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Catalytic Allylation

Mechanistic Insights into the Pd-Catalyzed Direct Amination of Allyl Alcohols: Evidence for an Outer-Sphere Mechanism Involving a Palladium Hydride Intermediate

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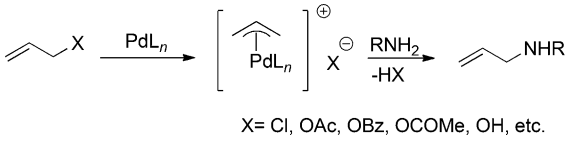
Dedicated to Professor Björn Åkermark on the occasion of his 80th birthday

Abstract: The mechanism of direct amination of allyl alcohol by a palladium triphenylphosphite complex has been explored. Labelling studies show that the reaction proceeds through a π-allylpalladium intermediate. A second-order dependence of reaction rate on allyl alcohol concentration was observed. Kinetic isotope effect studies and ESI-MS studies are in agreement with a reaction proceeding through a palladium hydride intermediate in which both O–H bond and C–O bond cleavages are involved in rate-determining steps. A stereochemical study supports an outer-sphere nucleophilic attack of the π-allylpalladium intermediate giving complete chiral transfer from starting material to product.

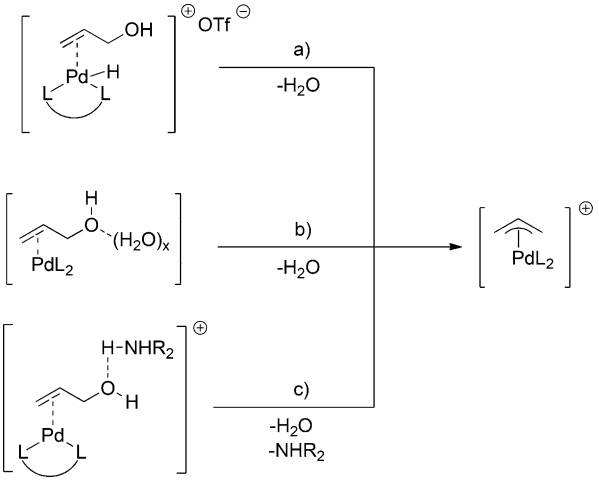
Palladium-catalyzed allylation is a powerful method to construct C–N bonds in organic synthesis.[1] Various allyl compounds such as halides,[2a] esters,[2b,c] ethers,[2d] and carbonates[2e] have been employed as substrates in this transformation. Direct amination of allyl alcohols (X = OH, Scheme 1), in which



Scheme 1. Palladium-catalyzed allylic amination with allyl substrates.

the hydroxyl group is not converted into a better leaving group in an additional synthetic step, has recently attracted attention due to economic and environmental advantages.[3] The poor leaving group ability of the hydroxyl group has led to only a limited number of conversions of unactivated allyl alcohols into allyl amines have been reported in the literature (Scheme 1).[4]

The key step in the direct amination of allyl alcohols by transition metal catalysts is the C–O bond cleavage of the hydroxyl group to generate a π-allylpalladium intermediate. Palladium complexes bearing phosphine ligands, for example, PPh_3, do not promote the C–O bond cleavage of allyl alcohols without the addition of Lewis acidic activators.[5] Instead, electron-deficient phosphorus ligands (phospholes, diphosphinidenecyclobutene, and triphenylphosphite) have successfully been used.[4,6] Different mechanistic pathways have been proposed to promote the C–O bond cleavage in allyl alcohol (**1**) by different Pd complexes as shown in Scheme 2.[7] Ozawa proposed that a hydridopalladium complex bearing the diphosphinidenecyclobutene ligand was responsible for this process (Scheme 2, path a).[7a] Theoretical calculations have supported water assisted hydrogen bonding based activation of the hydroxyl group in order to generate a π-allylpalladium intermediate (Scheme 2, path b).[7b] Theoretical calculations have also supported the formation of π-allylpalladium complex with different phosphorus ligands through the elimination of water, activated by an ammonium salt (Scheme 2, path c).[8]



Scheme 2. Proposed mechanisms for the C–O bond cleavage of the hydroxyl group of **1**.

