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Full Paper

Solvent-Free C–N Cross-Coupling

Solvent-Free Buchwald–Hartwig (Hetero)arylation of Anilines, Diarylamines, and Dialkylamines Mediated by Expanded-Ring N-Heterocyclic Carbene Palladium Complexes

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Abstract: A highly efficient solvent-free protocol for the Buchwald–Hartwig (hetero)arylation of anilines, diarylamines, and dialkylamines mediated by the expanded-ring N-heterocyclic carbene palladium complex (THP-Dipp)Pd(cinn)Cl [THP-Dipp = 1,3-bis(2,6-diisopropylphenyl)-3,4,5,6-tetrahydropyrimidin-2-ylidene; cinn = cinnamyl, 3-phenylallyl] was developed. The catalytic protocol was efficient for the coupling of amines and (hetero)aryl chlorides and bromides bearing donor, acceptor, and bulky substituents.

Introduction

The Buchwald–Hartwig amination reaction is a powerful tool in modern synthetic organic chemistry. This reaction has found a number of applications in the pharmaceutical and fine-chemical industries.[1] Thus, it is highly important to develop efficient, selective, high-yielding, and "green" environmentally friendly and safe protocols for this reaction.[2] The measure of "greenness" of a process is the *E* factor, introduced by Sheldon.[3] It is defined as the ratio of weight of waste to weight of product. The *E* factor for most fine chemicals exceeds 100. The largest contributors to the magnitude of the *E* factor are organic solvents, many of which are ecologically harmful and require expensive regeneration. Thus, elimination of solvents from organic synthesis is of high importance. In the last two decades, several approaches to eliminate solvents from organic synthesis were developed.[4] However, solvent-free methods for Buchwald–Hartwig amination remain rare.

The first example of the solvent-free amination of aryl bromides catalyzed by $Pd(OAc)_2$/DPEPhos [DPEPhos = (oydi-2,1-phenylene)bis(diphenylphosphine)] was reported in 2003 by Beletskaya et al.[5] The first example of the solvent-free amination of aryl chlorides catalyzed by $Pd_2(dba)_3$/IAPU (dba = dibenzylideneacetone; IAPU = 2,8,9-triisobutyl-2,5,8,9-tetraaza-1-phosphabicyclo[3.3.3]undecane) was reported in 2011 by Beccalli et al.[6] However, this protocol was limited to the use of indolines at high temperature and gave moderate yields of the products. In 2012, Tardiff and Stradiotto reported the solvent-free coupling of aryl chlorides efficiently catalyzed by the $[Pd(cinn)Cl]_2$/Mor-DalPhos [cinn = cinnamyl, 3-phenylallyl; Mor-DalPhos = di(1-adamantyl)-2-morpholinophenylphosphine] system.[7] The bulky N-heterocyclic carbene palladium complex [Pd(IPr*)(cinn)Cl] {IPr* = 1,3-bis[2,6-bis(diphenylmethyl)-4-methylphenyl]imidazol-2-ylidene} showed excellent activity in an efficient solvent-free protocol for the Buchwald–Hartwig amination of nonactivated aryl halides, as described by Nolan in 2013.[8] Yet, heteroaryl halides were out of the scope of this reaction, and only four examples of the coupling of secondary amines were presented. Recently, our group developed a highly efficient solvent-free protocol for the Buchwald–Hartwig amination of (hetero)aryl halides by using secondary amines. The reaction was mediated by the $Pd(OAc)_2$/RuPhos (RuPhos = 2-dicyclohexylphosphino-2′,6′-diisopropoxybiphenyl). catalytic system in air. Various (hetero)aryl halides were coupled with diaryl, alkyl–aryl, and dialkylamines in good to excellent yields.[9] Recently Khalafi-Nezhad demonstrated an efficient magnetically separable catalyst for the Buchwald–Hartwig coupling of secondary aliphatic amines and aryl halides under solvent-free conditions.[10]

In this contribution, we report on the development of a catalytic system for the Buchwald–Hartwig coupling of anilines and (hetero)aryl halides under solvent-free conditions. This reaction is mediated by the expanded-ring N-heterocyclic carbene palladium complex (THP-Dipp)Pd(cinn)Cl [THP-Dipp = 1,3-bis(2,6-diisopropylphenyl)-3,4,5,6-tetrahydropyrimidin-2-ylidene]. Together with the previously developed $Pd(OAc)_2$/RuPhos system,[9] these two catalysts constitute a toolbox for the highly efficient solvent-free coupling of anilines, diarylamines, and dialkylamines with (hetero)aryl halides.

