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Evaluation of Aromatic Amination Catalyzed by Palladium on Carbon: A Practical Synthesis of Triarylamines

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Abstract: A heterogeneous palladium on carbon (Pd/C)-catalyzed coupling between amines and aromatic halides including aromatic chlorides has been achieved using sodium *tert*-butoxide (NaO-*t*-Bu) and 1,1′-bis(diphenylphosphino)ferrocene (dppf) as a ligand in cyclopentyl methyl ether (CPME). The use of potassium *tert*-butoxide (KO-*t*-Bu) in place of NaO-*t*-Bu brought about the benzyne-mediated aromatic amination even without Pd/C and dppf, giving a mixture of regioisomers when 4-substituted bromobenzenes were employed as the substrate. The combination of Pd/C, dppf, NaO-*t*-Bu could be utilized for the syntheses of a broad range of triarylamines by replacing CPME with mesitylene which can provide a higher reaction temperature. The Pd/C could be quantitatively recovered and reused until at least the fourth cycle without any loss in catalytic activity. The quite low leaching of palladium ($<1.1\%$) was demonstrated by an inductively coupled plasma-atomic emission spectrometric analysis.

Keywords: amination; arylation; cross-coupling; palladium on carbon; triarylamines

Introduction

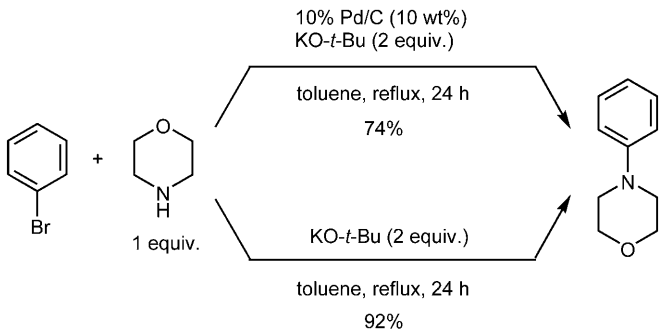
Arylamines are of increasing importance as synthons for the synthesis of artificial dyes, natural products, biologically active compounds such as pharmaceuticals and agrochemicals, and so on.[1] For the efficient preparation of arylamines, a variety of transition metal-mediated cross-coupling reactions between aryl halides and amines to create carbon-nitrogen bonds using copper,[2,3] palladium,[4–7] nickel,[8] and iron[9] catalysts have been recently reported. The homogeneous palladium-catalyzed aromatic aminations independently developed by Buchwald[5a] and Hartwig[5b] were a great success because of their wide range of applicability under relatively mild conditions.

Although the application of heterogeneous catalysts as alternatives to homogeneous ones has recently been investigated in a variety of organic chemical fields due to their reliable recyclability and avoidance of residual metals in the desired product which rends such catalysts most attractive from an environmental and toxicological point of view,[10,11] only a few heterogeneous catalysts were applied to the *N*-arylation of amines. Lipshutz utilized their handmade nickel on carbon (Ni/C) for the aromatic amination.[12] Very recently, Christensen[13] and Kobayashi[14] reported the applications of polymer-supported palladium catalysts for the aromatic amination; the former one used commercial fiber-supported palladium catalysts (FibreCat®), which were not reusable, while the latter one employed the newly investigated palladium catalyst which was embedded in a functionalized-polystyrene polymer, and was reusable. Palladium on carbon (Pd/C), which is a traditional heterogeneous catalyst, is readily available and was recently utilized for various kinds of cross-coupling reactions for carbon-carbon bond formations,[15] but it has not yet successfully been applied to the aromatic amination. Although Djakovitch utilized immobilized palladium catalysts including Pd/C for the aminations of aryl bromides, the regioselective introduction of amino groups was not achieved when the aryl bromides have a substituent on their benzene rings, because of the involvement of benzyne intermediates.[16] We now de-

scribe an efficient and *regioselective* Pd/C-catalyzed Buchwald–Hartwig amination, together with a practical synthetic protocol for the preparation of triarylamines.