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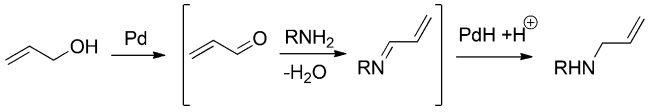
Recently, Ikariya and co-workers reported the use of Pd[P(OPh)$_3$]$_4$ as the catalyst for the direct activation of allyl alcohols with different nucleophiles.[7c] The methodology was recently expanded to a variety of anilines in combination with the ring-closing metathesis reaction to synthesize pyrrolines and hydrazines.[9] We became interested in exploring the reaction mechanism of the C–O bond cleavage of allyl alcohol and the C–N bond formation. The allylation of arylamines from unactivated allyl alcohols may proceed by different reaction mechanisms. One possibility is the formation of a π-allylpalladium intermediate (Scheme 1 and 2) followed by nucleophilic attack of an amine. Another possibility is the hydrogen borrowing mechanism to generate butenal, followed by condensation of the amine and subsequent palladium hydride insertion to give the final product (Scheme 3).[10]

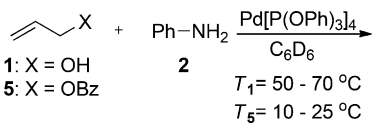


Scheme 3. Hydrogen borrowing mechanism.

To investigate the mechanism of the allylation of aniline (**2**) from unactivated **1** to generate allylaniline (**3**) and diallylaniline (**4**) catalyzed by Pd[P(OPh)$_3$]$_4$, several studies were performed. To determine whether the reaction proceeded via a π-allylpalladium intermediate or by a hydrogen borrowing pathway, labeling studies with allyl 1,1-D$_2$ alcohol ([D$_2$]-**1**) were performed. If the aldehyde was generated, the deuterium would be found only at the α-position. If a π-allylpalladium complex was formed, deuterium would be observed in both α- and γ-positions. When the reaction was performed, a 1:2:1 ratio (Scheme 4) of three deuterated products ([1,1-D$_4$]-**4**, [1,3-D$_4$]-**4**, and [3,3-D$_4$]-**4**) was obtained, supporting the intermediacy of a π-allylpalladium species. This encouraged us to study the activation mode of the hydroxyl group.

The initial rate of allylation of **2** with **1** was determined by ^{1}H NMR spectroscopy integrating the formation of **3** and **4** and comparing to an internal standard (Supporting Information). Kinetic measurements were performed at four different reaction temperatures between 50 and 70 °C to allow determination of activation parameters (Table 1). The Eyring plot

Table 1. Thermodynamic parameters for the allylation of **2** with **1** and **5** by Pd[P(OPh)$_3$]$_4$.



Substrate	$\Delta H^{\ddagger}$ [kcal mol^{-1}]	$\Delta S^{\ddagger}$ [cal mol^{-1} K^{-1}]
1	19.9	−21.2
5	14.2	−29.2

provided an activation enthalpy of $\Delta H^{\ddagger} = 19.9$ kcal mol^{-1} and an activation entropy of $\Delta S^{\ddagger} = -21.2$ cal mol^{-1} K^{-1}. The entropy ($\Delta S^{\ddagger}$) is less negative and the enthalpy is more positive for the amination of **1** compared to the amination of allyl benzoate (**5**) ($\Delta H^{\ddagger} = 14.2$ kcal mol^{-1} and $\Delta S^{\ddagger} = -29.2$ cal mol^{-1} K^{-1}) with a better leaving group.

As expected, the initial rate of the reaction showed a first-order dependence on Pd[P(OPh)$_3$]$_4$ concentration (see the Supporting Information). Interestingly, the rate of the reaction was independent of aniline concentration (see the Supporting Information). In order to examine the influence of the water, the reaction was performed separately with water-free C$_6$D$_6$ and C$_6$D$_6$ saturated with water. The result showed no difference in the rate of the reaction between dried or wet reaction conditions. Thereby, neither ammounium salt nor water are involved in the rate-determining step in the Pd[P(OPh)$_3$]$_4$ catalyzed allylic amination (Scheme 2, paths b and c).[5,8] Surprisingly, the allylation of **2** with **1** catalyzed by Pd[P(OPh)$_3$]$_4$ showed an unprecedented second-order dependence on allyl alcohol concentration (Figure 1).