Results and Discussion

To find optimal conditions for the full arylation of anilines to give triarylamines under solvent-free conditions, we tested vari-

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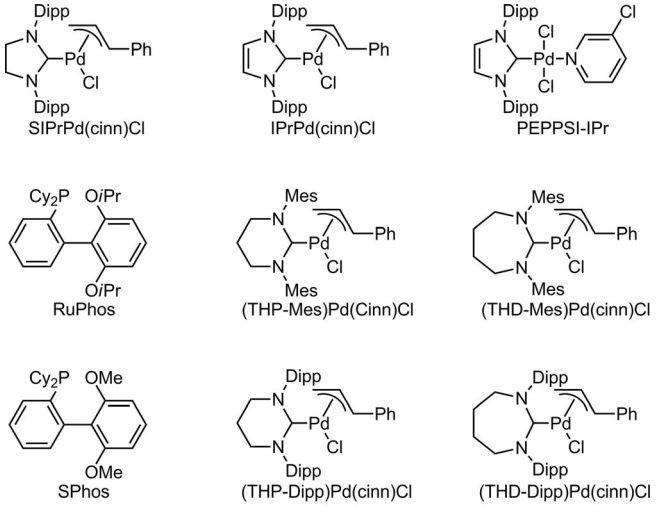
ous palladium sources as precatalysts (Figure 1): conventional $Pd(PPh_3)_4$, $(PPh_3)_2PdCl_2$, $[P(o\text{-Tol})_3]_2PdCl_2$; the well-defined phosphine-based catalytic systems $Pd(OAc)_2$/RuPhos and $Pd(OAc)_2$/2-dicyclohexylphosphino-2′,6′-dimethoxybiphenyl (SPhos);[11] the N-heterocyclic carbene (NHC) complexes SIPrPd(cinn)Cl, IPrPd(cinn)Cl,[12] and PEPPSI-IPr;[13] a mixture of $Pd(OAc)_2$ and IPr•HCl;[14] and complexes bearing expanded-ring NHCs (er-NHCs) such as (THP-Mes)Pd(cinn)Cl, (THP-Dipp)Pd(cinn)Cl, (THD-Mes)Pd(cinn)Cl, and (THD-Dipp)Pd(cinn)Cl.[15] After heating a mixture of aniline and bromobenzene (2.2 equiv.) in the presence of a palladium catalyst (2 mol-%) and *t*BuONa (2.4 equiv.) as a base under an atmosphere of argon at 110 °C for 24 h we were able to obtain triphenylamine in excellent yield by using the er-NHC complexes (THP-Mes)Pd(cinn)Cl, (THP-Dipp)Pd(cinn)Cl, and [(THD-Dipp)Pd(cinn)Cl] (see the Supporting Information; Table S1, entries 10–12). Other palladium sources that were tested were inefficient and either the starting materials were recovered or trace amounts of diphenylamine were obtained (Table S1, entries 1–9, 13, and 14). The highest activity was exhibited by (THP-Dipp)Pd(cinn)Cl, which gave an almost quantitative yield of the product.



SIPr = N,N'-bis(2,6-diisopropylphenyl)-4,5-dihydroimidazol-2-ylidene
IPr = N,N'-bis(2,6-diisopropylphenyl)imidazol-2-ylidene
THP-Mes = 1,3-bis(2,4,6-trimethylphenyl)-3,4,5,6-tetrahydropyrimidin-2-ylidene
THP-Dipp = 1,3-bis(2,6-diisopropylphenyl)-3,4,5,6-tetrahydropyrimidin-2-ylidene
THD-Mes = 1,3-bis(2,4,6-trimethylphenyl)-3,4,5,6-tetrahydrodiazepin-2-ylidene
THD-Dipp = 1,3-bis(2,6-diisopropylphenyl)-3,4,5,6-tetrahydrodiazepin-2-ylidene
cinn = cinnamyl, 3-phenylallyl
Mes = 2,4,6-trimethylphenyl
Dipp = 2,6-diisopropylphenyl

Figure 1. Structures of ligands.

