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An Efficient Synthesis of *N*-(Hetero)arylcarbazoles: Palladium-Catalyzed Coupling Reaction between (Hetero)aryl Chlorides and *N*-Carbazolylmagnesium Chloride

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Dedicated to Professor Stephen L. Buchwald for his 60th birthday.

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Abstract: An efficient method for the synthesis of *N*-(hetero)arylcarbazoles, useful compounds for functional materials, is reported. Various (hetero)aryl chlorides reacted with *N*-carbazolylmagnesium chloride in the presence of a palladium catalyst (0.05 to 0.2 mol%) prepared from allylpalladium(II) chloride dimer {[PdCl(allyl)]$_2$} and di-*tert*-butyl(2,2-diphenyl-1-methylcyclopropan-1-yl)phosphine (cBRIDP) under mild conditions (110 °C) in a short period of time (15 min to 2 h) to give *N*-(hetero)arylcarbazoles in high yields. The reactions of bromochlorobenzenes proceeded in favour of the bromo group to afford *N*-(chlorophenyl)carbazoles in a highly selective manner. Functional materials for use in organic light-emitting diodes, such as mCP, 26mcPy, CBP and TCB, were also obtained in high yields within 15 min by the reaction of (hetero)aryl polyhalides. Optimization of the reaction conditions and a postulated catalytic cycle for the reaction are also discussed.

Keywords: amination; conducting materials; cross-coupling; Grignard reaction; palladium; phosphane ligands

N-(Hetero)arylcarbazoles are useful as functional materials,[1] and various methods for the synthesis of these compounds have been reported to date.[2] Among these methods, the reaction between carbazole and a (hetero)aryl chloride[3–5] is attractive from an industrial perspective, since (hetero)aryl chlorides are generally inexpensive and readily available compared to other (hetero)aryl halides. With regard to the development of functional materials having *N*-(hetero)arylcarbazole moieties, it is important to be able to introduce the (hetero)aryl groups with a variety of *electron densities* to fine-tune the electronic properties of the materials. However, the scope of substrates in the reported methods has been mostly limited to *electron-deficient* aryl chlorides[3] and heteroaryl chlorides.[4] Although there have been a few reports on the use of *electron-neutral*/*electron-rich* aryl chlorides including our previous study,[5] the reactions required a stoichiometric amount of copper catalyst with light irradiation,[5a] or large quantities of a palladium (Pd) catalyst.[5b–d] Thus, a more universal and practical method that would enable the use of various (hetero)aryl chlorides regardless of their *electron density* is highly desired. This report describes (i) the discovery of an efficient Pd-catalyzed coupling reaction between various (hetero)aryl chlorides and *N*-carbazolylmagnesium chloride,[6] (ii) an investigation of the substrate scope and the successful application of this method to the synthesis of functional materials for use in organic light-emitting diodes (OLED), and (iii) a postulated catalytic cycle.

Initially, we investigated the unique behaviour of carbazole in the Buchwald–Hartwig reaction. When the reaction between chlorobenzene and diphenylamine was conducted with the use of sodium *tert*-butoxide (NaO-*t*-Bu) as a base in the presence of a Pd catalyst prepared from [PdCl(allyl)]$_2$ and Cy-vBRIDP,[7] the reaction went to completion within 2 h and gave triphenylamine in 99% yield. On the other hand, no coupling product was observed when carbazole was used in the place of diphenylamine under the same conditions (Scheme 1).[8]

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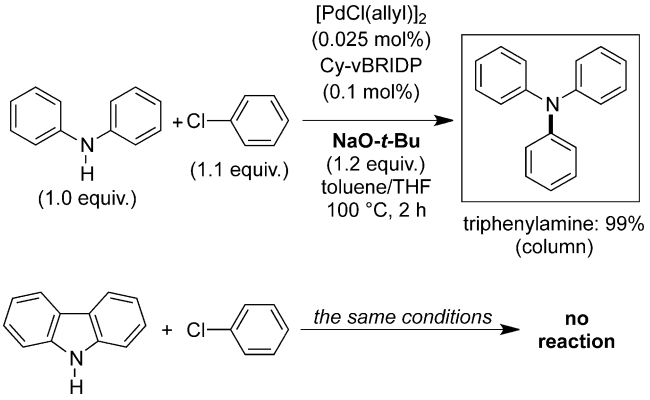
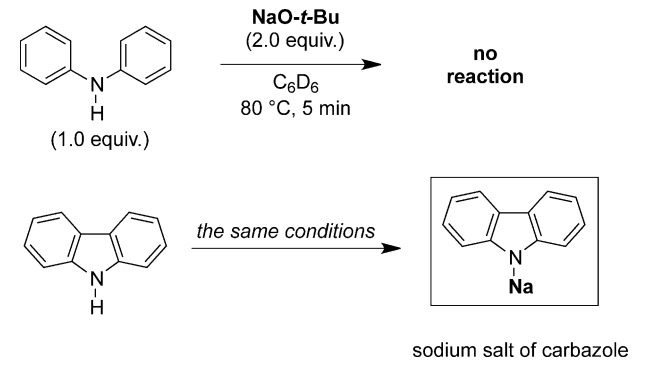


Scheme 1. Buchwald–Hartwig reaction between chlorobenzene and diphenylamine or carbazole.

