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Expanded ring diaminocarbene palladium complexes: synthesis, structure, and Suzuki–Miyaura cross-coupling of heteroaryl chlorides in water†

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A series of new 6- and 7-membered *N*-heterocyclic carbene (NHC) complexes of palladium (NHC)Pd(cinn)Cl (cinn = cinnamyl = 3-phenylallyl) were synthesized and characterized structurally in the solid state. The influence of ring size (5, 6 or 7) and bulkiness of *N*-aryl substituents (Mes = 2,4,6-trimethylphenyl, or Dipp = 2,6-diisopropylphenyl) in carbenes on palladium catalysed Suzuki–Miyaura cross-coupling was revealed. Due to the unique stereoelectronic properties of expanded ring NHCs, a versatile, highly efficient green protocol of coupling of heteroaromatic chlorides and bromides with boronic acids has been developed. High quantitative yields of biaryls were achieved with water as solvent, under air, using low catalyst and phase transfer agent loadings, and with mild and environmentally benign base $NaHCO_3$.

Introduction

N-Heterocyclic carbenes (NHCs) are nowadays ubiquitous ligands in organometallic chemistry as well as catalysis due to their unique properties.[1] Steric and electronic properties of NHCs can be tuned in a wide range by change of substituents and backbones.[2]

Palladium–NHC complexes exhibit a unique air and moisture stability, strong metal–ligand bonds and efficient steric protection of metal. Such factors favor catalyst lifetime and efficiency.[3] Numerous NHC–palladium catalytic systems for Suzuki–Miyaura reaction were developed by the groups of Herrmann,[4] Nolan,[5] Organ,[6] and Glorius.[7] A number of sulfonate-, carboxylate- and ammonium-functionalized NHCs were used in palladium catalyzed cross-coupling reactions in aqueous media.[8]

While the chemistry of imidazole-based NHCs is well documented, expanded ring (six and seven) NHCs are new and unexplored. Studies of their structure, chemical properties, and catalytic applications are now appearing.[9] Expanded ring NHCs offer markedly different steric and electronic properties when compared with their 5-membered ring counterparts. Expansion of the ring leads to a significant increase of donor properties, simultaneously the sterical demands of such ligands increase dramatically.[2] It is of particular interest to explore the influence of stereoelectronic properties of expanded ring NHCs on the stability of palladium complexes in air and moisture and their catalytic properties under "non-conventional" conditions.

Here we report the synthesis and characterization of a series of new 6- and 7-membered NHC palladium(II) complexes and their catalytic activity in Suzuki–Miyaura cross-coupling of heteroaryl chlorides in aqueous media under air.

Results and discussion

Synthesis

Recently we reported on the development of an efficient method for the synthesis of expanded ring amidinium salts bearing bulky aromatic substituents.[9c] This method was further optimized (Scheme 1). Amidinium tetrafluoroborates were obtained in excellent yields (80–90%) in two steps starting from commercially available reagents in decagram-scale.

A series of palladium–carbene complexes were obtained upon reaction of free carbenes with dimeric $[Pd(cinn)Cl]_2$ (Scheme 2).[10] Off-white to yellow powders were obtained upon stirring at room temperature. These complexes were found to be perfectly air- and moisture-stable and thus could be handled in air.

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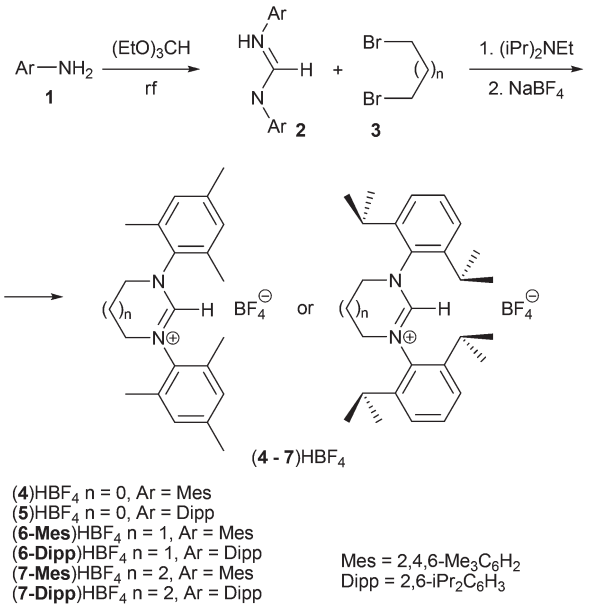
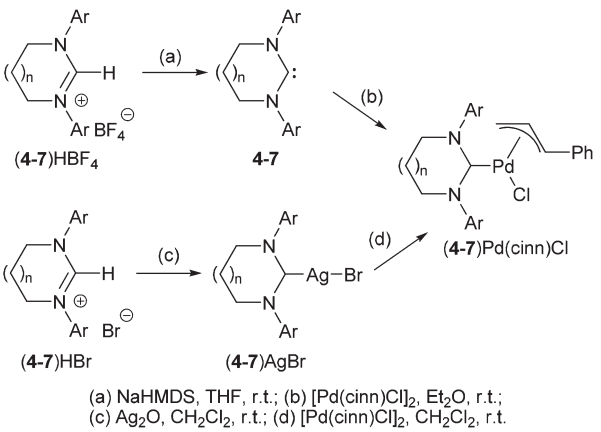
†Electronic supplementary information (ESI) available: Spectral data for the cross-coupling products and additional crystallographic data. CCDC 784539–784543. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt32860k



Scheme 1 Preparation of amidinium salts.



Scheme 2 Preparation of palladium complexes.

Elemental analyses confirmed the compositions of the complexes obtained. Contrary to five-membered ring carbenes,[11] synthesis of complexes using *in situ* generated expanded ring carbenes in reactions of amidinium salts and NaHMDS leads to a significant decrease in yields and the formation of dark-brown side products of unidentified nature.