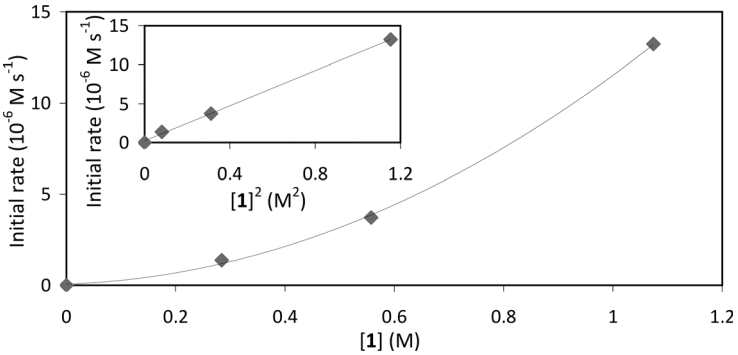
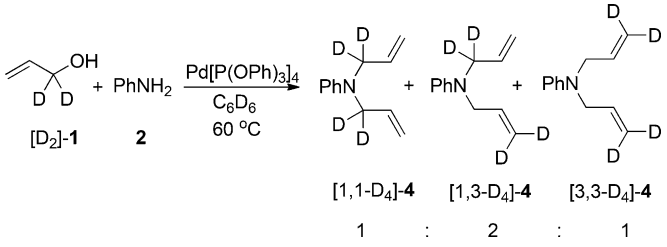


Figure 1. Second-order dependence of the initial rate on the concentration of **1** in the Pd[P(OPh)$_3$]$_4$ catalyzed the allylation of **2**. Reaction conditions: substrate **1** (0.174–0.696 M), **2** (0.174 M), Pd[P(OPh)$_3$]$_4$ (2 mol%), C$_6$D$_6$, 55 °C.



Scheme 4. Amination of deuterated allyl alcohol gives a statistical distribution of products as expected for a mechanism involving a π-allylpalladium intermediate.

From the kinetic data, a rate equation for the allylation of **2** by **1** catalyzed by Pd[P(OPh)$_3$]$_4$ under standard conditions is expressed in [Equation (1)]. The second order rate-dependence in **1** could be explained by a hydrogen bonding assistance promoted by **1** in analogy to what has previously been proposed for water or ammonium (Scheme 2, paths b and c). Alternative-

ly, the role of the second molecule of **1** is to act as a hydrogen source to generate a palladium hydride intermediate (Scheme 2, path a).

$$\text{rate} = k[\text{Pd}][\mathbf{1}]^2 \quad (1)$$

To get a better mechanistic understanding, deuterium kinetic isotope effect measurements for the allylation of **2** by **1** were carried out.[11] A deuterium kinetic isotope effect (KIE) was determined by comparing the rate of allylation of **2** by [D_2]-**1** and **1**. A large secondary deuterium KIE ($k_{CH}/k_{CD} = 1.34 \pm 0.01$) was observed (Table 2). The large secondary deuterium KIE is consistent with the proposal that the C–O bond cleavage occur either before or during the rate-determining step. For comparison, we carried out additional deuterium KIE experiments with **5** having a good leaving group. A secondary KIE for allyl benzoate ($k_{CH}/k_{CD} = 1.11 \pm 0.04$) was determined by preparing allyl [D_2]-1,1-benzoate ([D_2]-**5**) and comparing its rate of allylation to **5** at 25 °C.[12] The use of $CH_2=CHCH_2OD$ ([D_1]-**1**) for the allylation of **2** with Pd[$P(OPh)_3$]$_4$ gave a primary deuterium KIEs ($k_{OH}/k_{OD} = 2.06 \pm 0.08$) indicating that an O–H bond cleavage occurs either before or during the rate-determining step (Table 2).[13] To determine whether the cleavage of the O–H proceeds before, simultaneously, or after the C–O bond cleavage, the allylation of **2** was carried out with doubly labeled $CH_2=CHCD_2OD$ ([D_3]-**1**). Comparison of the rate constants for the reaction of amination with **1** and [D_3]-**1** gave deuterium KIEs of $k_{CHOH}/k_{CDOD} = 2.05 \pm 0.02$ (Table 2). Thereby, the doubly labeled allyl alcohol ([D_3]-**1**) showed a similar KIE (2.05) as observed for [D_1]-**1** (2.06).[14]