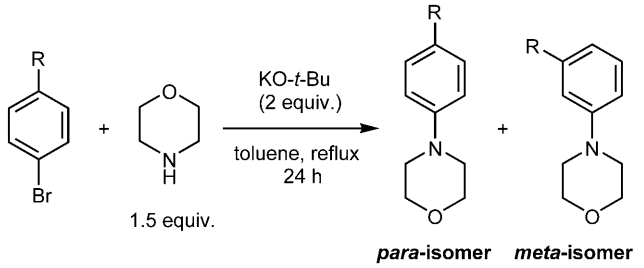
Results and Discussion

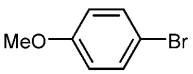
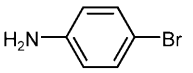
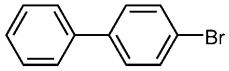
We initially investigated the Pd/C-catalyzed amination of bromobenzene with morpholine using KO-*t*-Bu as a base in toluene. The reaction successfully proceeded to give the desired *N*-phenylmorpholine in 74% yield, but the coupled product was obtained in 92% yield even without the Pd/C (Scheme 1). When the amination of bromobenzenes bearing a substituent at the 4 position was then examined in the absence of Pd/C (Table 1), the mixture of the 3- and 4-substituted aminobenzenes was obtained in each reaction, indicating that the reaction proceeded *via* the benzyne intermediates as Djakovitch observed.



Scheme 1. First attempt on aromatic amination.

Table 1. Aromatic amination *via* benzyne intermediate.



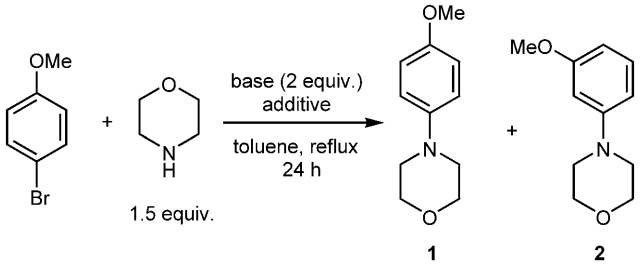
Entry	Ar–Br	Isolated Yield [%] *para*-isomer	*meta*-isomer
1		32	35
2		28	32
3		51	37

We next exchanged the base from KO-*t*-Bu to NaO-*t*-Bu (Table 2). The only difference in the counter cation of the base brought about a significant change in the reaction progress, and no coupled products were obtained without Pd/C (entry 2). When 10% Pd/C (2 mol%) was added to the reaction mixture, the formation of a trace amount of the desired *para*-adduct **1** was detected (entry 3), and the further addition of triphenylphosphine (3 mol%) afforded **1** in 3% yield without the formation of the corresponding *meta*-adduct **2** (entry 4). Since additional phosphine was expected to promote the reaction, we then screened a variety of phosphine ligands in the cross-coupling reaction between bromobenzene and morpholine (Table 3). Without Pd/C or ligands, no reaction took place (entries 1 and 2) indicating benzyne was never formed as an intermediate. The use of monodentate phosphine ligands (entries 3–12), including bulky and electron-rich biphenylphosphine ligands which achieved good conversions in homogeneous media[17] (entries 11 and 12), or flexible bidentate phosphine ligands (entries 13–15) led to a low yield of the *N*-phenylmorpholine, whereas the bulkier and stiffer bidentate phosphine ligands efficiently activated the catalysis (entries 16–18). Among these ligands 1,1′-bis(diphenylphosphino)ferrocene (dppf) was found to be the most effective for the reaction (entry 16), and the replacement of toluene with cyclopentyl methyl ether (CPME, bp 106 °C) completed the reaction to afford the desired phenylamine in 92% yield as the sole product (entry 19). Furthermore, the amount of NaO-*t*-Bu could be reduced to 1.5 equiv. to bromobenzene (entry 1, Table 4).