Palladium complexes (**6-Mes**)Pd(cinn)Cl, (**6-Dipp**)Pd(cinn)Cl and (7-**Dipp**)Pd(cinn)Cl were also obtained by the exchange reaction of (NHC)AgBr with $[Pd(cinn)Cl]_2$ (Scheme 2). Together with migration to Cu(I)[9c] and Au(I),[12] the observed reaction is one of the rare examples of migration of aryl-substituted expanded ring NHCs from Ag(I) to another metal. This observation contrasts with the previous observations of Buchmeiser,[13] Herrmann,[14] and our findings[9c] that expanded ring NHCs does not migrate from Ag(I) to Pd(II).

For more bulky **6-Dipp** and **7-Dipp** derivatives, transmetallation is reversible. Mixing of one equivalent of (NHC)AgBr with a half equivalent of $[Pd(cinn)Cl]_2$ at room temperature for 24 h leads to precipitation of one third of equivalent of AgBr. Filtration through Celite gives a transparent solution from which no precipitation was observed in 2 d. After evaporation, the product was extracted with diethyl ether. Upon dissolution of the residue in CH_2Cl_2, additional precipitation of AgBr was observed. The combined yields of (NHC)Pd(cinn)Cl complexes were 71–73% after three extractions.

The ^{13}C NMR resonances of carbenic carbons in complexes were observed at 213.8 ppm for six-membered ring carbenes, and at 221.4–225.5 ppm for seven-membered ring carbenes (in $CDCl_3$). These values differ from those obtained for 5-membered saturated ring carbenes **4** (211.0 ppm) and **5** (212.1 ppm).[10] Thus expansion of a carbene ring is accompanied with deshielding of carbenic carbon, and subsequent lower field ^{13}C NMR shifts are observed. The same trend was traced in Ru(II),[15] Rh(I),[13,16] Cu(I),[9c,17] Cu(II),[9i] and Ag(I)[9a,c] complexes.

Crystal structures

All new complexes were investigated by X-ray crystal structure analysis. Their molecular structures along with the atomic numbering schemes are shown in Fig. 1 and 2 and S1 and S3,† and selected geometrical parameters are given in Table S1.†

In general, the structures of the complexes are similar. In all cases, a distorted square-planar coordination around the palladium center was observed, with the chloride ligand located *cis* to the carbene. The allyl moiety is η^3-coordinated to

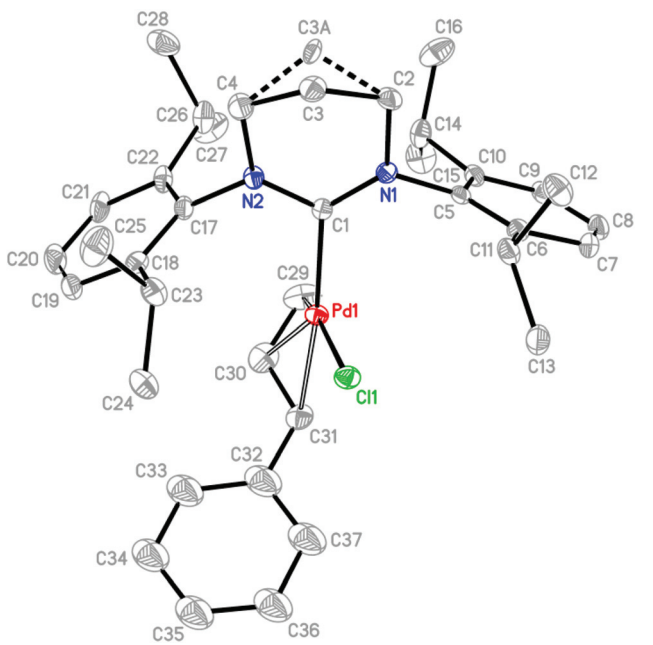


Fig. 1 X-Ray structure of (**6-Dipp**)Pd(cinn)Cl (hydrogen atoms and the solvate molecule are omitted for clarity, the alternative position of the disordered C3 atom is presented). Selected bond lengths (Å) and angles (°): Pd–C1: 2.042(4); Pd–Cl1 2.3351(9); Pd–C29 2.113(4); Pd–C30 2.134(4); Pd–C31 2.204(4); N1–C1–N2 117.1(3); C1–N–C_{Ar} 120.2(3), 121.2(3); C1–N–C_{ring} 124.6(3), 126.0(3); C_{Ar}–N–C_{ring} 113.6(3), 113.7(3); Pd–C1–N 115.6(3), 126.1(3); C5–N1–N2–C17 4.0.

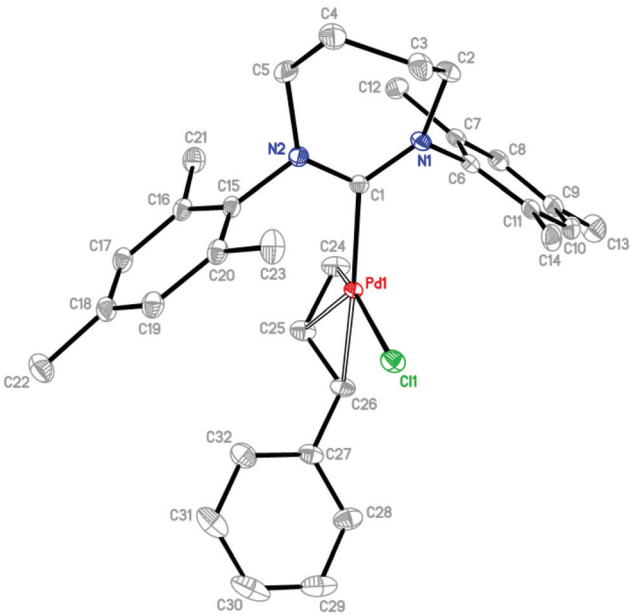


Fig. 2 X-Ray structure of (**7-Mes**)Pd(cinn)Cl (hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (°): Pd–C1: 2.0559(11); Pd–Cl1 2.3658(3); Pd–C24 2.1239(13); Pd–C25 2.1358(12); Pd–C26 2.2185(12); N1–C1–N2 119.46(10); C1–N–C_{Ar} 117.22(9), 117.36(9); C1–N–C_{ring} 123.31(10), 128.74(10); C_{Ar}–N–C_{ring} 113.95(9), 116.92(10); Pd–C1–N 118.60(8), 121.91(8); C6–N1–N2–C15 27.3.

