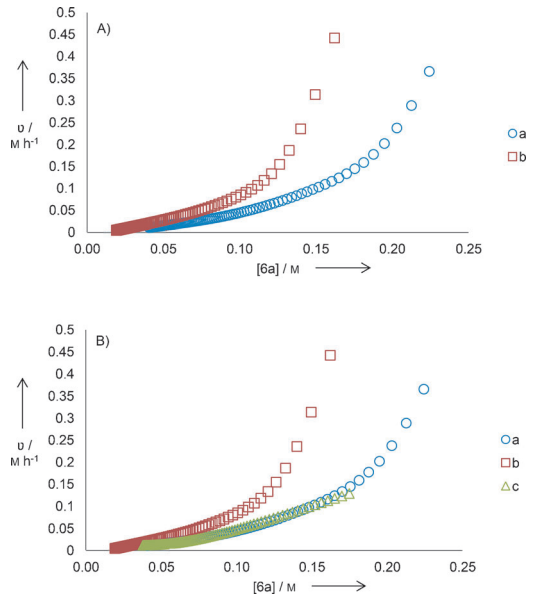


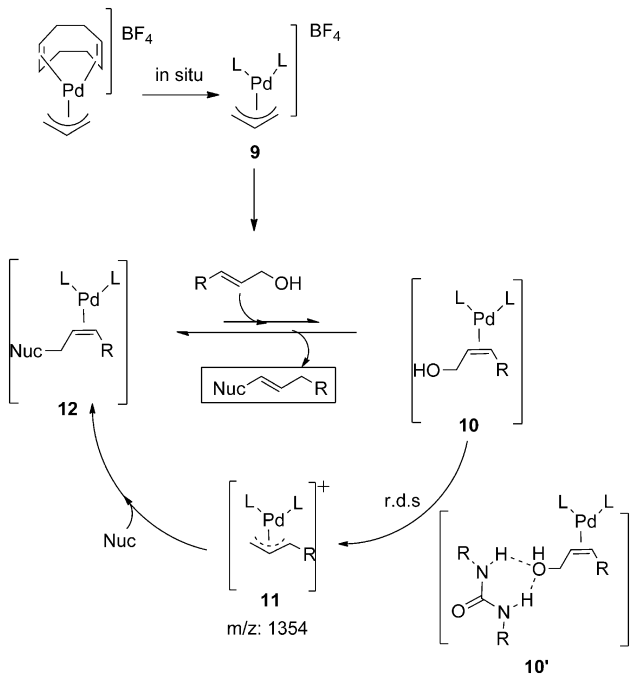
Figure 2. Same excess experiments A) Comparison of *run a*: [**6a**] = 0.24 M, [**8d**] = 0.36 M and *run b*: [**6a**] = 0.18 M, [**8d**] = 0.30 M, by reaction rate versus concentration of allylic alcohol, **6a**. B) Comparison of *run a* with product added reaction *run c*: [**6a**] = 0.18 M, [**8d**] = 0.30 M, [**8ad**] = 0.06 M.

served deviations from first order kinetics, which may indicate catalyst decomposition under these conditions (Figure 1b). Importantly, from the kinetic data it is clear that the presence of the urea additive increases the activity of the catalyst and the effect is stronger at higher concentration urea (Figure 1c). Above urea concentrations of 24 mM the reaction rate does not increase further. Notably, the reactions in the absence of urea gave less reproducible yields, indicating that the urea additive is also important to obtain reproducible results.

Recently, Blackmond developed progress kinetic analysis as a new methodology to analyze kinetic data.[20] In such approach the kinetic data are used to generate rate vs substrate concentration plots, from which one can directly see the order of the reaction. Interestingly, reactions that have different starting concentrations of the substrate should overlay in the event that there is no catalyst deactivation or product inhibition, important issues that are visualized in plots from two experiments. For reactions that have two different substrates such as in the current study, experiments are designed in which the excess of one of the two substrates remains the same, also allowing to make overlay plots to judge product inhibition/catalyst deactivation events. The parameter called the 'excess' is defined as initial concentration difference of two reactants that remains constant from beginning to the end. Accordingly, two reactions with same excess values with different absolute initial concentrations of the substrates were performed. From the plot of these two reactions (reaction rate versus substrate concentration) it is clear that these do not overlay, having a slower reaction rate for that with the highest concentration (Figure 2A). This indicates that we have catalyst decomposition or product inhibition. According to the Blackmond protocol, an additional experiment was performed with the same excess and in the presence of product. The concentrations were chosen as such that the amount of substrate is identical to that in experiment *b*, and the amount of product plus substrate is identical to that in experiment *a*. As is clear from the Figure 2B, the plots of reaction *a* and *c* are now nicely overlaying, indicating that the reaction suffers from product inhibition.

