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ARTICLE

Mixed er-NHC/Phosphine Pd(II) Complexes and Their Catalytic Activity in Buchwald-Hartwig Reaction under Solvent-Free Conditions

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A series of novel (NHC)$PdCl_2$-PR_3 complexes was synthesized and fully characterized by ^1H, ^{13}C, ^{31}P NMR and FT-IR spectroscopy. These complexes showed high catalytic activity toward solvent-free Buchwald-Hartwig amination. Both primary and secondary amines were efficiently utilized under the same reaction conditions. Solvent-free synthesis of valuable N-aryl carbazoles and similar N-heterocyclic systems was described.

Introduction

In the past 30 years, palladium-catalyzed cross-coupling reactions leading to formation of C–N bonds have become widely used in laboratory practice, as well as industrial fine organic synthesis.[1, 2] The Buchwald-Hartwig amination is one of the most popular cross-coupling reactions,[3, 4] allowing the efficient synthesis of N- and N,N-substituted arylamines, which are structural fragments of drugs[5, 6] and materials for organic electronics.[7-9]

Typically, cross-coupling reactions are performed in solutions, whereas the absence of solvent may be advantageous. Solvent-free cross-coupling reactions proceed at higher rates than conventional ones (in solvent); considerably higher reactant and catalyst concentrations drastically facilitate the reaction. The absence of frequently used green protic solvents reduces formation of aryl halide reduction byproducts. In case of virtually quantitative product yield, work-up is significantly simplified. Solvent-free conditions avoid hazards and toxicity associated with some aprotic solvents. Furthermore, energy costs of solvent-free reactions are reduced.

Reports on solvent-free Buchwald–Hartwig amination are quite limiting, only 14 works have been published on the topic.[10-23] A number of solvent-free mechanochemical Buchwald-Hartwig amination protocols have been published.[24-26] In continuation of our research on the development of new transition metals N-heterocyclic carbene (NHC) complexes and their performance under environmentally benign conditions,[21-23, 27-31] we decided to continue our study of the Buchwald–Hartwig amination (BHA) under solvent-free conditions. Earlier, in our works we have developed efficient catalytic systems for amination of aryl halides by secondary amines ($Pd(OAc)_2$/RuPhos)[21] and selective amination by primary arylamines to form diarylamines (expanded ring NHC complex (6-Dipp)Pd(cinn)Cl)[22, 23] under solvent-free conditions. Thus, we were interested in the development of catalytic system which would combine activity of both phosphine- and NHC-based systems, and be suitable for solvent-free monoarylation of primary and secondary amines and double arylation of primary amines.

Previously it was shown that the introduction of auxiliary ligands to NHC-Pd complexes can be beneficial and usually provides new features in their catalytic activity.[32-34] Thus, it was shown that introduction of the "throw-away" pyridyl ligands facilitate C–C bond formation,[35] substitution of pyridyl ligand to alkylamine ligand renders higher activity for both C–C and C–N cross-couplings.[36, 37] Also Cazin *et al.* showed that combination of NHC-Pd complex with phosphine ligand can enhance catalytic performance in Suzuki-Miyaura cross-coupling.[38] Wang *et al.* showed that NHC-Pd complex with arsine, stibine or phosphine auxiliary ligands are active catalysts for both Hiyama and Buchwald-Hartwig cross-coupling reactions.[39, 40] It can be assumed that combination of phosphine catalyst, active in one reaction, and NHC-catalyst, active in another one, may produce well-defined catalytic system active in both reactions.

From our results reported previously it could be assumed that combination of 6-Dipp and RuPhos ligands on a palladium centre would give the most efficient catalyst for the solvent-free amination reaction. However, introduction of phosphine

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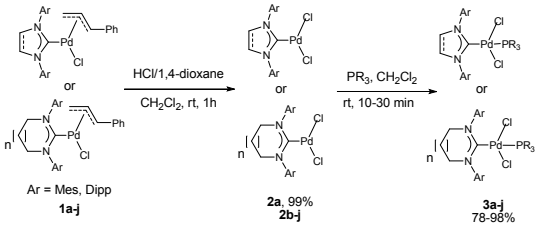
ligand inevitably causes alteration in both reactivity and selectivity of the resulting mixed NHC-phosphine palladium complex. That's why we decided to study a series of NHC-Pd-phosphine complexes with different combinations of NHC/phosphine ligands and find the most efficient catalyst for the reaction.