the palladium, with the phenyl-substituted carbon atom *trans* to the carbene ligand and the unsubstituted carbon atom *trans* to the chlorine ligand. The Pd–C_{allyl} bond opposite the NHC ligand is elongated by a strong *trans*-effect (Fig. 1 and 2). The Pd–C_{carb} distances in the complexes fall comfortably within the range obtained for palladium(II)–carbene complexes previously (1.91–2.10 Å)[5b] and increase upon passing from five- to seven-membered carbene rings.

The X-ray diffraction study reveals the characteristic *sofa* and *twist-sofa* conformations for the saturated six- and seven-membered carbene rings, respectively.[9a,c,i] Nitrogen atoms in five- and six-membered complexes adopt a nearly planar configuration, as evidenced by the observation that the sum of the C–N–C angles is close to 360°. However, the two nitrogen atoms of the seven-membered carbene rings have different configurations: the nitrogen N1 atom is planar, while the nitrogen N2 atom is slightly pyramidalized. Apparently, this fact could be explained by the steric reasons due to the presence of a phenyl substituent at the allyl ligand. The torsion angle α between the planes, defined by the C_{Ar}–N···N–C_{Ar} atoms, is different for five-, six- and seven-membered carbenes. This angle increases with the increasing of carbene ring size. The C–N–C angle distribution in the complexes is similar to that in the six- and seven-membered silver complexes described previously.[9a,c] They change in the range of C_{ring}–N–C_{carb} > C_{Ar}–N–C_{carb} > C_{ring}–N–C_{Ar} (Fig. 1 and 2).

The phenyl-substituted allyl ligand in the complexes has the *trans* conformation, with the phenyl plane twisted relative to the allyl plane. Due to the steric interactions of this ligand with the two aryl ligands of the carbene ring, the palladium coordination plane is not perpendicular to the N–C_{carb}–N plane, and the two Pd–C_{carb}–N angles have different values (Fig. 1 and 2). The geometries observed for the molecules of complexes are stabilized by the short intramolecular C_{Me}–H···Cl contacts (2.83, 2.61–2.78 and 2.57–2.63 Å for the five-, six- and seven-membered NHC complexes, respectively) as well as the crystal packing effects.

Catalytic tests in Suzuki–Miyaura reaction

Heteroaromatic compounds constitute a large and varied family of organic compounds. The wide scope of utilization of heteroaromatic compounds spans from medicinal chemistry to organic electronics.[18] Although Suzuki–Miyaura cross-coupling is one of the most powerful methods of making C–C bonds, the coupling of heteroaromatic compounds is still challenging. It is of particular interest to utilize heteroaromatic chlorides in cross-coupling reactions.[19]

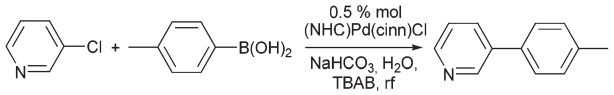
Substitution of organic solvents in cross-coupling reactions with water is a challenging task. Utilization of water as a solvent is ecologically friendly and might lead to significant cost reductions on a large scale. However, most current catalytic systems use mixtures of water with organic solvents.[20] Several catalytic systems based on phosphine or nitrogen containing ligands were developed for cross-coupling of heteroaromatic chlorides in aqueous media.[21] However such catalytic systems have significant drawbacks. To prevent rapid oxidation of phosphine ligand, the solvent should be neatly degassed. Moreover, the product is contaminated with toxic phosphine and products of side reactions of activations of C–P bonds.[22] Usually, reaction conditions are harsh: 12–24 h refluxing, large excess of strong base and boronic acid, high loadings of phase transfer agents and catalysts. No examples of cross-coupling of heteroaromatic chlorides in pure water were reported to date.

N-Heterocyclic carbene complexes of palladium are well documented active catalysts of cross-coupling reactions.[1a,b,23] Several examples of Suzuki–Miyaura coupling in aqueous media mediated by NHC palladium complexes were recently reported,[8a,24] two reports were devoted to coupling of heteroaromatic chlorides.[24d,e] In this work we set the target to develop an efficient catalytic system for Suzuki–Miyaura cross-coupling of heteroaromatic chlorides based on NHC–palladium complexes to meet the conditions of green chemistry: water as an environmentally friendly solvent, low loadings of catalysts and co-catalysts, low or no excess of boronic acid.

Catalytic tests were done in distilled water as solvent. $NaHCO_3$ was used as a base and $(Bu_4N)Br$ as a phase transfer agent. Initially we tested the activities of palladium complexes in the reaction of 3-chloropyridine with 4-tolylboronic acid (Table 1).

