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Allylic alkylation and amination using mixed (NHC)(phosphine) palladium complexes under biphasic conditions

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Abstract

A dramatic improvement of the catalytic activity was observed when a phosphine was added in allylic alkylation reactions catalyzed by (NHC)Pd(η^3-C_3H_5)Cl complexes. Consequently, several palladium complexes, generated in situ from different NHC–silver complexes, [Pd(η^3-C_3H_5)Cl]$_2$ and PPh_3, were tested in this reaction to evaluate their potential. High reaction rates and conversions could be obtained with this catalytic system in the alkylation of allylic acetates with dimethylmalonate, particularly under biphasic conditions using water/dichloromethane and KOH 1 M as the base. These conditions are experimentally more convenient and gave higher reaction rates than the classical anhydrous conditions (NaH/THF). In this system, the phosphine is essential since no conversion was obtained when it is not present. The steric hindrance of the carbene ligand has a great influence on the activity and the stability of the catalytic system. The best NHC ligands for this reaction are either 1-mesityl-3-methyl-imidazol-2-ylidene or 1-(2,6-diisopropylphenyl)-3-methyl-imidazol-2-ylidene which are less bulky among the NHC tested. These two ligands led in 5 min to a complete conversion at 20 °C. The Pd-catalyzed allylic amination reaction using (*E*)-1,3-diphenylprop-3-en-yl acetate and benzylamine was also tested with (NHC)(PPh_3)Pd complexes and under the biphasic conditions. This reaction was found to be slower than the alkylation with dimethylmalonate but a complete conversion could be reached in 6 h at 20 °C using K_2CO_3 1 M as the base. NMR experiments indicated that mixed (NHC)(PPh_3)Pd complexes are formed in situ but their structure could not be established exactly.

Keywords: *N*-heterocyclic carbenes; Allylic alkylation; (NHC)(phosphine)palladium complexes; Biphasic conditions

1. Introduction

Mixed (NHC)(phosphine) palladium complexes (NHC = *N*-heterocyclic carbene) have been used with success in CC or CN coupling reactions [1]. Their superior activity, compared to their bis(NHC) or bis(phosphine) analogues, has been demonstrated particularly in the Mizoroki-Heck, Suzuki-Miyaura or Stille reaction [1a,1b,1c,1g,1j]. However, the behaviour of such palladium complexes involving an NHC and a phosphine ligand has been very little studied in the Tsuji-Trost reaction. The first example of allylic alkylation catalyzed by NHC–palladium complexes was reported by Mori and Sato in 2003 [2]. Several enantioselective versions with chiral NHC ligands have been reported since, with enantiomeric excesses up to 92% [3]. A first example reported in 2005 by Douthwaite et al., describes the use of mixed NHC–P palladium complexes in this reaction [3b]. Chiral bidentate NHC–aminophosphine and NHC–phosphoramidate ligands were tested by the authors that noticed that the presence of the phosphine moiety increases the rate of the allylic substitution reaction compared to the related bis(NHC) or NHC–imino ligands. More recently, the use of chiral bidentate NHC–phosphine ligands in the Pd-catalyzed allylic amination reaction was also described. However, low reaction rates were observed with these ligands compared to isostructural P–N ligands [3f]. We have previously described the preparation and structure of palladium complexes bearing several types of chiral NHC [1g,3e,4].

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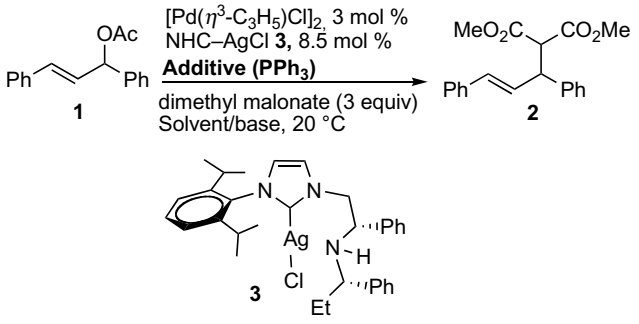
Chelating NHC–amino ligands were tested in the palladium-catalyzed asymmetric allylic alkylation reaction of (*E*)-1,3-diphenylprop-3-en-yl acetate with dimethyl malonate [3e]. However, although enantioselectivities up to 80% could be obtained, low reaction rates have also been observed with these ligands in the Tsuji-Trost reaction. We herein describe our study concerning the development of an efficient and convenient catalytic system for palladium catalyzed allylation reactions using in situ generated (NHC)(PPh_3)Pd complexes and biphasic conditions.

2. Results and discussion

We noticed recently that the addition of PPh_3 to preformed NHC–amino palladium complexes dramatically improved the efficiency of the catalytic system in the allylic alkylation reaction (Scheme 1). The influence of PPh_3 was studied in the reaction of (*E*)-1,3-diphenylprop-3-en-yl acetate **1** with dimethyl malonate, in anhydrous conditions or in biphasic conditions [5]. As previously reported [3e], the palladium complexes were generated in situ from the corresponding NHC–silver complexes and $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$. The results obtained with silver complex **3** [3e] are reported in Table 1.

