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Allylic Amination Using Well-Defined [(NHC)Pd(η^3-allyl)Cl] Complexes and PPh_3

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The allylic amination reaction catalyzed by [(NHC)Pd(allyl)Cl] complexes has been studied, and the presence of PPh_3 found to be essential for the catalytic system to be active. [(1-Mesityl-3-methylimidazol-2-ylidene)Pd(η^3-C_3H_5)Cl] has been used to optimize the conditions of the reaction with (*E*)-1,3-diphenylprop-3-enyl acetate and benzylamine under biphasic conditions (aqueous base/CH_2Cl_2). The best yields of isolated product (98%) were obtained using aqueous 1 M K_2CO_3. The influence of the NHC ligand and the allyl fragment on the pre-catalyst was also examined. Two new neutral [(NHC)Pd(η^3-1-RC_3H_4)Cl] complexes [NHC = 1-mesityl-3-methylimidazol-2-ylidene or 1-(2,6-diisopropylphenyl)-3-methylimidazol-2-ylidene; R = H or Ph] have been prepared and a decrease of the reaction time observed with the former. NMR studies have shown that this pre-catalyst is more easily activated than its η^3-allyl analogue and that the predominant activation pathway involves attack of the amine at the allyl fragment. This reaction occurs exclusively in the presence of PPh_3, thus suggesting that cationic [(NHC)Pd(allyl)(PPh_3)]$^+$ complexes, which are more electrophilic, are formed in situ and allow the amine to react with the allyl fragment. A tetrafluoroborate cationic complex has therefore been prepared from [(NHC)Pd(allyl)Cl], PPh_3, and $AgBF_4$ and fully characterized. This complex is an active pre-catalyst in the allylic amination reaction. The scope of the reaction was examined under the optimized reaction conditions with several different nitrogen nucleophiles and allylic acetates. The amination products were obtained in yields ranging from 73 to >98%, except for that from cyclohexenyl acetate and dibenzylamine. Finally, the reaction performed directly with the allylic alcohol and benzylamine led to a mixture of allylic amines in 9% yield.

Introduction

N-Heterocyclic carbenes (NHCs) have been found to be powerful ligands for transition-metal-catalyzed reactions.[1] In particular, NHC–palladium complexes have been developed as highly reactive pre-catalysts in C–C and C–N coupling reactions.[2] By comparison, their use in the Tsuji–Trost reaction has received less attention. The first example of an allylic alkylation reaction catalyzed by NHC–Pd complexes was reported by Mori and Sato in 2003.[3] Since then, many authors have studied the alkylation reaction using dimethyl malonate anions, particularly under anhydrous conditions, and numerous important advances have been reported in this field.[4] Most research groups have focused on enantioselective versions with chiral NHC ligands,[4a,4d–4j] and enantiomeric excesses of up to 92% have been reported.[4a] Initially, low catalytic activities were observed with these NHC–Pd complexes by comparison with traditional palladium complexes bearing phosphane ligands. NHC ligands are strong σ-donor ligands with a weak π-acidity[5] and probably render the intermediate cationic allylpalladium complexes poorly electrophilic, thereby disfavoring the nucleophilic addition step.[4d] Consequently, the use of palladium complexes in which the NHC ligand is associated with a more π-acceptor ligand, such as a phosphane, has been considered.[4d,4k,4l] Mixed (NHC)(phosphane)palladium complexes have been used with some success as catalysts in C–C and C–N coupling reactions.[6] Their superior activity with respect to their bis(NHC) or bis(phosphane) analogues has been demonstrated particularly for the Mizoroki–Heck, Suzuki–Miyaura, and Stille reactions.[6a–6c,6g,6j] By comparison, the behavior of such complexes in the Tsuji–Trost reaction has been less studied. The first example, reported in 2005 by Douthwaite and co-workers, describes the use of chiral bidentate NHC–aminophosphane and NHC–phosphoramidate ligands.[4d] In this case, the presence of the phosphane moiety increases the rate of the alkylation reaction compared to related bis(NHC) or NHC–imino ligands. In 2007, our group showed that palladium complexes, generated in situ from NHC–silver complexes, [{Pd(allyl)Cl}$_2$], and PPh_3, were very active catalytic species for the allylic alkylation reaction using dimethyl malonate.[4k] The use of such complexes under biphasic conditions[7] (aqueous 1 M KOH/CH_2Cl_2) led to high reaction rates and complete conversions within 5 min at 20 °C. A comparison of a few NHC ligands showed that the least bulky 1-mesityl-3-meth-

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ylimidazol-2-ylidene was the most efficient. The presence of PPh_3 was found to be essential, thereby suggesting that the active species is a palladium complex bearing both an NHC ligand and a phosphane or that PPh_3 is necessary to stabilize monoligated NHC–Pd^0 species.[8] In 2008, an asymmetric version of the allylic alkylation reaction, using palladium complexes bearing achiral NHC ligands and chiral monodentate P-ligands, was reported by Martin and Buono.[4l] A synergic effect between these two families of ligands was underlined. The presence on the palladium of a bulky achiral NHC ligand and a chiral diazaphospholidine resulted in increased enantiomeric excesses (up to 95.2% *ee*) and reaction rates in comparison with the reaction carried out with only one chiral P-ligand on the palladium.

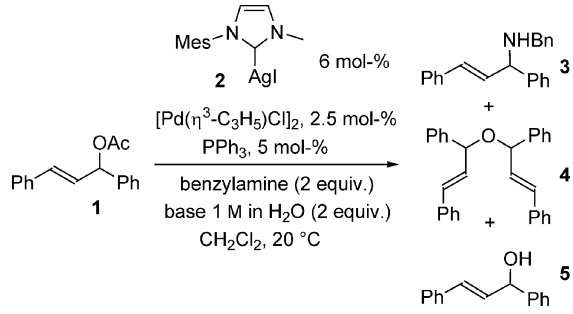
In contrast to allylic alkylation, the analogous amination reaction catalyzed by NHC–Pd complexes has been little investigated. It was initially reported that allylic substitution using NHC–Pd complexes seemed to be inapplicable to nitrogen nucleophiles.[4c] However, it was subsequently demonstrated that palladium complexes with chiral bidentate NHC–P ligands were active catalysts in the allylic amination reaction.[9] The authors noted that NHC–P ligands gave lower reaction rates than isostructural P–N ligands in the nucleophilic attack of amines on the cationic π-allylpalladium complex. Furthermore, the use of NHC–P ligands instead of P–N ligands induced a dramatic loss of enantioselectivity. This effect was attributed to the similar *trans* influence of phosphane and carbene ligands, which renders the corresponding *trans* allyl carbons electronically equivalent.

Having previously demonstrated that the combination of [(NHC)Pd(allyl)Cl] complexes, PPh_3, and biphasic conditions led to an efficient catalytic system for the allylic alkylation reaction, we decided to explore the application of this system to allylic amination. Herein we describe our results concerning the development of this reaction, its scope, and limitations. The preparation of a cationic $[(NHC)(PPh_3)(allyl)Pd]^+$ complex and its characterization is also discussed.