Reaction mixtures were refluxed in air for 1 h. The product was isolated using flash-chromatography. NHCs bearing bulky Dipp groups led to active pre-catalysts. (**6-Dipp**)Pd(cinn)Cl was found to be the most active, while (**5**)Pd(cinn)Cl exhibited slightly lower activity. Less bulky Mes derivatives exhibit low activities. The complex bearing **7-Dipp** carbene led to only

Table 1 Catalyst screening for Suzuki–Miyaura coupling of 3-chloropyridine and 4-tolylboronic acid[a]



Entry	NHC	Isolated yield (%)
1	**4**	3
2	**6-Mes**	33
3	**7-Mes**	15
4	**5**	84
5	**6-Dipp**	86
6	**7-Dipp**	25

[a] Reaction conditions: 3.27 mmol of 3-chloropyridine (1 eq.), 4-tolylboronic acid (1.04 eq.), $NaHCO_3$ (3.06 eq.), TBAB (0.095 eq.), 5 ml of distilled water and (NHC)Pd(cinn)Cl (0.5% mol); 1 h, reflux.

25% yield. We suppose that the decrease in catalytic activity is due to steric overprotection of the palladium atom.

We have chosen (**6-Dipp**)Pd(cinn)Cl for further detailed catalytic tests. A series of heteroaryl chlorides (Table 2) and heteroaryl bromides (Table 3) were reacted with 4-tolylboronic acid. In most cases reactions were run for 1 h in refluxing water in air. Cross-coupling products were isolated in high yields. All reactions are clean. No homo-coupling products were detected.

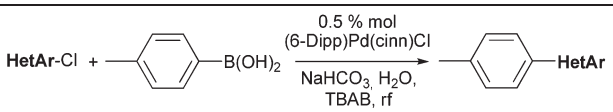
Coupling of 3-chloropyridine and phenylboronic acid was previously done by Nájera and coworkers using oxime-oxo palladacycles and bipyridine complexes of $PdCl_2$ as pre-catalysts. In their study, 1.5 fold excess of phenyl boronic acid and K_2CO_3 as a base was used. Reaction mixtures were refluxed for 3–7 h to give 50–90% yield depending on catalyst loading and the nature of the ligand at the palladium atom.[21a,c] Miyaura and coworkers reported on the synthesis of a 4-tolyl derivative in high yield upon heating of the reaction mixture to 80 °C for 16 h in the presence of K_3PO_4 as a base and 1 mol% of glycoside-substituted phosphine–palladium complex.[21d] Using (**6-Dipp**)Pd(cinnamyl)Cl, we were able to obtain high yield in 1 h using only a slight excess (0.04 eq.) of boronic acid (Table 2, entry 1). The coupling product of 4-chloropyridine with phenylboronic acid can be obtained in 56[21b] or 70% yield.[21d] We obtained the corresponding product in 77% yield under softer conditions (Table 2, entry 2).

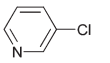
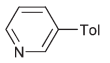
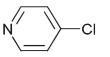
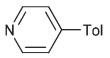
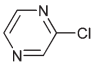
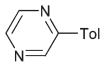
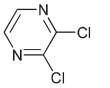
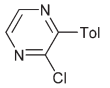
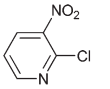
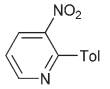
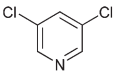
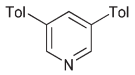
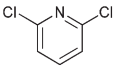
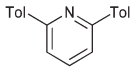
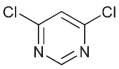
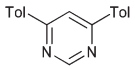
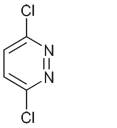
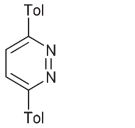
Couplings of chloropyrimidines, chloropyridazines, and chloropyrazines in pure water were successfully done for the first time (Table 2, entries 3, 4, 8, 9).

It is worth noting the coupling of dichlorides. In cases of dichloropyrazine, only the monoarylated product was isolated (Table 2, entries 4). While for 4,6-dichloropyrimidine and 3,6-dichloropyridazine, mono- and diarylated products were separately isolated (Table 2, entries 8 and 9). In cases of dichloropyridines, only diarylated products were obtained (Table 2, entries 6 and 7).

To widen the scope of substrates, we performed catalytic tests of (**6-Dipp**)Pd(cinn)Cl with heteroaryl bromides. As

Table 2 Suzuki–Miyaura coupling of heteroaryl bromides with 4-tolylboronic acid[a]



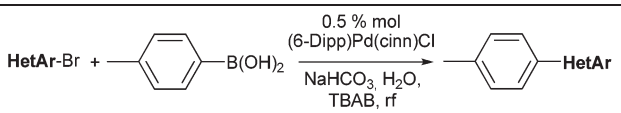
Entry	HetAr-Cl	Product	Time (h)	Isolated yield (%)
1			1	86
2			1	77
3			1	98
4			1	71
5			1	77
6			3	75
7			3	90
8			3	61[b]
9			3	39[b]

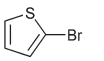
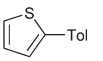
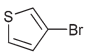
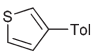
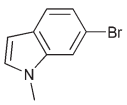
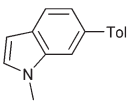
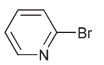
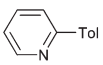
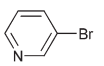
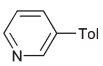
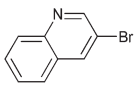
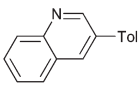
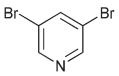
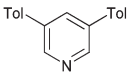
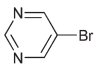
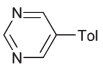
[a] Reaction conditions: 3.27 mmol of heteroaromatic chloride (1 eq.), 4-tolylboronic acid (1.04 eq.; 2.08 eq. for entries 6–9), $NaHCO_3$ (3.06 eq.), TBAB (0.095 eq.), 5 ml of distilled water and (**6-Dipp**)Pd(cinn)Cl (0.5% mol); reflux. [b] Monoarylated product was also isolated.

expected, bromides were more active than chlorides to give high yields in 1 h (Table 3).