In the absence of phosphine, the reaction afforded **2** in 33% conversion after 48 h at 20 °C in THF, using NaH as the base and anhydrous conditions (Table 1, entry 1). When the same reaction was performed by adding 7 mol% of PPh_3, a complete conversion was obtained after 1 h at 20 °C (entry 2). The effect of the phosphine was even more significant in biphasic conditions using KOH 1 M as the base and CH_2Cl_2 as the solvent. No reaction occurred in the absence of PPh_3 whereas a complete conversion was reached after 15 min in the presence of 7 mol% of this additive (entries 3 and 4). In both cases, the addition of PPh_3 led to a dramatic decrease of the enantioselectivity. We assumed that this effect could be due to the replacement of the chiral chelating amino side-chain on the palladium by PPh_3. In this case, mixed (NHC)(PPh_3)Pd complexes must be generated in situ leading to more active species than the starting NHC–amino complexes. Interestingly, the best conditions are achieved under the experimentally more convenient biphasic conditions (KOH 1 M, 7 mol% PPh_3, CH_2Cl_2), which afforded **2** quantitatively in only 15 min (entry 4). Similar results were obtained using the well-defined and isolated (NHC)Pd(η^3-C_3H_5)Cl complex **4** [4a] (Scheme 2). With NaH as the base and in the absence of PPh_3, no conversion was observed after 2 h whereas 100% conversion was obtained after 1.5 h with 6 mol% of phosphine. A complete conversion was reached in 15 min under biphasic conditions.

Although low enantioselectivities are obtained, these preliminary experiments seemed to demonstrate that this catalytic system, probably involving mixed (NHC)(PPh_3)Pd complexes, is much more efficient than those previously reported with NHC ligands [2,3]. Consequently, we decided to investigate the scope of this system by testing the behaviour of several achiral NHC ligands. Five new NHC–silver complexes **6a**–**e** having an aromatic substituent (mesityl or 2,6-diisopropylphenyl) on one nitrogen atom of the heterocycle and an alkyl group (more or less bulky) on the second nitrogen atom, were synthesized from the corresponding imidazolium salts **5a**–**e** and Ag_2O in CH_2Cl_2 [6]. The two silver complexes **6f**–**g**, already known [7], were also prepared to be tested (Scheme 3). The new silver complexes **6a**–**e** were characterized by NMR and HRMS. The elemental analyses obtained for these complexes were not in accordance with those calculated for the (NHC)AgX formulation. A minor species is detectable for some complexes by ^{1}H NMR. By comparison of elemental analyses and ^{1}H NMR spectra, we assumed that in addition to the major complex, 6–10% of a minor complex having probably the $(NHC)_2Ag^+/Cl^-$ form (for **6a**, **6b** and **6e**) or $(NHC)_2Ag^+/Br^-$ form (for **6c** and **6d**) is present. The majority of NHC silver complexes with monodentate NHC ligands are known to adopt one

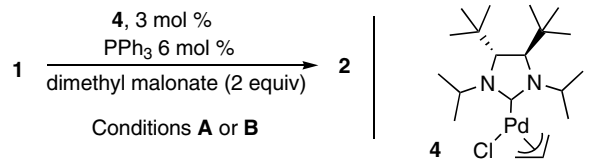


Scheme 1. Allylique alkylation using in situ generated NHC–amino–Pd complexes and PPh_3.

Table 1
Influence of PPh_3 in the allylic alkylation reaction using NHC–amino–Pd complexes

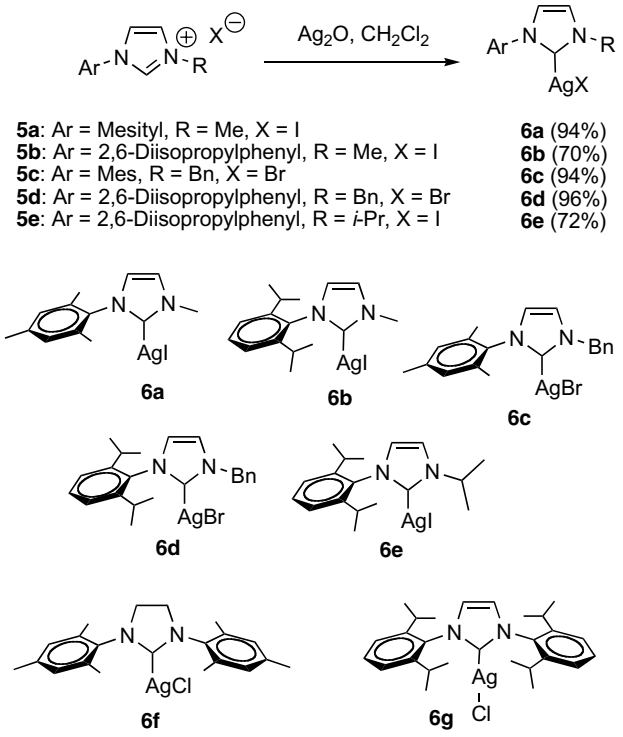
Entry	Solvent/base	Additive	*t* (h)	Conversion[a] (ee)
1	THF/NaH	None	48	33% (76%)
2	THF/NaH	PPh_3[b]	1	>98% (10%)
3	CH_2Cl_2/KOH[c]	None	16	0%
4	CH_2Cl_2/KOH[c]	PPh_3[b]	0.25	>98% (6%)

[a] Determined by ^{1}H NMR of the crude.
[b] PPh_3 7 mol%.
[c] KOH 1 M in H_2O, 2 equiv.



A: NaH (2 equiv), THF,20 °C, 90 min, convn >98% (*ee* 8%)
B: KOH 1M (5 equiv), CH_2Cl_2,20 °C, 15 min, convn >98% (*ee* 5%)

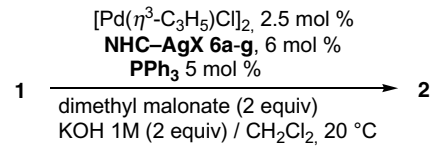
Scheme 2. Allylic alkylation using well-defined (NHC)Pd(η^3-C_3H_5)Cl complex **4** and PPh_3.