Table 2. Kinetic deuterium isotope effects on the allylation of **2** with **1** or **5** by Pd[$P(OPh)_3$]$_4$.

1/[D_2]-**1**	k_{CH}/k_{CD}	1.34 ± 0.01
1/[D_1]-**1**	k_{OH}/k_{OD}	2.06 ± 0.08
1/[D_3]-**1**	k_{CHOH}/k_{CDOD}	2.05 ± 0.02
[D_1]-**1**/[D_3]-**1**	k_{CDOH}/k_{CDOD}	1.00 ± 0.05
5/[D_2]-**5**	k_{CH}/k_{CD}	1.11 ± 0.04

The absence of a product isotope effect rules out the possibility that the second molecule of **1** activates the hydroxyl group of **1**, which is similar to what has been proposed for water or ammonium ions (Scheme 2, paths b and c).[15] The results are consistent with a mechanism in which the O–H bond cleavage occurs in a separate step, prior to the C–O bond cleavage, with either a negligibly lower (Figure 2, E_a') or with a similar (Figure 2, E_a'') activation energy (Figure 2). This would explain why the secondary KIE is not observed in the presence of the primary KIE.[16] These data are also consistent with the observed second-order dependence in **1**. Thus, the primary deuterium KIE of 2.06, may indeed indicate an insertion by palladium to the O–H bond of **1** to generate a palladium hydride intermediate in the rate-determining step. Similar KIE have been observed in rate-determining O–H bond cleavage by other transition metal catalysts.[13]

A palladium hydride intermediate that promotes the C–O bond cleavage to generate a π-allylpalladium complex has previously been proposed but never observed.[17] Attempts to detect a palladium hydride complex by ^{1}H NMR failed, probably due to a fast conversion (Figure 2).[17a] To overcome this problem, ESI-MS was used to analyze the hydride complex for the oxidative addition step. Attempts to detect the palladium hydride complex of **1** and [D_2]-**1** also failed. This is consistent with the negligibly lower energy barrier for the O–H bond cleavage, as compared to the C–O bond cleavage (Figure 2). Therefore, the more sterically crowded crotyl alcohol was subjected to the same reaction in the presence of Pd[$P(OPh)_3$]$_4$. The ESI-MS spectrum revealed a signal at *m/z* 899, which was consistent with the Pd hydride complex (PdH(OC_4H_7)NEt_3[$P(OPh)_3$]$_2$). The structure of the ion at *m/z* 899 was further confirmed by the MS/MS collision-induced-dissociation (CID), where ions of complexes with the masses that correspond to PdH(OC_4H_7) [$P(OPh)_3$]$_2$ and PdH(OC_4H_7)$P(OPh)_3$ were also observed (Figure 3).

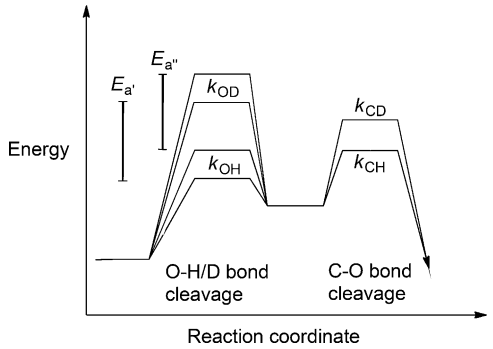


Figure 2. Energy profile of the O–H bond and the C–O bond cleavage reactions.