Expanded-ring NHCs offer markedly different steric and electronic properties than their five-membered-ring counterparts. Expansion of the ring leads to a significant increase in their donor properties; simultaneously, the steric demands of such ligands increase dramatically.[16] We suppose that these factors are the reasons why the er-NHC complexes have higher activities than five-membered-ring NHC and phosphine complexes in a number of catalytic transformations.[17a–17e,15a,15b,17f,15c,17g]

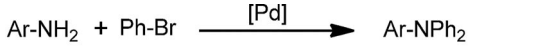
Different loadings of (THP-Dipp)Pd(cinn)Cl were tested. A 2 mol-% loading of the palladium catalyst was found to be optimal for efficient cross-coupling. A decrease in the amount of (THP-Dipp)Pd(cinn)Cl to 1 and 0.5 mol-% led to a significant decrease in the yields of triphenylamine to 59 and 37 %, respectively (see Table S2).

We examined the performance of bases other than *t*BuONa and found that in all cases the yields of triphenylamine decreased significantly (Table S3, entries 5–7). The use of *t*BuOK, *t*BuOLi, and K_2CO_3 as bases gave triphenylamine in yields of 85, 33, and 26 %, respectively. In the presence of KOH and NaOH, only starting materials were isolated from the mixture. Utilization of K_3PO_4 and Cs_2CO_3 provided trace amounts of triphenylamine (Table S3, entries 1–4).

A temperature of 110 °C was used in all experiments to melt the reaction mixture. In some cases, the mixture solidified at high levels of conversion.

The scope and limitations of the solvent-free protocol for the diarylation of anilines mediated by (THP-Dipp)Pd(cinn)Cl was studied for two model reactions: the diphenylation of various anilines by using phenyl bromide (Table 1) and the diarylation of aniline with various substituted (hetero)aromatic chlorides and bromides (Table 2).

Table 1. Coupling of various anilines with bromobenzene.[a]



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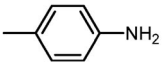
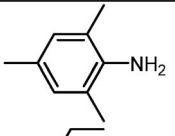
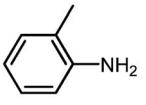
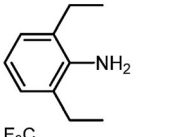
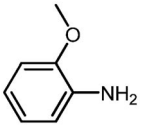
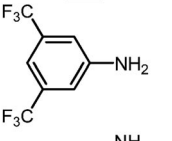
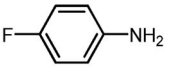
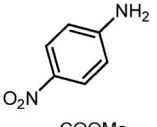
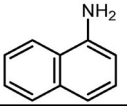
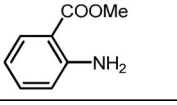
1		99	6		99
2		99	7		33
3		>99	8		>99
4		>99	9		–
5		97	10		–

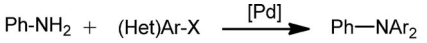
[a] Reaction conditions: (THP-Dipp)Pd(cinn)Cl (2 mol-%), PhBr (2.2 equiv.), *t*BuONa (2.4 equiv.), neat, 110 °C, 12 h, Ar. [b] Yield of isolated product.

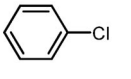
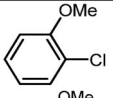
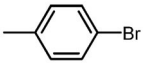
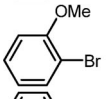
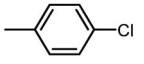
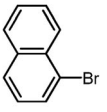
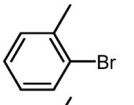
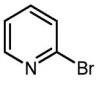
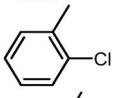
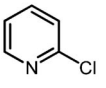
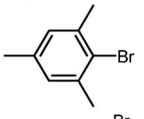
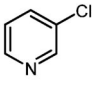
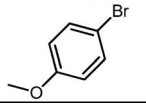
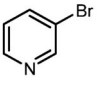
The diphenylation of alkyl-, donor-, and acceptor-substituted anilines proceeded in near-quantitative yields, except for 2,6-diethylaniline (Table 1, entry 7). The arylation of anilines sensitive to strong bases was unsuccessful (Table 1, entries 9 and 10).