Scheme 3. Synthesis and structures of NHC–silver complexes.

of the (NHC)AgX or $(NHC)_2Ag^+/AgX_2^-$ forms but the less frequent structure $(NHC)_2Ag^+/X^-$ was also reported [7,8]. It has also been shown that the reaction of imidazolium iodides with Ag_2O in CH_2Cl_2 could produce NHC silver complexes with chloride anion instead of iodide [8c].

In a first set of experiments, we examined the influence of the NHC ligand in the allylic alkylation reaction of **1** with dimethyl malonate (Scheme 4) in the presence of PPh_3. All reactions were carried out in biphasic conditions. The palladium complexes were generated in situ from silver complexes **6a–g**. In a typical procedure, a mixture of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (0.01 mmol, 2.5 mol%) and silver complex (6 mol%) in CH_2Cl_2 (1 mL) was stirred for 1 h at 20 °C under argon in the absence of light. PPh_3 (5 mol%) was then added and the solution was stirred for 1 h at the same temperature. To the mixture was added a solution of acetate **1** (0.4 mmol, 1 equiv.) in CH_2Cl_2 (1 mL), dimethyl malonate (2 equiv.), di-*tert*-butyl-4,4′-biphenyl (internal reference) and KOH 1 M (2 equiv.). The mixture was stirred vigorously at 20 °C. The reactions were followed by T.L.C. and ^{1}H NMR. The results are depicted in Table 2. To compare the stability and the efficiency of



Scheme 4. Allylic alkylation of **1** using (NHC)(phosphine)Pd complexes under biphasic conditions.

Table 2
Allylic alkylation using $(NHC)(PPh_3)Pd$ complexes: influence of the NHC ligand

Entry	NHC–AgX	t_1 (min)	Convn[a] (%)	t_2	Convn[a] (%)
1	**6a**	5	>98	–	–
2	None	5	16	1.5 h	16
3[b]	**6a**	5	0	1.5 h	0[c]
4[d]	**6a**	5	86	1.5 h	>98
5	**6b**	5	>98	–	–
6	**6c**	5	82	30 min	>98
7	**6d**	5	56	1.5 h	58[c]
8	**6e**	5	88	20 min	>98
9	**6f**	5	45	1.5 h	55[c]
10	**6g**	5	48	1.5 h	53[c]

[a] Determined by ^{1}H NMR. Di-*tert*-butyl-4,4′-biphenyl was used as internal reference.
[b] The reaction was performed in the absence of PPh_3.
[c] The same conversion was observed after 16 h.
[d] The reaction was performed with 2.5 mol of PPh_3.

the catalytic system for each ligand, samples were systematically taken at 5 min and, if the reaction is not complete, at 1.5 and 16 h. These samples were analysed by ^{1}H NMR and the conversion determined by comparison with the internal reference.

High reaction rates and conversions could be obtained with this catalytic system if the appropriate NHC ligand is used. A complete conversion was reached after 5 min using the less bulky silver complexes **6a** and **6b** bearing a methyl group on one of the two nitrogen atoms of the heterocycle (entries 1 and 5). These two complexes are without ambiguity the most efficient. A first control experiment performed with 6 mol% of PPh_3 in the absence of silver complex demonstrated that the carbene ligand was essential to get high reaction rates and conversions. In these conditions, only 16% conversion was measured after 1.5 h (entry 2). No formation of **2** was detected in a second control experiment carried out with 6 mol% of the silver complex **6a** but without PPh_3 (entry 3). Consequently, as previously observed (see Table 1, Schemes 1 and 2), both the carbene ligand and the phosphine play an important role in the reaction. Interestingly, the catalytic system was still efficient when less than 1 equiv. of PPh_3 was used. With a ratio PPh_3/Pd of 0.5 the reaction was slower but complete after 1.5 h (entries 4 and 1). The steric hindrance of the carbene ligand has an important influence on the reaction rate and the stability of the catalytic species. Silver complexes **6a** and **6b**, which lead to very efficient palladium catalysts, bear NHC ligands which are less bulky than the other ligands depicted in Scheme 3. The replacement of the methyl group on the nitrogen atom (complexes **6a**/**6b**) by a benzyl group (complexes **6c** and **6d**) significantly decreased the reaction rate: 30 min was necessary for the reaction to be complete with **6c**, instead of 5 min with **6a** (entries 6 and 1). The results obtained with complexes **6c** and **6d** allowed to distinguish the influence of the aryl group of the ligand (mesityl or 2,6-diisopropylphenyl). Using complex **6d** with a more bulky 2,6-diisopropylphenyl group instead of a mesityl group (complex **6c**), a maximum

of 58% conversion was reached after 1.5 h. This conversion is almost identical to the one observed after 5 min (56%). With this complex, the catalytic system seems to become rapidly inactive. The silver complex **6e** with an NHC ligand bearing a 2,6-diisopropylphenyl group and an isopropyl group leads to a more active palladium complex than its benzyl analogue **6d** (entries 8 and 7). However, a prolonged reaction time (20 min) was necessary to go to completion by comparison with its methyl analogue **6b** (entries 8 and 5). Finally, the more bulky silver complexes **6f** and **6g** gave moderate conversions after 16 h (entries 9 and 10) and no significant progress of the reaction was detected between 5 min and 16 h. This first set of experiments clearly shows that the more active palladium catalysts are generated from the less bulky silver complexes **6a** and **6b**. An increase of the steric hindrance leads in the best cases to a decrease of the reaction rate (silver complexes **6c**/**6e**) but can also lead to a rapid deactivation of the catalytic system (silver complexes **6d**, **6f** and **6g**) [9]. However, in contrast to our results, the bulky NHC ligand of complex **6g** was found by Mori and Sato as being efficient in their conditions. They could obtain **2** in almost quantitative yield (98%) after 2 h in anhydrous conditions (THF, 50 °C), using a palladium complex generated in situ from the imidazolium salt, $Pd_2dba_3 \cdot CHCl_3$ and Cs_2CO_3 [2].