Both[18] an inner-sphere mechanism,[19] in which the nucleophile coordinates the metal prior to attack, and an outer-sphere[2e,20] mechanism, in which the nucleophile attacks the π-allyl without prior coordination to the metal, have been suggested for the palladium-catalyzed allylation of amines. To determine whether the allylation of aromatic amines proceeds through an inner or outer-sphere mechanism, enantiomerically enriched allyl alcohol (*R*)-**6** was prepared and converted to the corresponding piperidine in the presence of Pd[$P(OPh)_3$]$_4$ (Scheme 5). The allylic substitution of (*R*)-**6** proceeded with an overall retention of stereochemistry (double inversion), as determined by chiral HPLC and single-crystal X-ray analysis of hydrochloride salt of the piperidine (*R*)-**7** (Figure 4). The formation of (*R*)-**7** indicated that the reaction proceeded through an outer-sphere mechanism. Moreover, the palladium-catalyzed intramolecular amination of enantioenriched allyl alcohol (*R*)-**6** to (*R*)-**7** proceeded with an excellent chirality transfer.

A mechanism for the palladium-catalyzed direct amination of allyl alcohols is proposed (Scheme 6). Palladium inserts into the O–H bond of **1** to generate palladium hydride intermediate **A**. This step has an activation barrier which is either negligibly lower or equal to the rate-determining step ($k_2 \geq k_1$). This is consistent with the observed primary KIE for the O–H bond cleavage ($k_{OH}/k_{OD} = 2.06$). The ion of the corresponding palladium hydride complex from crotyl alcohol was observed by ESI-

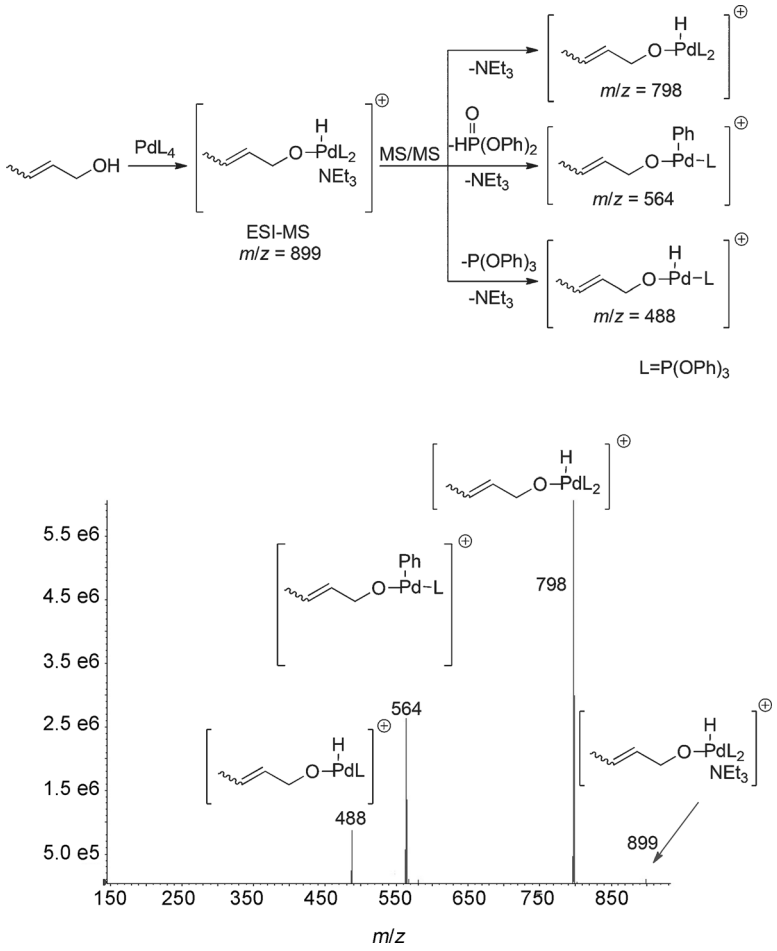
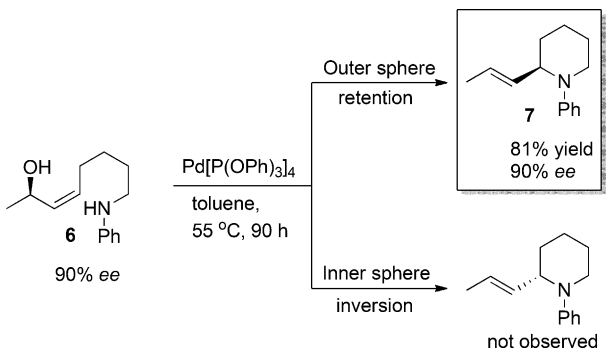


