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Diethylzinc-Mediated Allylation of Carbonyl Compounds Catalyzed by [(NHC)(PR_3)PdX_2] and [(NHC)Pd(η^3-allyl)Cl] Complexes

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Keywords: Allylation / Carbene ligands / Palladium / Reaction mechanisms

[(NHC)(PR_3)PdX_2] complexes (NHC = N-heterocyclic carbene) are active precatalysts in the palladium-catalyzed allylation of carbonyl compounds with allylic acetates and diethylzinc. A comparative study examining the catalytic activity of a series of six of these complexes was carried out with allyl and cinnamyl acetates. [(IMesMe)(PPh_3)PdI_2] was found to be the most versatile precatalyst (IMesMe = 1-mesityl-3-methylimidazol-2-ylidene) and the scope of the reaction was investigated with this complex. [(IMesMe)(PPh_3)PdI_2] catalyzes the allylation of aromatic (except 4-nitrobenzaldehyde) and aliphatic aldehydes (including enolizable aldehydes) with cinnamyl acetate to give the corresponding homoallylic alcohols in 57–98 % yields and diastereoselectivities ranging from 70:30 to 92:8. The allylation of acetone also takes place under the same conditions, leading to the expected adduct in 63 % yield. The reaction with cyclohexenyl acetate proceeds at room temperature to afford the homoallylic alcohols in 40–78 % yields with excellent diastereoselectivities (>98:2), but is limited to aromatic aldehydes. An experimental study concerning the mechanism of the transformation was also carried out. We first demonstrated that the phosphane ligand was not essential for the reaction to take place. [(NHC)Pd(allyl)Cl] complexes are active precatalysts and lead to similar yields in the presence or in the absence of PPh_3. Transmetalation of [(NHC)Pd(allyl)Cl] complexes with diethyl- or dimethylzinc, which is a determining step for the mechanism, was studied by ^{1}H NMR spectroscopy. The reaction of [(IPr)Pd(allyl)Cl] with dimethylzinc affords rapidly [(IPr)Pd(η^3-allyl)(Me)] but no detectable trace of allylzinc species [IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene]. [(IPr)Pd(η^3-allyl)(Me)] was found to be a nucleophilic species able to react smoothly at room temperature with an aldehyde in the absence of zinc to form the corresponding homoallylic alcohol.
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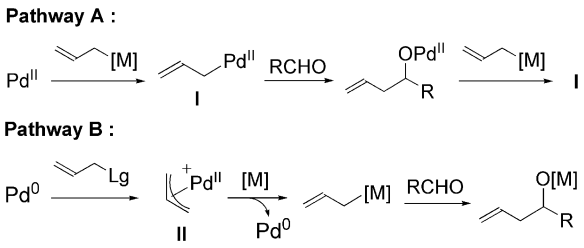
Introduction

Palladium-catalyzed transformations involving allylpalladium species represent an important area of homogeneous catalysis.[1] Among these, allylation of nucleophiles, commonly called the Tsuji–Trost reaction, has been widely studied.[1,2] In this reaction, it is clearly established that the allyl fragment of the transient cationic π-allyl palladium species behaves as an electrophile, allowing the formation of allylated products after attack of nucleophiles. Allylation reactions of electrophiles, catalyzed by Pd^{II} or Pd^0, have also been reported. Various efficient catalytic systems have been developed for the allylation of aldehydes, imines, ketones, or Michael acceptors.[3] Two main mechanisms, fundamentally different, have been proposed for these reactions (Scheme 1). In pathway A, (η^1-allyl)Pd^{II} **I** species, having a nucleophilic allyl moiety, are directly involved in the allylation step.[4] In pathway B, intermediate allylpalladium species **II** does not react directly with the electrophile but leads after transmetalation to the formation of nucleophilic allylmetal species. Therefore, in contrast to the Tsuji–Trost reaction, the direct participation of an allylpalladium species in the key step (reaction with the aldehyde) is not systematic. Moreover, in reactions where pathway A is considered, the nucleophilic behavior of the allyl moiety could not always be easily proved experimentally.



Scheme 1. Main pathways proposed for the allylation of aldehydes with allylpalladium complexes.

In the allylation reactions described by Yamamoto using catalytic bis(allyl)palladium (**1**) and allylstannanes (Figure 1),[5] the homoallylic alcohol resulting from the reaction of **1** with benzaldehyde was observed by NMR spectroscopy and isolated.[5a,7b] The nucleophilic properties of one of the allyl ligands was also confirmed by DFT calcula-

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tions.[6] Szabó reported allylation reactions of carbonyl compounds and imines by using catalytic Pd^{II} "pincer" complexes with tridentate P–C–P ligands.[7] This methodology was based on the in situ generation of nucleophilic (η^1-allyl)Pd^{II} species **2**, generally from allylstannanes.[8] In this case, the formation of **2** was confirmed by NMR spectroscopy[7a,7b,7d,9] and its reactivity studied by DFT calculations.[10] A low activation barrier was found for the reaction of the η^1-allyl complex with aldehydes.[7b,7e,11]

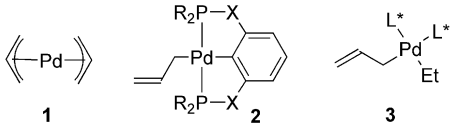

Figure 1. Nucleophilic allylpalladium complexes.

The palladium-catalyzed allylation reaction of carbonyl compounds or imines by using allylic acetates and diethylzinc was initially developed by Tamaru and many applications have been reported.[12] It was proposed for this transformation a mechanism corresponding to pathway B (Scheme 1) in which the intermediate cationic π-allyl palladium complex would react with Et_2Zn to form a nucleophilic allylzinc species.[12a] Phosphorous ligands are generally necessary in this reaction[3] and asymmetric versions have been reported with chiral monodentate P ligands.[12d,12g,12h,12j] In this case, the mechanism initially considered cannot easily account for the enantioselectivities obtained. In particular, when allyl or cinnamyl acetates are used, the reaction should proceed through achiral allylzinc species unable to generate any enantioselectivity.[3e] Therefore, Minnaard and Feringa proposed that nucleophilic [(L_2)(allyl)Pd(Et)] species **3** could be generated in situ after transmetalation by Et_2Zn and react directly with the aldehyde.[12h,13]

Recently, it has been considered that the strong σ-donor effect associated with the N-heterocyclic carbenes (NHCs)[14] could be exploited to confer nucleophilic properties on the allyl palladium complexes and promote the allylation of electrophiles such as aldehydes. Numerous applications of NHC–Pd complexes in the Tsuji–Trost reaction have been reported.[15] It has been generally observed that the allyl moiety of the intermediate [(NHC)Pd(allyl)(L)] cationic complexes was poorly electrophilic.[16] In contrast, Sigman showed in 2003 that the allyl fragment of [(NHC)Pd(allyl)Cl] complexes reacted with HCl to form propene.[17] Szabó described in 2004 the first application of NHC–Pd complexes in the allylation reaction of carbonyl compounds (Figure 2).[7b] However, a low catalytic activity was observed with the bis(NHC) "pincer" complex **4** tested.[18] In 2007, Jarvo showed that allylpalladium complexes of type **5**, bearing bidentate NHC ligands, behaved as nucleophiles and were able to react directly with aldehydes.[19] Complex **5** catalyzes allylations of aldehydes with allylstannanes[19] and conjugate allylation reactions of α,β-unsaturated *N*-acylpyrroles using allylboronic esters.[20] Later, Shi and co-workers reported that bis(NHC)Pd^{II} complexes **6** were efficient precatalysts in the allylation reaction of aldehydes.[21] In the presence of allylstannanes,[21a] the transient formation of (η^1-allyl)Pd species was shown by NMR spectroscopy, and a mechanism similar to that proposed by Szabó was considered (pathway A, Scheme 1).

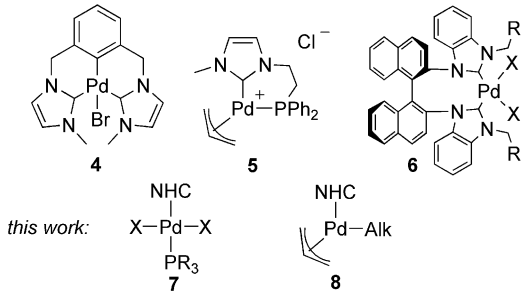

Figure 2. NHC–Pd complexes used in allylation reactions of carbonyl compounds.