The scope and limitation of the catalytic system were examined by testing the allylic alkylation reaction of acetates **7**–**9** (Fig. 1) with dimethyl malonate. The results, depicted in Table 3, demonstrate that the steric hindrance due to the substituents of the allylic acetates, is as important as the one of the NHC ligand. For example, using the palladium catalyst generated from silver complex **6c**, the reaction is faster with the acetates **7** and **8** than with the more bulky acetate **1** (entries 1–3). For similar reasons, the most bulky silver complex **6g** afforded the allylated products in low conversions from the acetates **1** and **7** (entries 4 and 5) but gave a complete conversion after 5 min with the less bulky acetate **8** (entry 6). To summarize, with acetates **1**, **7** and **8**, high conversions and reaction rates can be achieved if the appropriate silver complex is chosen to minimize the steric hindrance. The unsymmetrically substituted acetate **7** afforded exclusively the linear product **10** (entries 2 and 5). A limitation of this catalytic system was found when the reaction was performed with the cyclic acetate **9** which led to low conversions. The best result (26% conversion) was obtained with the less bulky silver complex **6a** using KOH 50% as the base (entry 7).

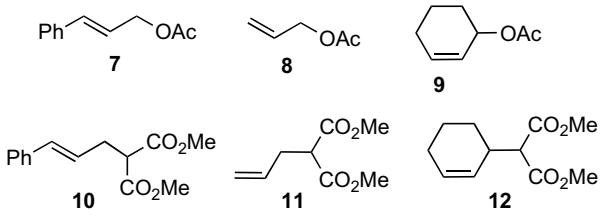


Fig. 1. Allylic acetates and allylation products.

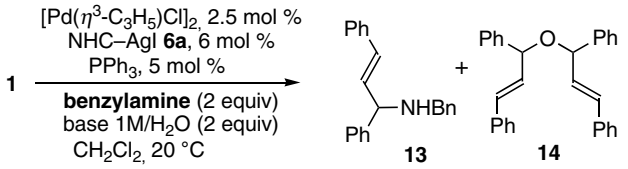
Table 3
Allylic alkylation of acetates **1**, **7**–**9** using (NHC)(PPh_3)Pd complexes

Entry	Acetate	NHC–AgX	Product	*t*	Convn[a] (%)
1	**1**	**6c**	**2**	30 min	>98
2	**7**	**6c**	**10**	5 min	>98
3	**8**	**6c**	**11**	5 min	>98
4	**1**	**6g**	**2**	16 h	53[b]
5	**7**	**6g**	**10**	1.5 h	30[b,c,d]
6	**8**	**6g**	**11**	5 min	>98
7[e]	**9**	**6a**	**12**	16 h	26[b]

[a] Determined by ^{1}H NMR of the crude. Di-*tert*-butyl-4,4′-biphenyl was used as internal reference.
[b] The remaining proportion corresponds to the starting acetate.
[c] The linear product **10** was the sole addition product detectable in the crude.
[d] The same conversion was observed after 16 h.
[e] KOH 50% (0.8 mL) was used.

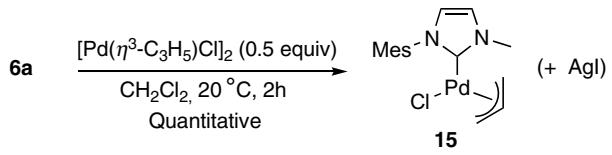
We next investigated the reaction of benzylamine with acetate **1**. It was first reported that the allylic substitution using NHC–Pd complexes seems to be inapplicable to nitrogen nucleophiles [2b]. Contrary to this observation, it was demonstrated in 2007 that bidentate NHC–P ligands led to active palladium catalysts in the allylic amination reaction. However, low reaction rates were observed in the anhydrous conditions that have been used (THF, 40 °C) [3f]. In a preliminary experiment, the reaction was tested in the conditions developed for the alkylation, using silver complex **6a** and KOH 1 M as the base. We could obtain the expected product **13** in 66% yield after 16 h at 20 °C (Scheme 5). The amination reaction is slower than the alkylation with dimethylmalonate and 15% of the ether **14** was obtained as a by-product. The conditions were optimized by replacing KOH by K_2CO_3 (1 M) and by changing the concentration in acetate **1** from 0.2 M in CH_2Cl_2 to 0.4 M. A complete conversion was then obtained after 6 h at ambient temperature and the homoallylic amine **13** was isolated in 95% yield.

Finally, we attempted to determine the exact nature of the palladium species generated in situ. The experiments were performed with silver complex **6a**. The reaction of **6a** with 0.5 equiv. of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ in CH_2Cl_2 at 20 °C afforded quantitatively, after filtration of the silver



Base	Products		
	1	13	14
KOH		68 %	16 %
K_2CO_3		>98 %	

Scheme 5. Amination of **1** using (NHC)(phosphine)Pd complexes and biphasic conditions.



Scheme 6. Synthesis of well-defined (NHC)Pd(η^3-C_3H_5)Cl complex **15**.

salts, the palladium complex **15** that was fully characterized (Scheme 6). The NMR characteristics of this complex are in accordance with those reported in the literature for similar complexes with monodentate NHC ligands [3c,4a,10]. This complex is stable in solution in CH_2Cl_2 and in CD_2Cl_2.