Results and discussion

Mixed N-heterocyclic carbene/phosphine complexes are accessible in a few ways: introduction of NHC into phosphine-Pd complex ($Pd(PR_3)_2Cl_2$), introduction of phosphine ligand into NHC-Pd complex ($[(NHC)PdCl_2]_2$) and one-pot synthesis from NHC·HCl, palladium(II) chloride and phosphine in presence of weak base. Whereas relatively high acidity of five-membered NHC precursors allows easy generation of free NHC, er-NHC's ones are considerably less acidic,[41, 42] favoring only second synthetic way as the most feasible. Following this strategy, a series of novel er-NHC-$PdCl_2$-PR_3 complexes was synthesized by reaction of bridged $[(NHC)PdCl_2]_2$ with a tertiary phosphine according to a reported technique.[43] Introduction of phosphine into bridged palladium dichloride complex proceeds quickly and smoothly, affording corresponding mixed NHC-phosphine complex in less than half an hour. Complexes (**3a–j**) were easily obtained in high to quantitative yields (Scheme 1). All complexes are yellow or yellowish solids, light, moisture and air stable. X-ray quality crystals of complexes **3a** and **3f** were grown by slow evaporation of pentane/dichloromethane solutions.



Scheme 1 Synthesis of er-NHC-$PdCl_2$-PR_3 complexes.

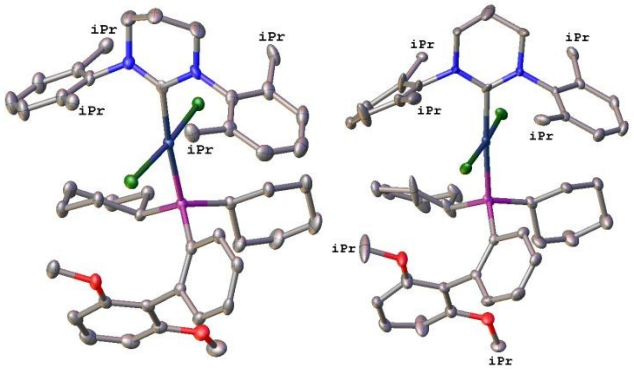


Figure 1 Molecular structure of complexes **3a** (left) and **3f** (right). Hydrogen atoms and iPr groups are omitted for clarity.

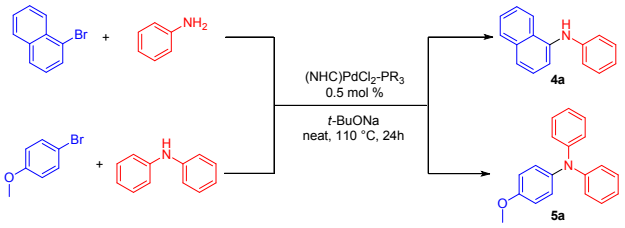
All complexes were characterized by ^1H, ^{13}C, ^{31}P NMR and FT-IR spectroscopy and HRMS. ^{13}C NMR spectra of complexes **3a-j** showed signal of C2-atom as doublet with $^2J_{CP}$ coupling constant from 175 to 192 Hz, which is characteristic for the *trans* position of the phosphine and NHC ligands.[44-46] ^{31}P NMR spectra of all complexes except **3j** (signal was broadened) expectedly showed sharp singlets shifted downfield when compared to free phosphine at room temperature (Table 1). Chemical shift of ^{31}P atom was in accordance with donor ability of phosphine ligands, whereas electronic and steric properties of NHC-ligands have almost no effect on phosphorus chemical shift of coordinated phosphine. Previously it was shown, that ^{13}C chemical shift of carbene atom (C2) may be a sensitive tool for measurement of donating ability of *trans*-ligand in square Pd(II) complexes.[47] In case of complexes **3a**, **3f-j** ^{13}C NMR spectra provided the following series of phosphine ligands based on their donating ability was obtained: RuPhos>SPhos~DavePhos>CyJohnPhos> >PPh_3>P(*o*-Tol)$_3$. Similar trend was observed for complexes **3a**, **3f-j** from ^{31}P NMR spectra: SPhos>RuPhos~ DavePhos>CyJohnPhos>>PPh_3>P(*o*-Tol)$_3$.