Herein we wish to present our study concerning the use of [$(NHC)(PR_3)PdX_2$] complexes **7** as precatalysts in the diethylzinc-mediated palladium-catalyzed allylation of carbonyl compounds as well as an experimental study of the mechanism, carried out with [(NHC)Pd(allyl)Cl] complexes, demonstrating that nucleophilic [(NHC)Pd(allyl)(Alk)] species **8** are likely involved in the key step of the reaction.

Results and Discussion

A series of six [$(NHC)(PR_3)PdX_2$] complexes **7a**–**f** with different phosphorus, NHC, and halides ligands was prepared (Figure 3). We initially selected this family of complexes for several reasons. We assumed that (i) the π-accepting properties of the phosphorus ligand could favor the reduction of Pd^{II} species into Pd^0; (ii) the oxidative addition of allylic acetates that generates [(NHC)Pd(allyl)(OAc)] complexes could be favored by the σ-donor effects of both the NHC and the P-ligand; (iii) the phosphorus ligand could stabilize underligated $(NHC)Pd^0$ complexes but could also dissociate to free a coordination site; (iv) a single [$(NHC)(PR_3)PdX_2$] precatalyst may allow the formation of various transient [(NHC)Pd(η^3-R-allyl)OAc] complexes and therefore of a wide range of homoallylic alcohols; (v) these complexes must be more appropriate than [(NHC)-Pd(allyl)Cl] precatalysts, as contamination by unexpected homoallylic alcohols arising from the transfer of the allyl fragment initially present on the precatalyst cannot take place. We decided to compare the influence of two NHC ligands, IPr and IMesMe (Figure 3), which had given significantly different results in the Tsuji–Trost reaction.[15l] In allylic alkylation reactions catalyzed by [(IMesMe)Pd(allyl)-Cl], high reaction rates and yields were observed with various allylic acetates, whereas the efficiency of [(IPr)Pd(allyl)-Cl] was limited to allyl acetate.

Complexes **7a**–**e**, bearing IPr as ligand, were obtained in 68–94% yields by reaction of the phosphorus ligand [PPh_3, $P(n\text{Bu})_3$ or $P(OPh)_3$] with the appropriate [$\{(IPr)PdX_2\}_2$]

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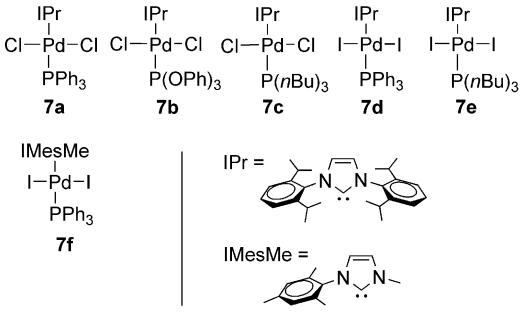
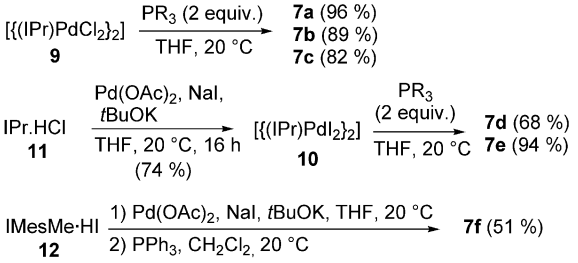


Figure 3. [(NHC)(PR_3)PdX_2] complexes and NHC ligands. IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene; IMesMe = 1-mesityl-3-methylimidazol-2-ylidene.

dimeric complex **9** or **10** (Scheme 2).[22] [{(IPr)PdI_2}$_2$] (**9**) was synthesized in 74% yield from imidazolium salt **11** (IPr·HCl) by using a reported procedure.[23] Complex **7f** was obtained in 51% yield in two steps from imidazolium salt **12** (IMesMe·HI) by the same procedure as that used for **7d** and **7e**. In this case, the intermediate dimeric complex [{(IMesMe)PdI_2}$_2$] is not stable enough to be isolated analytically pure in reasonable yields and fully characterized. It was directly engaged in the second step after rapid purification by filtration through silica gel. Slow evaporation of a diluted solution of **7f** in Et_2O afforded small red crystals suitable for X-ray diffraction analysis. As shown in Figure 4, **7f** is a *trans* complex with a distorted square-planar coordination around the palladium center.



Scheme 2. Synthesis of complexes **7a**–**f**.

The efficiency of [(NHC)(PR_3)PdX_2] complexes **7a**–**f** was first investigated in the allylation reaction of benzaldehyde and 4-bromobenzaldehyde with allylic acetate (**13**) under standard reaction conditions usually reported for this transformation[12] (Scheme 3). All reactions were stirred for 16 h at 20 °C in the presence of **7a**–**f** (5 mol-%) and 3.5 equiv. of diethylzinc. The allylation of benzaldehyde with **13** has been described previously using Pd(PPh_3)$_4$[12a] or palladium complexes generated from Pd(PhCN)$_2$Cl$_2$ and phosphoramidites ligands as catalysts.[12h] Homoallylic alcohol **14a** was obtained in 77 and 73% yield, respectively. Allylation reactions using **13** have not been reported with NHC–Pd complexes. As shown in Table 1, complexes **7a**–**f** proved to be suitable precatalysts for this Et_2Zn-mediated reaction. In preliminary experiments performed with benzaldehyde and complexes **7a**, **7b**, or **7d**, homoallylic alcohol **14a** was obtained in 23–60% yields (Table 1, Entries 1–3). The best yield was achieved with [(IPr)(PPh_3)PdI_2] (**7d**) (60%; Table 1, Entry 3). In a second set of experiments with 4-bromobenzaldehyde and complexes **7a**–**f**, higher yields ranging from 45 to 75% were obtained (Table 1, Entries 4–9) and [(IPr)(PPh_3)PdCl_2] (**7a**) was found to be the most efficient complex, affording homoallylic alcohol **14b** in 75% yield (Table 1, Entry 4). A close but slightly lower yield of 70% was obtained with [(IMesMe)(PPh_3)PdI_2] (**7f**) (Table 1, Entry 9). In reactions catalyzed by **7a**–**e**, bearing the same NHC ligand (IPr), no straightforward influence of the electronic properties of the phosphorus ligand and of the nature of the halide ligand on the yields could be evidenced (Table 1, Entries 1–8). However, PPh_3 appeared to be the most appropriate phosphorus ligand: in reactions using benzaldehyde as the electrophile, triphenylphosphanyl complexes **7a** and **7d** led to the formation of 1-phenyl-3-buten-1-ol (**14a**) in 54 and 60% yields (Table 1, Entries 1 and 3), whereas a lower yield of 23% was obtained with [(IPr){P(OPh)$_3$}PdCl_2] (**7b**) (Table 1, Entry 2); When 4-bromobenzaldehyde was used as the electrophile and dichlorido complexes **7a**–**c** as the precatalysts (Table 1, Entries 4–6), the best yield was also achieved with **7a** bearing PPh_3 as the phosphorus ligand (75%; Table 1, Entry 4) and the replacement of PPh_3 by P(OPh)$_3$ (complex **7b**) or P(nBu)$_3$ (complex **7c**) led to a significant decrease in the yields (Table 1, Entries 5 and 6). In contrast to these observations, the effect of the phosphorus ligand [PPh_3 or P(nBu)$_3$] was found to be negligible in reactions catalyzed by the diiodido complexes **7d** and **7e** (Table 1, Entries 7 and 8). Finally, the influence of the NHC ligand was compared under the same conditions using the diiodido complexes [(IPr)(PPh_3)PdI_2] (**7d**) and [(IMesMe)(PPh_3)PdI_2] (**7f**). Homoallylic alcohol **14b** was obtained in 70% yield with **7f** (Table 1, Entry 9) but in a lower yield of 55% with **7d** (Table 1, Entry 7), thus suggesting that IMesMe should be more appropriate.