Results and Discussion

Study and Optimization of the Reaction Conditions

In preliminary experiments, the reaction of (*E*)-1,3-diphenylprop-3-enyl acetate (**1**; 0.4 M in CH_2Cl_2) with benzylamine (2 equiv.) was tested in the presence of a [(NHC)Pd(allyl)Cl] complex generated in situ from the silver complex **2**, $[\{Pd(\eta^3\text{-allyl})Cl\}_2]$, and PPh_3 (Scheme 1 and Table 1). The reaction was first performed under the biphasic conditions developed for the alkylation with dimethyl malonate[4k] using aqueous 1 M KOH as the base and CH_2Cl_2. This procedure afforded the expected allylic amine **3** with a conversion of 59% after 16 h at 20 °C (Table 1, entry 1). The amination reaction is much slower than the alkylation reaction, and ether **4** and allylic alcohol **5** were obtained as by-products in 27% and 12% yields respectively. The conditions were optimized by replacing KOH with 1 M K_2CO_3 or $NaHCO_3$, which allowed us to obtain complete conversions after 4–6 h at 20 °C (Table 1, entries 2 and 3). Although the reaction is faster with $NaHCO_3$ (Table 1, entry 2), the best yield of isolated product (95%) was obtained using K_2CO_3 (Table 1, entry 3).



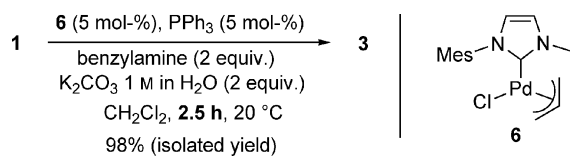
Scheme 1. Allylic amination using an [(NHC)Pd(allyl)Cl] complex generated in situ in the presence of PPh_3.

Table 1. Influence of the aqueous base on the allylic amination reaction.

Entry	Base	*t* [h]	% **1**[a]	% **3**[a]	% **4**[a]	% **5**[a]
1	KOH	16	2	59	27	12
2	$NaHCO_3$	4	–	>98 (83)[b]	–	–
3	K_2CO_3	6	–	>98 (95)[b]	–	–

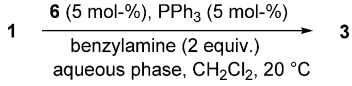
[a] Determined from the ^1H NMR spectrum of the crude reaction mixture by comparison with an internal standard. [b] Yield of isolated product.

The procedure for generating the [(NHC)Pd(allyl)Cl] precatalyst from **2** in situ releases silver iodide, which remains in the reaction medium, and it has been shown for the allylic alkylation reaction that silver salts can have a notable influence on enantioselectivity and yield.[4i,10] Consequently, we examined the use of the well-defined and isolated [(NHC)Pd(allyl)Cl] complex **6**, whose synthesis has been reported previously.[4k] No silver salt is present in the reaction medium under these conditions, and a significant decrease of the reaction time from 6 h to 2.5 h was observed using aqueous K_2CO_3 as the base (Scheme 2). We have shown previously that PPh_3 is essential for the formation of active palladium species in the allylic alkylation reaction. In the presence of AgI, the competitive formation of a Ph_3P–AgI complex could lead to a decrease of the amount of active species and therefore to an increase in the reaction time. Consequently, the use of isolated [(NHC)Pd(allyl)Cl] complexes rather than complexes generated in situ seems more appropriate.



Scheme 2. Allylic amination using the well-defined [(NHC)Pd(allyl)Cl] complex **6** and PPh_3 under biphasic conditions.

Further experiments were performed with complex **6** under various conditions (Scheme 3). The results are presented in Table 2. An initial reaction was carried out with 5 mol-% of complex **6** without PPh_3 (Table 2, entry 2). No conversion was observed, thus indicating, as for the alkylation reaction, that the phosphane is indispensable for the reaction to take place. No precipitation of palladium black was detected, which suggests that the dramatic effect of PPh_3 cannot exclusively be due to the stabilization of $(NHC)Pd^0$ species, thereby avoiding their decomposition and the precipitation of palladium. The formation of **3** was not detected either in a second control experiment carried out with 5 mol-% of PPh_3 but without palladium complex **6** (Table 2, entry 3). The use of 10 mol-% of PPh_3 (PPh_3/Pd = 2) led to a decrease of the reaction time (Table 2, entry 4), and a complete conversion was observed by TLC after 1 h. However, the conversion measured by ^1H NMR spectroscopy (92%) and the yield of isolated product (86%) were both lower than under the standard conditions (K_2CO_3 1 M, 98%; Table 2, entry 1). Next, the influence of the base and water was examined (Table 2, entries 1 and 4–8). No difference in reaction time or conversion was observed when $NaHCO_3$ or K_2CO_3 were used (Table 2, entries 1 and 5). However, the best yield of isolated product (98%) was still obtained with aqueous K_2CO_3 (Table 2, entry 1). Interestingly, the reaction carried out with water instead of aqueous K_2CO_3 led to a complete conversion after 2.5 h (Table 2, entry 6). This result is in contrast with our previous study concerning the allylic alkylation reaction, where no reaction occurred in the absence of aqueous KOH.[4k] The reaction was then performed in pure CH_2Cl_2 (Table 2, entry 7). These conditions furnished the allylic amine **3** in 98% isolated yield after 2.5 h, thus indicating that the presence of K_2CO_3 and water is not necessary. In this case, the use of 1.1 equiv. of benzylamine instead of 2 equiv. decreased the conversion slightly (90% after 2.5 h) and **3** was isolated in 82% yield (Table 2, entry 8). This study with complex **6** and PPh_3 shows that the best results are obtained either under biphasic conditions (aqueous 1 M K_2CO_3/CH_2Cl_2) or in pure CH_2Cl_2, with two equivalents of amine. These two experimental conditions were therefore selected to examine the influence of the [(NHC)Pd(allyl)Cl] pre-catalyst.



Scheme 3. Influence of the conditions on the allylic amination reaction with complex **6**.

Table 2. Influence of the conditions on the allylic amination reaction with the [(NHC)Pd(allyl)Cl] complex **6**.

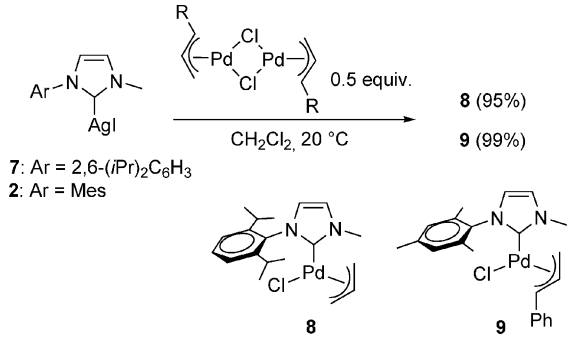
Entry	Aqueous phase	*t* [h]	% Conv.[a]	% Yield[b]
1	1 M K_2CO_3/H_2O	2.5	>98	98
2[c]	1 M K_2CO_3/H_2O	2.5	0	–
3[d]	1 M K_2CO_3/H_2O	2.5	0	–
4[e]	1 M K_2CO_3/H_2O	1	92	86
5	1 M $NaHCO_3/H_2O$	2.5	>98	84
6	H_2O	2.5	>98	92
7	none	2.5	>98	98
8[f]	none	2.5	90	82

[a] Determined from the ^1H NMR spectrum of the crude reaction mixture by comparison with an internal standard. [b] Yield of isolated product. [c] Pd complex (5 mol-%) without PPh_3. [d] PPh_3 (5 mol-%) without Pd complex. [e] PPh_3 (10 mol-%). [f] 1.1 equiv. of benzylamine was used.