Next, we varied the nature of arylboronic acids. 2-Chloropyridine was used for the catalytic test since 2-substituted pyridines are useful building blocks for organic synthesis. Synthesis of 2-arylated pyridines *via* heterocyclization is not straightforward, while 2-chloropyridines are easily accessible. Additionally, it is known that 2-chloropyridines have a tendency to hydrolyze under basic conditions.[25] It was of interest to determine whether the hydrolysis of 2-chloropyridine affects cross-coupling reactions. It is worth mentioning that in the conditions reported by Nájera and coworkers, the reaction of phenylboronic acid with 2-chloropyridine results in only 66% of the coupling product.[21b] Miyaura and coworkers obtained 2-(4-tolyl)pyridine in 88% yield.[21d] In addition, Plenio and coworkers obtained good yields in cross-coupling of 2-chloropyridine with 4-tolylboronic acid, however they used strong bases such as KOH and K_2CO_3 under reflux conditions for 12 h.[21f,24d]

Table 3 Suzuki–Miyaura coupling of heteroaryl bromides with 4-tolylboronic acid[a]



Entry	HetAr-Br	Product	Isolated yield (%)
1			97
2			99
3			99
4			89
5			97
6			98
7			82
8			92

[a] Reaction conditions: 3.27 mmol of heteroaromatic bromide (1 eq.), 4-tolylboronic acid (1.04 eq.), $NaHCO_3$ (3.06 eq.), TBAB (0.095 eq.), 5 ml of distillated water and (**6-Dipp**)Pd(cinn)Cl (0.5 mol%); 1 h, reflux.

We found that in all cases, reactions were free from side products. Target products were obtained in high or near quantitative yields (Table 4). The use of (**6-Dipp**)Pd(cinn)Cl is efficient in cross-coupling of donor aryl boronic acids (Table 4, entries 1, 2), as well as deactivated acceptor aryls (Table 4, entries 3–5) and bulky (Table 4, entry 6) boronic acids.

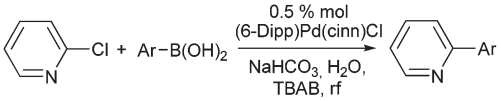
Conclusions

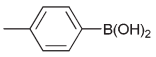
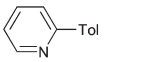
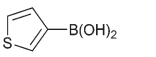
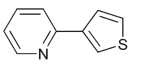
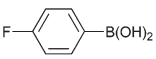
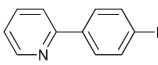
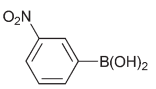
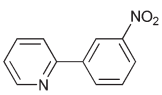
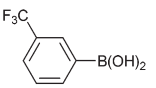
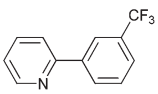
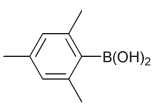
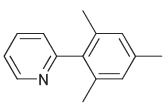
A series of expanded ring NHC–palladium complexes were synthesized and characterized structurally in the solid state. These complexes can be obtained by direct interaction of free carbenes with a palladium source or *via* transmetallation in (NHC)AgCl.

The catalytic activities of the complexes in the Suzuki–Miyaura cross-coupling reaction of heteroaryl chlorides and bromides in aqueous media were tested. The (**6-Dipp**)Pd(cinn)Cl complex based on six-membered ring carbene bearing bulky Dipp substituents was found to be the most active pre-catalyst. Catalytic reaction conditions were optimized to meet the requirements of "green chemistry". The developed cross-coupling protocol has several prominent features:

a. The reaction takes place in water with no addition of organic solvents.

Table 4 Suzuki–Miyaura coupling of 2-chloropyridine with arylboronic acids[a]



Entry	Ar–$B(OH)_2$	Product	Isolated yield (%)
1			97
2			99
3			82
4			98
5			86
6			90

[a] Reaction conditions: 3.27 mmol of 2-chloropyridine (1 eq.), boronic acid (1.04 eq.), $NaHCO_3$ (3.06 eq.), TBAB (0.095 eq.), 5 ml of distillated water and (**6-Dipp**)Pd(cinn)Cl (0.5 mol%); reflux.

b. The reaction is carried out under air, no degasation of water is needed.

c. Mild, cheap, environmentally benign $NaHCO_3$ is used as a base.

d. Low loadings of phase transfer agent $(Bu_4N)Br$.

e. Only a slight excess of boronic acid is used.

f. The reaction is fast.

g. The reaction is clean and no homo-coupling products are formed.

Thus, we developed a versatile, robust, highly active catalytic system for the coupling of heteroaromatic chlorides and bromides. Boronic acids bearing donor, acceptor as well as sterically bulky substituents can be efficiently used as coupling partners. As an additional advantage, the precatalyst (**6-Dipp**)-Pd(cinn)Cl is air- and moisture-stable and can be prepared in multigram quantities in high yields.

Experimental

General information

Unless otherwise stated, all manipulations were carried out using standard Schlenk technique under argon atmosphere. Dichloromethane was distilled prior to use over CaH_2 in argon atmosphere. Diethyl ether was distilled over sodium-benzophenone. Unsaturated amidinium precursors were prepared by the method published by Hintermann.[26] Free *N*-heterocyclic carbenes were prepared from the corresponding amidinium salts by the method published by Cavell *et al.*[9a] Bis(palladium-

(λ_3-cinnamyl)chloride) was prepared using the published procedure.[27] Other chemicals and solvents were obtained from commercial sources and used without further purification. NMR spectra were obtained on a Bruker "Avance 400" (400 MHz 1H, 101 MHz 13C) and Bruker "Avance 600" (600 MHz ^{1}H, 151 MHz ^{13}C). The chemical shifts are frequency referenced relative to the solvent peaks.[28] Coupling constants J are given in Hertz as positive values regardless of their real individual signs. The multiplicity of the signals is indicated as "s", "d", or "m" for singlet, doublet, or multiplet, respectively. The abbreviation "br" is given for broadened signals. Elemental analyses were performed on a Carlo Erba EA1108 CHNS-O elemental analyzer at the Institute of Petrochemical Synthesis, Russian Academy of Sciences.