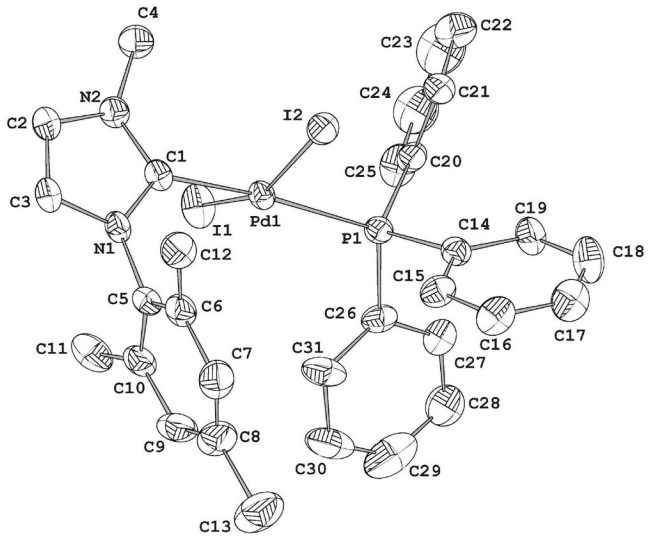


Figure 4. Molecular structure of **7f**. Selected angles [°] C1–Pd1–P1 174.91(16), I1–Pd1–I2 157.49(2), I1–Pd1–P1 90.84(4), I1–Pd1–C1 88.44(14), I2–Pd1–P1 93.31(4), I2–Pd1–C1 89.27(14). Selected bond lengths [Å]: Pd1–C1 2.023(5), Pd1–P1 2.3459(14), Pd1–I1 2.6326(5), Pd1–I2 2.6352(5).

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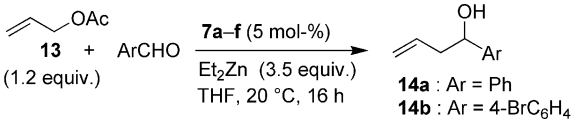


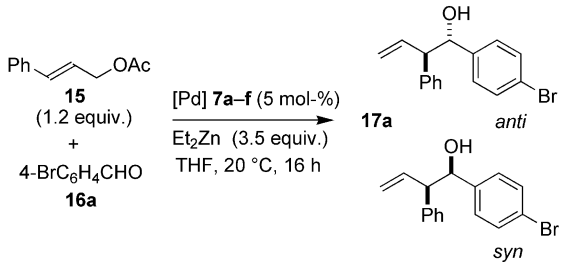
Scheme 3. Diethylzinc-mediated allylation of aldehydes with allylic acetate (**13**) catalyzed by **7a**–**f** (diethylzinc 1 M in hexanes).

Table 1. Allylation of aromatic aldehydes catalyzed by **7a**–**f** by using allylic acetate (**13**).

Entry	Complex	Ar	Product	Yield [%][a]
1	**7a**	Ph	**14a**	54
2	**7b**	Ph	**14a**	23
3	**7d**	Ph	**14a**	60
4	**7a**	4-BrC_6H_4	**14b**	*75*
5	**7b**	4-BrC_6H_4	**14b**	50
6	**7c**	4-BrC_6H_4	**14b**	45
7	**7d**	4-BrC_6H_4	**14b**	55
8	**7e**	4-BrC_6H_4	**14b**	52
9	**7f**	4-BrC_6H_4	**14b**	*70*

[a] Yields determined by analysis of the ^{1}H NMR spectrum of the crude reaction mixture by comparison with the internal standard (di-*tert*-butyl-4,4′-biphenyl).

Next, we examined the catalytic activity of **7a**–**f** in the allylation of 4-bromobenzaldehyde with cinnamyl acetate (**15**; Scheme 4). The results are presented in Table 2. In this study, a clear and dramatic effect of the NHC ligand was observed. Yields ranging from 10 to 34% were obtained with complexes **7a**–**e** bearing IPr as the NHC ligand, whereas **7f** afforded homoallylic alcohol **17a** in a significantly higher yield of 76%. A similar influence of the NHC ligand was previously observed by our group in allylic alkylation reactions with cinnamyl acetate and dimethyl malonate.[15l] A diastereomeric ratio (*dr*) of 92:8 (*anti*/*syn*) was obtained for **17a** in the reaction catalyzed by complex **7f**, and the linear product was not detected in the crude reaction mixture.



Scheme 4. Allylation of aldehydes with cinnamyl acetate (**15**) and complex **7f**.

The scope of the reaction was then examined with cinnamyl acetate (**15**), complex **7f**, and various aromatic or aliphatic aldehydes **16b**–**l** (Scheme 5, Figure 5, and Table 3). The Et_2Zn-mediated allylation of benzaldehyde was initially described with the benzoate analogue of **15** and $Pd(PPh_3)_4$. Under these conditions, the homoallylic alcohol was obtained in 83% yield and an *anti*/*syn* ratio of 91:9.[3a] To the best of our knowledge, cinnamyl acetate (**15**) was mainly used in the asymmetric version of the reaction with chiral

Table 2. Comparison of complexes **7a**–**f** in the allylation of 4-bromobenzaldehyde with cinnamyl acetate.

Entry	Complex	Yield [%][a]	*anti*/*syn*[b]
1	**7a**	12	n.d.[c]
2	**7b**	10	n.d.[c]
3	**7c**	22	36:64
4	**7d**	32	62:28
5	**7e**	34	91:9
6	**7f**	*76*	92:8

[a] Yield determined by analysis of the ^{1}H NMR spectrum of the crude reaction mixture by comparison with the internal standard. [b] Ratio determined by analysis of the ^{1}H NMR spectrum of the crude reaction mixture. [c] Not determined.

monophosphane ligands.[12d] Aromatic aldehydes led to the formation of the homoallylic alcohols in 70–80% yield but a lower yield of 55% was reported with 2,2-dimethylpropanal. The *anti* isomer was obtained as the major product with excellent diastereoselectivities (98:2–99:1). The reaction was not described with enolizable aldehydes or ketones. In 2009, the allylation of benzaldehyde with **15**, catalyzed by chiral bis(NHC)–Pd^{II} complexes **6**, was reported. The corresponding homoallylic alcohol **17c** was obtained in 72% yield with a low *anti*/*syn* ratio of 55:45.[21b] As shown in Table 3, our conditions proved to be ineffective with 4-nitrobenzaldehyde (**16b**) but led in the other cases to the expected adducts **17c**–**k** in 57–98% yield and diastereoselectivites ranging from 59:41 to 88:12. The results obtained with aromatic aldehydes suggested that the electronic properties of the substituent on the aryl group could have a significant effect on the yield. The allylation product was not detected by using 4-nitrobenzaldehyde (**16b**), whereas 4-methoxybenzaldehyde (**16f**) led to the corresponding adduct **17f** in 95% yield (Table 3, Entries 1 and 4). Similar results were reported by Onomura.[12j] However, the influence of the substitution was found to be less marked with aromatic aldehydes **16c**, **16d**, and **16g**, which led to the corresponding homoallylic alcohols in yields ranging from 57 to 75% (Table 3, Entries 4–6). Similar diastereomeric ratios (85:15–92:8) were observed with aldehydes **16c**, **16f**, and **16g** derived from benzaldehyde, whereas 1-naphthylaldehyde (**16d**) gave a lower *dr* of 70:30. Nonaromatic aldehydes, including crotonaldehyde (**16h**) and aliphatic aldehydes **16i**–**k**, furnished the branched products in 60–67% yields with *dr* values varying from 59:41 to 85:15 (Table 3, Entries 6–9). Interestingly, enolizable aldehydes **16i** and **16j** are compatible with the catalytic system (65–67% yield; Table 3, Entries 7 and 8). The more bulky aldehydes **16j** and **16k** gave the best diastereoselectivities with *anti*/*syn* ratios of 85:15 and 83:17, respectively. 2,2-Dimethylpropanal (**16k**) gave the highest yield (98%) but a significant amount of linear product **18k** (38%) was produced during the reaction (Table 3, Entry 9). The lowest *anti*/*syn* ratios were obtained with crotonaldehyde (**16h**) and butyraldehyde (**16i**; Table 3, Entries 6 and 7). The Lewis basicity of the carbonyl compound seems to have a significant effect on the reaction, as the best conversions were achieved by using the more electron-rich aldehydes **16f** and **16k**.

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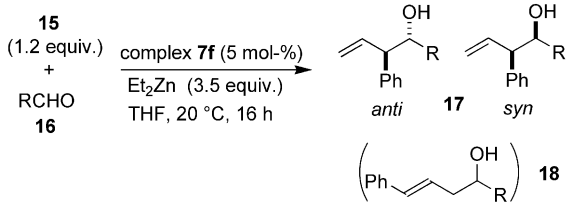


Scheme 5. Allylation of aldehydes with cinnamyl acetate (**15**) and complex **7f**.