Influence of the Pre-Catalyst

When Pd^{II} pre-catalysts are used, the efficiency of the activation step can have a significant effect on the reaction time by altering the concentration of the catalytically active Pd^0 species. In the case of allylpalladium(II) complexes, zero-valent palladium species can be generated by addition of nucleophiles.[11] This procedure was used in 2001 by Caddick and Cloke for the formation of $(NHC)_2Pd^0$ complexes from $[\{Pd(\eta^3\text{-}C_3H_5)Cl\}_2]$.[12] Since then, the syntheses of many [(NHC)Pd(allyl)Cl] complexes have been reported in the literature as well as their use as pre-catalysts for the generation of active $(NHC)Pd^0$ complexes in situ.[4,12,13] The most efficient nucleophiles used as initiators in C–C or C–N cross-coupling reactions are usually alkoxide anions such as *t*BuO$^-$ or MeO$^-$. It has been postulated that the activation of [(NHC)Pd(allyl)Cl] complexes for catalysis occurs through a nucleophilic attack at the allyl moiety or through a chloride/alkoxide σ-metathesis followed by reductive elimination.[13a,13i] [(NHC)Pd(R-allyl)Cl] complexes possessing a modified and more labile allyl moiety (R-allyl = crotyl, prenyl, or cinnamyl) have been shown to be more easily activated than their [(NHC)Pd(allyl)Cl] analogues, thus allowing the development of more efficient catalytic systems for Suzuki–Miyaura and Buchwald–Hartwig cross-coupling reactions.[13i] For these reasons, we decided to prepare the two new neutral [(NHC)Pd(R-allyl)Cl] complexes **8** and **9** (Scheme 4) to compare their activity with the initial complex **6**. Complex **8** differs from **6** by the presence of the more bulky 1-{2,6-diisopropylphenyl}-3-methylimidazol-2-ylidene ligand, whereas complex **9** contains the same NHC ligand as **6** but an η^3-cinnamyl moiety instead of an η^3-allyl. These complexes were obtained, following a reported procedure,[13e] by treating the silver complexes **2** or **7** with 0.5 equiv. of $[\{Pd(\eta^3\text{-}PhC_3H_4)Cl\}_2]$ or $[\{Pd(\eta^3\text{-}C_3H_5)Cl\}_2]$ in CH_2Cl_2 at 20 °C. This method produced the palladium complexes **8** and **9**, which were fully characterized, in 95–99% yields. Their NMR characteristics are in accordance with those reported in the literature for similar complexes.[13] A single set of signals is detectable in solution by ^1H NMR spectroscopy at 20 °C for **6**, **8**, and **9**. Some representative ^{13}C NMR spectroscopic data for these three complexes are presented in Table 3. Complexes **6** and **8** show very similar chemical shifts, with the carbon *trans* to the chloride at about δ = 49 ppm and the carbon *trans* to the NHC moiety at δ = 71–73 ppm. For **9**, the carbon *trans* to the NHC moiety appears at δ = 89.5 ppm due to the presence of the phenyl group on the allyl fragment. Similar chemical shifts have been reported for [(IPr)Pd(cinnamyl)-

Cl] [IPr = 1,3-bis(2,6-diisopropylphenyl)imidazole].[13i] The elemental analyses for **8** and **9** deviate from the calculated values for [(NHC)Pd(R-allyl)Cl] complexes even after prolonged drying under vacuum. Analyses performed on several different samples gave similar results. We found that the observed values correspond to the expected complexes together with about 20% of residual CH_2Cl_2. Ionic CH_2Cl_2 solvates of [(NHC)Pd(η^3-allyl)X] complexes were reported in 2007.[13j]



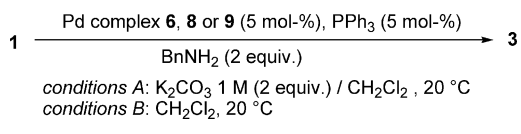
Scheme 4. Synthesis of well-defined [(NHC)Pd(allyl)Cl] complexes **8** and **9**.

Table 3. Selected ^{13}C NMR spectroscopic data for complexes **6**, **8**, and **9**.

Complex	^{13}C Chemical shifts [ppm]			
	C allyl			*C carbene*
	C trans to NHC	*C central*	*C trans to Cl*	
6[a]	71.1	114.5	48.6	181.3
8[b]	73.1	114.6	48.9	182.5
9[a]	89.5	109.3	45.6	180.4

[a] Recorded in CD_2Cl_2. [b] Recorded in $CDCl_3$.

In the amination reaction, nucleophilic attack of the amine at the allyl fragment could lead to the formation of active Pd^0 species. However, the different nucleophiles present in the reaction medium (including PPh_3) can also potentially be involved in activation of the pre-catalyst. For this reason, we supposed that in addition to the structure of the complex, the reaction conditions, particularly the presence of aqueous K_2CO_3, could also have an influence on the activation step and thus on the reaction time. Consequently, complexes **6**, **8**, and **9** were compared in the two optimized protocols discussed above (Scheme 5). The results are presented in Table 4.



Scheme 5. Comparison of complexes **6**, **8**, and **9** in the allylic amination reaction.

A first series of experiments was performed under biphasic conditions (Table 4, entries 1–3). A decrease of the reaction time from 2.5 h to 1 h was observed when **9** was used as the pre-catalyst (Table 4, entry 3) instead of its [(NHC)Pd(η^3-allyl)Cl] analogues **6** and **8** (Table 4, entries 2 and 3), thus indicating that the activation step could be favored. In these three experiments, the conversions measured by ^1H NMR spectroscopy are superior to 98%, but **6** led to a better isolated yield (98%) than **8** (83%) and **9** (89%; Table 4, entries 1–3 respectively). A second set of experiments was performed in pure CH_2Cl_2. The isolated yields and reaction times obtained with complexes **6** and **8** were similar to those obtained under biphasic conditions, with complete conversion being achieved after 2.5 h (Table 4, entries 1, 2, 4 and 5). The use of a more bulky NHC ligand (complex **8**) has no significant effect on the reaction. Next, the reaction in CH_2Cl_2 with pre-catalyst **9** was examined. Surprisingly, after 2.5 h the reaction produced the allylic amine **3** in only 49% yield (Table 4, entry 6). This result is in contrast with the improved activity observed under biphasic conditions (Table 4, entry 3) and suggests that the activation of complex **9** may depend on the presence of aqueous K_2CO_3. This is also in contrast with the observation made with **6** and **8**, where the conditions have a negligible influence on the reaction time and yield. Cinnamylbenzylamine or cinnamyl alcohol, which should be formed during the activation of **9**, could not be detected in the ^1H NMR spectra of the crude reaction mixtures.[14] To further study the activation pathway, the reaction of complex **6** with benzylamine was examined by ^1H NMR spectroscopy. Two equivalents of benzylamine were added to a solution of **6** in CD_2Cl_2. The spectrum recorded after 5 min showed the presence of benzylamine and **6** exclusively. The signals corresponding to the allyl fragment of **6** are slightly broader than in the initial spectrum (without $BnNH_2$), thereby suggesting a change in the allyl dynamics.[15] A similar spectrum was obtained after 2 h at 20 °C. One equivalent of PPh_3 was then added to the solution. After 5 min, a pale-yellow coloration was observed and the ^1H NMR spectrum showed the formation of about 16% of allylbenzylamine. Upon standing at 20 °C, the solution became progressively red. A conversion of 30% was measured after 40 min and 40–45% after 2.5 h. The same experiment was carried out with complex **9**. Two equivalents of benzylamine were added to a solution of **9** in CD_2Cl_2 and the resultant solution was analyzed by ^1H NMR spectroscopy. No formation of cinnamylbenzylamine (linear product) or 3-(benzyl-

Table 4. Comparison of [(NHC)Pd(allyl)Cl] complexes **6**, **8**, and **9**.