Table 1. ^{13}C and ^{31}P NMR data for complexes **3a–j** (δ in ppm, *J* in Hz)[a]

(NHC)$PdCl_2$-PR_3 complex	C (carbene)		^{31}P	
	δ_C	$^2J_{CP}$	δ_P (complex)	δ_P (PR_3)
(6-Dipp)$PdCl_2$-SPhos (**3a**)	198.5	182.6	39.0	
IPr$PdCl_2$-SPhos (**3b**)	175.0	187.2	40.1	
SIPr$PdCl_2$-SPhos (**3c**)	202.0	176.2	39.4	-12.6
IMes$PdCl_2$-SPhos (**3d**)	172.6	186.6	38.9	
SIMes$PdCl_2$-SPhos (**3e**)	200.1	175.1	38.5	
(6-Dipp)$PdCl_2$-RuPhos (**3f**)	198.9	182.7	38.7	–12.7
(6-Dipp)$PdCl_2$-DavePhos (**3g**)	198.4	182.8	38.7	–13.3
(6-Dipp)$PdCl_2$-PPh_3 (**3h**)	197.2	192.4	17.5	–9.0
(6-Dipp)$PdCl_2$-P(*o*-Tol)$_3$ (**3i**)[b]	195.0	191.1	15.9	–33.2
(6-Dipp)$PdCl_2$-CyJohnPhos (**3j**)	197.8	182.7	32.2	–16.8

[a] NMR were recorded at 298 K. [b] NMR were recorded at 323 K.

Table 2. Screening of catalytic systems in BHA reaction



Entry	Catalyst	Isolated yield (%)	
		4a	**5a**
1	**(6-Dipp)$PdCl_2$-SPhos (3a)**	98	95
2	IPr$PdCl_2$-SPhos (**3b**)	86	84
3	SIPr$PdCl_2$-SPhos (**3c**)	90	82
4	IMes$PdCl_2$-SPhos (**3d**)	0	85
5	SIMes$PdCl_2$-SPhos (**3e**)	0	92
6	(6-Dipp)$PdCl_2$-RuPhos (**3f**)	86	93
7	(6-Dipp)$PdCl_2$-DavePhos (**3g**)	86	84
8	(6-Dipp)$PdCl_2$-PPh_3 (**3h**)	48	15
9	(6-Dipp)$PdCl_2$-P(*o*-Tol)$_3$ (**3i**)	98	14
10	(6-Dipp)$PdCl_2$-CyJohnPhos (**3j**)	98	70

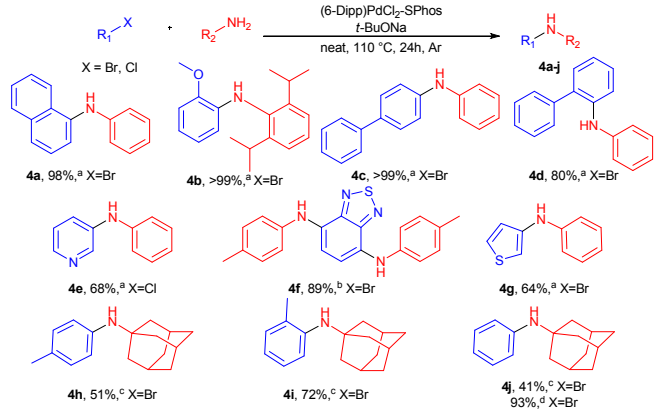
In order to find the most efficient catalyst in arylation reaction of both RNH_2 and R_2NH under solvent-free conditions, synthesized complexes were tested in the BHA reaction of 1-

bromonaphthalene with aniline (primary amine) and 1-bromo-4-methoxybenzene with diphenylamine (secondary amine) (Table 2).