A wide range of haloarenes was examined for the coupling with morpholine under the optimized conditions [10% Pd/C (2 mol%), dppf (3 mol%), morpholine (1.5 equiv.), NaO-*t*-Bu (1.5 equiv.), CPME, reflux] (Table 4). Bromobenzenes bearing an electron-donating group, and naphthyl and pyridinyl bromides were effectively cross-coupled with morpholine (entries 2–5 and 11–13). The bromo group of 4-chlorobromobenzene was selectively replaced with morpholine (entry 6). For the phenyl bromides possessing an electron-withdrawing group on the benzene ring, Cs_2CO_3 was used as a base because NaO-*t*-Bu caused the decomposition of the electrophilic substituents due to its strong nucleophilicity (entries 7–10 and 16). Although the catalytic system was inactive towards conversions of electron-neutral chloroarenes (entries 14 and 15), the use of 4-cyanochlorobenzene possessing a relatively electron-poor benzene ring due to the electron-withdrawing cyano substituent afforded the cross-coupling product in 88% yield (entry 16).

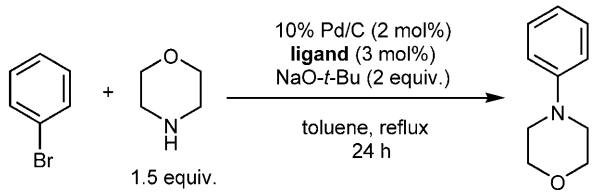
A variety of amines was applied to the Pd/C-catalyzed aromatic amination (Table 5). Primary, cyclic secondary, and aromatic amines were found to be good substrates for the reaction (Table 4 and en-

Table 2. Effect of base and additive.



Entry	Base	Additive	Isolated Yield [%]	
			1	**2**
1	KO-*t*-Bu	–	32	35
2	NaO-*t*-Bu	–	no reaction	
3	NaO-*t*-Bu	10% Pd/C (2 mol%)	trace	0
4	NaO-*t*-Bu	10% Pd/C (2 mol%), PPh_3 (3 mol%)	3	0

Table 3. Screening of ligands for the *N*-phenylation of morpholine.

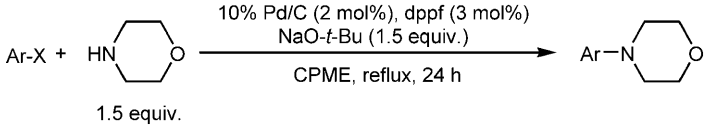


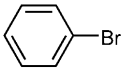
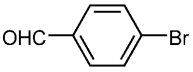
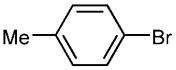
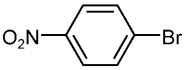
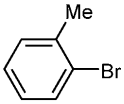
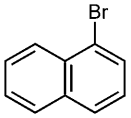
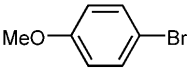
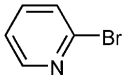
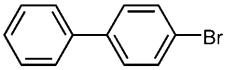
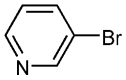
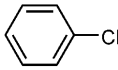
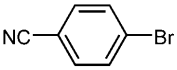
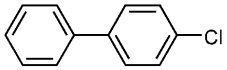
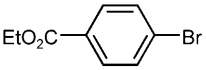
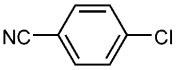
Entry	Ligand[a]	Yield [%][b]	
		unreacted PhBr	*N*-phenylmorpholine
1[c]	–	100	0
2	–	92	0
3	PPh_3	73	13
4	tri-2-tolylphosphine	88	3
5	tri-4-tolylphosphine	82	11
6	tris(4-methoxyphenyl)phosphine	80	8
7	tris(2,6-dimethoxyphenyl)phosphine	89	7
8	tris(4-chlorophenyl)phosphine	79	16
9	tricyclohexylphosphine	89	4
10	isopropyldiphenylphosphine	82	10
11	(2-biphenyl)dicyclohexylphosphine	68	25
12	(2-biphenyl)di-*tert*-butylphosphine	70	21
13	dppe	95	0
14	dppp	97	3
15	dppb	87	8
16	dppf	4	96
17	BINAP	2	84
18	Xantphos	30	61
19[d]	dppf	0	92[e]