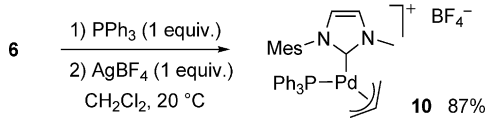
Entry	Complex	Aqueous phase	*t* [h][a]	% Conv.[b] (% yield)[c]
1	**6**	1 M K_2CO_3	2.5	>98 (98)
2	**8**	1 M K_2CO_3	2.5	>98 (83)
3	**9**	1 M K_2CO_3	1	>98 (89)
4	**6**	none	2.5	>98 (98)
5	**8**	none	2.5	>98 (77)
6	**9**	none	2.5	50 (49)

[a] The reaction was stirred for a further 0.5 h after it appeared to be complete by TLC analysis. [b] Determined from the ^1H NMR spectrum of the crude reaction mixture by comparison with an internal standard. [c] Yield of isolated product.

amino)-3-phenylpropene (branched product) was detected. The addition of benzylamine to **9** led to a broadening of most of the signals in the ^{1}H NMR spectrum. Furthermore, the signals corresponding to the protons at the extremities of the allyl were not visible anymore, whereas the signal for the central proton of the allyl, although broad, was still clearly identifiable. After 2 h, no significant change in the spectrum was observed. One equivalent of PPh_3 was then added. After 5 min, the NMR analysis showed the formation of 50% of cinnamylbenzylamine and bis(cinnamyl)-benzylamine (ratio 2:1). The color of the solution changed progressively from pale-yellow to deep red within 10–15 min. After 40 min, the conversion reached 70%. The formation of allylic amines demonstrates that the nucleophilic addition of benzylamine to the allyl fragment, which generates NHC–Pd^0 complexes, is the predominant activation pathway (the allylic amines were not obtained with complete conversions). The NMR spectra recorded 5 min after the addition of PPh_3 showed that the addition of benzylamine to the cinnamyl fragment in complex **9** is faster than that to the allyl fragment of complex **6**, thus indicating that the activation of **9** must be favored by comparison with **6**. The fact that nucleophilic addition of the amine occurs exclusively in the presence of PPh_3 shows that the latter is essential for activation of the pre-catalyst. We assumed that cationic [(NHC)(PPh_3)Pd(allyl)][Cl] complexes, which must be more electrophilic and allow nucleophilic attack of the amine at the allyl fragment, were generated in situ in the presence of phosphane. To confirm this hypothesis, we decided to prepare the cationic complex containing a non-coordinating tetrafluoroborate ligand from **6** and PPh_3 and to test its activity in the catalytic reaction.

Synthesis and Catalytic Activity of [(1-Mesityl-3-methylimidazol-2-ylidene)(PPh_3)Pd(allyl)] Tetrafluoroborate

A few [(NHC)(phosphane)Pd(allyl)X] complexes have been described with bidentate NHC–P ligands. They have been isolated and characterized as their η^3-allyl cationic form.[9,16] In 2008, cationic [(NHC)(PR_3)Pd(allyl)][BF_4] complexes containing monodentate NHC and phosphane ligands were reported by Cavell and co-workers. NHCs with lower steric bulk than our ligands were selected by these authors in order to favor the reductive elimination of 2-allylimidazolium salts and generate monoligated phosphane–Pd^0 active species.[17] In our previous studies, we attempted to determine the nature of the palladium species generated after addition of one equivalent of PPh_3 to the [(NHC)Pd(allyl)Cl] complex **6** by NMR spectroscopy.[4k] The ^{1}H NMR spectrum of the mixture recorded at room temperature showed the complete disappearance of the starting complex **6** but exhibited mainly very broad signals. A relatively slow interconversion of the *exo* and *endo* coordination modes of the allyl ligand could account for the broad signals observed by ^{1}H NMR spectroscopy.[15] The ^{31}P NMR spectrum recorded at 20 °C shows a single signal at δ = 24.8 ppm, in accordance with those reported in the literature for (NHC)(phosphane)Pd^{II} complexes.[6a,6g,6j,9,16,17] However, the structure of the palladium species could not be exactly determined. The cationic complex **10** was then synthesized by addition of PPh_3 (1 equiv.) and $AgBF_4$ (1 equiv.) to a solution of **6** in CH_2Cl_2 (Scheme 6). Filtration of AgCl and removal of the solvent afforded, in quantitative yield, an off-white solid, which was characterized by HRMS, ^{1}H, ^{13}C, ^{31}P and ^{19}F NMR spectroscopy, and elemental analysis.



Scheme 6. Synthesis of the cationic complex **10**.

The formation of complex **10** was confirmed by its positive mode ESI mass spectrum, which shows an isotopic pattern centered at *m*/*z* 609.16512 corresponding to the [(NHC)Pd(allyl)PPh_3]$^+$ cation [M^+ – BF_4]. The ^{1}H NMR spectrum of **10** recorded at 24 °C exhibits very broad signals. At –15 °C, however, two major sets of sharper peaks in a 1.6:1 ratio are visible (see Figure 1 for the area of the central allyl proton; **A**: 55%, **B**: 32%). These two major sets of signals, which represent 87% of the mixture, were assigned to the two isomers (*endo* and *exo* coordination mode of the allyl) of the expected [(NHC)(PPh_3)Pd(η^3-allyl)][BF_4] complex (Figure 2). This was confirmed by the ^{1}H-2D COSY spectrum, which shows five nonequivalent allyl protons signals for each isomer **A** and **B** (Figure 3). However, as shown in Figure 1, minor signals corresponding to three other Pd(allyl) complexes (**C**, **D**, and **E**) are detectable in solution for the central proton of the allyl moiety. The nature of **D** and **E** could not be determined, whereas **C**, the major impurity in solution, was found to be the cationic

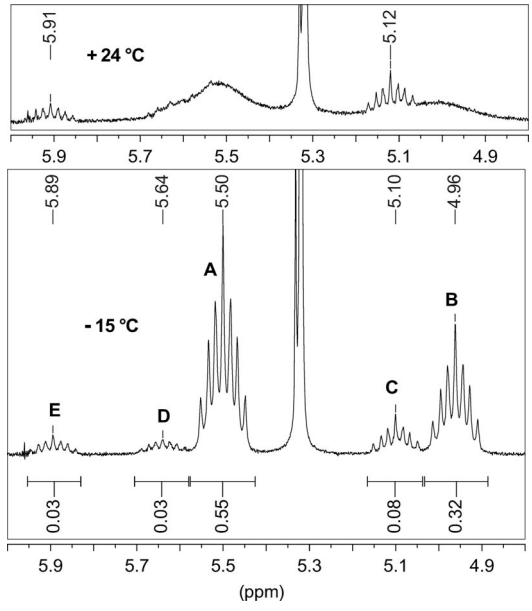


Figure 1. ^{1}H NMR spectra of complex **10** recorded at +24 and –15 °C (central allylic C*H*).

complex $[(NHC)_2Pd(allyl)][Cl]$.[18] The elemental analysis results deviate from the calculated values even after prolonged drying under vacuum but correspond to complex **10** with about 20% of CH_2Cl_2. The ^{31}P NMR spectrum recorded at –15 °C shows two peaks at δ = 24.6 and 25.4 ppm with a 1.6:1 ratio, which is similar to the ratio observed by ^1H NMR spectroscopy for the two isomers **A** and **B**. In the ^{13}C NMR spectrum recorded at 19 °C, only one carbon resonance (at δ = 121.2 ppm) is found for the allyl ligand, which corresponds to the central carbon. At –15 °C, however, two sets of three signals corresponding to the allyl fragments of the two isomers are visible. The coupling with the phosphorus confirmed the coordination of PPh_3 at the palladium center. Representative ^{13}C NMR spectroscopic data are presented in Table 5. In contrast with the neutral complexes **6**, **8**, and **9**, and as observed by Visentin, Togni,[9] and Cavell,[17] the two allyl termini have similar ^{13}C chemical shifts, thus suggesting that the carbene and phosphorus donors have similar *trans* influences.