To elucidate the cause of this difference in reactivity, we performed an NMR study. Diphenylamine and carbazole were, respectively, treated with NaO-*t*-Bu in benzene-d_6 (C_6D_6) at 80 °C for 5 min in an NMR tube, and analyzed by ^{1}H NMR. As a result, the spectrum for diphenylamine did not differ from that without NaO-*t*-Bu, whereas in the case of carbazole, the peak for the proton on the nitrogen atom disappeared along with the slight downfield shifts of each peak for the proton on the carbon atom.[8] This meant that carbazole was acidic enough ($pK_a = 19.9$ in dimethyl sulfoxide[9]) to react with NaO-*t*-Bu under these conditions to form its sodium salt (Scheme 2).



Scheme 2. NMR study: treatment of diphenylamine or carbazole with NaO-*t*-Bu in benzene-d_6.

The results of the NMR study suggested that the *transmetalation* of the sodium salt of carbazole to an arylpalladium(II) halide was involved in the catalytic cycle of the Buchwald–Hartwig reaction between carbazole and aryl halides with the use of NaO-*t*-Bu. According to the pioneering work by Hartwig et al., the arylpalladium(II) halide was transformed into an *anionic* bis(*N*-pyrrolyl)arylpalladate(II), which was less active toward reductive elimination than a *neutral* mono(*N*-pyrrolyl)arylpalladium(II), by the *transmetalation* of an excess of potassium salt of pyrrole.[10] In the coupling reaction of the sodium salt of carbazole, the Pd catalyst would be deactivated by the generation of a similar *anionic* palladate(II) complex. Thus, we hypothesized that the activity of the Pd catalyst could be compensated by the use of a magnesium salt of carbazole as a reactant, the nucleophilicity of which is estimated to be weaker than that of alkali metal salts due to the higher electronegativity of magnesium ($\chi = 1.31$) compared to those of alkali metals ($\chi = 0.79$ for caesium to 0.98 for lithium).[11] Based on the above working hypothesis, we attempted the coupling reaction between chlorobenzene and *N*-carbazolylmagnesium chloride [prepared *in situ* by the treatment of carbazole with *tert*-butylmagnesium chloride (*t*-BuMgCl)] using Pd catalysts prepared from $[PdCl(allyl)]_2$ and various ligands (Table 1).[8]

As expected, *N*-carbazolylmagnesium chloride reacted smoothly in the presence of the Pd catalyst derived from a proper ligand. Among the monophosphine ligands tested, those having a di-*tert*-butylphosphino [$(t\text{-Bu})_2$P] group (entries 2, 4, 6, 7, 9 and 11) were much superior in their activity to those having a dicyclohexylphosphino (Cy_2P) group (entries 1, 3, 5, 8 and 10). Especially, when cBRIDP,[5b] *t*BuXPhos[12] or BippyPhos[5c,13] was used as a ligand (0.4 mol%), the reaction went to completion with 0.1 mol% of $[PdCl(allyl)]_2$ within 2 h under reflux conditions (85 °C) to give *N*-phenylcarbazole (entries 4, 9 and 11). Unexpectedly, $(t\text{-Bu})_3$P, which is reportedly useful for the coupling reaction between carbazole and *electron-deficient* aryl chlorides,[3a] was inferior to monophosphine ligands having a $(t\text{-Bu})_2$P group (entry 12). In addition, the use of diphosphine ligands (DtBPF,[14] Xantphos[15] and *t*Bu-Xantphos[16]) or N-heterocyclic carbenes (NHCs) (IMes[17a] and SIPr[17b]), which have been reported to be suitable for the Buchwald–Hartwig amination as ligands (except for *t*Bu-Xantphos), resulted in no conversion (entries 13 to 17).