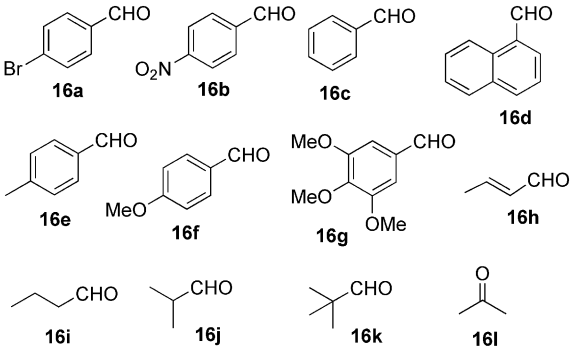


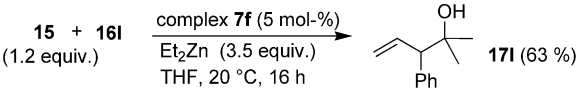
Figure 5. Carbonyl compounds **16** used in this study.

Table 3. Allylation of aldehydes with cinnamyl acetate catalyzed by **7f**.

Entry	RCHO	Product	Yield [%][a]	*anti*/*syn*[b]
1	**16b**	**17b**	<5	n.d.[b]
2	**16c**	**17c**	75	85:15
3	**16d**	**17d**	57	70:30
4	**16f**	**17f**	95	87:13
5	**16g**	**17g**	75	88:12
6	**16h**	**17h**	63	59:41
7	**16i**	**17i**	67	65:35
8	**16j**	**17j**	65	85:15
9	**16k**	**17k**	60 (98)[c]	83:17

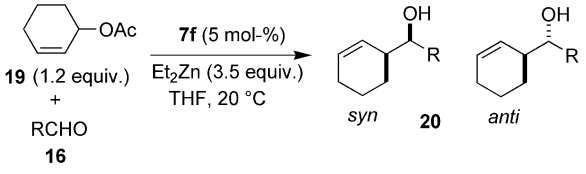
[a] Determined by analysis of the ^{1}H NMR spectrum of the crude reaction mixture by comparison with the internal standard. [b] Not determined. [c] Yield including linear product **18k**.

Interestingly, the reaction is also effective with acetone (**16l**) as the electrophile. The corresponding homoallylic alcohol **17l** was obtained in 63% yield (Scheme 6).



Scheme 6. Allylation of acetone with cinnamyl acetate (**15**) and complex **7f**.

The scope of the reaction with **7f** was further studied with cyclohexenyl acetate (**19**) (Scheme 7 and Table 4). Palladium-catalyzed allylation reactions of aldehydes with **19** in the presence of Et_2Zn have been reported with chiral monophosphane or phosphoramidite ligands.[12d,12h,12k] Aromatic aldehydes are generally the most appropriate electrophiles, leading to the homoallylic alcohols in good to excellent yields and diastereoselectivities. The reaction with aliphatic aldehydes was generally found to be more difficult. The allylation of 3-phenylpropanal catalyzed by palladium complexes bearing [2,2]paracyclophane monophosphane ligands was reported. The expected homoallylic alcohol was obtained in 38% yield (*dr* = 91:9).[12k] Phosphoramidite ligands proved to be ineffective for the allylation of aliphatic aldehydes.[12h] Interestingly, bis(NHC)–Pd^{II} complexes **6** were recently shown to catalyzed the allylation of aromatic and aliphatic aldehydes in THF at 50 °C with acetate **19**. By using 10 mol-% of catalyst, aromatic aldehydes furnished the homoallylic alcohols in 74–96% yield with diastereomeric ratios varying from 90:10 to >99:1, whereas aliphatic aldehydes produced the corresponding adducts in lower yields (58–61%) and *syn*/*anti* ratios ranging from 84:16 to 90:10.[21b] As shown in Table 4, complex **7f** (5 mol-%) catalyzes the allylation of aromatic aldehydes with cyclohexenyl acetate (**19**) at room temperature and leads to the formation of the homoallylic alcohols in 40–78% yields (Table 4, Entries 1–7). High diastereoselectivities were obtained in all cases with *syn*/*anti* ratios superior to 98:2. The best result was reached with 4-bromobenzaldehyde (**16a**), which led to **20a** in 78% yield after 16 h (Table 4, Entry 1). Prolonged reaction times in this case did not improve significantly the yield. The allylation reaction is slower with benzaldehyde (**16c**), which led to homoallylic alcohol **20c** in 32% yield after 16 h and 76% after 45 h (Table 4, Entries 2 and 3). Surprisingly, the more electron-rich aldehydes **16e** and **16f** gave the lowest results, maximum yields of 59 and 40%, respectively, being reached after 45 h (Table 4, Entries 5 and 7). No important evolution of the yields was observed between 16 and 45 h (Table 4, Entries 4–7). Our conditions proved to be ineffective with aliphatic aldehydes **16i**–**k** (Table 4, Entries 8–10) and the maximum yield (12%) was obtained with *n*-butanal (**16i**) (Table 4, Entry 8). Attempts to optimize the conditions with **16j** were unsuccessful. Prolonged reaction times (20 °C, 120 h) or higher temperatures (50 °C, 48 h) did not improve the yield.



Scheme 7. Allylation of aldehydes with cyclohexenyl acetate and complex **7f**.

Having investigated the scope and limitations of the reaction, we decided to focus our attention on the study of its mechanism. As presented in the introduction, two fundamentally different pathways have been proposed for this reaction. Transmetalation of the π-allylpalladium intermediates by Et_2Zn is one of the key steps of the transformation. The outcome of this reaction must determine if allylzinc or (allyl)Pd(Et) species are formed, and consequently, if the reaction proceeds through pathway A or pathway B (Scheme 1). In reactions catalyzed by **7f**, the π-allyl intermediates can be either neutral [(NHC)Pd(η^3-allyl)(OAc)] or cationic [(NHC)(PPh_3)Pd(η^3-allyl)][OAc] complexes generated, as in the Tsuji–Trost reaction, by oxidative addition

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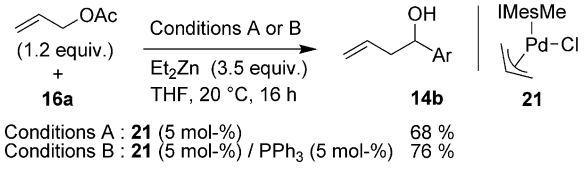
Table 4. Allylation of aldehydes with cyclohexenyl acetate (**19**) and complex **7f**.

Entry	RCHO	Product	*t* [h]	Yield [%][a]	*syn*/*anti*[a]
1	**16a**	**20a**	16	78	>98:2
2	**16c**	**20c**	16	32	>98:2
3	**16c**	**20c**	45	76	>98:2
4	**16e**	**20e**	16	53	>98:2
5	**16e**	**20e**	45	59	>98:2
6	**16f**	**20f**	16	33	>98:2
7	**16f**	**20f**	45	40	>98:2
8	**16i**	**20i**	16	12	n.d.[b]
9	**16j**	**20j**	16	7	n.d.[b]
10	**16k**	**20k**	16	<2	n.d.[b]

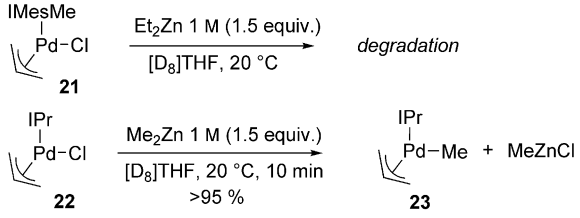
[a] Determined by analysis of the ^{1}H NMR spectrum of the crude reaction mixture by comparison with the internal standard. [b] Not determined.

of the allylic acetate to (NHC)Pd^0 or (NHC)(PPh_3)Pd^0 species. We assumed that either of these complexes (neutral or cationic) must be involved in the transmetalation step. This prompted us to study the mechanism with [(NHC)Pd(η^3-allyl)Cl] complexes, which are structurally similar to the neutral complex cited above and should be directly involved in the catalytic cycle. Firstly, it was necessary to control their catalytic activity and to determine the importance of the phosphane ligand. The allylation of 4-bromobenzaldehyde (**16a**) with allylic acetate (**13**) was then tested by using [(IMesMe)Pd(η^3-allyl)Cl] (**21**)[24] as the catalyst (Scheme 8, conditions A). The reaction led to expected homoallylic alcohol **14b** in 68% yield. This demonstrated that **21** could catalyze the reaction and that PPh_3 was not essential for this one to take place. Performed in the presence of PPh_3 (conditions B), the same reaction afforded **14b** in a slightly better yield of 76%. However, comparison of these results with that obtained with [(IMesMe)(PPh_3)PdI_2] (**7f**) (70% yield; Table 1, Entry 9) suggested that this difference is not significant.[25]



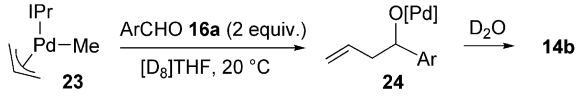
Scheme 8. Allylation of 4-bromobenzaldehyde catalyzed by complex **21**. Influence of the phosphane.