Figure 3. CID mass spectrum of the signal at *m/z* 899 of crotyl alcohol.



Scheme 5. Palladium-catalyzed intramolecular amination with retention of configuration, supporting an outer-sphere mechanism.

MS and MS/MS CID. The palladium hydride intermediate (**A**) coordinates to a second molecule of **1** to generate intermediate **B**, which is proposed to be responsible for the cleavage of the C–O bond of **1** to generate the π-allylpalladium intermediate **C**.[7d] This barrier is visible by a large secondary KIE ($k_{CH}/k_{CD}=1.34$) with the deuterated [D_2]-**1** compound, but not with the doubly deuterated [D_3]-**1** ($k_{CHOH}/k_{CDOD}=2.05$), in accordance with the fact that the C–O bond cleavage occurs after the O–H bond cleavage. The second-order dependence in **1** is also consistent with two separate steps with equal energy barriers ($k_2 \geq k_1$). Addition of an aromatic amine to either terminal carbon of the π-allyl occurs through an outer-sphere mechanism, without prior coordination to palladium, to generate intermediate **D**, consistent with the observed double inversion in transforming alcohol (*R*)-**6** to (*R*)-**7**. Proton transfer from the amine and ligand exchange produce the allylamine and regenerate the $Pd[P(OPh)_3]_2$.

Experimental Section

General procedure

A flame-dried Schlenk tube containing a stir bar was charged with $Pd(dba)_2$ (30 mg, 0.0525 mmol). The tube was capped with a rubber septum, evacuated and backfilled with argon. 0.8 mL of CH_2Cl_2 and $P(OPh)_3$ (108 μL, 0.42 mmol) was added by syringe. The slurry was degassed by three freeze-pump-thaw cycles and stirred at room temperature for 30 min. The formation of $Pd[P(OPh)_3]_4$ complex was confirmed by ^{31}P NMR spectroscopy. The complex gives a characteristic singlet at $\delta = 139$ ppm. The residual solvent was evaporated in vacuo. Aniline solution (0.4 mL, 0.435 M in C_6D_6) was added to an the NMR tube with 0.2 mL of $Pd[P(OPh)_3]_4$ (2.9 mM in C_6D_6) under an argon atmosphere. Degassed allylic alcohol (47 μL, 0.696 mmol) was added by syringe; the NMR tube was shaken, and inserted into the spectrometer preheated to 65 °C. The initial rate method was used