Further investigation revealed that the catalytic activity increased with elevated reaction temperature.[8] To raise the reflux temperature of reaction mixture (85 °C to 110 °C), a mixture of xylenes was chosen as a main solvent in the place of toluene, and the amount of tetrahydrofuran (THF) as a co-solvent was reduced by changing Grignard reagents from *t*-BuMgCl (1 mol/L in THF) to methylmagnesium chloride (MeMgCl) (3 mol/L in THF).[18] After investigation on the substrate ratio, we found that the catalytic activity further increased with the use of a slight excess of carbazole relative to aryl chlorides.[8] In addition, a competing methylation of aryl chlorides (Kumada–Tamao–Corriu coupling[19]) could be suppressed by the use of a slight excess of carbazole relative to MeMgCl. As a result of these investigations, we established the optimal substrate ratio as follows; aryl chloride (1.0 equiv.), carbazole (1.03 equiv.),

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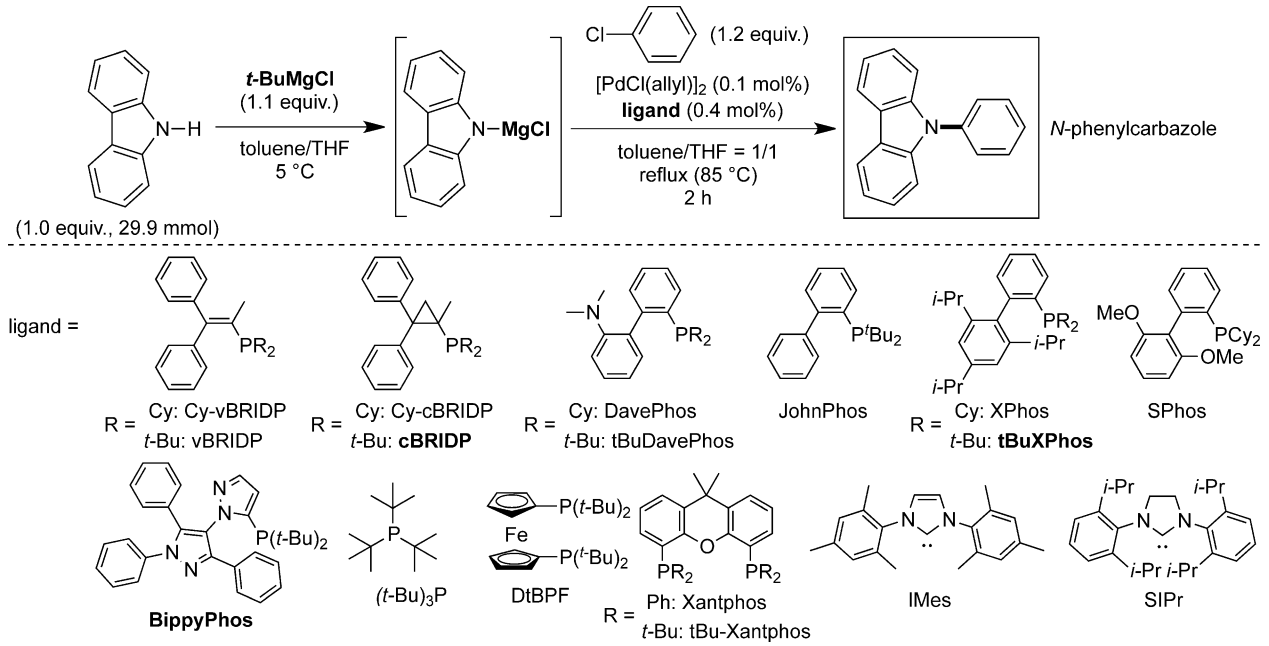
Table 1. Coupling reaction between chlorobenzene and *N*-carbazolylmagnesium chloride: screening of ligands.



Entry	Ligand	Conv. [%]	Entry	Ligand	Conv. [%]	Entry	Ligand	Conv. [%]
1	Cy-vBRIDP	1.0	7	JohnPhos	35.9	13	DtBPF[b]	0
2	vBRIDP	63.8	8	XPhos	3.4	14	Xantphos[b]	0
3	Cy-cBRIDP	0.2	9	***t*BuXPhos**	**>99.9**	15	*t*Bu-Xantphos[b]	0
4	**cBRIDP**	**>99.9**	10	SPhos	0.1	16	IMes[c]	0
5	DavePhos	0.1	11	**BippyPhos**	**>99.9**	17	SIPr[c]	0
6	*t*BuDavePhos	31.2	12	$(t\text{-Bu})_3$P[a]	15.7			

[a] Well-defined Pd[$(t\text{-Bu})_3$P]$_2$ (0.2 mol%) was used in the place of [PdCl(allyl)]$_2$/$(t\text{-Bu})_3$P.
[b] Diphosphine ligands were used in an amount of 0.2 mol%.
[c] Well-defined PdCl(allyl)(NHC) (0.2 mol%) was used in the place of [PdCl(allyl)]$_2$/NHC (NHC = IMes or SIPr).

MeMgCl (1.02 equiv.), xylenes (total 7 vol. per weight of carbazole) and THF (total 5 equiv.) (Table 2).