We hypothesized that the participation of monoligated NHC–Pd complexes rather than (NHC)(PPh_3)Pd complexes in the rate-determining step could account for the negligible influence of the phosphane. Consequently, in order to simplify our study, the transmetalation step was investigated with [(NHC)Pd(η^3-allyl)Cl] complexes in the absence of phosphane. The transmetalation of Pd^{II} complexes with dialkylzinc has been scarcely studied although it is of importance in catalytic reactions, particularly in Negishi couplings. The first experimental observations on this reaction was reported in 2007.[26] We first attempted to determine the species generated by addition of a stoichiometric amount of Et_2Zn to complex **21**. The reaction was performed at 20 °C in [D_8]THF and monitored by ^{1}H NMR spectroscopy (Scheme 9). Unfortunately, a rapid degradation of the complex was observed, with precipitation of Pd black. We decided then to study the reaction with [(IPr)Pd(η^3-allyl)(Cl)] (**22**), bearing the same NHC ligand as complexes **7a**–**e**, and to use Me_2Zn instead of Et_2Zn to avoid β-H elimination reactions. In this case, we observed the rapid formation of [(IPr)Pd(η^3-allyl)(Me)] (**23**), and complete conversion was achieved within 10 min (Scheme 9). Complex **23** is a stable complex whose synthesis and characterization was reported by Pörschke in 2005.[27] In the ^{1}H NMR spectrum, we observed the characteristic singlet of the Pd–Me at δ = –0.34 ppm ([D_8]THF). This spectrum also showed the presence of $ZnMe_2$ (δ = –0.86 ppm)[28] and MeZnCl (δ = –0.82 ppm)[29] although their respective amounts could not be exactly determined. More importantly, allylzinc species that could be formed during the reaction were not detectable. A single set of signals corresponding to a single allyl fragment, which is that of **23**, was visible. It has been suggested that zinc–palladium aggregates could be involved in the R_2Zn-mediated allylation reaction.[12h,30] However, we were unable to detect such species in the reaction medium by ^{1}H NMR spectroscopy.



Scheme 9. Transmetalation reactions with Et_2Zn or Me_2Zn (1 M in hexanes). Solution of Pd complex (0.08 M in [D_8]THF).

The reactivity of **23** in the absence of zinc was then investigated. Complex **23** was synthesized and isolated according to a reported procedure by reaction of **22** with methyllithium.[27] The reaction of **23** with 4-bromobenzaldehyde (**16a**) was monitored by ^{1}H NMR spectroscopy in [D_8]THF at 20 °C (Scheme 10). As shown in Figure 6, **23** reacts smoothly with the aldehyde to form homoallylic adduct **24**. Conversions of 45 and 73% were measured after 45 min and 6.5 h, respectively, the maximum (77%) being reached after 24 h. The exact nature of intermediate **24** was not determined. However, its ^{1}H NMR spectrum is very close to that of **14b** except for the hydrogen on the carbon bearing the oxygen atom. The formation of **14b** was confirmed by adding D_2O to the NMR sample at the end of the reaction.



Scheme 10. Reaction of **23** with aldehyde **16a**.

These experiments support the mechanism depicted in Figure 7, in which nucleophilic [(NHC)Pd(allyl)(R)] species (R = Et or Me), would be involved. This catalytic cycle is

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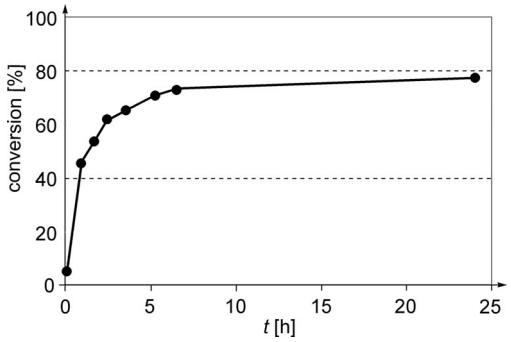


Figure 6. ^{1}H NMR monitoring of the reaction of **23** (0.17 M in [D_8]-THF) with **16a** at 20 °C. Yield of homoallylic adduct **24** determined by integration of the central allyl proton and comparison with the internal reference (TMS).

basically identical to that considered by Minnaard and Feringa with phosphoramidite ligands,[12h] except for the L/Pd ratio and the coordination mode of the allyl moiety in the nucleophilic allylpalladium intermediate. In our study, the transmetalation reaction was found to be faster than the allylation reaction. In addition, we previously observed high reaction rates in the allylic alkylation by using dimethyl malonate and allylic acetate catalyzed by similar complexes,[15l] an indication that the oxidative addition must also be fast. Although the concentrations in the catalytic reaction are different, this suggests that the rate-determining step could be the allylation step.

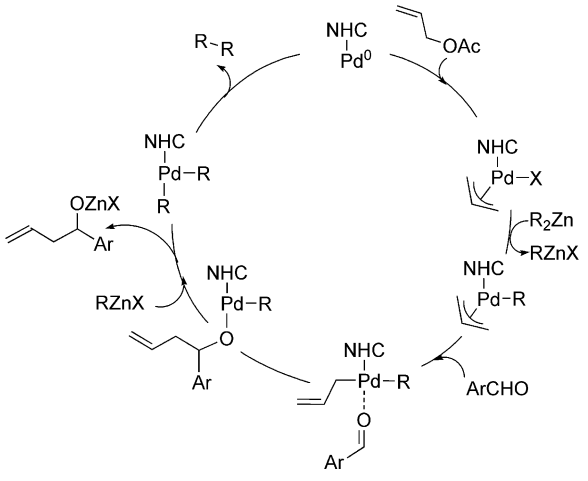
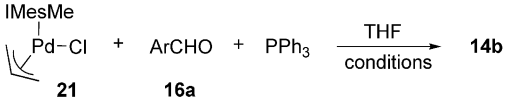


Figure 7. Proposed catalytic cycle of the diethylzinc-mediated allylation reaction with [(NHC)Pd(allyl)X] complexes (X = Cl or AcO; R = Me or Et).

Finally, we decided to control the reactivity of [(NHC)-Pd(η^3-allyl)Cl] complexes toward aldehydes without Et_2Zn. Indeed, as presented in the introduction, it was reported that cationic allylpalladium complexes **5**, bearing bidentate NHC–P ligands, were able to react directly with stoichiometric amounts of aldehydes in various solvents at 60–70 °C to form the corresponding homoallylic alcohols.[19] We tested the reaction of complex **21** with a stoichiometric amount of aldehyde **16a**, in the presence of PPh_3 (Scheme 11). However, whatever the conditions used (THF, 20 °C or reflux), no formation of **14b** was detected after 16 h (Table 5, Entries 1 and 2) and a degradation of the complex was observed. In contrast, addition of Et_2Zn to the same mixture at 20 °C led to the rapid formation of **14b**, a conversion of 59% being achieved within 30 min (Table 5, Entry 3). As shown previously in Scheme 9, the direct addition of Et_2Zn to complex **21** in the absence of aldehyde leads instantaneously to the degradation of the complex. Comparison of these two reactions shows, as observed by Tamaru,[12a] that the application of Barbier-type procedure is essential for the allylation.



Scheme 11. Reaction of **21** with aldehyde **16a**. Reagents: **21** (0.02 mmol), **16a** (0.02 mmol), PPh_3 (0.02 mmol) in THF (0.5 mL).

Table 5. Stoichiometric reactions of complex **21** with aldehyde **16a**.

