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Palladium-Catalyzed Intramolecular Hydroamination of Allenes Coupled to Aerobic Alcohol Oxidation

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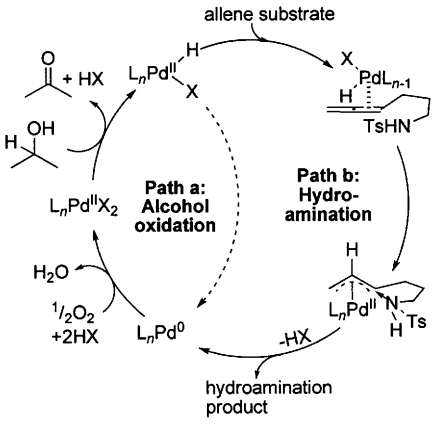
The direct addition of a nitrogen–hydrogen bond across an unsaturated carbon–carbon bond (hydroamination) is a powerful strategy to generate nitrogen–carbon bonds and an effective way to synthesize biologically active nitrogen-containing heterocycles.[1] The development of catalyst systems for this type of transformation has been extensively studied. Although lanthanides[2] and Group IV transition metals[3] are among the most reactive catalyst systems, the synthetic utility of these protocols is compromised by the poor functional group compatibility and excessive air and moisture sensitivity. In contrast, late transition metals have been shown to have better tolerance. For instance, some late transition metals catalyze the addition of amines to vinylarenes;[4] the catalysis of the addition of amides and sulfonamides to alkenes, allenes, and dienes[5,6] has also been reported recently. Most late-transition-metal-catalyzed hydroaminations require the use of phosphine ligands, and, hence, are not compatible with aerobic reaction conditions owing to rapid degradation of phosphine ligands. On the other hand, nitrogen-containing ligands, which are generally stable under oxidative reaction conditions,[7] have rarely been used in hydroamination reactions.[8] Herein, we report the first Pd^{II}-catalyzed intramolecular hydroamination of allenes under a dioxygen atmosphere, in which bathocuproine[9] is used as the ligand.

During the past ten years, many effective palladium catalyst systems, which have been based on nitrogen-containing ligands, have been developed for the aerobic oxidation of alcohols[10] and in which a Pd^{II}–hydride species was generated as an intermediate.[11] However, the Pd^{II}–hydride species is generally considered to undergo rapid reductive elimination to yield Pd^0, especially in the presence of base (Scheme 1, Path a).[12] We reasoned that if allenes could coordinate to the Pd^{II} center before the Pd^{II}–hydride intermediate undergoes reductive elimination, a π-allyl–Pd^{II} intermediate could form through the allene insertion into Pd–H bond.[13,14] Subsequent intramolecular attack by a nitrogen nucleophile (e.g., tosylamide) at the π-allyl–Pd^{II} intermediate would then lead to the corresponding hydroamination product and a Pd^0 species, which could readily be reoxidized by *molecular dioxygen* to complete the catalytic cycle (cf. Scheme 1, Path b).[15]



Scheme 1. Hypothesis of hydroamination of allenes.

We set out to examine the above hypothesis by testing the reaction of *N*-(γ-allenyl)tosylamide (**1a**) with the proposed Pd^{II}–hydride species formed in aerobic oxidation of isopropyl alcohol. Several nitrogen-containing ligands that have been reported in palladium-catalyzed aerobic alcohol oxidation were tested in our initial studies. Treatment of **1a** (0.1 mmol) with $Pd(OAc)_2$ (5 mol%) and (−)-sparteine

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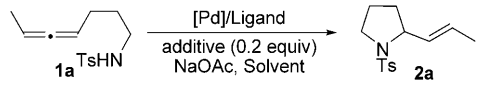
(10 mol%) in isopropyl alcohol (1 mL) under 1 atm O_2 afforded cyclic hydroamination product *E*-**2a** with high regioselectivity in low yield (26%; Table 1, entry 1), along with

Table 1. Screen results of palladium-mediated hydroamination of allene.[a]



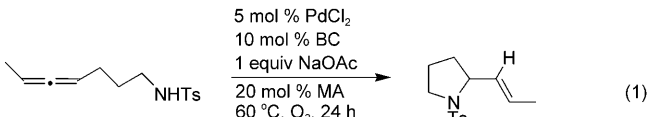
Entry	[Pd]	Ligand	Additive	Solvent	Yield [%][b]
1	$Pd(OAc)_2$	(−)-sparteine	–	*i*PrOH	26
2	$Pd(OAc)_2$	BC[f]	–	*i*PrOH	24
3	$Pd(OAc)_2$	pyridine	–	*i*PrOH	0
4	$Pd(OAc)_2$	Et_3N	–	*i*PrOH	0
5	$Pd(OAc)_2$	bipy	–	*i*PrOH	trace
6	$Pd(OAc)_2$	phen[g]	–	*i*PrOH	trace
7	$Pd(OAc)_2$	–	–	*i*PrOH	0
8	$PdCl_2$	BC	–	*i*PrOH	50
9	$PdCl_2$	BC	MA[h]	*i*PrOH	67
10	$PdCl_2$	BC	BQ[i]	*i*PrOH	35
11	$PdCl_2$	BC	NQ[j]	*i*PrOH	15
12[c]	$PdCl_2$	BC	MA	*i*PrOH	83
13[c,d]	$PdCl_2$	BC	MA	*i*PrOH	56
14[c,e]	$PdCl_2$	BC	MA	*i*PrOH	0
15	$PdCl_2$	BC	MA	MeOH	27
16	$PdCl_2$	BC	MA	*n*PrOH	69
17	$PdCl_2$	BC	MA	BnOH	10
18	$PdCl_2$	BC	MA	toluene	0