X-Ray structure determination

Data were collected on a Bruker SMART APEX II CCD and a Bruker SMART 1K CCD diffractometer (λ(MoK$_\alpha$)-radiation, graphite monochromator, ω and φ scan mode) and corrected for absorption using the *SADABS* program (versions 2.01[29] and 2.03[30]). For details, see Table S2.† The structures were solved by direct methods and refined by full-matrix least squares technique on F^2 with anisotropic displacement parameters for non-hydrogen atoms. The crystallographically independent parts of the unit cells of (**6-Mes**)Pd(cinn)Cl, (**6-Dipp**)Pd(cinn)Cl and (**7-Dipp**)Pd(cinn)Cl contain one methylene chloride, one diethyl ether, and a half hexane solvate molecule, respectively. The capping-C3 carbon atoms of six-membered carbene rings in one of the two independent molecules of (**6-Mes**)Pd(cinn)Cl and in the molecule of (**6-Dipp**)Pd(cinn)Cl are disordered over two sites with the occupancies of 0.6 : 0.4 and 0.7 : 0.3, respectively. The allyl ligand and hexane solvate molecule in (**7-Dipp**)-Pd(cinn)Cl are strongly disordered. The allyl ligand was successfully split by two positions with occupancies of 0.8 : 0.2, whereas the contribution to the scattering by the hexane solvent molecule was removed by the use of the utility SQUEEZE in *PLATON98*.[31] The hydrogen atoms in all compounds were placed in calculated positions and refined within the riding model with fixed isotropic displacement parameters (U_{iso}(H) = 1.5U_{eq}(C) for the CH_3-groups and U_{iso}(H) = 1.2U_{eq}(C) for the other groups). All calculations were carried out using the *SHELXTL* program.[32] Crystallographic data for the complexes have been deposited with the Cambridge Crystallographic Data Center. CCDC 784539–784543 contain the supplementary crystallographic data for this paper.

General method of synthesis of saturated amidinium salts

In air, to the mixture of formamidine (1.0 eq.), alkyldibromide (1.5 eq.), and DIPEA (1.2 eq.) was added a small amount of toluene which is necessary for easy mixing (approx. 15 ml to 0.1 mol of formamidine). The reaction mixture was heated at 120 °C for 1 h, then dissolved in CH_2Cl_2, and washed in 3 × 100 ml of a diluted solution of potassium carbonate. The organic layer was dried and dissolved in acetone (200 ml × 0.1 mol). To the solution was added a solution of $NaBF_4$ (2 eq.) in water (10 ml × 1 g) and acetone was evaporated; the precipitated product was filtered off and dried for a few days in a vacuumed desiccator over P_2O_5.

General method of synthesis of silver complexes

Silver complexes were prepared by a modified method reported earlier.[9c] A mixture of amidinium salt (1 eq.) and silver(I) oxide in a Schlenk flask was dissolved in dichloromethane (20 ml × 1 mmol) in the absence of light. The reaction mixture was stirred for 3 days, filtered through a short pad of Celite and evaporated at half. Methanol (5 ml × 1 mmol) was then added to the solution and the mixture was evaporated at 2/3. A white precipitate of the target complex was filtered off and dried.

General methods of synthesis of palladium complexes

Method A. A solution of *N*-heterocyclic carbene (1 eq.) in diethyl ether (30 ml) was added to a suspension of Bis(palladium(η_3-cinnamyl)chloride) (0.5 eq.) in a small amount of diethyl ether. The reaction was stirred for 1 h, then filtered off (if the solution is not clear), evaporated to dryness, grinded with hexane and the precipitate was filtered off and dried *in vacuo*. If the product is not pure according to the analytical data, it could be purified by recrystallization from hexane–DCM or by flash chromatography, using DCM as an eluent.

Method B. In air, the NHC–silver(I) complex (1 eq.) and bis-(palladium(η_3-cinnamyl)chloride) (0.5 eq.) were dissolved in DCM (20 ml × 1 mmol) and stirred for 24 h in the absence of light. The mixture was evaporated, dissolved in diethyl ether, filtered off through a short pad of Celite (for separation of the product solution from AgBr, unreacted starting silver complex and [Pd(cinn)Cl]$_2$), and evaporated to give the pure palladium complex. In the case of **6-Dipp** and **7-Dipp**, the pad of Celite was extracted with DCM (for dissolution of the remaining starting materials) and the filtrate was stirred for 24 h. Then all processes were repeated two more times.

(4)Pd(cinn)Cl. Yield: 0.57 g, 48%, white powder (Method A). Anal. Calcd for $C_{30}H_{35}ClN_2Pd$: C, 63.72; H, 6.24; N, 4.95. Found: C, 63.94; H, 6.31; N, 5.03. ^{1}H NMR ($CDCl_3$, 400 MHz): δ_{ppm} 7.09–7.15 (m, 3H, Ph), 7.04–7.08 (m, 2H, Ph), 6.97 (br.s, 2H, Ar-Mes-H), 6.95 (br.s, 2H, Ar-Mes-H), 5.09 (ddd, J = 18.6, 12.5, 10.3 Hz, 1H, Allyl), 4.27 (d, J = 12.6 Hz, 1H, Allyl), 3.99 (d, J = 3.4 Hz, 4H, CH_2-N), 3.27 (d, J = 6.3 Hz, 1H, Allyl), 2.46 (s, 6H, CH_3-Mes), 2.42 (s, 6H, CH_3-Mes), 2.32 (s, 6H, CH_3-Mes), 1.93 (d, J = 11.7 Hz, 1H, Allyl).