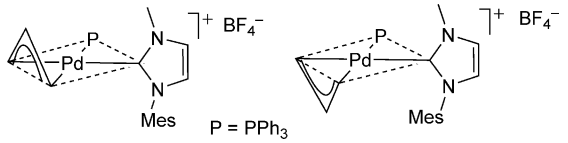


Figure 2. Coordination modes of the allyl ligand in complex **10**.

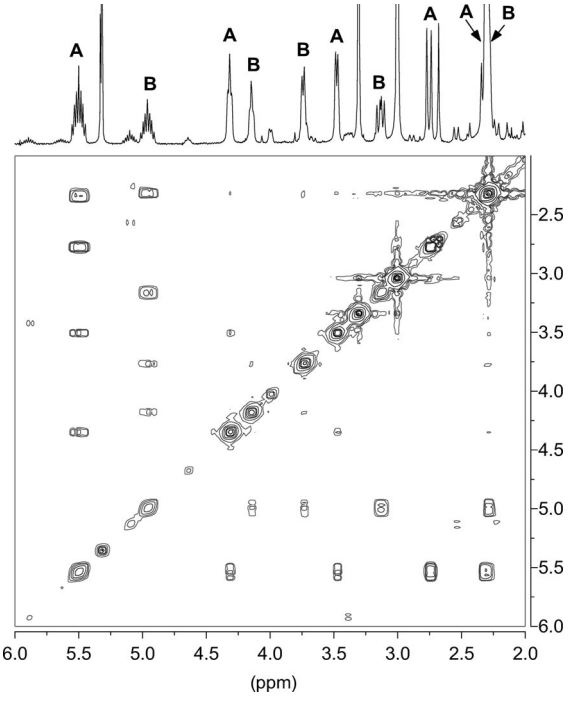


Figure 3. 2D ^1H-COSY spectrum of complex **10** at –15 °C.

The catalytic activity of **10** was tested in the reaction of **1** with benzylamine under our two standard reaction conditions. Under biphasic conditions (aqueous 1 M K_2CO_3/CH_2Cl_2), **10** led to the formation of the expected allylic amine **3** in 86% isolated yield after 3 h. A lower yield of 57% was obtained after 4 h in pure CH_2Cl_2. These results showed that cationic $[(NHC)(PPh_3)Pd(allyl)]$ complexes are active pre-catalysts in the amination reaction.

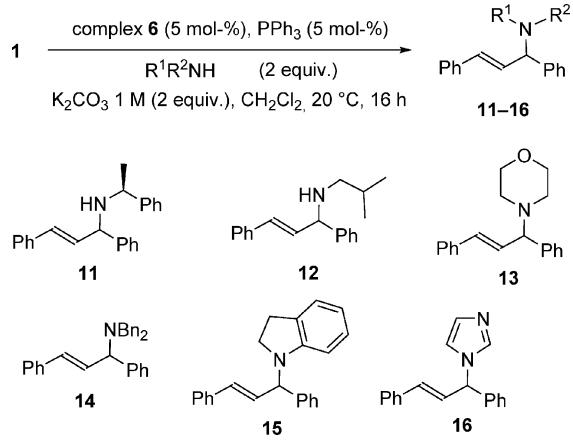
Table 5. Selected ^{13}C NMR spectroscopic data for the two isomers **A** and **B** of complex **10**: allyl fragment and carbene (CD_2Cl_2, –15 °C).

	^{13}C Chemical shifts [ppm]/$J_{C,P}$ [Hz]			
	C allyl			*C carbene*
	C trans to NHC	*C central*	*C trans to PPh_3*	
A	71.7	120.8/4	66.8/30	177.1/18
B	68.3	120.8/4	69.3/29	176.9/18

As stated above, [(NHC)Pd(allyl)Cl] complexes associated with PPh_3 lead to active palladium catalysts for the allylic amination reaction using (*E*)-1,3-diphenylprop-3-enyl acetate (**1**) and benzylamine. In the best case, complete conversions could be achieved after 1 h at 20 °C. The most active pre-catalyst was found to be complex **9** under biphasic conditions. However, complex **6** always leads to better isolated yields under the standard reaction conditions used (anhydrous or biphasic).[19] For this reason, and because its synthesis can be carried out from commercially available $[\{Pd(\eta^3\text{-allyl})Cl\}_2]$, complex **6** was chosen to study the scope of the reaction with various substrates. The biphasic conditions (aqueous 1 M K_2CO_3/CH_2Cl_2), which generally provide improved isolated yields, were also selected (see Table 3).

Scope of the Reaction

The reaction of various nitrogen nucleophiles with (*E*)-1,3-diphenylprop-3-enyl acetate (**1**) was investigated first. Primary, secondary, and aromatic amines as well as aromatic heterocycles were tested (Scheme 7). The results are presented in Table 6. Isolated yields ranging from 40 to 95% were obtained. Chiral (*S*)-α-methylbenzylamine led to the allylic amine **11** with the best isolated yield (95%; Table 6, entry 1) but a low diastereomeric ratio of 1:1.[20]



Scheme 7. Scope of the reaction: nitrogen nucleophiles.

The reaction is slower than with benzylamine, probably due to the increased steric bulk, and a reaction time of 16 h was necessary to reach completion. Isobutylamine and morpholine afforded the allylic amines **12** and **13**, respectively, in 86 and 79% yields (Table 6, entries 2 and 3). A lower yield (40%) was obtained with dibenzylamine (Table 6, entry 4) although no trace of **1** was visible in the crude reaction mixture. Finally, the reaction with indoline and imidazole produced the allylic compounds **15** and **16**, respectively, in 80 and 73% yields (Table 6, entries 5 and 6).

Table 6. Scope of the reaction: nitrogen nucleophiles.

Entry	Nucleophile	% Yield[a] (product) *dr*[b]
1	(*S*)-α-methylbenzylamine	95 (**11**) 1:1
2	isobutylamine	86 (**12**)
3	morpholine	79 (**13**)
4	dibenzylamine	40 (**14**)
5	indoline	80 (**15**)
6	imidazole	73 (**16**)

[a] Yield of isolated product. [b] Determined by ^{1}H NMR spectroscopy.

The reaction of benzylamine with various allylic substrates (Figure 4, compounds **17**–**21**) was then investigated under the same conditions. The results are summarized in Table 5.

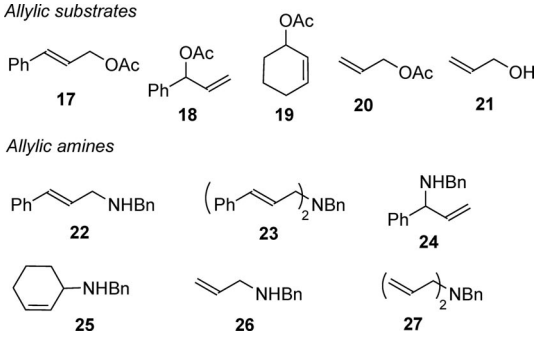


Figure 4. Allylic acetates, alcohol, and amines.