[a] dppe = 1,2-bis(diphenylphosphino)ethane, dppp = 1,3-bis(diphenylphosphino)propane, dppb = 1,4-bis(diphenylphosphino)-butane, dppf = 1,1′-bis(diphenylphosphino)ferrocene, BINAP = 2,2′-bis(diphenylphosphanyl)-1,1′-biphenyl, Xantphos = 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene.
[b] Determined by GC analyses using *n*-undecane as the internal standard.
[c] Without Pd/C.
[d] CPME (1 mL) was used as a solvent.
[e] Isolated yield.

tries 1–3, 5, and 6, Table 5), while the use of dibutylamine, acyclic and aliphatic secondary amines, exhibited a very low reactivity presumably due to the high tendency for β-hydride elimination (entry 4).[18] The formation of diphenyloctylamine or triphenylamine as a by-product was observed for entries 1 and 5 based

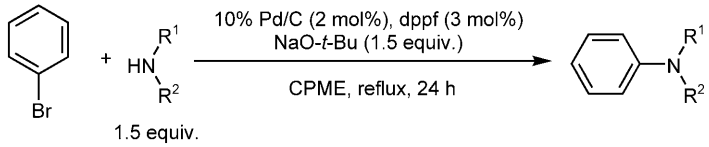
Table 4. Pd/C-catalyzed coupling of aryl halides with morpholine.

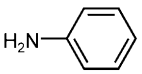
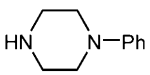
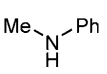


Entry	Ar-X	Yield [%][a]	Entry	Ar-X	Yield [%][a]
1		92	9[e]		42
2		86	10[d]		68
3		76	11		89
4[b]		72	12		97
5		80	13		77
6		90[c]	14		0
7[d]		100	15		3
8[d]		99	16[d]		88

[a] Isolated yield.
[b] 4 mol% of 10% Pd/C, 6 mol% of dppf, and 2 equiv. of NaO-*t*-Bu were used.
[c] 4-(4-Chlorophenyl)morpholine was obtained.
[d] 1.5 equiv. of Cs_2CO_3 was used instead of NaO-*t*-Bu.
[e] 2.5 equiv- of morpholine and 2 equiv- of Cs_2CO_3 were used.

Table 5. Pd/C-catalyzed coupling of bromobenzene with amines.



Entry	Amine	Yield [%][a]	Entry	Amine	Yield [%][a]
1[b]	H_2NOct	83	4[c]	$HNBu_2$	19
2		98	5[b]		96
3		81	6		78

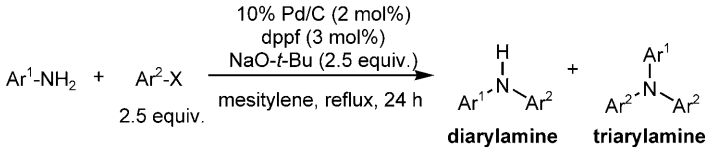
[a] Isolated yield.
[b] 5 equiv. of amine was used.
[c] 4 mol% of Pd/C, 6 mol% of dppf, and 2 equiv. of NaO-*t*-Bu were used.