Under the optimized conditions, re-screening of ligands and bases was conducted by means of the coupling reaction between 4-chlorotoluene and carbazole as an evaluation system. Among the prescreened ligands, cBRIDP having a characteristic cyclopropane ring showed high performance even at a low catalyst loading (entries 1 to 5); the reaction with MeMgCl went to completion within 1 hour to give *N*-(4-methylphenyl)carbazole quantitatively in the presence of Pd catalyst prepared from 0.025 mol% of [PdCl(allyl)]$_2$ and 0.1 mol% of cBRIDP (entry 1). As expected, bases derived from alkali metals such as NaO-*t*-Bu[5b–d] and potassium carbonate (K_2CO_3[3a]) were scarcely effective under the same conditions (entries 6 and 7). The lower efficiency of NaO-*t*-Bu was not improved by the addition of anhydrous magnesium chloride ($MgCl_2$) (entry 8). The use of magnesium oxide (MgO), which had been used to prepare *N*-indolylmagnesium hydroxide from indole in 1,4-dioxane,[20] resulted in no conversion (entry 9). In addition, magnesium di-*tert*-butoxide [Mg(O-*t*-Bu)$_2$] was found to be ineffective regardless of the amount used; although Mg(O-*t*-Bu)$_2$ gave slightly better results in conversion than those from NaO-*t*-Bu (entries 10 and 11). The possible reasons for the inefficiency of these magnesium compounds were their lower solubility and/or basicity in aromatic hydrocarbons than those of MeMgCl.

With the protocol in hand, we then expanded the substrate scope to various aryl chlorides (Table 3). The reactions of *electron-rich* (entries 1 and 2), *electron-neutral* (entries 3 to 5) and *electron-deficient* aryl chlorides (entries 6 to 9) went to completion within 15 min to 2 h in the presence of the Pd catalyst prepared from [PdCl(allyl)]$_2$ and cBRIDP [i.e., PdCl(allyl)(cbridp):[3b,21] Pd-cBRIDP catalyst) (0.05 to 0.2 mol%) to give the corresponding *N*-arylcarbazoles in yields of 93 to 99%, respectively. However, no coupling products were observed in the reactions of aryl chlorides having a substituent at the *ortho* position

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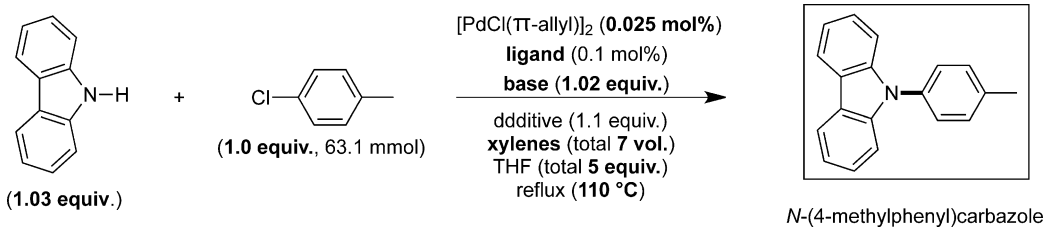
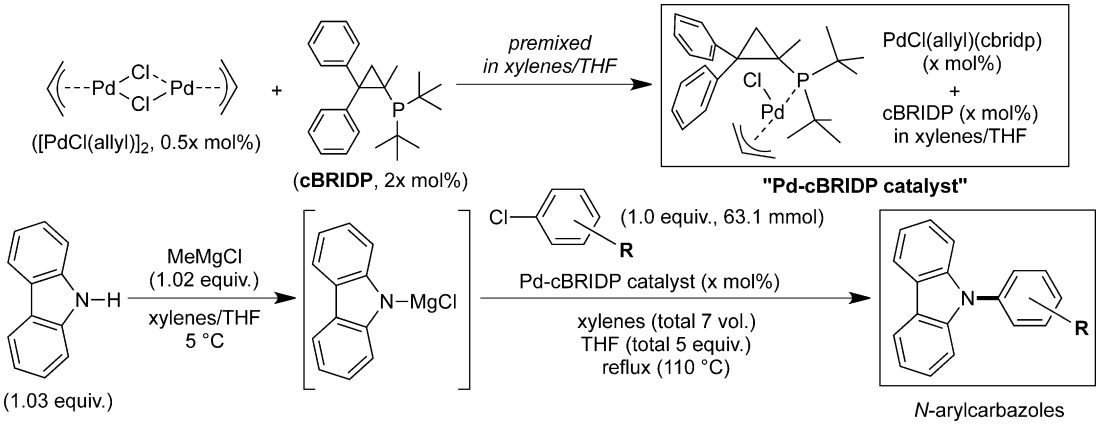
Table 2. Coupling reaction of carbazole and 4-chlorotoluene under the optimized conditions: re-screening of ligands and bases.