The most efficient complex for both types of solvent-free Buchwald-Hartwig amination was (6-Dipp)$PdCl_2$-SPhos. Interestingly, that catalytic performance of complexes with (6-Dipp) carbene ligand (**3a**, **3f-j**) in arylation of N,N-diarylamine was in agreement with donor ability as judged from ^{31}P NMR.

Investigation of complex **3a** catalytic activity in reactions of primary (Table 3) and secondary amines (Table 4) was the next stage of our study.

Table 3. Coupling of primary amines with various aryl halides



[a] Reaction conditions: ArX or (Het)ArX (1.0 mmol, 1 equiv.), primary amine (1.0 mmol, 1 equiv.), (6-Dipp)$PdCl_2$-SPhos (0.5 mol %), *t*-BuONa (1.2 equiv.), neat, 110 °C, 24h. [b] Primary amine (2.0 mmol, 2 equiv.), (6-Dipp)$PdCl_2$-SPhos (2 mol %), *t*-BuONa (2.4 equiv.), [c] (6-Dipp)$PdCl_2$-SPhos (1 mol %). [d] PhBr (2 equiv.), (6-Dipp)$PdCl_2$-SPhos (2 mol %).

Cross-coupling of primary amines resulted in a series of diarylamines (**4a–d**) and arylheteroaryl amines (**4e–g**) in good to quantitative yields (Table 3). The elaborated catalyst system allowed amination of sterically loaded aryl bromides (**4a**, **4b**, **4d**, **4i**) and heteroaryl chlorides (**4e**). Amination of 4,7-dibromobenzol[c][1,2,5]thiadiazole allowed to obtain **4f** with high (89%) yield; analogues of which are may be used for designing of new efficient red thermally activated delayed fluorescence emitters (TADF)[48] and in synthesis of stable π-conjugated polymers based on polyanilines demonstrating excellent electronic properties.[49] Bulky and high-melting 1-adamantylamine afforded products **4h** and **4i** in somewhat lower yields, whereas arylation in presence of 2 equivalents of bromobenzene afforded product **4j** in 93%.

Table 4. Coupling of secondary amines with various aryl halides.

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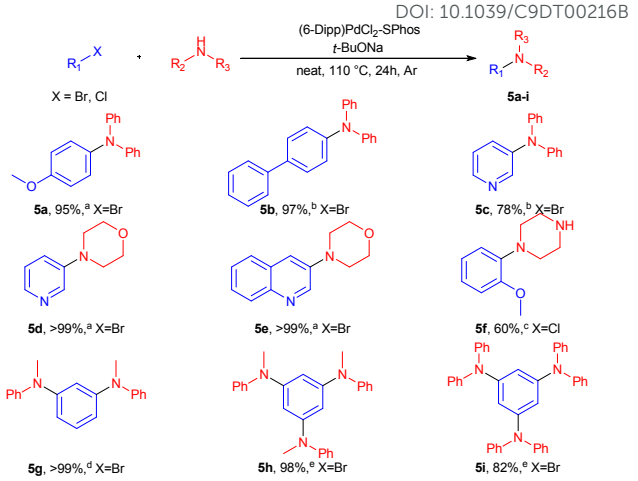
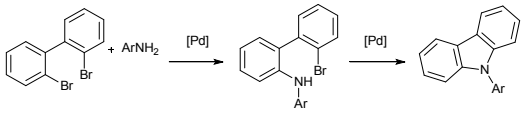


[a] Reaction conditions: ArX or (Het)ArX (1.0 mmol, 1 equiv.), secondary amine (1.0 mmol, 1 equiv.), (6-Dipp)$PdCl_2$-SPhos (0.5 mol %), *t*-BuONa (1.2 equiv.), neat, 110 °C, 24h. [b] (6-Dipp)$PdCl_2$-SPhos (1 mol %). [c] Reaction time 10 min. [d] Secondary amine (2.0 mmol, 2 equiv.), (6-Dipp)$PdCl_2$-SPhos (2 mol %), *t*-BuONa (2.4 equiv.). [e] Secondary amine (3.0 mmol, 3 equiv.), (6-Dipp)$PdCl_2$-SPhos (3 mol %), *t*-BuONa (3.6 equiv.).