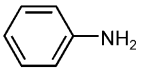
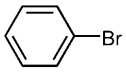
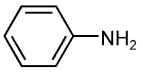
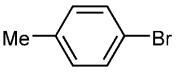
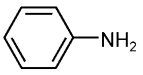
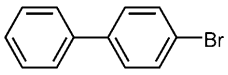
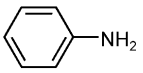
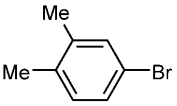
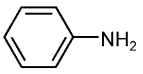
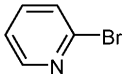
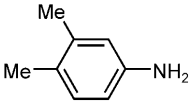
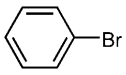
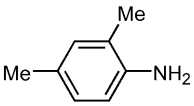
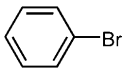
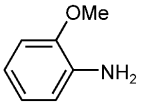
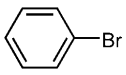
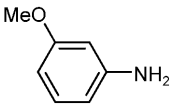
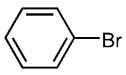
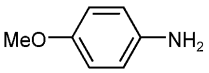
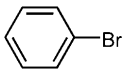
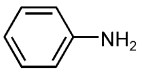
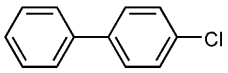
upon the second aromatic amination between the resulting (desired) secondary amine and bromobenzene although the use of an excess amount (5 equiv.) of the amines overcame the problem.

Application to Triarylamine Synthesis

Triarylamines have been attracting significant attention as charge transfer materials and are in use as a component of organic light-emitting diodes,[19,20] solar cells,[21] organic photoconductors,[22] etc. We next investigated the development of a practical synthetic method for the preparation of triarylamines using the present Pd/C-catalyzed aromatic amination (Table 6). The aromatic amination of bromobenzene and 4-bromotoluene (2.5 equiv.) with aniline using NaO-*t*-Bu (2.5 equiv.) and boiling mesitylene (bp 163 °C) as a solvent instead of CPME afforded the corresponding triarylamines in good yields (entries 1 and 2), although the use of 4-bromobiphenyl, 3,4-dimethylbromobenzene, and 2-bromopyridine as substrates gave a mixture of the desired triarylamine and the corresponding diarylamine (entries 3–5). The reaction of electron-rich dimethylanilines with bromobenzene gave only the triarylamines without any by-products (entries 6 and 7). Three regioisomers of anisidine were also used for the arylation (entries 8–10), on which the steric effect of the *ortho*-substituted methoxy group was observed. On the other hand, even

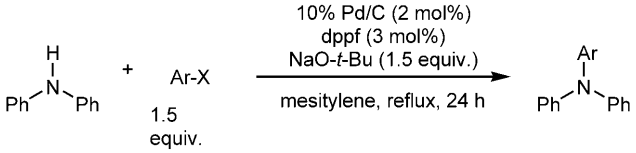
Table 6. Synthesis of triarylamines from aniline derivatives.

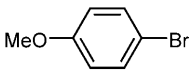
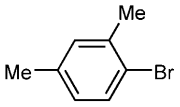
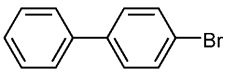
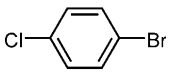
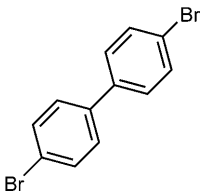
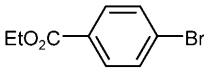
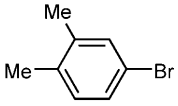
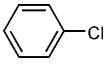
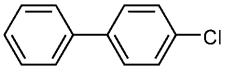


Entry	Ar^1-NH_2	Ar^2-X	Yield [%][a] diarylamine	triarylamine
1			0	92
2			0	78
3			23	77
4			59	32
5			38	62
6			0	94
7			0	84
8			53	33
9			25	73
10			41	45
11			38	43

[a] Isolated yield.

Table 7. Synthesis of triarylamines from diphenylamine.



Entry	Ar-X	Yield [%][a]	Entry	Ar-X	Yield [%][a]
1[b]		92	5		0
2[c]		91	6		100[f]
3[d]		73[e]	7[g]		75
4		83	8		62
			9		100

[a] Isolated yield.
[b] 4 mol% of Pd/C and 6 mol% of dppf were used.
[c] 1.2 equiv. of 4-bromobiphenyl was used.
[d] 2.5 equiv. of NaO-*t*-Bu and diphenylamine were used.
[e] Yield of *N*,*N*,*N*′,*N*′-tetraphenyl-[1,1′-biphenyl]-4,4′-diamine.
[f] (4-Chlorophenyl)diphenylamine was obtained.
[g] Cs_2CO_3 was used as the base.