To study the nature of the species formed in the presence of phosphine, 1 equiv. of PPh_3 was added in an NMR tube to a solution of complex **15** in CD_2Cl_2. After the addition, ^1H and ^{31}P NMR spectra were recorded at different times. The ^1H NMR spectrum recorded at 19 °C after 5 min showed the complete disappearance of the starting complex **15** but exhibited mainly very broad signals, difficult to analyse. A similar spectrum was obtained after 30 min. The ^{31}P NMR spectra recorded at 5 min and 30 min always exhibit a single signal at 24.8 ppm. This indicates that PPh_3 reacts rapidly with **15** to form a single phosphine–Pd species, stable in solution in CD_2Cl_2 at room temperature [11]. The ^{31}P resonance observed is in accordance with those reported in the literature for mixed (NHC)(phosphine)Pd^{II} complexes [1a,1g,1j,12]. A slow equilibration rate between several forms could account for the broad resonances observed by ^1H NMR. To our knowledge, (NHC)(phosphine)Pd–allyl complexes have been only isolated and characterized as their η^3-allyl cationic form by using noncoordinating counterions [3f,13]. With a coordinating counterion such as chloride, the presence of η^3 and η^1-allyl species must be considered [14]. In addition, different η^1-allyl species could also be in equilibrium by *cis–trans* isomerization [12] (Scheme 7). ^1H NMR experiments performed at 30 and 42 °C did not provide more precise information even if some signals slightly sharpen upon increase of the temperature. These experiments and the fact that both the phosphine and the NHC are essential in the reaction confirm that mixed (NHC)(PPh_3)Pd complexes are formed in situ although their structure could not be determined.

The exact role of the phosphine remains to be determined. Its σ-donating effect in association with the strong σ-donating effect of the NHC could favor the oxidative addition (ionization) step if an associative mechanism is involved [15]. The phosphine could also accelerate the nucleophile addition step: it was suggested that the low activity of NHC–Pd complexes in the Tsuji-Trost reaction (in the absence of phosphine) could be due to the strong σ-donating properties of the NHC leading to poorly electrophilic cationic π-allyl palladium complexes [3b,16]. In this case, the π-acidity of the phosphine could promote the second step of the reaction by reducing the electron density at the Pd center [17]. In our conditions, we attempted to replace PPh_3 by the more π-acidic $P(OPh)_3$ ligand. In this case, the alkylation reaction carried out with silver complex **6a** and acetate **1** led to only 4% conversion.

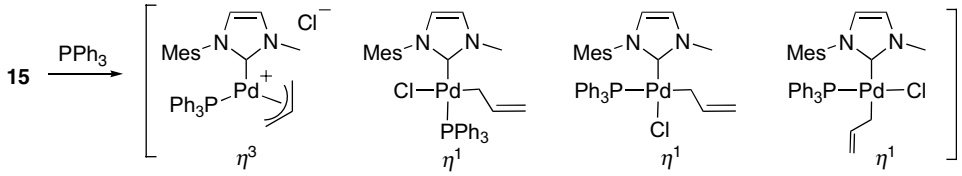
3. Conclusion

We have developed an efficient and convenient catalytic system for the allylic alkylation and amination reaction using mixed (NHC)(phosphine) palladium complexes and biphasic conditions. The superior activity of NHC–P complexes compared to other NHC–palladium complexes seems to be even more significant in this reaction than in Mizoroki-Heck or Suzuki-Miyaura reactions. We could demonstrate that under these biphasic conditions, the presence of a phosphine is absolutely necessary to get active NHC–palladium species and that the steric interactions between the NHC ligand and the allylic acetate must be minimized to get high reaction rates and conversions. Further studies are ongoing to determine precisely the role of the phosphine and to expand the use of this catalytic system.

4. Experimental

4.1. General considerations

All experiments were performed under argon using standard Schlenk techniques unless stated otherwise. Solvents were dried over the appropriate drying agent and distilled under dinitrogen. Sodium benzophenone ketyl (THF), CaH_2 (CH_2Cl_2). Reagents were purchased from Acros or Aldrich and used as received unless otherwise stated. 1-Mesitylimidazole, 1-[2,6-(*i*-Pr)$_2$C$_6$H$_3$]-imidazole [18], 1-mesityl-3-methyl-imidazolium iodide **5a** [19], 1,3-bis(mesityl)-imidazolin-2-ylidene silver chloride **6f** [7] and 1,3-bis(2,6-diisopropylphenyl)-imidazol-2-ylidene silver chloride **6g** [7] were prepared according to reported procedures. ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Brucker ARX-400



Scheme 7. Possible palladium species formed in the presence of triphenylphosphine.

spectrometer, in $CDCl_3$, CD_2Cl_2 or DMSO-d_6 as the solvent. IR spectra were recorded on a Brucker Tensor 27 (pike) instrument and only the structurally most important peaks are listed. Melting points are uncorrected and were measured on a Stuart Scientific apparatus SMP3. The NMR data for products **2** [20], **10** [21], **11** [22], **12** [23,24], **13** [24] and **14** [25] were in accordance with those reported in the literature.