The reaction with cinnamyl acetate (**17**) led, with complete conversion, to a mixture of linear and branched products (**22**, **23**, and **24**; Table 7, entry 1). The major products are the linear products **22** and **23**, which were obtained in a combined 93% yield. A poor selectivity was observed between mono- and diallylation, with a **22**/**23** ratio of 45:55. Regiochemical memory effects have been reported in the allylic alkylation reaction using crotyl carbonates and palladium complexes bearing bulky NHC ligands [NHC = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene or 1,3-di-*tert*-butylimidazol-2-ylidene].[4b] Consequently, we examined the reaction of the branched acetate **18** (Table 7, entry 2). This reaction still gave the linear isomers (**22** and **23**) as the major products (78% yield), although the linear/branched ratio observed (6:1) is slightly different than in the previous reaction with the linear acetate **17** (linear/branched = 13:1). This difference can be attributed to a weak memory effect, although much less marked than that observed by Faller.[4b] However, the use of allylic acetates instead of allylic carbonates and of a less bulky NHC ligand could account for this difference. The reaction carried out with cyclohexenyl acetate (**19**) led to no conversion and the acetate was recovered quantitatively (Table 7, entry 3). We had already observed in the allylic alkylation reaction with **6**[4k] that **19** is significantly less reactive than the other acetates tested. Allylic acetate **20** led to the expected amines **26** and **27** in 95% yield (Table 7, entry 4). As observed before with **17**, the selectivity between mono- and diallylation is poor, with a **26**/**27** ratio of 54:46. Finally, we attempted the allylic amination with allylic alcohol **21**. Different procedures for palladium-catalyzed allylations of amines with allylic alcohols have been reported.[21] Among them, several examples of reactions at room temperature have been described and it has been shown that the presence of water can have a significant influence on the efficiency of the process. We thought that our aqueous conditions, associated with the strong σ-donor effect of the NHC ligand, could favor the formation of the η^3-allyl intermediate and thus favor the reaction. Unfortunately, under our conditions, the reaction performed with **21** for 16 h at 20 °C led to a mixture of allylic amines (**26** and **27**) in only 9% yield (Table 7, entry 5).

Table 7. Allylic acetates and allylic alcohol.[a]

Entry	Substrate	*t* [h]	Linear[b] [%] (mono/di)	Branched[b] [%]
1	**17**	16	93 (**22**/**23** = 45:55)	7
2	**18**	16	78 (**22**/**23** = 51:49)	14
3	**19**	16	0	–
4	**20**	2.5	95 (**26**/**27** = 54:46)	–
5	**21**	16	9 (**26**/**27** = 30:70)	–

[a] Conditions: **6** (5 mol-%), PPh_3 (5 mol-%), $BnNH_2$ (2 equiv.), 1 M K_2CO_3 (2 equiv.), acetate or alcohol (1 equiv.) 0.4 M in CH_2Cl_2, 20 °C. [b] Yields and ratio determined from the ^{1}H NMR spectrum of the crude reaction mixture by comparison with an internal standard.

Conclusions

The combination of [(NHC)Pd(allyl)Cl] complexes and PPh_3 leads to active catalytic species for the allylic amination reaction under biphasic or anhydrous conditions. The reaction occurs exclusively in the presence of PPh_3. This suggests the in situ formation of $[(NHC)Pd(allyl)(PPh_3)]^+$ complexes, which are more electrophilic than [(NHC)Pd(allyl)X] complexes (X = Cl or AcO) and allow the attack of the amine at the allyl fragment. Complete conversions have been obtained within 1 h at room temperature using a [(NHC)Pd(η^3-cinnamyl)] complex, which is more easily activated. ^{13}C NMR studies of $[(NHC)Pd(allyl)(PPh_3)][BF_4]$ suggest that the carbene and phosphorus donors have similar *trans* influences, as already reported in the literature. This catalytic system is compatible with various nitrogen nucleophiles and allylic acetates. Interestingly, an allylic alcohol produces the corresponding allylic amines, although only a low conversion is obtained.

Experimental Section

General: All experiments were performed under argon using standard Schlenk techniques unless stated otherwise. CH_2Cl_2 (RECTAPUR, stabilized with 0.1% of EtOH) was degassed by vacuum/argon cycles. Reagents were purchased from Acros, Aldrich, or Strem and used as received. 1-Mesityl-3-methylimidazolium iodide[22] and 1-(2,6-diisopropylphenyl)-3-methylimidazolium iodide[4k] were prepared according to literature procedures. ^1H and ^{13}C NMR spectra were recorded with a Bruker ARX-250 or ARX-400 spectrometer, in $CDCl_3$ or CD_2Cl_2 as solvent. In CD_2Cl_2, proton chemical shifts (δ) are reported relative to residual protonated solvent (δ = 5.32 ppm), whereas tetramethylsilane (TMS) was used as internal reference (δ = 0.00 ppm) in $CDCl_3$. ^{13}C chemical shifts (δ) are reported relative to the NMR solvent (CD_2Cl_2: δ = 54.00 ppm; $CDCl_3$: δ = 77.23 ppm). Melting points are uncorrected and were measured with a Stuart Scientific apparatus SMP3. Elemental analyses were performed at the ICSN (microanalytical service).

(1-Mesityl-3-methylimidazol-2-ylidene)silver Iodide (2): The reported procedure[4k] was modified as follows. Ag_2O (95 mg, 0.41 mmol) was added to a solution of 1-mesityl-3-methylimidazolium iodide (258 mg, 0.79 mmol) in CH_2Cl_2 (18 mL) and the mixture stirred at 20 °C for 3 h with exclusion of light. The silver complex is partially insoluble in CH_2Cl_2. The mixture was concentrated under reduced pressure (without filtration) and dried under vacuum to give 342 mg (99%) of a white solid. ^1H NMR (250 MHz, $CDCl_3$): δ = 1.98 (s, 6 H), 2.34 (s, 3 H), 3.97 (s, 3 H), 6.94 (d, J = 2 Hz, 1 H), 6.96 (s, 2 H), 7.15 (d, J = 2 Hz, 1 H) ppm.

[1-(2,6-Diisopropylphenyl)-3-methylimidazol-2-ylidene]silver Iodide (7): The reported procedure[4k] was modified as follows. Ag_2O (121 mg, 0.52 mmol) was added to a solution of 1-(2,6-diisopropylphenyl)-3-methylimidazolium iodide (370 mg, 1 mmol) in CH_2Cl_2 (20 mL) and the mixture stirred at 20 °C for 5.5 h with exclusion of light. It was then filtered through celite, concentrated under reduced pressure, and dried under vacuum to give 435 mg (91%) of an off-white solid. ^1H NMR (250 MHz, $CDCl_3$): δ = 1.11 (d, J = 6.8 Hz, 6 H), 1.22 (d, J = 6.8 Hz, 6 H), 2.37 (m, J = 6.8 Hz, 6 H), 3.99 (s, 3 H), 6.98 (d, J = 1.5 Hz, 1 H), 7.17 (d, J = 1.5 Hz, 1 H), 7.26 (d, J = 8 Hz, 2 H), 7.47 (t, J = 8 Hz, 1 H) ppm.