The diarylation of aniline with (hetero)aryl chlorides and bromides gave high yields, except for aryls bearing *ortho* substituents. Thus, coupling with 2-bromotoluene and 2-chlorotoluene led to moderate yields of the products (Table 2, entries 4

and 5), whereas for mesityl bromide, 2-chloroanisole, and 2-bromoanisole no diarylation products were obtained (Table 2, entries 6, 8, and 9). In these cases, monoarylation took place. We suppose that steric crowding by the *ortho* substituents hindered addition of the second aryl group.

Table 2. Coupling of aniline with various haloarenes.[a]



#	(Het)ArAr-X	Yield[b] [%]	#	(Het)ArAr-X	Yield[b] [%]
1		99	8		0[c]
2		99	9		0[c]
3		99	10		94
4		62	11		99
5		53	12		99
6		0[c]	13		99
7		95	14		99

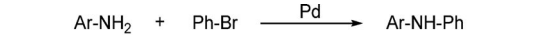
[a] Reaction conditions: (THP-Dipp)Pd(cinn)Cl (2 mol-%), (Het)ArX (2.2 equiv.), *t*BuONa (2.4 equiv.), neat, 110 °C, 12 h, Ar. [b] Yield of isolated product. [c] Monoarylated product in high yield was obtained, see Table 4.

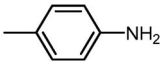
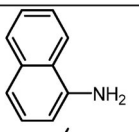
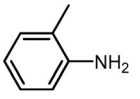
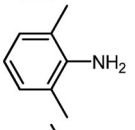
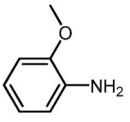
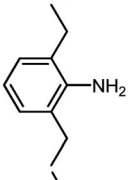
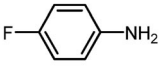
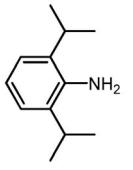
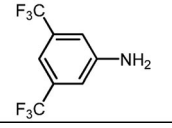
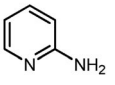
Given that the diarylation reaction was highly efficient only for *ortho*-unsubstituted substrates, we studied the first and second arylation steps in more detail. Monoarylation was studied for two model reactions: the phenylation of various anilines by using bromobenzene (Table 3) and the monoarylation of aniline with various substituted (hetero)aromatic chlorides and bromides (Table 4).

In all cases, except for challenging 2-aminopyridine[18] (Table 3, entry 10), the addition of the phenyl group to the anilines proceeded in near-quantitative yields. Notably, monoarylation proceeded efficiently for donor, acceptor, and even highly sterically encumbered (Table 3, entries 7–9) anilines.

The monoarylation of aniline with (hetero)aryl chlorides and bromides mediated by (THP-Dipp)Pd(cinn)Cl proceeded with high efficiency. In most cases, high to quantitative yields were obtained for acceptor- and donor-substituted substrates in addition to sterically encumbered substrates. Even 3-halo-substituted pyridines[18] and 3-bromothiophene,[19] which are challenging substrates for the Buchwald–Hartwig amination, were coupled in good yields (Table 4, entries 15–17). A nonquantitative yield was obtained for the activated 1-bromo-4-nitrobenzene substrate. Most probably, this was due to its instability in the presence of a strong base (Table 4, entry 10).

Table 3. Coupling of arylamines with bromobenzene.[a]



#	ArNH$_2$	Yield[b] [%]	#	ArNH$_2$	Yield[b] [%]
1		99	6		99
2		99	7		99
3		99	8		99
4		99	9		99
5		96	10		60

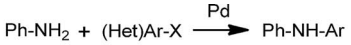
[a] Reaction conditions: (THP-Dipp)Pd(cinn)Cl (1 mol-%), PhBr (1 equiv.), *t*BuONa (1.2 equiv.), neat, 110 °C, 12 h, Ar. [b] Yield of isolated product.