4.2. 1-(2,6-Diisopropylphenyl)-3-methyl imidazolium iodide (**5b**)

An oven-dried screw-cap tube flushed with argon was charged with 1-(2,6-diisopropylphenyl)-imidazole (114 mg, 0.5 mmol), dichloromethane (1 mL) and iodomethane (62 μL, 1 mmol). The mixture was stirred at 30–35 °C (oil bath) for 16 h. After cooling, the imidazolium salt was precipitated by several washings of the residue with pentane (2 × 15 mL) and ether (2 × 10 mL). After drying under vacuum, a white solid was obtained (181 mg, 98%). M.p. 81–82 °C. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 9.92$ (s, 1H), 8.17 (s, 1H), 7.46 (t, 1H, $J = 7.8$ Hz), 7.22 (d, 2H, $J = 7.8$ Hz), 7.18 (s, 1H), 4.32 (s, 3H), 2.22 (m, 1H, $J = 6.8$ Hz), 1.14 (d, 3H, $J = 6.8$ Hz), 1.06 (d, 3H, $J = 6.8$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 145.3$, 137.3, 131.9, 129.8, 125.3, 124.6, 124.2, 37.9, 28.5, 24.4, 24.3. HRMS: *m*/*z* calcd for $C_{16}H_{23}N_2$243.18558, found 243.18549. Anal. Calc. for $C_{16}H_{23}IN_2$ ($M_w = 370.27$): C, 51.90; H, 6.26; N, 7.57. Found: C, 51.61; H, 6.33; N, 7.41%.

4.3. 1-Mesityl-3-benzyl-imidazolium bromide (**5c**)

An oven-dried screw-cap tube flushed with argon was charged with 1-mesityl-imidazole (186 mg, 1 mmol), dichloromethane (1 mL) and benzyl bromide (238 μL, 2 mmol). The mixture was stirred at 30–35 °C (oil bath) for 16 h. After cooling, the imidazolium salt was precipitated by several washings of the residue with pentane (2 × 15 mL) and ether (2 × 10 mL). After drying under vacuum, a white solid was obtained (360 mg, 100%). M.p. = 237–238 °C. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 10.69$ (s, 1H), 7.65–7.55 (m, 3H), 7.45–7.40 (m, 3H), 7.12 (s, 1H), 7.01 (s, 2H), 6.01 (s, 2H), 2.35 (s, 3H), 2.09 (s, 6H). ^{3}C NMR (100 MHz, $CDCl_3$): $\delta = 141.2$, 137.7, 134.1, 133.6, 130.7, 129.8, 129.3, 129.1, 123.2, 123.0, 53.3, 21.0, 17.6. HRMS: *m*/*z* calcd for $C_{19}H_{21}N_2$ 277.16993, found 217.16950. Anal. Calc. for $C_{19}H_{21}BrN_2$ ($M_w = 357.29$): C, 63.87; H, 5.92; N, 7.84. Found: C, 63.47; H, 5.91; N, 7.74%.

4.4. 1-(2,6-Diisopropylphenyl)-3-benzyl imidazolium bromide (**5d**)

An oven-dried screw-cap tube flushed with argon was charged with 1-(2,6-diisopropylphenyl)-imidazole (228 mg, 1 mmol), dichloromethane (1 mL) and benzyl bromide (238 μL, 2 mmol). The mixture was stirred at 30 °C (oil bath) for 16 h. After cooling, the imidazolium salt was precipitated by several washings of the residue with pentane (2 × 15 mL) and ether (2 × 10 mL). After drying under vacuum, a pale yellow solid was obtained (396 mg, 99%). M.p. = 114–115 °C. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 10.65$ (s, 1H), 7.75 (t, 1H, $J = 1.7$ Hz), 7.65–7.62 (m, 2H), 7.55 (t, 1H, $J = 7.8$ Hz), 7.46–7.41 (m, 3H), 7.31 (d, 2H, $J = 7.8$ Hz), 7.13 (t, 1H, $J = 1.7$ Hz), 6.09 (s, 2H), 2.28 (m, 2H, $J = 6.8$ Hz), 1.24 (d, 6H, $J = 6.8$ Hz), 1.14 (d, 6H, $J = 6.8$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 145.3$, 138.1, 133.8, 131.9, 131.2, 129.4, 129.1, 124.6, 124.1, 123.1, 53.4, 28.7, 24.4, 24.0. HRMS: *m*/*z* calcd for $C_{22}H_{27}BrN_2$ 319.21688, found 319.21642. Anal. Calc. for $C_{22}H_{27}BrN_2$ ($M_w = 399.37$): C, 66.16; H, 6.81; N, 7.01. Found: C, 66.02; H, 7.00; N, 6.92%.

4.5. 1-(2,6-Diisopropylphenyl)-3-isopropyl imidazolium iodide (**5e**)

An oven-dried screw-cap tube flushed with argon was charged with 1-(2,6-diisopropylphenyl)imidazole (228 mg, 1 mmol) and 2-iodopropane (1 mL, 10 mmol). The mixture was stirred under argon at 50 °C (oil bath) for 50 h. After cooling, the solution was diluted with CH_2Cl_2 (20 mL) and washed with aqueous $Na_2S_2O_3$ (2 × 5 mL) then with water (2 × 10 mL). The organic layer was dried over $MgSO_4$, filtered and concentrated. After drying under vacuum, a pale yellow hygroscopic solid was obtained (350 mg, 60%). M.p. = 207–208 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.16 (t, 1H, $J = 1.5$ Hz), 8.08 (t, 1H, $J = 1.8$ Hz), 7.55 (t, 1H, $J = 8$ Hz), 7.32 (d, 2H, $J = 8$ Hz), 7.29 (s, 1H), 5.63 (m, 1H, $J = 6.6$ Hz), 2.28 (m, 2H, $J = 6.8$ Hz), 1.72 (d, 3H, $J = 6.6$ Hz), 1.25 (d, 3H, $J = 6.8$ Hz), 1.17 (d, 3H, $J = 6.8$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.2, 136.5, 131.8, 130.0, 124.7, 124.6, 121.4, 53.7, 28.7, 24.4, 24.2, 23.4, 23.4. HRMS: *m*/*z* calcd for $C_{18}H_{27}N_2$ 271.21688, found 271.21668. Anal. Calc. for $(C_{18}H_{27}IN_2)_2(H_2O)$: C, 53.08; H, 6.93; N, 6.88. Found: C, 53.03; H, 6.78; N, 6.91%.