Complex 6: The reported procedure[4k] was modified as follows. A mixture of the silver complex **2** (107 mg, 0.25 mmol) and [{Pd(η^3-C_3H_5)Cl}$_2$] (48 mg, 0.13 mmol) in degassed CH_2Cl_2 (5 mL) was stirred for 2.5 h at 20 °C. The AgI precipitate was removed by filtration through a short pad of celite, and evaporation of CH_2Cl_2 and drying under vacuum afforded 95 mg (99%) of an off-white solid; m.p. 179–180 °C. ^1H NMR (250 MHz, $CDCl_3$): δ = 1.76 (d, J = 11.6 Hz, 1 H), 2.04 (s, 3 H), 2.20 (s, 3 H), 2.32 (s, 3 H), 3.02 (d, J = 13.5 Hz, 1 H), 3.15 (dd, J = 7.2, 1.5 Hz, 1 H), 4.03 (s, 3 H), 4.09 (dd, J = 7.5, 1.5 Hz, 1 H), 5.01 (m, 1 H), 6.89 (d, J = 1.7 Hz, 1 H), 6.92 (s, 1 H), 6.95 (s, 1 H), 7.08 (d, J = 1.7 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 17.3, 18.1, 20.8, 38.1 (N-*C*H$_3$), 48.6 (*C*H$_{2\ allyl}$), 71.1 (*C*H$_{2\ allyl}$), 114.5 (*C*H$_{allyl}$), 122.2, 122.6, 128.6, 128.9, 135.3, 135.7, 136.4, 138.8, 181.3 ($C_{carbene}$) ppm. $C_{16}H_{21}ClN_2Pd$ (383.22): calcd. C 50.15, H 5.52, N 7.31; found C 49.91, H 5.39, N 7.28.

Complex 8: A mixture of the silver complex **7** (100 mg, 0.21 mmol) and [{Pd(η^3-C_3H_5)Cl}$_2$] (38 mg, 0.10 mmol) in degassed CH_2Cl_2 (5 mL) was stirred for 2.5 h at 20 °C. The AgI precipitate was removed by filtration through a short pad of celite, and evaporation of CH_2Cl_2 and drying under vacuum afforded 85 mg (95%) of an off-white solid; m.p. 159–161 °C. ^1H NMR (400 MHz, $CDCl_3$: δ = 1.07 (d, J = 6.8 Hz, 3 H), 1.10 (d, J = 6.8 Hz, 3 H), 1.29 (d, J = 6.8 Hz, 3 H), 1.37 (d, J = 6.6 Hz, 3 H), 1.65 (d, J = 11.6 Hz, 1 H), 2.59 (m, 1 H), 2.96 (m, 1 H), 3.01 (d, J = 13.6 Hz, 1 H), 3.08 (d, J = 6.4 Hz, 1 H), 4.09 (s, 3 H), 4.13 (d, J = 7.4 Hz, 1 H), 5.01 (m, 1 H), 6.98 (d, J = 1.7 Hz, 1 H), 7.10 (d, 1 = H, J = 1.7 Hz), 7.20–7.28 (m, 2 H), 7.42 (t, J = 7.7 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 23.0, 23.4, 26.1, 26.5, 28.2, 28.3, 38.8, 48.9 (*C*H$_{2\ allyl}$), 73.1 (*C*H$_{2\ allyl}$), 114.6 (*C*H$_{allyl}$), 122.2, 123.6, 124.0, 124.1, 129.9, 136.1, 146.0, 147.1, 182.5 ($C_{carbene}$) ppm. ($C_{19}H_{27}ClN_2Pd$)-(CH_2Cl_2)$_{0.3}$ (450.78): calcd. C 51.42, H 6.17, N 6.21; found C 51.54, H 6.19, N 6.21.

Complex 9: A mixture of the silver complex **2** (95 mg, 0.22 mmol) and [{Pd(cinnamyl)Cl}$_2$] (56 mg, 0.11 mmol) in degassed CH_2Cl_2 (5 mL) was stirred for 2.5 h at 20 °C. The AgI precipitate was removed by filtration through a short pad of celite, and evaporation of CH_2Cl_2 and drying under vacuum afforded 100 mg (99%) of a pale-yellow solid; m.p. 176–178 °C. ^1H NMR (250 MHz, $CDCl_3$): δ = 1.80 (d, J = 11.5 Hz, 1 H), 2.05 (s, 3 H), 2.25 (s, 3 H), 2.35 (s, 3 H), 3.11 (d, J = 6 Hz, 1 H), 4.01 (s, 3 H), 4.58 (d, J = 12.6 Hz, 1 H), 5.43 (m, 1 H), 6.90 (d, J = 1.6 Hz, 1 H), 6.96 (s, 1 H), 7.00 (s, 1 H), 7.07 (d, J = 1.6 Hz, 1 H), 7.15–7.40 (m, 5 H) ppm. ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 17.8, 18.2, 20.8, 38.3 (N-*C*H$_3$), 45.6 (*C*H$_{2\ cinnamyl}$), 89.5 (Ph-*C*H$_{cinnamyl}$), 109.3 (CH$_2$-*C*H$_{cinnamyl}$), 122.4, 122.7, 126.6, 127.2, 128.3, 128.6, 128.9, 135.3, 135.9, 136.4, 138.5, 138.9, 180.4 ($C_{carbene}$) ppm. ($C_{22}H_{25}ClN_2Pd$)(CH_2Cl_2)$_{0.3}$ (476.31): calcd. C 55.98, H 5.38, N 5.88; found C 56.14, H 5.39, N 5.64.

Complex 10: PPh_3 (70 mg, 0.27 mmol) was added to a solution of complex **6** (103 mg, 0.27 mmol) in degassed CH_2Cl_2 (3 mL). The mixture was stirred for 5 min and $AgBF_4$ (52 mg, 0.27 mmol) was added and the mixture stirred for 2 h at 20 °C. The AgCl precipitate was removed by filtration through a short pad of celite, and evaporation of CH_2Cl_2 and drying under vacuum afforded, quantitatively, 190 mg of a pale-grey solid; m.p. 112–114 °C. ^1H NMR (400 MHz, CD_2Cl_2, –15 °C, complexes **A** and **B**): δ = 1.35 (s, 1.8 H, C*H*$_3$ mesityl **B**), 1.48 (s, 3 H, C*H*$_3$ mesityl **A**), 1.91 (s, 3 H, C*H*$_3$ mesityl **A**), 1.93 (s, 1.8 H, C*H*$_3$ mesityl **B**), 2.25–2.35 (m, 6.4 H, C*H*$_3$ mesityl **A**+**B** and C*H*H allyl **A**+**B**), 2.76 (d, J = 13.3 Hz, 1 H, C*H*H allyl **A**), 3.01 (s, 3 H, C*H*$_3$-N **A**), 3.14 (dd, J = 13.3, 9.8 Hz, 0.6 H, C*H*H allyl **B**), 3.31 (s, 1.8 H, C*H*$_3$-N **B**), 3.48 (d, J = 6.7 Hz, 1 H, C*H*H allyl **A**), 3.74 (d, J = 7.4 Hz, 0.6 H, C*H*H allyl **B**), 4.15 (s broad, 0.6 H, C*H*H allyl **B**), 4.32 (t, J = 5.1 Hz, 1 H, C*H*H allyl **A**), 4.96 (m, 0.6 H, C*H* allyl **B**), 5.50 (m, 1 H, C*H* allyl **A**), 6.65 (s, 0.6 H, **B**), 6.79 (s, 1 H, **A**), 6.90–7.65 (m, 28.8 H) ppm. ^{31}P NMR (162 MHz, CD_2Cl_2, –15 °C): δ = 25.4 (**B**), 24.6 (**A**) ppm. ^{13}C NMR (100 MHz, CD_2Cl_2): spectra recorded at +20 °C and –15 °C did not allow the assignment of all signals. See Table 5 for representative chemical shifts (allyl fragment and carbene) ppm. ^{19}F NMR (376 MHz, CD_2Cl_2, –15 °C): δ = –152.88 ($^{10}BF_4$, 20%), –152.93 ($^{11}BF_4$, 80%) ppm. HRMS: *m*/*z* calcd. for $C_{34}H_{36}N_2PPd$: 609.16455; found 609.16512. ($C_{34}H_{36}BF_4ClN_2PPd$)(CH_2Cl_2)$_{0.3}$ (713.86): calcd. C 57.54, H 5.14, N 3.92; found C 57.52, H 5.27, N 3.96.