The perfect overlap observed in Figure 2B also shines light on the effect of water as additive under these conditions. In principle water, which is released during the reaction, could play a role in the activation of allylic alcohols, as has been observed for other systems.[13b] However, in our system water is not playing a major role, as otherwise the experimental kinetic curves of experiment *b* and *c* would not have over-layed. Full overlap of these kinetic curves suggests that the water that is formed during the reaction is neither participating significantly in product inhibition nor in allyl alcohol activation.

Based on the kinetic data we propose the mechanism for direct activation of allylic alcohols for the amination reactions as depicted in Scheme 5. In situ formed cationic phosphoramidite palladium precursor **9** reacts with the nucleophile to generate species **12.** Alkene exchanges leads to the formation Pd intermediate **10**. Subsequently, oxidative addition leads to the allyl intermediate **11**, which can undergo nucleophilic attack to



Scheme 5. Proposed mechanism for amination reactions of allylic alcohols.

form the product. Product inhibition is explained by the equilibrium between **12** and **10**. Zero order kinetics in nucleophile and first order kinetics in allylic alcohol, Pd and 1,3-diethylurea indicate that the oxidative addition is the rate determining step. This oxidative addition reaction is facilitated by the urea additive. Preliminary DFT calculations suggest that both in **10** and **10′** a hydrogen bond is formed between the substrate and the ligand, whereas in **10′** also hydrogen bonds are formed between the urea N-H and the alcohol (Figure 3).

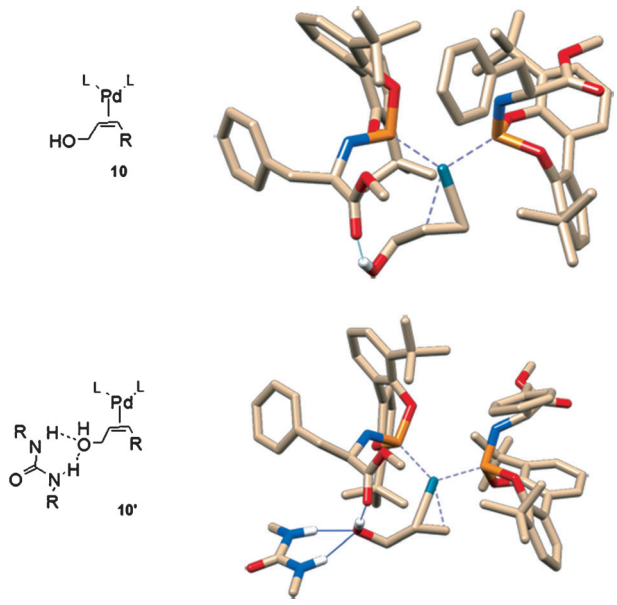


Figure 3. DFT-calculated intermediates of **10** and **10′**, displaying hydrogen bonds that are crucial according to kinetic analysis of reaction mechanism (Scheme 5).

Further calculations should demonstrate the effect of these hydrogen bonds on the transition states that lead to **11**.

Conclusions

We report a new, efficient, regioselective Pd catalyst system for direct activation of allylic alcohols that can be applied in alkylation and amination reactions. The catalyst has a broad substrate scope and is tolerant towards different functional groups. The phosphoramidite ligand with phenyl alanine moiety has functional groups that form supramolecular interactions with the substrate. In addition, the 1,3-diethylurea building also forms hydrogen bonds with the allylic alcohol, which leads to activation of the allylic alcohols. Detailed kinetic studies for amination reactions show that this reaction is first order in allyl alcohol, urea, and palladium, supporting that oxidative addition is the rate determining step and this step facilitated by urea. This simple catalyst system opens up new synthetic routes to functionalize allylic alcohols with a minimum of waste formation, including those based on biorenewable terpenols.

Experimental Section

General procedure for alkylation and amination reactions: Allylic alcohol, **6a**, (0.5 mmol) and nucleophile, **8a**, (0.75 mmol) added to the mixture of 3 mol% [(η^3-allyl)Pd(cod)]BF_4, 3 mol% 1,3-diethylurea and 6 mol% ligand **4** in toluene (2.5 mL). Reactions were completed in 20 h at 80 °C. Products were isolated in pure form after column chromatography.

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Keywords: alkylation · aminations · homogeneous catalysis · hydrogen bonding · palladium

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