Entry	Ligand	Base	Additive	Time	Conv. [%]	Yield [%][a]
1	**cBRIDP**	**MeMgCl**	**none**	**1 h**	**>99.9**	**99**
2	vBRIDP	MeMgCl	none	3 h	>99.9	98
3	*t*BuXPhos	MeMgCl	none	3 h	96.4	88
4	JohnPhos	MeMgCl	none	3 h	80.8	–
5	BippyPhos	MeMgCl	none	3 h	62.4	–
6	cBRIDP	NaO-*t*-Bu	none	1 h	0.9	–
7	cBRIDP	K_2CO_3	none	1 h	2.2	–
8	cBRIDP	NaO-*t*-Bu	$MgCl_2$	1 h	1.2	–
9	cBRIDP	MgO	none	1 h	0	–
10	cBRIDP	$Mg(O\text{-}t\text{-}Bu)_2$[b]	none	1 h	3.0	–
11	cBRIDP	$Mg(O\text{-}t\text{-}Bu)_2$	none	1 h	4.8	–

[a] Isolated by silica gel column chromatography.
[b] $Mg(O\text{-}t\text{-}Bu)_2$ was used in an amount of 0.51 equiv.

Table 3. Coupling reactions of various aryl chlorides under the optimized conditions.



Entry	R	Catalyst	Time	Yield [%]	Entry	R	Catalyst	Time	Yield [%]
1	4-OMe	0.2 mol%	2 h	93[a]	9	4-CN	0.05 mol%	30 min	93[a]
2	3-OMe	0.1 mol%	30 min	99[b]	10	2-Me	0.05 mol%	1 h	–[c]
3	4-Me	0.05 mol%	1 h	99[b]	11	2-Cl	0.05 mol%	1 h	–[c]
4	3-Me	0.05 mol%	1 h	99[b]	12	4-CHO	0.05 mol%	1 h	–[d]
5	H	0.05 mol%	30 min	99[b]	13	4-COMe	0.05 mol%	1 h	–[c]
6	4-F	0.05 mol%	30 min	99[b]	14	$4\text{-}CO_2Me$	0.05 mol%	1 h	–[d]
7	$4\text{-}CF_3$	0.05 mol%	15 min	94[a]	15	4-NHCOMe	0.05 mol%	1 h	–[c]
8	4-COPh	0.05 mol%	15 min	99[b]					

[a] Isolated by recrystallization.
[b] Isolated by silica gel column chromatography.
[c] No reaction.
[d] Complex mixture.

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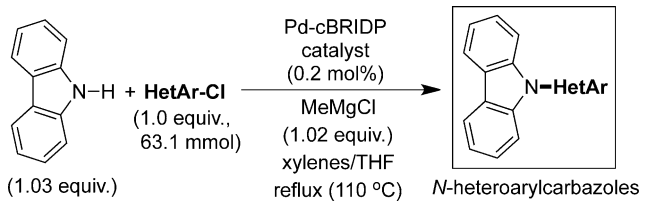
Table 4. Coupling reactions of heteroaryl chlorides.



Entry	HetAr	Time	Conv. [%]	Yield [%][a]
1	2-thienyl	2 h	>99.9	98
2	2-pyridyl	1 h	>99.9	98
3	2-pyridyl	1 h	0[b]	–
4	2-quinolyl	15 min	>99.9	99
5	2-quinolyl	15 min	0[b]	–

[a] Isolated by silica gel column chromatography.
[b] The experiment was conducted in the absence of Pd-cBRIDP catalyst.

(entries 10 and 11). In contrast to the result of entry 10, *o*-chlorotoluene reacted with diphenylamine under the same conditions to give *N*-(*o*-tolyl)diphenylamine quantitatively. These results suggested that the steric repulsion between the rigid *N*-carbazolylmagnesium chloride and *o*-tolylpalladium(II) chloride as an intermediate in the reaction was the cause of the inactivity of *o*-chlorotoluene. Although a cyano and benzoyl group tolerated the reaction conditions (entries 8 and 9), formyl, acetyl, methoxycarbonyl and acetylamino groups were incompatible due to the basicity and/or nucleophilicity of *N*-carbazolylmagnesium chloride (entries 12 to 15).

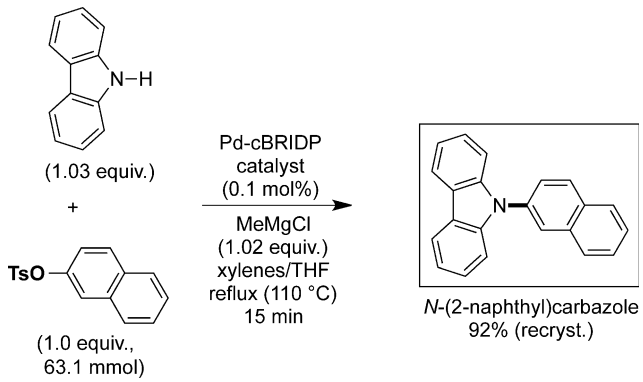
Heteroaryl chlorides could be used in the reaction (Table 4). The reactions between *N*-carbazolylmagnesium chloride and *electron-rich* 2-chlorothiophene, *electron-deficient* 2-chloropyridine or 2-chloroquinoline in the presence of Pd-cBRIDP catalyst (0.2 mol%) gave the corresponding *N*-heteroarylcarbazoles quantitatively (entries 1, 2 and 4). Control experiments in the absence of Pd-cBRIDP catalyst, where no coupling products were observed, showed that the reaction was catalytic rather than a nucleophilic aromatic substitution (entries 3 and 5).