Typical Procedure for the Palladium-Catalyzed Allylic Amination Under Biphasic Conditions: PPh_3 (5.3 mg, 0.02 mmol) was added to a solution of complex **6** (7.7 mg, 0.02 mmol) in CH_2Cl_2 (0.5 mL) and the mixture stirred for 15 min at 20 °C. A solution of (*E*)-1,3-diphenylprop-3-en-yl acetate (**1**; 100 mg, 0.4 mmol, 1 equiv.) in CH_2Cl_2 (0.5 mL), the amine (0.8 mmol, 2 equiv.), and 1 M K_2CO_3 in H_2O (0.8 mL, 2 equiv.) were then added to the mixture, which was stirred vigorously at 20 °C for the indicated time (see Tables 2, 3, 4, and 5). The mixture was diluted with Et_2O, the organic layer separated, and the aqueous phase extracted with Et_2O. The com-

bined organic layers were dried with K_2CO_3 and filtered through celite. Di-*tert*-butyl-4,4′-biphenyl (35 mg, 0.33 equiv., 0.13 mmol, internal reference) was then added and the solvents evaporated. The conversion was determined from the ^{1}H NMR spectrum of the residue by comparison with the internal reference. Compounds **3** and **11**–**16** were purified by flash chromatography on silica gel. NMR spectroscopic data for **3**,[23] **11**,[20c] **13**,[24] **14**,[25] **22**, **23**, **24**,[26] **25**,[27] **26**,[28] and **27**[29] have been reported in the literature.

***N*-[(*E*)-1,3-Diphenylprop-2-en-1-yl]benzylamine (3):** The same procedure was used starting from 86 μL of benzylamine (0.8 mmol, 2 equiv.). The mixture was stirred for 2.5 h at 20 °C. After work-up, the crude mixture was purified by flash chromatography on silica gel (pentanes:Et_2O, 9:1) to afford 118 mg (98%) of the title compound as a colorless oil. Spectral data are consistent with the reported literature.[23]

(*S*)-*N*-[(*E*)-1,3-Diphenylprop-2-en-1-yl]-1-methylbenzylamine (11): The same procedure was used starting from 103 μL of (*S*)-(α)-methylbenzylamine (0.8 mmol, 2 equiv.). The mixture was stirred for 16 h at 20 °C. After work-up, the crude mixture was purified by flash chromatography on silica gel (pentanes:Et_2O, 9:1) to afford 119 mg (95%) of the title compound as a colorless oil. Spectral data are consistent with the reported literature.[20c]

***N*-[(*E*)-1,3-Diphenylprop-2-en-1-yl]isobutylamine (12):** The same procedure was used starting from 80 μL of isobutylamine (0.8 mmol, 2 equiv.). The mixture was stirred for 16 h at 20 °C. After work-up, the crude mixture was purified by flash chromatography on silica gel (pentanes:Et_2O, 1:1) to afford 91 mg (86%) of the title compound as a colorless oil. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.91 (d, J = 6.6 Hz, 6 H), 1.48 (br. s, 1 H), 1.76 (m, 1 H), 2.34 (dd, J = 11.5, 6.9 Hz, 1 H), 2.46 (dd, J = 11.5, 6.6 Hz, 1 H), 4.31 (d, J = 7.3 Hz, 1 H), 6.28 (dd, J = 15.7, 7.3 Hz, 1 H), 6.56 (d, J = 15.7 Hz, 1 H), 7.10–7.43 (m, 10 H) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 21.2, 21.3, 29.0, 56.2, 66.2, 126.9, 127.6, 127.7, 127.8, 128.9, 129.0, 130.4, 133.6, 137.5, 143.8 ppm. $C_{19}H_{23}N$ (265.40): calcd. C 85.99, H 8.74, N 5.28; found C 86.16, H 8.77, N 5.26.

***N*-[(*E*)-1,3-Diphenylprop-2-en-1-yl]morpholine (13):** The same procedure was used starting from 70 μL of morpholine (0.8 mmol, 2 equiv.). The mixture was stirred for 16 h at 20 °C. After work-up, the crude mixture was purified by flash chromatography on silica gel (pentanes:Et_2O, 8:2 then 1:1) to afford 88 mg (79%) of the title compound as a colorless oil. Spectral data are consistent with the reported literature.[24]

***N*-[(*E*)-1,3-Diphenylprop-2-en-1-yl]dibenzylamine (14):** The same procedure was used starting from 155 μL of dibenzylamine (0.8 mmol, 2 equiv.). The mixture was stirred for 16 h at 20 °C. After work-up, the crude mixture was purified by flash chromatography on silica gel (pentanes:Et_2O, 99:1) to afford 63 mg (40%) of the title compound as a colorless oil. Spectral data are consistent with the reported literature.[25]

***N*-[(*E*)-1,3-Diphenylprop-2-en-1-yl]indoline (15):** The same procedure was used starting from 90 μL of indoline (0.8 mmol, 2 equiv.). The mixture was stirred for 16 h at 20 °C. After work-up, the crude mixture was purified by flash chromatography on silica gel (pentanes:Et_2O, 9:1) to afford 100 mg (80%) of the title compound as a colorless oil. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.93 (t, J = 8.2 Hz, 2 H), 3.35–3.42 (m, 2 H), 5.09 (d, J = 7.4 Hz, 1 H), 6.34 (d, J = 8 Hz, 1 H), 6.46 (dd, J = 15.8, 7.4 Hz), 6.61 (dt, J = 7.4, 1.5 Hz, 1 H), 6.64 (d, J = 15.8 Hz, 1 H), 6.93 (t, J = 7.7 Hz, 1 H), 7.05 (dd, J = 7.2, 1 Hz, 1 H), 7.15–7.38 (m, 8 H), 7.45 (d, J = 7.4 Hz, 2 H) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 28.9, 51.2, 64.6, 109.0, 118.1, 124.9, 127.0, 127.6, 127.8, 128.2, 128.3, 131.0, 133.3, 137.2, 141.3 ppm. $C_{23}H_{21}N$ (311.43): calcd. C 88.71, H 6.80, N 4.50; found C 88.98, H 6.87, N 4.36.

***N*-[(*E*)-1,3-Diphenylprop-2-en-1-yl]imidazole (16):** The same procedure was used starting from 55 mg of imidazole (0.8 mmol, 2 equiv.). The mixture was stirred for 16 h at 20 °C. After work-up, the crude mixture was purified by flash chromatography on silica gel (EtOAc then thf) to afford 104 mg (73%) of the title compound as a colorless oil. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 5.93 (d, J = 6.6 Hz, 1 H), 6.57 (dd, J = 16.2, 6.6 Hz, 1 H), 6.93 (s, 1 H), 7.11 (s, 1 H), 7.20–7.75 (m, 10 H), 7.57 (s, 1 H) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 63.6, 119.0, 127.1, 127.2, 127.8, 128.9, 129.0, 129.1, 129.5, 129.8, 134.5, 135.9, 137.1, 139.1 ppm. $C_{18}H_{16}N_2$ (260.34): calcd. C 83.05, H 6.20, N 10.76; found C 83.37, H 6.24, N 10.66.

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