Thus, we developed an efficient catalytic system, that is, (THP-Dipp)Pd(cinn)Cl, for the monoarylation of anilines (Tables 3 and 4). (Hetero)aryl halides and anilines bearing donor, acceptor, and sterically bulky substituents were efficiently used as coupling partners.

To note, monoarylated products were obtained with high selectivity. No measurable signals of diarylated products were detected in the ^{1}H NMR and ^{13}C NMR spectra (see the Supporting Information). TLC monitoring of the reactions revealed that the er-NHC-catalyzed first arylation is fast, whereas the second arylation is much slower. Thus, no significant contamination of monoarylated products with triarylamines was observed, even at high conversion levels.

To find optimal conditions for the arylation of diarylamines under solvent-free conditions, we re-examined the catalytic activities of the er-NHC precatalysts (THP-Mes)Pd(cinn)Cl, (THP-Dipp)Pd(cinn)Cl, (THD-Dipp)Pd(cinn)Cl, and (THD-Mes)Pd(cinn)Cl that showed the best performance in the diarylation of anilines (Table S1, entries 10–13). After heating a mixture of diphenylamine and bromobenzene (1.0 equiv.) in the presence of the palladium catalyst (1 mol-%) and *t*BuONa (1.2 equiv.) as the base under an atmosphere of argon for 24 h we were able to obtain triphenylamine in excellent yields by using (THP-

Table 4. Coupling of aryl halides with aniline.[a]



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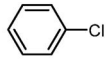
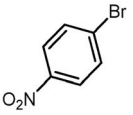
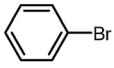
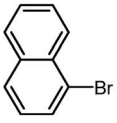
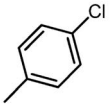
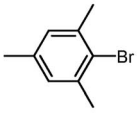
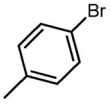
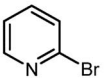
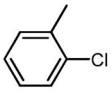
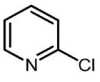
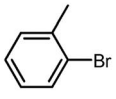
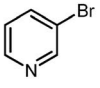
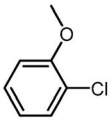
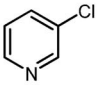
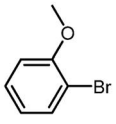
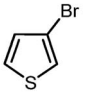
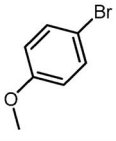
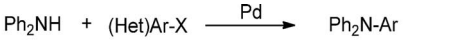
1		99	10		60
2		99	11		88
3		92	12		99
4		97	13		99
5		96	14		99
6		95	15		76
7		95	16		85
8		99	17		77
9		95			

[a] Reaction conditions: (THP-Dipp)Pd(cinn)Cl (1 mol-%), (Het)ArX (1 equiv.), *t*BuONa (1.2 equiv.), neat, 110 °C, 12 h, Ar. [b] Yield of isolated product.

Mes)Pd(cinn)Cl, (THP-Dipp)Pd(cinn)Cl, and (THD-Dipp)Pd(cinn)Cl (Table S4, entries 1–3). (THD-Mes)Pd(cinn)Cl was inefficient and the starting materials were recovered (Table S4, entry 4). The highest catalytic activity was exhibited by (THP-Dipp)Pd(cinn)Cl, which gave the desired product in near-quantitative yield (Table S4, entry 2).

The second arylation step was studied for the model diphenylamine substrate and various (hetero)aryl halides (Table 5). (Hetero)aryl chlorides and bromides unsubstituted in the *ortho* position give good to near-quantitative yields, whereas *ortho*-substituted substrates (Table 5, entries 11–14) did not provide any coupling products.