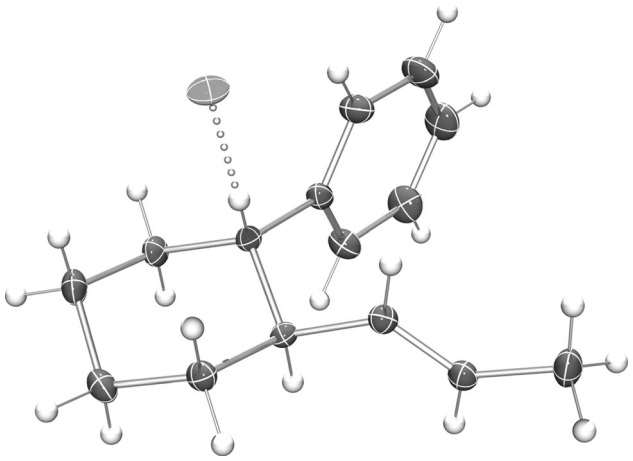
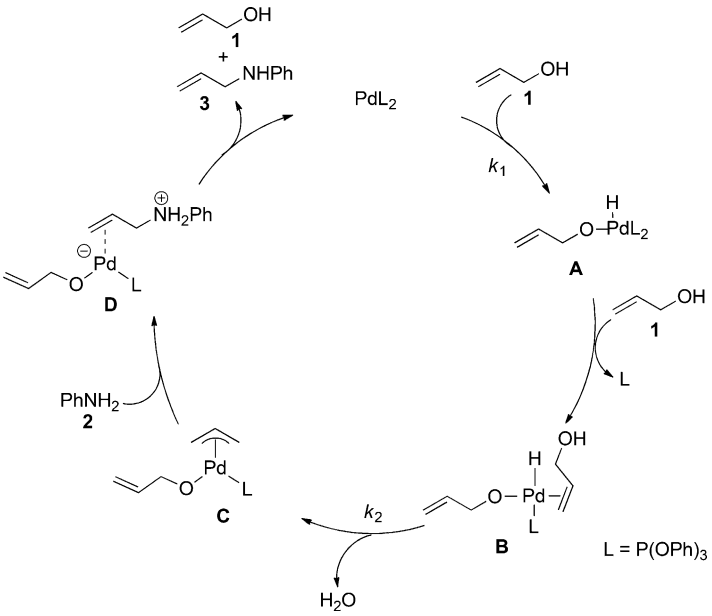


Figure 4. X-ray structure of piperidine **7**·HCl with thermal ellipsoids drawn at the 50% probability level.



Scheme 6. Proposed mechanism for Pd-catalyzed direct aminations of allyl alcohols.

to determine the kinetic dependence on reactant concentrations. Initial rates were estimated from the slope of a plot of the concentration of allylated product (< 15% conversion) against time. The kinetics of the allylation were determined by ^{1}H NMR spectroscopy. The reaction was followed by ^{1}H NMR spectroscopy by integrating the ratio of *N*-allylaniline at $\delta = 3.35$ ppm, and *N,N*-diallylaniline at $\delta = 3.60$ ppm and the ferrocene signal at $\delta = 4.00$ ppm. Because, we could not integrate the aniline directly due to overlap of chemical shifts, the concentration of aniline was determined indirectly. After each kinetic run, the sample was taken out of the probe and let to react to completion in an oil-bath. By this method, the total amount of product could be measured and thereby initial concentration of aniline could be determined. Thereby at a given reaction time the concentration of aniline was determined by subtracting the concentration of mono- and diallylated product.

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Keywords: alcohols · allylation · kinetics · palladium · reaction mechanisms

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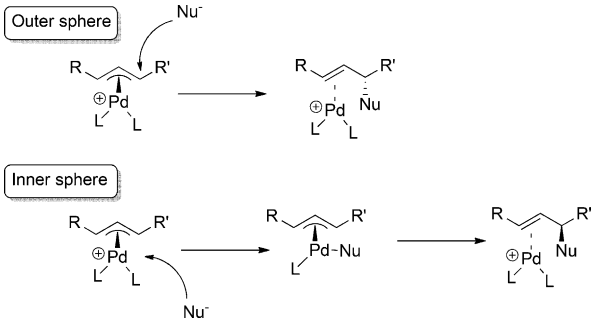
[18] There are two possible pathways for nucleophilic addition to π-allylpalladium intermediate: one is that the nucleophile first coordinates the metal center, followed by a bond-forming reductive elimination (inner-sphere mechanism). The other is that the nucleophile first attacks the allylic carbon center and substitutes the palladium complex (outer-sphere mechanism). For review of inner-sphere and outer-sphere mechanisms, see: a) B. M. Trost, D. L. VanVranken, *Chem. Rev.* **1996**, *96*, 395 – 422; b) B. M. Trost, T. Zhang, J. D. Sieber, *Chem. Sci.* **2010**, *1*, 427 – 440; c) J.-E. Bäckvall, *Acc. Chem. Res.* **1983**, *16*, 335 – 342.



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