Under the reaction conditions, 2-naphthyl tosylate also reacted with *N*-carbazolylmagnesium chloride for 15 min to give *N*-(2-naphthyl)carbazole in 92% yield (Scheme 3). To the best of our knowledge, this is the first example of the coupling reaction between aryl tosylate and carbazole. Unfortunately, the reaction lacked generality with respect to the substrate; 1-naphthyl tosylate and 4-biphenyl tosylate were not reactive under the same conditions. The reaction of 2-naphthyl mesylate[22] gave *N*-mesylcarbazole and 2-naphthol instead of the coupling product.

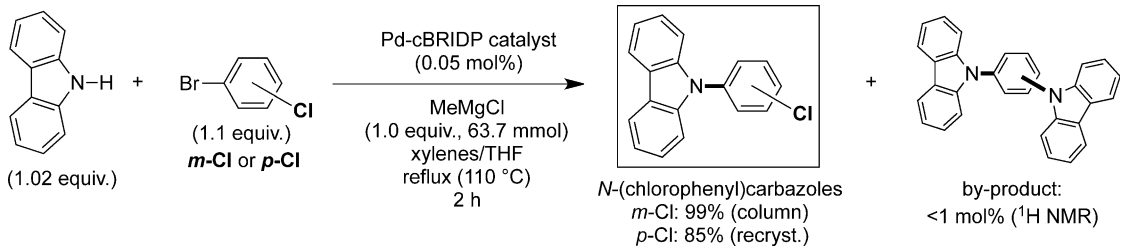
Aryl bromides as well as aryl chlorides could be understandably used in the reaction. Interestingly, the coupling reactions between bromochlorobenzenes and *N*-carbazolylmagnesium chloride gave *N*-(chlorophenyl)carbazoles, which are potentially useful as intermediates for functional materials, in high yields (>85%) with remarkable selectivity (>99%) (Scheme 4). These result suggested that the oxidative addition of Pd(0) species derived from Pd-cBRIDP catalyst to bromochlorobenzenes proceeded in favour of the bromo group in a highly selective manner.

The reaction was applied to the synthesis of functional materials for use in OLED (Scheme 5). When (hetero)aryl polyhalides were allowed to react with *N*-carbazolylmagnesium chloride in the presence of Pd-cBRIDP catalyst [0.1 mol% per halogeno group on the (hetero)aryl polyhalides], OLED materials such as mCP,[1c–e,7] 26mcPy,[1f] CBP[1a,b] and TCB[1g,h] were obtained within 15 min in high yields (>90%).[8]

The postulated catalytic cycle of the coupling reaction between carbazole and chlorobenzene is depicted in Figure 1. First, the oxidative addition of Pd(0) spe-



Scheme 3. Coupling reaction of 2-naphthyl tosylate.



Scheme 4. Bromo-selective coupling reactions of bromochlorobenzenes.

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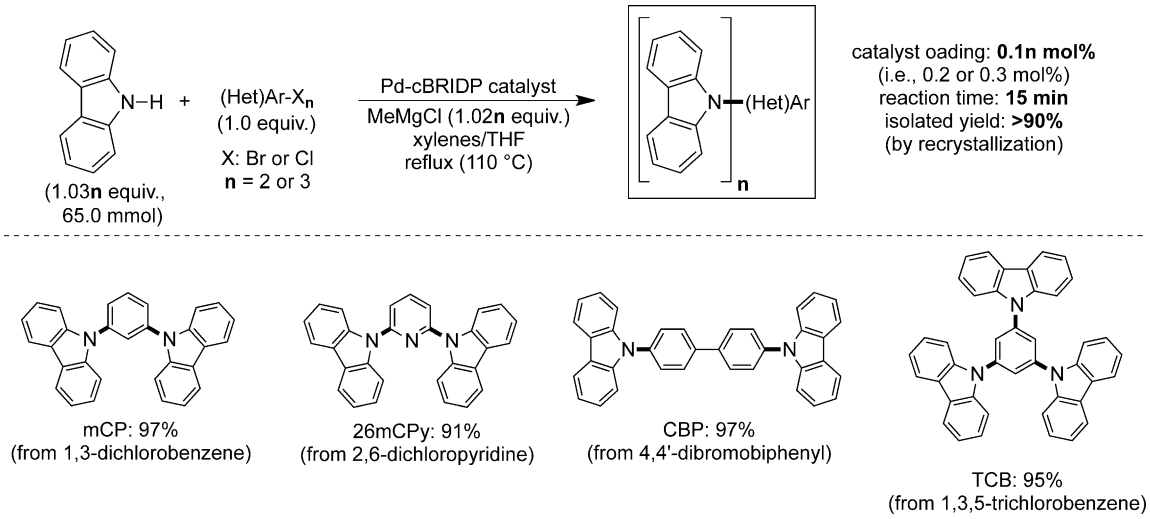

Scheme 5. Efficient synthesis of functional materials for use in OLED.