[a] Reaction conditions: **1a** (0.1 mmol), [Pd] (5 mol%), ligand (10 mol%), NaOAc (1 equiv), solvent (1 mL) at 60°C. [b] GC yield, tetradecane as internal standard. [c] *i*PrOH (2 mL). [d] Under air. [e] Under N_2. [f] BC = bathocuproine. [g] phen = 1,10-phenanthroline. [h] MA = maleic anhydride. [i] BQ = 1,4-benzoquinone. [j] NQ = 1,4-naphthoquinone.

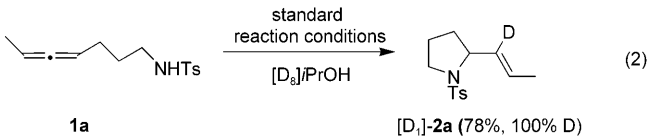
the formation of acetone. Utilization of bathocuproine (BC, 10 mol%) as a ligand led to the similar result (entry 2). Other commonly used nitrogen-containing ligands such as pyridine (Py), triethyl amine (TEA), bipyridine (Bipy) and 1,10-phenanthroline (phen) were not effective (entries 3–6). No reaction occurred in the absence of ligand (entry 7). During the optimization of reaction conditions, we found that the reaction with bathocuproine afforded better reproducibility than (−)-sparteine. Palladium source screen indicated that $PdCl_2$ was a more efficient catalyst than $Pd(OAc)_2$ (entry 8). Alkenes with electron-withdrawing groups[16] were tested as additives in this reaction; maleic anhydride (MA, 20 mol%) was found to give better result (67%, entry 9) than other additives, such as benzoquinone (BQ) and 1,4-naphthoquinone (NQ) (entries 10 and 11). Lower substrate concentration seemed beneficial to this reaction: the reaction of **1a** gave the best yield (83%) when the reaction was conducted in a 0.05 M solution of isopropyl alcohol (entry 12). The same reaction under air still afforded the hydroamination product in moderate yield (entry 13). No reaction occurred under a nitrogen atmosphere (entry 14). Finally, isopropyl alcohol was proven to be superior to other alcohols, such as methanol, *n*-propanol and benzyl alcohol (entries 15–17). It is also worth noting that no reaction was observed in toluene (entry 18).[17]

Based on the optimized reaction condition, the substrate scope of this hydroamination reaction was then investigated with a variety of allene substrates. Substrates bearing different protecting groups were tested. The reaction with nosylamide **1b** afforded significantly lower conversion than tosylamide **1a** (Table 2, entries 1-2). When *N*-tosylimide **1c**, which has an acidic N−H proton, was treated under standard conditions, no reaction occurred (entry 3). These observations could be attributed to the inhibitory effect of acidic proton on aerobic alcohol oxidation.[18] A number of internal allene substrates bearing two or three substituents (**1d–i**) underwent effective intramolecular hydroamination to afford the corresponding products with high regioselectivity, and the configuration of the resulting double bonds in the products was exclusively *trans* (entries 4–9). For allene **1f**, the mixture of **2f** and **2f′** (ratio of 1:1.2) was generated due to alkene isomerization (entry 6). It is worth noting that the substrates **1j** and **1k**, bearing hydroxyl and ester groups, respectively, both afforded hydroamination products in good yields, indicating that this catalytic system has better functional group tolerance (entries 10 and 11). For terminal allene **1l**, compound **2l** was obtained in a slightly low yield (41%; entry 12). However, terminal allene substrates bearing two substituents (**1m** and **1n**) afforded moderate yields of the five-membered cylic products (entries 13 and 14). For the reaction of **1o**, which has one more carbon atom tethered between amide and allene, the substituted piperidine product **2o** was obtained in 61% yield (entry 15).

To explore our initial mechanism hypothesis, two deuterium-labeled solvents were used to determine the origin of the proton incorporated into the cyclic product. When $(CH_3)_2CHOD$ was used as solvent, no deuterium was incorporated into the product [Eq. (1)]. In the case of $(CD_3)_2CDOD$, the reaction afforded hydroamination product [D_1]-**2a** in 78% yield and 100% deuterium incorporation [Eq. (2)]. These observations are consistent with the hypothesis that the intermediate Pd^{II}-hydride is generated from β-hydride elimination of alkoxypalladium species in Pd-catalyzed alcohol oxidation,[11] rather than from oxidative addition of HX (acid proton) to Pd^0 center.[13,19]