Next, we evaluated performance of developed catalyst **3a** in arylation of secondary amines with mono- (**5a-f**), di- (**5g**) and trihalo (hetero)aryls (Table 4, **5h**, **5i**). All products were isolated in high to virtually quantitative yields, demonstrating high catalytic efficiency of complex **3a** for arylation of secondary amines. It is worth mentioning that our catalytic system **3a** afforded **5i** in 82% yield from 1,3,5-tribromobenzene and diphenylamine, whereas previously reported yield was as low as 25%.[50]

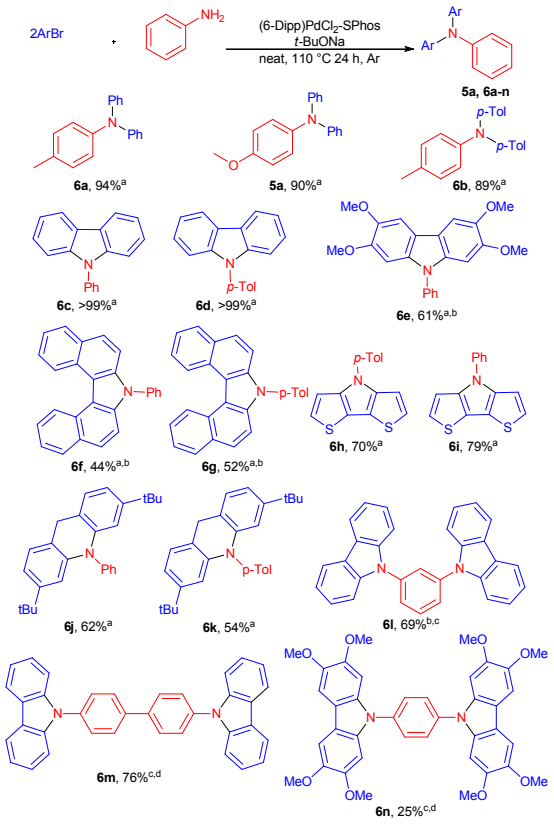
All the examples described above clearly showed that the developed catalyst **3a** was efficient in arylation of both primary and secondary amines. Thus, it was interesting if our catalyst is suitable for one-pot sequential double arylation of primary amines (Table 5). We verified this approach to produce triarylamines. The commercially available tri-*p*-tolylamine (TTA, **6b**), a hole transport molecule[51, 52] was obtained in high yield, similar to 4-methyl-*N*,*N*-diphenylaniline (**6a**) and 4-methoxy-*N*,*N*-diphenylaniline (**5a**).

The success of one-pot solvent-free double arylation of primary amines prompted us to investigate applicability of our conditions to the synthesis of N-aryl carbazole derivatives via one-pot solvent-free diarylative cyclization (Scheme 2). Carbazoles have earned popularity as structural fragments of organic molecules used in electronic and optoelectronic devices,[51, 53-58] since they demonstrate unique thermal, electric, and optic properties,[59-63] they also demonstrate wide scope of biological activity.[64, 65]



Scheme 2. One-pot diarylative cyclization reaction.

Table 5. Double arylation of arylamines.



[a] Reaction conditions: arylbromide (1.0 mmol, 2 equiv.), arylamine (0.5 mmol, 1 equiv.), (6-Dipp)$PdCl_2$-SPhos (2 mol %), *t*-BuONa (2.4 equiv.), neat, 110 °C, 24h. [b] 150 °C.[c] aryldiamine (0.5 mmol, 1 equiv.), 2,2'-dibromobiphenyl (1.0 mmol, 2 equiv.), (6-Dipp)$PdCl_2$-SPhos (4 mol %), *t*-BuONa (4.8 equiv.). [d] 170 °C.