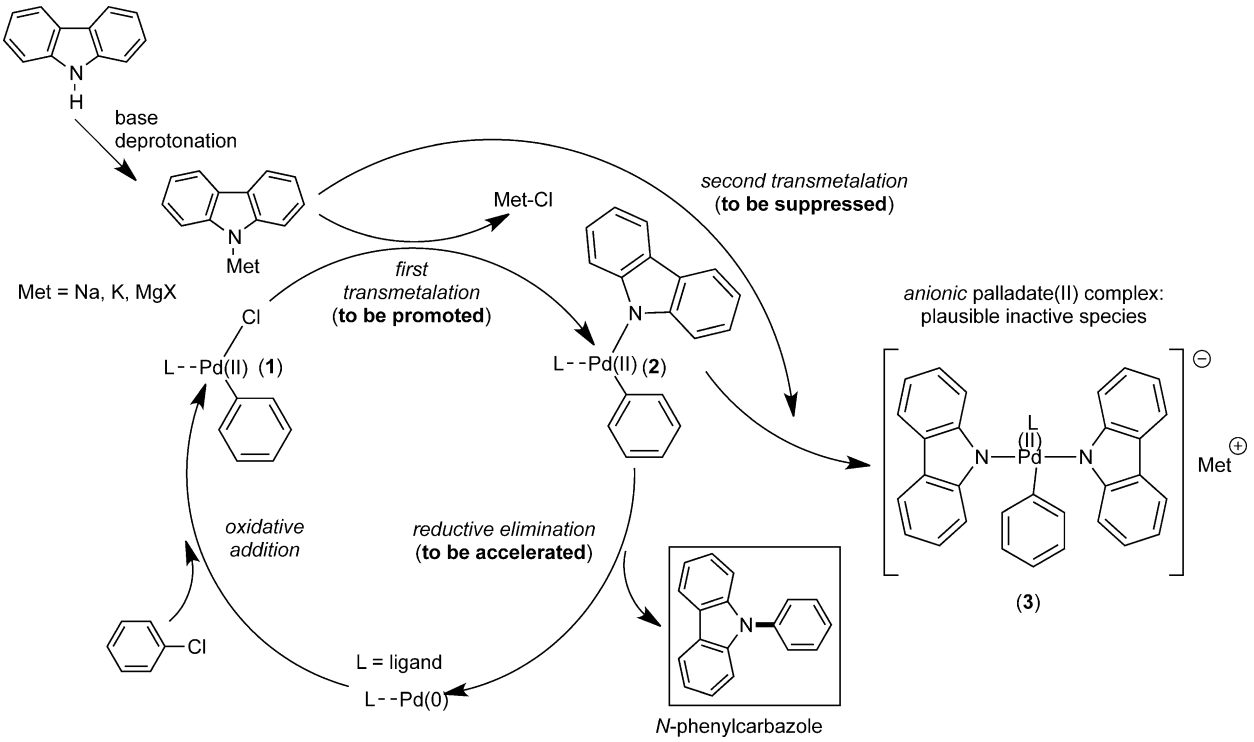

Figure 1. Postulated catalytic cycle of the coupling reaction between carbazole and chlorobenzene.

cies to chlorobenzene gives a phenylpalladium(II) chloride (**1**). Next, the *first transmetalation* of a salt of carbazole to complex **1** affords a *neutral* mono(*N*-carbazolyl)phenyl-palladium(II) (**2**). The excess salt would react with complex **2** (i.e., *second transmetalation*) to give an *anionic* bis(*N*-carbazolyl)phenylpalladate(II) (**3**) as the plausible inactive species. The role of the Grignard reagent is to decrease the nucleophilicity of the salt of carbazole and suppress the *second transmetalation*. Finally, *N*-phenylcarbazole is generated by the reductive elimination of Pd(0) species from complex **2**. However, the reductive elimination from *neutral* mono(*N*-pyrrolyl)arylpalladium(II), the electronic structure of which is similar to that of complex **2**, is known to be much slower than that from arylpalladium(II) amide, which is the intermediate for the Buchwald–Hartwig reaction of ordinary amines.[10] Therefore, higher temperature and ligands with suitable bulkiness, such as cBRIDP, are required to accelerate the reductive elimination with promoting the *first transmetalation*; diphosphine ligands (DtBPF, Xantphos and *t*Bu-Xantphos) and NHCs (IMes and

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SIPr) are thought to be so bulky that the *first transmetalation* is inhibited.