4.6. Preparation of NHC–silver(I) complexes. General procedure

To a solution of imidazolium salt (1 mmol) in dry CH_2Cl_2 (15 mL) was added Ag_2O (0.55 mmol). The mixture was stirred at 20 °C for 16 h with exclusion of light, filtered through celite and concentrated under reduced pressure. The solid was washed with pentane and dried under vacuum.

4.7. 1-Mesityl-3-methyl-imidazol-2-ylidene silver iodide (**6a**)

567 mg (94%) of a beige solid was obtained starting from 500 mg (1.5 mmol) of **5a**. M.p. = 82–83 °C. ^{1}H

NMR (400 MHz, $CDCl_3$): $\delta = 7.27$ (s, 1H), 6.90 (s, 2H), 6.88 (m, 1H), 3.91 (s, 3H), 2.33 (s, 3H), 1.86 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 183.6$, 139.2, 135.3, 134.7, 129.2, 122.5, 122.4, 38.9, 21.0, 17.7. HRMS: $[(NHC)_2Ag]$ $[AgI_2]$ *m/z* calcd for $C_{26}H_{32}N_4Ag$ (cation) 507.1672, found 507.16763. Anal. Calc. for $(C_{13}H_{16}AgIN_2)_{10}(C_{26}H_{32}AgClN_4)$: C, 38.28; H, 3.95; N, 6.87. Found: C, 38.34; H, 3.96; N, 6.76%.

4.8. 1-(2,6-Diisopropylphenyl)-3-methyl-imidazol-2-ylidene silver iodide (**6b**)

90 mg (70%) of a white solid was obtained starting from 100 mg (0.27 mmol) of **5b**. M.p. 94–95 °C. ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.44$ (t, 3H, $J = 15.6$ Hz), 7.25 (s, 1H), 7.23 (s, 1H), 7.21 (s, 1H), 6.96 (d, 1H), 3.93 (s, 3H), 2.34 (m, 2H, $J = 6.8$ Hz), 1.14 (d, 6H, $J = 6.8$ Hz), 1.09 (d, 6H, $J = 6.8$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 145.7$, 134.5, 130.4, 124.1, 123.8, 38.9, 28.1, 24.6, 24.5, 24.3, the carbene carbon was not detected. HRMS: $[(NHC)_2Ag]$ $[AgI_2]$ *m/z* calcd for $C_{32}H_{44}N_4Ag$ (cation) 591.26114, found 591.26137. Anal. Calc. for $(C_{16}H_{22}AgIN_2)_9(C_{32}H_{44}AgClN_4)$: C, 42.95; H, 4.96; N, 6.26. Found: C, 43.04; H, 4.96; N, 6.03%.

4.9. 1-Mesityl-3-benzyl-imidazol-2-ylidene silver bromide (**6c**)

345 mg (94%) of a beige solid was obtained starting from 297 mg (0.79 mmol) of **5c**. M.p. 64–65 °C. ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.36$ (m, 3H), 7.25 (m, 2H), 7.12 (s, 1H), 6.93 (m, 3H), 5.39 (s, 2H), 2.32 (s, 3H), 1.97 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 139.8$, 135.5, 135.2, 134.6, 129.4, 129.2, 128.7, 127.6, 123.1, 121.0, 55.7, 21.0, 17.7, the carbene carbon was not detected. HRMS: $[(NHC)_2Ag]$ $[AgBr_2]$ *m/z* calcd for $C_{38}H_{40}N_4Ag$ (cation) 659.2298, found 659.2300. Anal. Calc. for $(C_{19}H_{20}AgBrN_2)_{15}(C_{38}H_{40}AgBrN_4)$: C, 50.36; H, 4.45; N, 6.18. Found: C, 50.53; H, 4.52; N, 6.14%.

4.10. 1-(2,6-Diisopropylphenyl)-3-benzyl-imidazol-2-ylidene silver bromide (**6d**)

415 mg (96%) of an off-white solid was obtained starting from 340 mg (0.85 mmol) of **5d**. M.p. 78–79 °C. ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.51$–7.27 (m, 8H), 7.13 (d, 1H, $J = 1.5$ Hz), 7.02 (d, 1H, $J = 1.5$ Hz), 5.46 (s, 2H), 2.41 (m, 2H, $J = 6.8$ Hz), 1.27 (d, 6H, $J = 6.8$ Hz), 1.14 (d, 6H, $J = 6.8$ Hz). ^{13}C NMR (100 MHz, CD_2Cl_2) $\delta = 146.2$, 136.2, 135.2, 130.8, 129.5, 128.9, 127.8 (broad), 124.9, 124.5, 121.8 (broad), 55.7 (broad), 28.7, 24.7, 24.3, the carbene carbon was not detected. HRMS: $[(NHC)_2Ag]$ $[AgBr_2]$ *m/z* calcd for $C_{44}H_{52}N_4Ag$ (cation) 743.32374, found 743.32197. Anal. Calc. for $(C_{22}H_{26}AgBrN_2)_{13}(C_{44}H_{52}AgBrN_4)$: C, 53.52; H, 5.31; N, 5.67. Found: C, 53.66; H, 5.38; N, 5.61%.