Entry	Conditions	Conv. [%][a]
1[a]	16 h, 20 °C	0[b]
2[a]	16 h, reflux	0[b]
3	Et_2Zn[c], 30 min, 20 °C	59[d]

[a] [D_8]THF was used as the solvent. [b] Compound **14b** was not detectable by ^{1}H NMR spectroscopy. [c] Et_2Zn (1 M in hexanes, 0.02 mmol). [d] Conversion determined by analysis of the ^{1}H NMR spectrum of the crude reaction mixture by comparison with the amount of residual aldehyde. The reaction was quenched with NH_4Cl, extracted with Et_2O, dried ($MgSO_4$), and concentrated.

Conclusions

In conclusion, we demonstrated that [(NHC)(PR_3)PdX_2] and [(NHC)Pd(η^3-allyl)Cl] complexes are suitable catalysts for the allylation reaction of carbonyl compounds by using allylic acetates and diethylzinc. The investigation of the reaction scope with complex **7f** revealed interesting results but also showed limitations. This complex catalyzes the allylation of various aldehydes, including enolizable aliphatic aldehydes, as well as acetone, by using cinnamyl acetate. The reaction with cyclohexenyl acetate was found to be limited to aromatic aldehydes but led to excellent diastereoselectivities. We also demonstrated experimentally for the first time that transmetalation of π-allylpalladium intermediates with dialkylzinc led to the formation of nucleophilic (allyl)(alkyl)Pd^{II} species able to react directly with aldehydes in the absence of zinc. The rate-determining step of the catalytic reaction is very likely the allylation step, which, interestingly, is also the stereodetermining step. This may allow the development of asymmetric versions by using easily accessible chiral monodentate NHC ligands. Investigations concerning this topic are currently underway as are DFT calculations on the mechanism.

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Experimental Section

General: All experiments were performed under an atmosphere of argon by using standard Schlenk techniques unless stated otherwise. THF was dried with sodium benzophenone ketyl under an atmosphere of argon and distilled prior to use. CH_2Cl_2 (RECTAPUR, stabilized with 0.1% of EtOH) and THF were degassed by vacuum/argon cycles. Reagents were purchased from Acros, Aldrich, or Strem and used as received. [{(IPr)PdCl$_2$}$_2$] (**9**),[31] 1,3-(2,6-diisopropylphenyl)imidazolium chloride (**11**),[32] 1-mesityl-3-methylimidazolium iodide (**12**),[33] and [(IPr)Pd(allyl)Cl] (**22**)[34] were prepared according to literature procedures. ^{1}H NMR and ^{13}C NMR spectra were recorded with a Bruker ARX-250 or Avance-400 spectrometer. Proton chemical shifts (δ) are reported relative to TMS. Carbon chemical shifts are reported relative to the NMR solvent ($CDCl_3$, 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). Compounds **14a**,[35,36] **14b**,[36] **17a**,[7f] **17b**,[7f,37] **17c**,[7f,12g,38] **17d**,[12g] **17f**,[12g] **17h**,[38] **17i**,[39] **17j**,[40] **17k**,[12f] **17l**,[41] **18k**,[12f] **20c**,[42] **20e**,[43] **20f**,[37] **20i**,[43,44] **20j**,[42,35b] and **20k**[35b] have previously been described in the literature.

[(IPr)(PPh$_3$)PdCl$_2$] (7a): To a solution of [{(IPr)PdCl$_2$}$_2$] (**9**; 113 mg, 0.1 mmol) in THF (2 mL) was added PPh_3 in one portion (52.5 mg, 0.2 mmol). The resulting mixture was stirred at 20 °C for 20 min. The color of the solution changed from orange to yellow. The mixture was concentrated, and the solid residue was purified by flash chromatography on silica gel (pentane/Et_2O, 9:1) to give a pale-yellow solid (159 mg, 96%). M.p. 222–224 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.47 (t, J = 7.8 Hz, 2 H), 7.28 (d, J = 7.8 Hz, 4 H), 7.23–7.15 (m, 9 H), 7.11–7.05 (m, 8 H), 3.12 (m, 4 H, C*H* *i*Pr), 1.23 (d, J = 6.5 Hz, 12 H, CH_3 *i*Pr), 1.00 (d, J = 6.8 Hz, 12 H, CH_3 *i*Pr) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.9 (d, $^2J_{C,P}$ = 198 Hz, *C* carbene), 146.8 (*i*Pr-*C* Ar), 135.5 (N-*C* Ar), 134.9 (d, $J_{C,P}$ = 10.3 Hz, *C*H Ph), 130.3 (d, $^1J_{C,P}$ = 44.5 Hz, *C* Ph), 129.8 (*C*H Ar), 129.7 (d, $^4J_{C,P}$ = 1.7 Hz, *C*H Ph), 127.5 (d, $J_{C,P}$ = 10.3 Hz, *C*H Ph), 124.2 (d, $^4J_{C,P}$ = 6 Hz, N-*C*H=*C*H-N), 123.8 (*C*H Ar), 28.6 (*i*Pr), 26.3 (*i*Pr), 22.9 (*i*Pr) ppm. ^{31}P NMR (75 MHz, $CDCl_3$): δ = 21.6 ppm. HRMS (ESI) calcd. for $C_{45}H_{51}Cl_2N_2PPdNa$ [M$^+$ + Na] 847.20995; found 847.21019. $C_{45}H_{51}Cl_2N_2PPd$ (828.2): calcd. C 65.26, H 6.21, N 3.38; found C 65.37, H 6.35, N 3.44.

[(IPr){P(OPh)$_3$}PdCl$_2$] (7b): To a solution of [{(IPr)PdCl$_2$}$_2$] (**9**; 113 mg, 0.1 mmol) in THF (2 mL) was added P(OPh)$_3$ (53 µL, 0.2 mmol). The color of the solution changed from orange to yellow. The resulting mixture was stirred at 20 °C for 20 min. The mixture was concentrated, and the solid residue was purified by flash chromatography on silica gel (pentane/Et_2O, 9:1) to give a pale-yellow solid (156 mg, 89%). M.p. 74–76 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.54 (t, J = 7.6 Hz, 2 H), 7.28 (d, J = 7.6 Hz, 4 H), 7.10–6.95 (m, 17 H), 3.01 (m, 4 H, C*H* *i*Pr), 1.22 (d, J = 6.6 Hz, 12 H, CH_3 *i*Pr), 1.04 (d, J = 6.8 Hz, 12 H, CH_3 *i*Pr) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.1 (d, $^2J_{C,P}$ = 300 Hz, *C* carbene), 150.8 (d, $^2J_{C,P}$ = 5.14 Hz, P-O-*C* Ph), 146.7 (*i*Pr-*C* Ar), 134.9 (N-*C* Ar), 130.0 (*C*H Ar), 129.3 (*C*H Ar), 124.6 (d, $^4J_{C,P}$ = 8.6 Hz, N-*C*H=*C*H-N), 124.3 (*C*H Ar), 123.9 (*C*H Ar), 120.4 (d, $^3J_{C,P}$ = 5.1 Hz, *C*H Ph), 28.5 (*i*Pr), 26.3 (*i*Pr), 22.8 (*i*Pr) ppm. ^{31}P NMR (75 MHz, $CDCl_3$): δ = 92.3 ppm. $C_{45}H_{51}Cl_2N_2O_3PPd$ (876.2): calcd. C 61.68, H 5.87, N 3.20; found C 61.36, H 5.88, N 3.07.