Table 5. Coupling of aryl halides with diphenylamine.[a]



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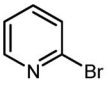
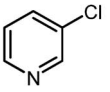
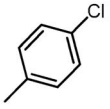
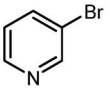
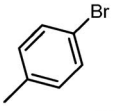
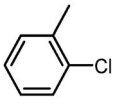
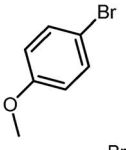
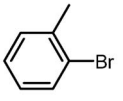
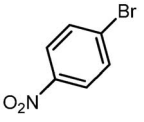
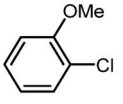
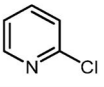
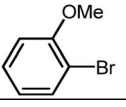
1		95	8		98
2		99	9		86
3		76	10		80
4		81	11		0
5		50	12		0
6		90	13		0
7		99	14		0

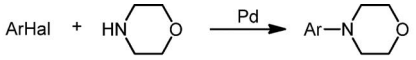
[a] Reaction conditions: (THP-Dipp)Pd(cinn)Cl (1 mol-%), (Het)ArX (1 equiv.), *t*BuONa (1.2 equiv.), neat, 110 °C, 12 h. [b] Yield of isolated product.

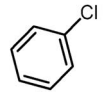
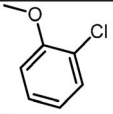
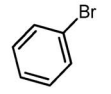
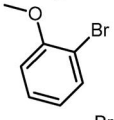
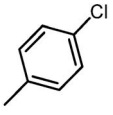
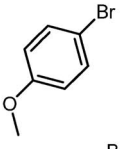
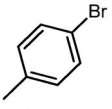
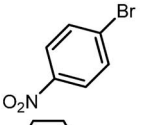
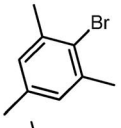
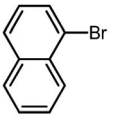
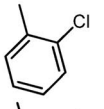
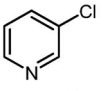
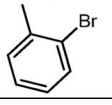
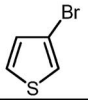
Consequently, the limitations of the solvent-free protocol by using (THP-Dipp)Pd(cinn)Cl as the precatalyst include the instability of the substrates in the presence of a strong base and *ortho*-substituted substrates for the second arylation step. The latter problem could be solved for solvent-free conditions by using the $Pd(OAc)_2$/RuPhos catalytic system.[9] *ortho*-Substituted haloarenes were coupled with diarylamines in high to quantitative yields. To note, $Pd(OAc)_2$/RuPhos was virtually inactive in the arylation of monoarylamines (Table S1, entry 6), whereas it was highly active in the arylation of diaryl, alkylaryl, and dialkylamines under solvent-free conditions.

To broaden the scope of the substrates, we tested the activity of (THP-Dipp)Pd(cinn)Cl in the coupling of dialkylamines. Morpholine was used as a model substrate (Table 6). In all cases, we were able to obtain near-quantitative yields. Thus, under our conditions secondary aliphatic amines were efficiently coupled with acceptor-substituted, donor-substituted, and sterically encumbered (hetero)aryl halides.

It was of particular interest for us to exhibit the utility of a developed protocol in real-life applications. Triarylamines are building blocks in many organic materials exhibiting optoelectronic properties.[20] The developed solvent-free method was tested in the synthesis of commercially available TTA,[21] MeO-TPD,[22] DDP,[23] and TPD (Figure 2),[24] all of which are used in organic light-emitting diodes (OLEDs).

Table 6. Coupling of aryl halides with morpholine.[a]



#	ArHal	Yield [%]	#	ArHal	Yield [%]
1		99	8		99
2		99	9		99
3		99	10		99
4		99	11		99
5		99	12		99
6		99	13		99
7		99	14		99

[a] Reaction conditions: (THP-Dipp)Pd(cinn)Cl (1 mol-%), (Het)ArX (1 equiv.), morpholine (1.2 equiv.), *t*BuONa (1.2 equiv.), neat, 110 °C, 12 h. [b] Yield of isolated product.