^{13}C NMR (151 MHz, $CDCl_3$): δ_{ppm} 211.2 (N-C-N), 138.1 (Ar), 136.4 (Ar), 129.4 (Ar), 128.3 (Ar), 127.4 (Ar), 126.6 (Ar), 109.7 (Allyl), 90.2 (Allyl), 51.3 (CH_2-N), 46.8 (Allyl), 21.2 (CH_3-Mes), 18.64 (CH_3-Mes), 18.56 (CH_3-Mes).

(5)Pd(cinn)Cl. Yield: 0.82 g, 63%, light-yellow powder (Method A). Anal. Calcd for $C_{36}H_{47}ClN_2Pd$: C, 66.56; H, 7.29; N, 4.31. Found: C, 67.13; H, 7.01; N, 4.24. ^{1}H NMR ($CDCl_3$, 600 MHz): δ_{ppm} 7.38 (t, J = 7.8 Hz, 2H, *p*-Ar-Dipp-H), 7.25 (d, J = 7.6 Hz, 4H, *m*-Ar-Dipp-H), 7.15–7.11 (m, 5H, Ph), 5.06 (dt, J = 13.1, 9.2, 1H, Allyl), 4.34 (d, J = 13.2 Hz, 1H, Allyl), 4.04 (s, 4H, CH_2-N), 3.45 (br.s, 4H, CH-*i*Pr), 2.89 (br.s, 1H, Allyl), 1.58 (br.s, 1H, Allyl), 1.47 (d, J = 5.9 Hz, 6H, CH_3-*i*Pr), 1.42 (d, J = 6.2 Hz, 6H, CH_3-*i*Pr), 1.28 (d, J = 6.8 Hz, 12H, CH_3-*i*Pr). ^{13}C NMR

($CDCl_3$, 151 MHz): δ_{ppm} 212.0 (N-C-N), 147.1 (Ar), 137.6 (Ar), 136.3 (Ar), 129.0 (Ar), 128.2 (Ar), 127.2 (Ar), 126.6 (Ar), 124.1 (Ar), 109.0 (Allyl), 91.6 (Allyl), 54.0 (CH_2-N), 46.0 (Allyl), 28.5 (CH-*i*Pr), 26.6 (CH-*i*Pr), 23.7 (CH_3-*i*Pr).

(6-Mes)Pd(cinn)Cl. Yield 0.31 g, 62% (Method A); 0.88 g 88% (Method B), light-yellow powder. Anal. Calcd for $C_{31}H_{37}ClN_2Pd$: C, 64.25; H, 6.44; N, 4.83. Found: C, 64.02; H, 6.59; N, 4.93. ^{1}H NMR(DMSO-d_6, 400 MHz): δ_{ppm} 6.99–7.09 (m, 3H, Ph), 6.95 (br.s, 2H, Ar-Mes-H), 6.87 (br.s, 2H, Ar-Mes-H), 6.68 (d, J = 6.4 Hz, 2H, Ph), 4.61 (ddd, J = 19.3, 11.8, 9.4 Hz, 1H, Allyl), 3.62 (d, J = 12.0 Hz, 1H, Allyl), 3.37 (s, 4H, CH_2-N), 2.39–2.43 (m, 2H, Allyl), 2.34 (br.s, 6H, CH_3-Mes), 2.28 (br.s, 12H, CH_3-Mes), 2.15–2.23 (m, 2H, CH_2) (one of the allyl protons was not observed). ^{13}C NMR(DMSO-d_6, 101 MHz): δ_{ppm} 206.7 (N-C-N), 139.5 (Ar), 136.6 (Ar), 136.4 (Ar), 134.4 (Ar), 129.3 (Ar), 128.9 (Ar), 128.7 (Ar), 128.0 (Ar), 127.7 (Ar), 127.0 (Ar), 125.5 (Ar), 109.5 (Allyl), 83.7 (Allyl), 48.3 (CH_2-N), 45.9 (allyl), 31.0 (CH_2), 22.1 (CH_3-Mes), 20.6 (CH_3-Mes), 19.0 (CH_3-Mes), 17.5 (CH_3-Mes), 14.0 (CH_3-Mes). ^{13}C NMR (151 MHz, $CDCl_3$) δ_{ppm} 213.8 (N-C-N), 146.7 (Ar), 143.5 (Ar), 138.9 (Ar), 128.5 (Ar), 127.9 (Ar), 127.3 (Ar), 126.0 (Ar), 124.1 (Ar), 108.7 (allyl), 86.7 (allyl), 65.7 (N-CH_2), 49.3 (allyl), 31.5 (CH_2), 28.6 (CH_3-Mes), 26.9 (CH_3-Mes), 23.6 (CH_3-Mes), 22.6 (CH_3-Mes), 20.8 (CH_3-Mes), 15.2 (CH_3-Mes).

(7-Mes)Pd(cinn)Cl. Yield: 0.94 g, 93% (Method B), light-yellow powder. Anal. Calcd for $C_{32}H_{39}ClN_2Pd$: C, 64.75; H, 6.62; N, 4.72. Found: C, 64.38; H, 6.31; N, 4.83. ^{1}H NMR ($CDCl_3$, 400 MHz): δ_{ppm} 7.07 (br.s, 2H, Ar-Mes-H), 6.96 (br.s, 5H, Ph), 6.75 (br.s, 2H, Ar-Mes-H), 4.63 (dd, J = 19.1, 11.7 Hz, 1H, Allyl), 4.09 (d, J = 11.0 Hz, 1H, Allyl), 3.60–3.90 (m, 4H, CH_2-N), 3.32 (d, J = 5.6 Hz, 1H, Allyl), 2.02–2.80 (m, 22H, CH_3-Mes + CH_2CH_2), 1.54 (d, J = 12.3 Hz, 1H, Allyl). ^{13}C NMR ($CDCl_3$, 101 MHz): δ_{ppm} 221.4 (N-C-N), 139.1 (Ar), 137.0 (Ar), 130.1 (Ar), 129.6 (Ar), 128.9 (Ar), 128.1 (Ar), 127.9 (Ar), 127.1 (Ar), 126.0 (Ar), 109.6 (Allyl), 86.0 (Allyl), 53.8 (Allyl), 48.5 (CH_2-N), 25.3 (CH_2CH_2), 20.9 (CH_3-Mes), 20.02–20.37 (m, CH_3-Mes), 19.55–20.02 (m, CH_3-Mes), 18.10–19.02 (m, CH_3-Mes).