4.11. 1-(2,6-Diisopropylphenyl)-3-isopropyl-imidazol-2-ylidene silver iodide (**6e**)

202 mg (72%) of a pale beige solid was obtained starting from 150 mg (0.554 mmol) of **5e**. M.p. 88–89 °C. ^1H NMR (400 MHz, DMSO-d_6, the complex is little soluble in $CDCl_3$ and CD_2Cl_2). A mixture of isomers is observed, major isomer (~90%): $\delta = 7.79$ (d, 1H, $J = 1.5$ Hz), 7,69 (d, 1H, $J = 1.5$ Hz), 7.57 (t, 1H, $J = 7.8$ Hz), 7.38 (d, 2H, $J = 7.8$ Hz), 3.87 (m, 1H), 2.25–2.10 (m, 2H), 1.30–0.95 (m, 18H). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 145.9$, 135.1, 130.4, 124.1, 123.7, 53.9, 28.2, 24.4, 24.3, 24.2, 24.0, the carbene carbon was not detected. HRMS: $[(NHC)_2Ag]$ $[AgI_2]$ *m/z* calcd for $C_{36}H_{52}N_4Ag$ (cation) 647.32374, found 647.32238. Anal. Calc. for $(C_{18}H_{26}AgIN_2)_{12}(C_{36}H_{52}AgClN_4)$: C, 44.29; H, 5.39; N, 5.74. Calc. for $(C_{18}H_{26}AgIN_2)_{12}(C_{36}H_{52}AgIN_4)$: C, 44.26; H, 5.37; N, 5.74. Found: C, 44.33; H, 5.23; N, 5.57%.

4.12. Typical procedure for allylic alkylation reactions in biphasic conditions

A mixture of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (3.6 mg, 0.01 mmol, 2.5 mol%) and silver complex (0.024 mmol, 6 mol%) in CH_2Cl_2 (1 mL) was stirred for 1 h at 20 °C under argon in the absence of light. PPh_3 (5.2 mg, 0.02 mmol, 5 mol%) was then added and the solution was stirred for 1 h at the same temperature. To the mixture was added a solution of (*E*)-1,3-diphenylprop-3-en-yl acetate **1** (100 mg, 0.4 mmol, 1 equiv.) in CH_2Cl_2 (1 mL), dimethyl malonate (91 μL, 0.8 mmol, 2 equiv.), di-*tert*-butyl-4,4′-biphenyl (34.8 mg, 0.33 equiv., 0.13 mmol, internal reference) and KOH 1 M in H_2O (0.8 mL, 2 equiv.). The mixture was stirred vigorously for the indicated time at 20 °C. The mixture was diluted with Et_2O and the organic layer was separated. The residue was extracted with Et_2O. The combined organic layers were filtered through a short pad of silicagel, dried over Na_2SO_4 and concentrated. The conversion was determined by ^1H NMR of the residue by comparison with the internal reference.

4.13. Allylic amination reaction with benzylamine in biphasic conditions

A mixture of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (3.6 mg, 0.01 mmol, 2.5 mol%) and silver complex **6a** (10.5 mg, 0.024 mmol, 6 mol%) in CH_2Cl_2 (0.5 mL) was stirred for 1 h at 20 °C under argon in the absence of light. PPh_3 (5.2 mg, 0.02 mmol, 5 mol%) was then added and the solution was stirred for 1 h at the same temperature. To the mixture was added 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), benzylamine (87 μL, 0.8 mmol, 2 equiv.), di-*tert*-butyl-4,4′-biphenyl (34.8 mg, 0.33 equiv., 0.13 mmol, internal reference) and K_2CO_3 1 M in H_2O (0.8 mL, 2 equiv.). The mixture was stirred vigorously for 6 h at 20 °C. The mix-

ture was diluted with Et_2O, solid NaCl was added and the organic layer was separated. The residue was extracted with Et_2O. The combined organic layers were dried over K_2CO_3, filtered through a short pad of silicagel and concentrated. A complete conversion was determined by ^1H NMR of the crude by comparison with the internal reference. The residue was purified by column chromatography (SiO_2, pentane/Et_2O;9/1) to afford 114 mg (95%) of the expected product **13** as a colorless oil.

4.14. Synthesis of (NHC)Pd(allyl)Cl complex (**15**)

A mixture of silver complex **6a** (100 mg, 0.23 mmol) and $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (42 mg, 0.115 mmol) in degassed CH_2Cl_2 (5 mL) was stirred for 2 h at 20 °C. The silver salts were removed by filtration through a short pad of Celite. Evaporation of the CH_2Cl_2 and drying under vacuum afforded quantitatively 92 mg of an off-white solid. M.p. = 179–180 °C. ^1H NMR (400 MHz, $CDCl_3$) $\delta = 7.10$ (d, 1H, $J = 1.8$ Hz), 6.97 (s, 1H), 6.94 (s, 1H), 6.91 (d, 1H, $J = 1.8$ Hz), 5.03 (m, 1H), 4.11 (dd, 1H, $J = 7.4$ and 2 Hz), 4.10 (s, 3H), 3.15 (d, 1H, $J = 6.6$ Hz), 3.03 (d, 1H, $J = 13.4$ Hz), 2.34 (s, 3H), 2.22 (s, 3H), 2.06 (s, 3H). ^{13}C NMR (100 MHz, CD_2Cl_2): $\delta = 181.3$ ($C_{carbene}$), 139.7, 136.4, 135.7, 135.3, 128.9, 128.6, 122.6, 122.2, 114.5 (CH_{allyl}), 71.1 (CH_2), 48.6 (CH_2), 38.1 (N–CH_3), 20.8 (CH_3, Mes), 18.1 (CH_3, Mes), 17.3 (CH_3, Mes). Anal. Calc. for $C_{16}H_{21}ClN_2Pd$ ($M_w = 383.22$): C, 50.15; H, 5.52; N, 7.31. Found: C, 49.91; H, 5.39; N, 7.28%.

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