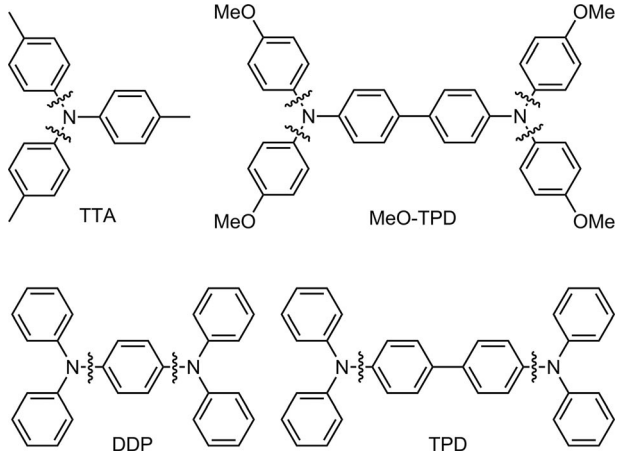
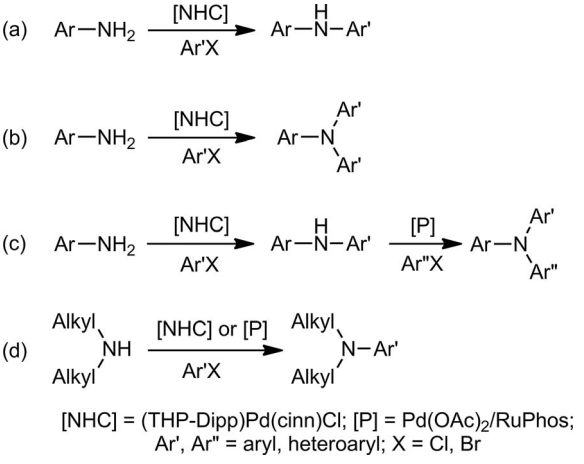


Figure 2. Structures of the synthesized OLED materials.

By using the (THP-Dipp)Pd(cinn)Cl catalyst, TTA was synthesized from *p*-toluidine and 4-bromotoluene in 99 % yield, and MeO-TPD was synthesized from benzidine and 4-bromoanisole in one step (see the Supporting information) in 95 % yield. Large-scale reactions followed by distillation of the products from the mixtures allowed pure TTA (95 %) and MeO-TPD (89 %) to be obtained without the use of organic solvents. Calculated *E* factors for the large-scale reactions were very low: 1.66 and 1.94 for TTA and MeO-TPD, respectively. DDP and TPD were obtained, both in 99 % yield, by reaction of diphenylamine with 1,4-dibromobenzene and 4,4′-dibromobiphenyl, respectively, by using the $Pd(OAc)_2$/RuPhos catalytic system.[9]

Conclusions

In conclusion, we developed a toolbox for the Buchwald–Hartwig arylation of primary and secondary arylamines and secondary alkylamines under solvent-free conditions. The results are summarized in Scheme 1. Anilines were mono(hetero)arylated with (hetero)aryl chlorides and bromides bearing donor, acceptor, and bulky substituents by using the er-NHC precatalyst (THP-Dipp)Pd(cinn)Cl (Scheme 1, a). For cases in which the (hetero)aryl halide was unsubstituted in the *ortho* position, we were the first to show that anilines could be di(hetero)arylated with the same catalyst in one step (Scheme 1, b). To note, reactions (a) and (b) were mediated only by expanded-ring NHC complexes. Conventional palladium sources, five-membered-ring carbene complexes, and well-defined bulky phosphine catalysts were not active under the solvent-free conditions. The introduction of *ortho*-substituted (hetero)aryl groups into the anilines was performed over two steps: first, (hetero)arylation mediated by (THP-Dipp)Pd(cinn)Cl; second, (hetero)arylation mediated by $Pd(OAc)_2$/RuPhos (Scheme 1, c).[9] Dialkylamines were (hetero)arylated in near-quantitative yields by using both the (THP-Dipp)Pd(cinn)Cl and $Pd(OAc)_2$/RuPhos catalytic systems (Scheme 1, d).



Scheme 1.

The developed protocol has a number of advantages: one, no solvent is used; two, a low catalyst loading is used; three, the bases are readily available; four, the reaction is activated by conventional heating (no milling, sonication, or other means needed). Thus, we developed a versatile, robust, highly active catalytic system for Buchwald–Hartwig amination. Furthermore, the reaction protocol can be scaled with no significant loss in efficiency.