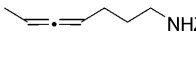
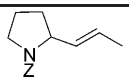
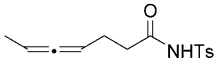
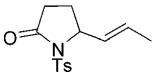
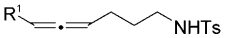
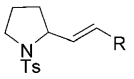
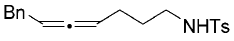
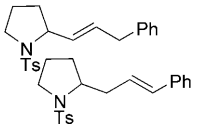
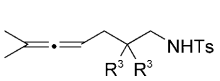
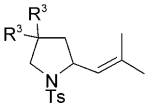
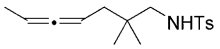
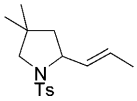
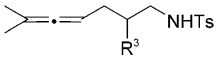
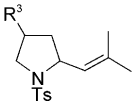
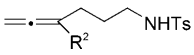
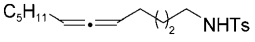
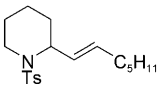
(1)



(2)

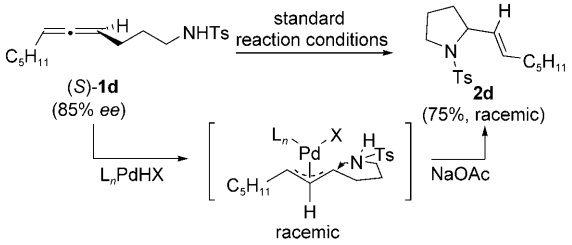
To confirm the formation of the proposed intermediate π-allyl–Pd^{II} species, chiral substrate (*S*)-**1d** was synthesized

Table 2. Pd-catalyzed hydroamination of allenes.[a]

Entry	Substrate (**1**)		Product (**2**)		Yield [%][b]
1		**1a** Z = Ts		**2a**	82
2		**1b** Z = Ns		**2b**	20[g]
3		**1c**		**2c**	0
4		**1d** $R^1 = C_5H_{11}$		**2d**	72
5[c,d]		**1e** $R^1 = i$Pr		**2e**	71
6[c]		**1f**		**2f**+ **2f′**	64 (1:1.2)[h]
7		**1g** $R^3 = H$		**2g**	85
8[c]		**1h** $R^3 = Me$		**2h**	78
9[c,e]		**1i**		**2i**	67
10[c]		**1j** $R^3 = CH_2OH$		**2j**	62 (2:1)[i,j]
11		**1k** $R^3 = CH_2OAc$		**2k**	69 (5:3)[i]
12		**1l** $R^2 = H$		**2l**	41
13[c]		**1m** $R^2 = Me$		**2m**	69
14[c]		**1n** $R^2 = C_5H_{11}$		**2n**	52
15[f]		**1o**		**2o**	61

[a] Reaction conditions: **1** (0.1 mmol), $PdCl_2$ (5 mol%), BC (10 mol%), MA (20 mol%) and NaOAc (1 equiv) in *i*PrOH (2 mL) at 60°C under 1 atm O_2. [b] Isolated yield; [c] MA (10 mol%). [d] 13% **1e** was recovered. [e] 50°C; [f] 75°C. [g] 50% **1b** was recovered. [h] The ratio of **2f** and **2f′**. [i] The ratio of *cis* and *trans* isomers. [j] 13% substituted tetrahydrofuran product was obtained.

and submitted under standard condition. A racemic product is expected if the π-allyl–Pd^{II} species was involved as a key intermediate.[20] The reaction of (*S*)-**1d** (85% *ee*) indeed afforded racemic product **2d** in 75% yield [Eq. (3)], which strongly supports our proposed mechanism which features a π-allyl–Pd^{II} complex as a key intermediate (Scheme 1, path b).



(3)

In summary, we have developed a fundamentally different approach to Pd-catalyzed intramolecular hydroamination of allenes using nitrogen-based ligands. The reaction is initiated by Pd^{II}-mediated alcohol oxidation, followed by allene insertion into a Pd^{II}–hydride intermediate to afford π-allyl–Pd^{II} intermediate. Subsequent intramolecular nucleophilic attack by amide leads to the corresponding hydroamination product and a Pd^0 species. This transformation is performed under aerobic conditions wherein the reoxidation of Pd^0 species by O_2 is necessary to complete the catalytic cycle. Investigation of asymmetric hydroamination is in progress.

Experimental Section

A representative procedure: $PdCl_2$ (0.005 mmol, 5 mol%), bathocuproine (0.01 mmol, 10 mol%), maleic anhydride (0.02 mmol, 20 mol%), NaOAc (0.1 mmol, 100 mol%), and allene **1** (0.1 mmol) were combined in a glass tube. The tube was evacuated under reduce vacuo and refilled with O_2 five times. Then isopropyl alcohol (*i*PrOH, 2 mL) was added. The mixture was stirred under O_2 at room temperature for 30 min and then heated up to 60°C. The reaction was monitored by thin-layer chromatography. After the reaction was completed, the solvent was concentrated and the residue was purified by silica gel column chromatography to give the corresponding hydroamination product **2**.

Acknowledgements

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Keywords: alcohols · allenes · hydroamination · aerobic oxidation · palladium

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