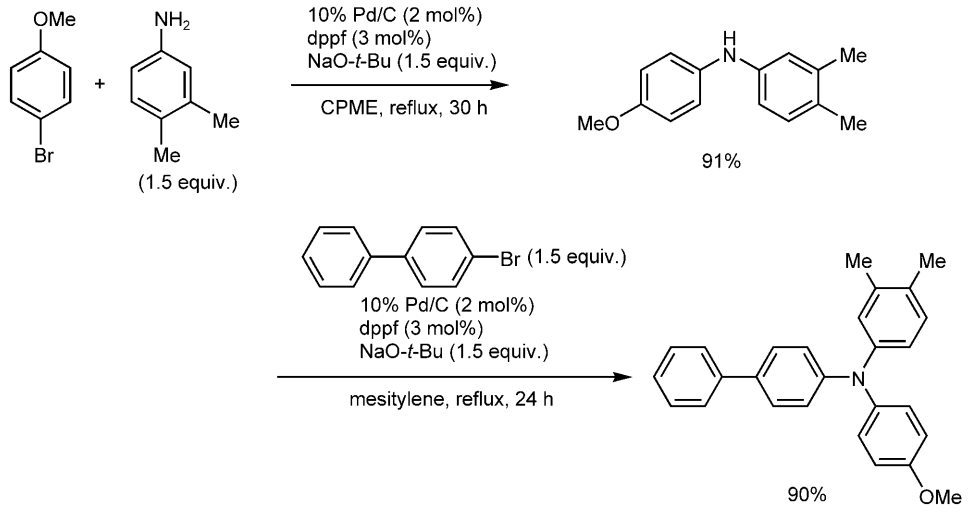
4-chlorobiphenyl, an aromatic chloride, was susceptible to amination under these conditions while a mixture of di- and triarylamines was obtained (entry 11).

The synthesis of triarylamines using a diphenylamine instead of a monoarylamine with aryl bromide was also investigated and the desired triarylamines were obtained in good yields (Table 7, entries 1–4), although the reaction never proceeded in the case of an *ortho*-methyl-substituted benzene due to the steric hindrance of the methyl group to the access of the bulky diphenylamine (entry 5). It is noteworthy that aryl chlorides could also be used for the coupling reaction with diphenylamine (entries 8 and 9).

Based on these results, a stepwise synthesis of an asymmetrical triarylamine was demonstrated (Scheme 2). First, 4-bromoanisole was coupled with 3,4-xylidine (1.5 equiv.) in refluxing *CPME* to give the corresponding diarylamine in 91% yield and subsequent coupling with 4-bromobiphenyl (1.5 equiv.) in refluxing *mesitylene* afforded the desired asymmetrical triarylamine in 90% yield (82% yield in two steps).

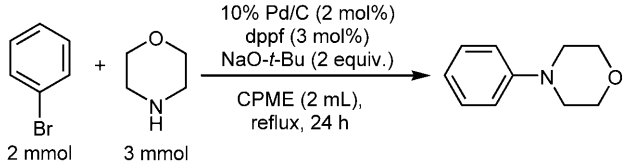
Reusability of 10% Pd/C

The reusability of heterogeneous Pd/C is an important factor in developing an economically and environmentally friendly process. The reuse test of Pd/C was carried out in the *N*-phenylation of morpholine using 3 mol% of dppf and 2 equiv. of NaO-*t*-Bu. The catalyst was recovered after a 24-h reaction, washed successively with H_2O and CH_2Cl_2, dried, and then subjected to the second run of the same reaction process. It was found that 10% Pd/C could be quantitatively recovered and reused at least until the fourth run without any declination of the catalyst activity (Table 8). Furthermore, the very low level of palladium leaching in the reaction media was confirmed by an inductively coupled plasma-atomic emission spectrometric analysis (0.68 and 1.1% of total palladium amount, Table 9).