Implementation of our solvent-free conditions allowed us to obtain broad spectrum of N-arylcarbazole derivatives. Amination of 2,2'-dibromobiphenyl with aniline and *p*-toluidine afforded carbazoles **6c** and **6d** in virtually quantitative yields. In some cases used dibromobiaryles have melting points above 150 °C, in such cases reactions were performed at 150 or 170 °C as indicated in Table 5. Interestingly, such harsh reaction conditions did not diminish catalytic activity of the complex **3a**. Thus, tetra-methoxycarbazole derivative **6e** was isolated in 61% yield when reaction was performed at 150 °C. The same reaction conditions were employed for synthesis of dibenzo[*c,g*]carbazole derivatives **6f** and **6g**, yielding the products in 44 and 52%, respectively, whereas the only reported yield of **6f** synthesis was only 1 %.[66] These molecules, containing flat bis-naphthelene fragment, can be applied to produce materials for excimer emission. [56, 59]

Dithieno[3,2-*b*:2',3'-*d*]pyrrole derivatives **6h** and **6i**, congeners of carbazole, were isolated in 70 and 79% yields, respectively. These compounds are also interesting from the prospect of their unique physical properties.[67-71] The main synthesis method of this class of compounds has been intramolecular palladium-catalyzed ($Pd_2(dba)_3$/P*t*Bu_3[56, 72] or $Pd_2(dba)_3$/BINAP[73] systems) amination of 3,3'-dibromo-2,2'-bithiophene in toluene. Our approach allows to produce these compounds with comparable yields, but does not require solvents usage.

Analogous diarylative cyclization of 2,2'-dibromo-4,4'di-*tert*-butyldiphenylmethane afforded novel N-arylated dihydroacridines **6j** and **6k** in good yields. Derivatives of N-aryl dihydroacridine are valuable source for the synthesis of acrydinium type photocatalysts[74] and useful building blocks in supramolecular chemistry for assembly of molecular nanomotors.[75] Previously, the most popular method of dihydroacridines synthesis was a multistep approach: reduction of acridinon to dihydroacridine with further *N*-arylation of NH-dihydroacridine.[76, 77] Our approach allows to reduce the synthesis to a single step.

Finally, we tried diarylative cyclization to obtain different bis(9*H*-carbazole-9-yl)arenes, which have a numerous applications in a field of organic electronics. [57, 78-80] Because of high melting points of both starting materials, syntheses of **6m** and **6n** were performed at 170 °C, whereas **6l** was synthesized at 150 °C. Our conditions allowed solvent-free synthesis of these compounds for the first time.

Conclusions

In summary, a series of novel mixed er-NHC/phosphine palladium(II) complexes was synthesized and tested in solvent-free Buchwald-Hartwig amination reaction of primary and secondary amines. Complex **3a**, bearing (6-Dipp) NHC and SPhos as ligands, was found to be the most efficient catalyst for both types of amination reactions.

It turned out, that complex **3a** was capable to effectively catalyze solvent-free diarylative cyclization between arylamines and dibromobiaryls / dibromodiphenylmethane/ dibromodithiophen affording N-arylated carbazoles, dihydroacridines and dithieno[3,2-*b*:2',3'-*d*]pyrroles. These types of compounds were synthesized via solvent-free approach for the first time.

Hence, our study is a valuable proof of concept for catalytic activity synergistic enhancement by NHC/phosphine combination on the same palladium centre.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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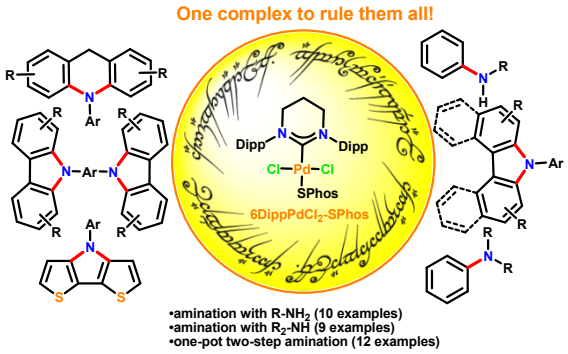

Single catalyst for solvent-free Buchwald-Hartwig amination with both primary and secondary amines and diarylative cyclizations.