In conclusion, we have developed an efficient method for the synthesis of *N*-(hetero)arylcarbazoles by the Pd-catalyzed coupling reactions between (hetero)aryl chlorides and *N*-carbazolylmagnesium chloride. The reaction could be applied to various (hetero)aryl halides regardless of their *electron density*. The reaction proceeded under mild conditions in a short period of time with a smaller amount of catalyst compared to the conventional methods. The key to success was the use of Grignard reagent as a base to suppress the *second transmetalation* and cBRIDP as a ligand to accelerate the reductive elimination without inhibiting the *first transmetalation*. This method was used to efficiently synthesize known OLED materials, and could be useful for the development of new functional materials.

Experimental Section

Procedure for the Coupling Reaction between 4-Chlorotoluene and *N*-Carbazolylmagnesium Chloride: Synthesis of *N*-(4-Methylphenyl)carbazole

Preparation of Pd-cBRIDP catalyst: $[PdCl(allyl)]_2$ (5.8 mg, 0.025 mol%) and cBRIDP (22.2 mg, 0.1 mol%) were placed in a 50-mL, two-necked, round-bottomed flask, and the flask was equipped with a three-way stopcock, evacuated and filled with nitrogen. To the flask were added dehydrated THF (2.9 mL, 35.8 mmol, 0.57 equiv.), and the mixture was shaken for 1 min at room temperature under nitrogen and then diluted with dehydrated xylenes (11 mL) to prepare a mixture of PdCl(allyl)(cbridp) (0.05 mol%) and cBRIDP (0.05 mol%) in xylenes/THF (i.e., a Pd-cBRIDP catalyst solution) as a pale-yellow liquid; yield: 13.9 mL.

Preparation of N-carbazolylmagnesium chloride: A 200-mL, four-necked, round-bottomed flask equipped with a Teflon®-coated magnetic stirring bar, condenser, dropping funnel, thermometer, and a three-way stopcock was evacuated and filled with nitrogen. Carbazole (10.9 g, 65.0 mmol, 1.03 equiv.), dehydrated xylenes (55 mL) and dehydrated THF (5.3 mL, 65.0 mmol, 1.03 equiv.) were charged into the flask successively, and the resulting white slurry was cooled to 5 °C with the use of an ice-water bath. A THF solution of MeMgCl (3.22 mol/L, 20.0 mL, 64.4 mmol, 1.02 equiv.), containing 17.3 mL of THF (213.6 mmol, 3.39 equiv.), was placed in the dropping funnel and added dropwise to the slurry over 10 min at a rate so that the internal temperature was kept at 20 °C or lower with vigorous stirring under nitrogen; the slurry dissolved rapidly with the formation of bubbles of methane to afford a solution of *N*-carbazolylmagnesium chloride (1.02 equiv.) with a trace of carbazole as a dark-gray liquid. The dropping funnel was then washed with dehydrated xylenes (11 mL).

Coupling reaction: 4-Chlorotoluene (7.5 mL, 63.1 mmol, 1.0 equiv.) and the Pd-cBRIDP catalyst solution (13.9 mL, containing 0.05 mol% of the catalyst) were added to the solution of *N*-carbazolylmagnesium chloride prepared above, and the mixture was warmed to reflux temperature (*ca.* 108 to 112 °C) by the use of a silicone oil bath under nitrogen. The reaction mixture was then stirred for 1 hour under reflux conditions; as the coupling reaction proceeded, magnesium chloride precipitated. GC analysis of the sample prepared by washing of the diluted reaction mixture (*ca.* 30 μL) in toluene (*ca.* 1 mL) with saturated aqueous NH_4Cl (*ca.* 0.5 mL) indicated that 4-chlorotoluene was completely consumed after the coupling reaction.

Post treatment and isolation: After the reaction mixture had been cooled to room temperature by the use of a water bath, to the mixture were added tap-water (25 mL) and NH_4Cl (1.7 g, 31.8 mmol, 0.5 equiv.). The mixture was stirred for 5 min at room temperature and filtered by suction with filter paper and Celite® to remove insoluble materials. The aqueous layer was separated off from the filtrate by the use of a separating funnel. The filtrate was concentrated under vacuum to afford a residue, which was purified by silica gel column chromatography (eluent: *n*-hexane/toluene = 2/1) to give *N*-(4-methylphenyl)carbazole as a colorless solid; yield: 16.0 g (62.2 mmol, 99%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.14 (dt, *J* = 7.5, 0.9 Hz, 2H), 7.45–7.35 (m, 8H), 7.27 (ddd, *J* = 2.4, 5.7, 8.1 Hz, 2H), 2.48 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 141.1, 137.3, 135.0, 130.4, 127.0, 125.8, 123.2, 120.2, 119.7, 109.8, 21.2.

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