This protocol meets the demands of "green" chemistry; Sheldon's *E* factors for given examples are presented above. We

believe that our findings will lead to broader and more efficient use of the Buchwald–Hartwig amination reaction in laboratory practice and the development of "green" industrial technologies.

Experimental Section

General Information: Unless otherwise stated, all reactions were performed under an argon atmosphere. All starting compounds, catalysts, and *t*BuONa were weighed in air. Chemicals and solvents were obtained from commercial sources and were used without further purification.

General Procedure for the Solvent-Free Preparation of Diarylamines by Diarylation of Primary Arylamines: A one-necked, round-bottomed, 10 mL flask equipped with a reflux condenser with an argon inlet and a magnetic stir bar was charged with the arylamine (1 mmol), the aryl halide (2.2 mmol), (THP-Dipp)Pd(cinn)Cl (13.2 mg, 0.02 mmol), and finally powdered *t*BuONa (230.6 mg,2.4 mmol). The mixture was degassed with freeze–pump–thaw cycles (3×). The flask was then transferred to a preheated oil bath (110 °C). After 12 h, the mixture was cooled, dissolved in CH_2Cl_2, and filtered through a short pad of silica gel. In some cases, additional purification by flash chromatography (hexanes/dichloromethane) was required.

General Procedure for the Solvent-Free Preparation of Diarylamines by Arylation of Primary Arylamines: A one-necked, round-bottomed, 10 mL flask equipped with a reflux condenser with an argon inlet and a magnetic stir bar was charged with the arylamine (1 mmol), the aryl halide (1 mmol), (THP-Dipp)Pd(cinn)Cl (6.6 mg, 0.01 mmol), and finally powdered *t*BuONa (115.3 mg,1.2 mmol). The mixture was degassed with freeze–pump–thaw cycles (3×). The flask was transferred to a preheated oil bath (110 °C). After 12 h, the mixture was cooled, dissolved in CH_2Cl_2, and filtered through short pad of silica gel. Flash chromatography (hexanes/dichloromethane) yielded the pure product.

General Procedure for the Solvent-Free Preparation of Diarylamines by Arylation of Diarylamines: Under an ambient atmosphere, a screw-cap vial equipped with a magnetic stir bar was charged with diphenylamine (169 mg, 1 mmol), the aryl halide (1 mmol), (THP-Dipp)Pd(cinn)Cl (6.6 mg, 0.01 mmol), and finally powdered *t*BuONa (115.3 mg, 1.2 mmol). The vial was transferred to a preheated oil bath (110 °C). After 12 h, the mixture was cooled, dissolved in CH_2Cl_2, and filtered through short pad of silica gel. In some cases, additional purification by flash chromatography (hexanes/dichloromethane) was required.

General Procedure for the Solvent-Free Synthesis of *N*-Arylmorpholines by Arylation of Morpholine: Under an ambient atmosphere, a screw-cap vial equipped with a magnetic stir bar was charged with morpholine (95.8 mg, 1.2 mmol), the aryl halide (1 mmol), (THP-Dipp)Pd(cinn)Cl (6.6 mg, 0.01 mmol), and finally powdered *t*BuONa (115.3 mg, 1.2 mmol). *CAUTION: In some cases a strong exothermic reaction was observed*. The vial was transferred to a preheated oil bath (110 °C). After 12 h, the mixture was cooled, dissolved in CH_2Cl_2, and filtered through short pad of silica gel.

General Procedure for the Solvent-Free Arylation of Diphenylamine with Dibromoarenes: Under an ambient atmosphere, a screw-cap vial equipped with a magnetic stir bar was charged with diphenylamine (341 mg, 2.02 mmol), the dibromoarene (1 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 2 mol-%), RuPhos (18.7 mg, 0.04 mmol, 4 mol-%), and finally powdered *t*BuONa (231 mg,2.4 mmol). The vial was transferred to a preheated oil bath (110 °C). After 12 h, the mixture was cooled, dissolved in CH_2Cl_2, and filtered through short pad of silica gel.

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Keywords: Green chemistry · Cross-coupling · Amination · Palladium · Carbene ligands

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