[(IPr){P(*n*Bu)$_3$}PdCl$_2$] (7c): To a solution of [{(IPr)PdCl$_2$}$_2$] (**9**; 50 mg, 0.044 mmol) in THF (2.5 mL) was added P(*n*Bu)$_3$ (22 µL, 0.088 mmol). The resulting mixture was stirred at 20 °C and monitored by TLC. After 3.5 h, a second portion of P(*n*Bu)$_3$ (22 µL, 0.088 mmol) was added. After 30 min, the mixture was concentrated, and the solid residue was purified by flash chromatography on silica gel (cyclohexane/EtOAc, 8:2) to give a yellow solid (56 mg, 82%). M.p.149–154 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45 (t, J = 7.6 Hz, 2 H), 7.30 (d, J = 7.6 Hz, 4 H), 7.08 (d, J = 1.5 Hz, 2 H, N-C*H*=*CH*-N), 3.13 (m, 4 H, C*H* *i*Pr), 1.51–1.42 (m, 6 H, P-CH_2 *n*Bu), 1.39 (d, J = 6.6 Hz, 12 H, CH_3 *i*Pr), 1.26–1.12 (m, 12 H, CH_2 *n*Bu), 1.08 (d, J = 7.1 Hz, 12 H, CH_3 *i*Pr), 0.77 (t, J = 6.9 Hz, 9 H, CH_3 *n*Bu) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 175.6 (d, $^2J_{C,P}$ = 193 Hz, *C* carbene), 146.7 (*C* Ar), 135.5 (*C* Ar), 129.6 (*C*H Ar), 124.0 (d, $^4J_{C,P}$ = 5.1 Hz, N-*C*H=*C*H-N), 123.5 (*C*H Ar), 28.6 (*i*Pr), 26.3 (*i*Pr), 25.8 (*C*H$_2$ *n*Bu), 24.1 (d, $J_{C,P}$ = 13.7 Hz; *C*H$_2$ *n*Bu), 22.9 (*i*Pr), 20.4 (d, $J_{C,P}$ = 26.6 Hz; *C*H$_2$ *n*Bu), 13.7 (*C*H$_3$ *n*Bu) ppm. ^{31}P NMR (75 MHz, $CDCl_3$): δ = 8.9 ppm. $C_{39}H_{63}Cl_2N_2PPd$ (768.23): calcd. C 60.97, H 8.27, N 3.65; found C 60.74, H 8.05, N 3.49.

[{(IPr)PdI$_2$}$_2$] (10): To a solution of 1,3-(2,6-diisopropylphenyl)-imidazolium chloride (**11**; 219 mg, 0.5 mmol) in THF (40 mL) was added $Pd(OAc)_2$ (113 mg, 0.5 mmol) and sodium iodide (300 mg, 2 mmol). Potassium *tert*-butoxide (67 mg, 0.6 mmol) was then added in portions, and the mixture was stirred for 16 h at 20 °C. The mixture was directly poured in a short column of silica gel, and the orange-brown fraction was collected by elution with THF. The solvent was evaporated, and the brown solid obtained was dissolved in hot cyclohexane with a few drops of EtOAc and purified by flash chromatography on silica gel (pentane/Et_2O, 9:1) to give an orange-brown solid (246 mg, 74%). M.p. >280 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.52 (t, J = 7.7 Hz, 4 H, C*H* Ar), 7.34 (d, J = 7.7 Hz, 8 H, C*H* Ar), 7.09 (s, 4 H, N-C*H*=*CH*-N), 3.27 (m, 4 H, C*H* *i*Pr), 2.74 (m, 4 H, C*H* *i*Pr), 1.47 (d, J = 6.6 Hz, 12 H, CH_3 *i*Pr), 1.25 (d, J = 6.3 Hz, 12 H, CH_3 *i*Pr), 1.08 (d, J = 6.9 Hz, 12 H, CH_3 *i*Pr), 0.93 (d, J = 6.6 Hz, 12 H, CH_3 *i*Pr) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 166.0 (*C* carbene), 146.8, 146.4, 135.8, 130.7, 125.8, 125.1, 124.7, 29.5 (*i*Pr), 26.9 (*i*Pr), 24.4 (*i*Pr) ppm. $C_{54}H_{72}I_4N_4Pd_2$ (1497.63): calcd. C 43.31, H 4.85, N 3.74; found C 43.51, H 4.74, N 3.57.

[(IPr)(PPh$_3$)PdI$_2$] (7d): To a solution of {[(IPr)PdI$_2$]$_2$} (**10**; 322 mg, 0.215 mmol) in THF (15 mL) was added PPh_3 (113 mg, 0.43 mmol) in one portion. The resulting mixture was stirred at 20 °C for 3 h. The color of the solution changed from brown-red to orange-red. The mixture was concentrated, and the solid residue was purified by flash chromatography on silica gel (pentane/Et_2O, 9:1) to give an orange solid (345 mg, 68%). M.p. 193–197 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.46 (t, J = 7.6 Hz, 2 H), 7.28–7.08 (m, 21 H), 3.35 (m, 4 H, C*H* *i*Pr), 1.27 (d, J = 6.6 Hz, 12 H, CH_3 *i*Pr), 1.00 (d, J = 6.8 Hz, 12 H, CH_3 *i*Pr) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.3 (d, $^2J_{C,P}$ = 198 Hz, *C* carbene), 146.6 (*C* Ar), 136.5 (*C* Ar), 135.3 (d, $J_{C,P}$ = 10.3 Hz, *C*H Ph), 133.9 (d, $^1J_{C,P}$ = 48 Hz, *C* Ph), 129.9 (*C*H Ar), 129.6 (d, $^4J_{C,P}$ = 1.7 Hz, *C*H Ph), 127.1 (d, $J_{C,P}$ = 10.3 Hz, *C*H Ph), 125.0 (d, $^4J_{C,P}$ = 6.0 Hz, N-*C*H=*C*H-N), 124.1 (*C*H Ar), 29.3 (*i*Pr), 26.4 (*i*Pr), 23.6 (*i*Pr) ppm. ^{31}P NMR (75 MHz, $CDCl_3$): δ = 16.2 ppm. $C_{45}H_{51}I_2N_2PPd$ (1011.1): calcd. C 53.45, H 5.08, N 2.77; found C 53.98, H 5.08, N 2.62.

[(IPr){P(*n*Bu)$_3$}PdI$_2$] (7e): To a solution of [{(IPr)PdI$_2$}$_2$] (**10**; 35 mg, 0.023 mmol) in THF (1.6 mL) was added P(*n*Bu)$_3$ (12 µL, 0.047 mmol). The resulting mixture was stirred at 20 °C and monitored by TLC. After 15 h, a second portion of P(*n*Bu)$_3$ (12 µL, 0.047 mmol) was added. After 30 min, the mixture was concentrated, and the solid residue was purified by flash chromatography

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on silica gel (*c*Hex/EtOAc, 98:2) to give a yellow solid (42 mg, 94%). M.p. 129–131 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44 (t, J = 7.8 Hz, 2 H), 7.29 (d, J = 7.8 Hz, 4 H), 7.20 (d, J = 1.3 Hz, 2 H, N-C*H*=C*H*-N), 3.41 (m, 4 H, C*H* *i*Pr), 1.95 (m, 6 H, P-CH_2 *n*Bu), 1.44 (d, J = 6.8 Hz, 12 H, CH_3 *i*Pr), 1.30–1.05 (m, 12 H, CH_2 *n*Bu), 1.08 (d, J = 6.5 Hz, 12 H, CH_3 *i*Pr), 0.80 (t, J = 6.9 Hz, 9 H, CH_3 *n*Bu) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.5 (d, $^2J_{C,P}$ = 189 Hz, *C* carbene), 145.4 (*C* Ar), 135.3 (*C* Ar), 128.7 (*C*H Ar), 123.8 (d, $^4J_{C,P}$ = 5.1 Hz, N-*C*H=*C*H-N), 122.8 (*C*H Ar), 28.1 (*i*Pr), 25.9 (d, $J_{C,P}$ = 29.1 Hz, *C*H$_2$ *n*Bu), 25.6 (*C*H$_2$ *n*Bu), 25.5 (*i*Pr), 23.1 (d, $J_{C,P}$ = 13.7 Hz, *C*H$_2$ *n*Bu), 22.5 (*i*Pr), 12.7 (*C*H$_3$ *n*Bu) ppm. ^{31}P NMR (75 MHz, $CDCl_3$): δ = –1.03 ppm. $C_{39}H_{63}I_2N_2PPd$ (951.13): calcd. C 49.25, H 6.68, N 2.95; found C 49.31, H 6.54, N 2.81.