(6-Dipp)Pd(cinn)Cl. Yield: 0.15 g, 34% (Method A); 0.85 g, 71% (Method B), light-yellow powder. Anal. Calcd for $C_{37}H_{49}ClN_2Pd$: C, 66.96; H, 7.44; N, 4.22. Found: C, 67.19; H, 7.53; N, 4.13. ^{1}H NMR ($CDCl_3$, 400 MHz): δ_{ppm} 7.35 (t, J = 7.6 Hz, 2H, *p*-Ar-Dipp-H), 7.25 (d, J = 7.3 Hz, 4H, *m*-Ar-Dipp-H), 7.04–7.11 (m, 3H, Ph), 6.83–6.88 (m, 2H, Ph), 4.62 (dt, J = 12.2, 9.4 Hz, 1H, Allyl), 3.88 (d, J = 12.2 Hz, 1H, Allyl), 3.62–3.69 (t, J = 5.6 Hz, 4H, CH_2-N), 3.55 (dt, J = 13.4, 6.6 Hz, 4H, CH-*i*Pr), 2.36 (ddd, J = 11.2, 6.0, 5.7 Hz, 2H, CH_2), 1.42 (d, J = 6.6 Hz, 12H, CH_3-*i*Pr), 1.22 (d, J = 6.8 Hz, 12H, CH_3-*i*Pr), 1.18 (d, J = 6.6 Hz, 1H, Allyl) (one of the allyl protons was not observed). ^{13}C NMR ($CDCl_3$, 151 MHz): δ_{ppm} 213.8 (N-C-N), 146.6 (Ar), 143.5 (Ar), 138.9 (Ar), 128.5 (Ar), 127.8 (Ar), 127.3 (Ar), 126.0 (Ar), 124.1 (Ar), 108.7 (Allyl), 86.7 (Allyl), 65.7 (Allyl), 49.3 (CH_2-N), 31.5 (CH_2), 28.6 (CH-*i*Pr), 26.9 (CH-*i*Pr), 23.6 (CH_3-*i*Pr), 22.5 (CH_3-*i*Pr), 20.8 (CH_3-*i*Pr), 15.2 (CH_3-*i*Pr).

(7-Dipp)Pd(cinn)Cl. Yield: 0.46 g, 42% (Method A); 0.185 g, 73% (Method B), light-yellow powder. Anal. Calcd for $C_{38}H_{51}ClN_2Pd$: C, 67.35; H, 7.59; N, 4.13. Found: C, 67.38; H, 7.35; N, 4.28. ^{1}H NMR ($CDCl_3$, 600 MHz): δ_{ppm} 7.31 (t, J = 7.6 Hz, 2H, *p*-Ar-Dipp-H), 7.23 (d, J = 7.6 Hz, 4H, *m*-Ar-Dipp-H), 7.01–7.11 (m, 3H, Ph), 6.69–6.76 (m, 2H, Ph), 4.58 (dt, J = 21.1, 9.4 Hz, 1H, Allyl), 4.04 (br.s, 4H, CH_2-N), 3.80 (d, J = 12.0 Hz, 1H, Allyl), 3.61 (br.s, 4H, CH-*i*Pr), 2.35 (br.s, 4H, CH_2CH_2), 1.45 (d, J = 6.7 Hz, 12H, CH_3-*i*Pr), 1.24 (d, J = 6.5 Hz, 12H, CH_3-*i*Pr) (two of the allyl protons were not observed). ^{13}C NMR ($CDCl_3$, 151 MHz): δ_{ppm} 225.5 (N-C-N), 146.4 (Ar), 145.7 (Ar), 139.2 (Ar), 128.2 (Ar), 127.8 (Ar), 127.4 (Ar), 125.9 (Ar), 124.1 (Ar), 109.1 (Allyl), 85.6 (Allyl), 56.7 (Allyl), 48.3 (CH_2-N), 31.7 (CH_2CH_2), 28.9 (CH-*i*Pr), 28.8 (CH-*i*Pr), 27.3 (CH-*i*Pr), 25.5-(CH-*i*Pr), 23.9 (CH_3-*i*Pr).

General method of Suzuki–Miyaura cross-coupling reaction in water

In air, heteroaromatic halide (3.27 mmol, 1 eq.), boronic acid (3.40 mmol, 1.04 eq.), $NaHCO_3$ (0.84 g, 10 mmol, 3.06 eq.), TBAB (0.1 g, 0.31 mmol, 0.095 eq.) and (**6-Dipp**)Pd(cinn)Cl (10.9 mg, 0.0164 mmol, 0.005 eq.) were mixed with 5 ml of distillated water in a 25 ml round bottomed flask equipped with a magnetic stirring bar and a reflux condenser. The reaction mixture was refluxed for 1 h, cooled to room temperature and extracted with 3 × 20 ml CH_2Cl_2. The crude product obtained from evaporation of the combined organic phase was purified by flash chromatography using hexane–$CHCl_3$ or acetone–$CHCl_3$ mixture as eluent.

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