[(IMesMe)(PPh$_3$)PdI$_2$] (7f): To a solution of 1-methyl-3-mesitylimidazolium iodide (**12**; 164 mg, 0.5 mmol) in THF (40 mL) was added, under a nitrogen atmosphere, $Pd(OAc)_2$ (113 mg, 0.5 mmol) and sodium iodide (300 mg, 2 mmol). Potassium *tert*-butoxide (67 mg, 0.6 mmol) was then added in portions, and the mixture was stirred for 6 h at 20 °C with exclusion of light. The mixture was directly poured onto a short column of silica gel, and the orange fraction was collected by elution with THF. Evaporation of the solvent and drying afforded an orange-red solid (225 mg). The solid was dissolved in CH_2Cl_2 (20 mL) and PPh_3 (94 mg, 0.36 mmol) was added in one portion. The mixture was stirred for 15 min at 20 °C. The color of the solution changed from dark-red to orange. Evaporation of the solvent and drying afforded an orange solid (310 mg). ^{1}H NMR analysis of this solid in $CDCl_3$ showed the presence of 96% of the expected complex **7f**, 4% of the bis(carbene) complex [(IMesMe)$_2$PdI$_2$], and trace amounts of PPh_3. The orange solid was dissolved in ethyl acetate (20 mL) and stirred for 15 min. The pale-yellow precipitate that appeared {[(IMesMe)$_2$PdI$_2$]} was separated by filtration, and the solution was concentrated to dryness. The residue was dissolved in CH_2Cl_2 (3 mL) and pentane (20 mL) was added slowly. The red-orange precipitate formed was collected by filtration, washed with pentane, and dried to afford an orange solid (208 mg, 51%). The sample contained less than 2% of the bis(carbene) complex [(IMesMe)$_2$PdI$_2$]. Small red crystals suitable for X-ray analysis were obtained by slow evaporation of a diluted Et_2O solution of the complex containing a small amount of CH_2Cl_2. M.p. 203–206 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.55–7.25 (m, 15 H), 7.08 (t, J = 1.7 Hz, 1 H, N-C*H*=C*H*-N), 6.96 (s, 2 H, C*H* Ar), 6.95 (t, J = 1.7 Hz, 1 H, N-CH=*CH*-N), 4.00 (s, 3 H, N-CH_3), 2.44 (s, 3 H, CH_3 Mes), 2.31 (s, 6 H, CH_3 Mes) ppm. ^{13}C NMR (62.5 MHz, CD_2Cl_2): δ = 160.9 (d, $^2J_{C,P}$ = 195.0 Hz, *C* carbene), 139.9 (*C* Mes), 137.1 (*C* Mes), 135.9 (d, $J_{C,P}$ = 10.8 Hz, *C*H Ph), 134.1 (d, $^1J_{C,P}$ = 45.5 Hz, *C* Ph), 130.7 (d, $^4J_{C,P}$ = 2.2 Hz, *C*H Ph), 129.9 (*C*H Mes), 128.3 (d, $J_{C,P}$ = 9.8 Hz, *C*H Ph), 125.6 (d, $^4J_{C,P}$ = 5.5 Hz, N-*C*H=CH-N), 123.5 (d, $^4J_{C,P}$ = 6.5 Hz, N-CH=*C*H-N), 40.5 (N-*C*H$_3$), 22.2 (*C*H$_3$ Mes), 21.8 (*C*H$_3$ Mes) ppm. ^{31}P NMR (75 MHz, CD_2Cl_2): δ = 16.2 ppm. HRMS (ESI): calcd. for $C_{31}H_{31}I_2N_2P^{104}PdNa$ [M$^+$ + Na] 842.92468; found 842.92472. $C_{31}H_{31}I_2N_2PPd$ (822.79): calcd. C 45.25, H 3.80, N 3.40; found C 45.10, H 3.80, N 3.52. Data for the minor complex [(IMesMe)$_2$PdI$_2$]: Pale-yellow solid. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 6.96 (d, J = 1.9 Hz, 2 H), 6.79 (s, 4 H), 6.72 (d, J = 1.9 Hz, 2 H), 4.09 (s, 6 H, N-CH_3), 2.44 (s, 6 H, CH_3 Mes), 2.00 (s, 12 H, CH_3 Mes) ppm. HRMS (ESI): calcd. for $C_{26}H_{32}I_2N_4PdNa$ [M$^+$ + Na] 782.96434; found 782.96489. The complex is little soluble in most organic solvents.

Typical Procedure for the Palladium-Catalyzed Allylation of Carbonyl Compounds: To a solution of 4,4′-di-*tert*-butylbiphenyl (17.6 mg, 0.066 mmol, internal standard), palladium complex (5% mol), allylic acetate (0.24 mmol), and aldehyde or ketone (0.2 mmol) in dry THF (1.5 mL) was added dropwise at 20 °C a solution of Et_2Zn (1 M in hexanes, 0.7 mL, 0.7 mmol, 3.5 equiv.). The mixture was stirred for 16 h (or 45 h) at 20 °C before quenching with aqueous saturated NH_4Cl (5 mL). The mixture was stirred vigorously for 30 min. Et_2O (5 mL) was added, and the organic layer was separated. The aqueous layer was extracted with Et_2O (2 × 5 mL). The combined organic layer was dried (Na_2SO_4), filtered through Celite, and concentrated under reduced pressure (15 Torr, 20 °C). The yield was determined by ^{1}H NMR spectroscopy of the crude reaction mixture by comparison with the internal standard.

1-(3,4,5-Trimethoxyphenyl)-2-phenyl-3-buten-1-ol (17g): The crude was purified by flash chromatography on silica gel (pentane/Et_2O, 1:1) to give a colorless oil. Data for the *anti* isomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.18–7.05 (m, 3 H, C*H* Ph), 6.96 (d, J = 8.3 Hz, 2 H, C*H* Ph), 6.18 [s, 2 H, $(MeO)_3C_6H_2$], 6.19 (ddd, J = 8.8, 10.3, 19.3 Hz, 1 H, C*H*=CH$_2$), 5.24–5.17 (m, 2 H, CH=CH_2), 4.67 (d, J = 8.1 Hz, 1 H, C*H*-OH), 3.70 (s, 3 H, Me), 3.61 (s, 6 H, Me), 3.38 (t, J = 8.3 Hz, 1 H, C*H*-Ph), 2.45 (br. s, 1 H, O*H*) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.6 (*C* Ar), 140.6 (*C* Ar), 137.9 (*C*H), 137.3 (*C* Ar), 128.4 (*C*H Ph), 128.3 (*C*H Ph), 126.6 (*C*H), 118.5 (*C*H$_2$), 103.6 (C*H*), 77.3 (*C*H-OH), 60.8 (*C*H$_3$ OMe), 59.5 (*C*H-Ph), 55.9 (*C*H$_3$ OMe) ppm. Data for the *syn* (visible and representative signals): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.87 (ddd, J = 18.0, 10.5, 7.7 Hz, 1 H, C*H*=CH$_2$), 4.98 (dt, J = 10.3, 1.3 Hz, 1 H, CH=CH_2), 4.86 (dt, J = 17.1, 1.3 Hz, 1 H, CH=CH_2), 4.78 (d, J = 7.7 Hz, 1 H, C*H*–OH) ppm. HRMS (ESI): calcd. for $C_{19}H_{22}O_4Li$ [M$^+$ + Li] 321.16731; found 321.16625. $C_{19}H_{22}O$ (266.38): calcd. C 72.59, H 7.05; found C 72.68, H 7.11.

***syn*-1-Cyclohex-2-enyl(4-bromophenyl)methanol (20a):** The crude was purified by flash chromatography on silica gel (pentane/Et_2O, 8:2) to give a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.46 (d, J = 8.3 Hz, 2 H, C*H* Ph), 7.21 (d, J = 8.3 Hz, 2 H, C*H* Ph), 5.84 (ddd, J = 10.2, 6.0, 2.6 Hz, 1 H, CH$_2$-C*H*=CH), 5.38 (dd, J = 10.2, 2.0 Hz, 1 H, CH=C*H*-CH), 4.57 (d, J = 6.1 Hz, 1 H, C*H*-OH), 2.45 (m, 1 H, C*H*-CH-OH), 1.98 (m, 2 H, CH_2-CH=CH), 1.80–1.70 (m, 1 H, CH_2), 1.69–1.58 (m, 1 H, CH_2), 1.55–1.45 (m, 2 H, CH_2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.2 (*C* Ar), 131.7 (*C*H Ar), 131.4 (CH$_2$-*C*H=CH), 128.6 (*C*H Ar), 127.9 (CH=C*H*-CH), 121.5 (*C* Ar), 77.0 (*C*H-OH), 43.5 (*C*H-CH-OH), 25.6 (*C*H$_2$), 23.9 (*C*H$_2$), 21.4 (*C*H$_2$) ppm. HRMS (ESI): calcd. for $C_{13}H_{15}BrONa$ [M$^+$ + Na] 289.01985; found 289.02251. $C_{13}H_{15}BrO$ (267.16): calcd. C 58.44, H 5.66; found C 58.08, H 5.97.

CCDC-723321 (for **7f**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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