Scheme 2. Synthesis of asymmetrical triarylamine.

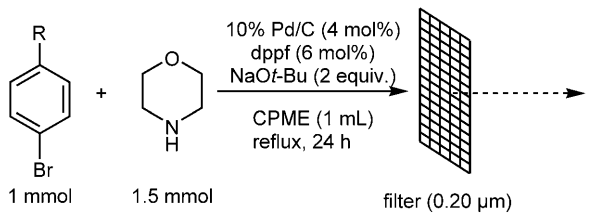
Table 8. Reuse test of Pd/C.



Recycle	1st	2nd	3rd	4th
Yield [%][a]	82	89	90	95
recovered Pd/C [mg][b]	48.6	48.0	43.5	42.5

[a] Isolated yield.
[b] 42.6 mg of Pd/C was used for the 1 st cycle.

Table 9. Measurement of leached Pd.



Entry	R	Pd in filtrate ppm[a]	μmol	Leached Pd/used Pd [%]
1	H	4.6	0.43	1.1
2	OMe	2.9	0.27	0.68

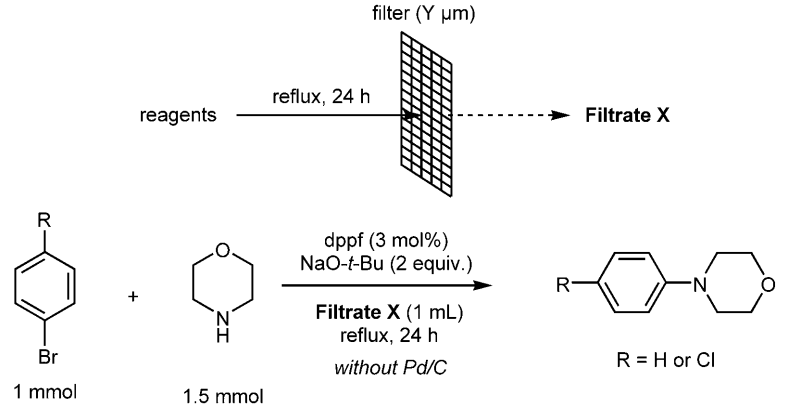
[a] Measured by ICP-AES (SPS3000, SII NanoTechnology Inc.).

What are the Active Catalyst Species?

In our previous study on the Pd/C-catalyzed, ligand-free Suzuki–Miyaura coupling, we demonstrated that the reaction would proceed in a heterogeneous way on the basis of absolutely no detection of the palladium leaching.[11,23] On the other hand, the catalytic activity may be attributed to the small amount of leached palladium in the present Pd/C-catalyzed aromatic amination.[12b,24] Therefore, we investigated what are the real active catalyst species. First, 10% Pd/C (0.04 mmol) was pretreated with dppf (0.06 mmol) and NaO-*t*-Bu (4 mmol) in boiling CPME for 24 h, and the mixture was filtered using a 0.45 μm membrane filter to give Filtrate 1. A mixture of bromobenzene (1 mmol) and morpholine (1.5 mmol) in 1 mL of Filtrate 1 was then heated at reflux together with dppf (0.03 mmol) and NaO-*t*-Bu (2 mmol) in the absence of 10% Pd/C to afford the *N*-phenylmorpholine in 72% yield (Table 10, entry 1). Since the equivalent results were obtained when the reaction was carried out using the filtrate (Filtrate 2) which was prepared by further filtration of the Filtrate 1 with a finer 0.20 μm membrane filter (entry 2), it is obvious that the reaction was not catalyzed by the fine 10% Pd/C particles passed through the 0.45 μm filter. The reaction of morpholine with 4-chlorobromobenzene in Filtrate 2 proceeded with strict regioselectivity to give only the *para*-substituted isomer in 79% yield (entry 3). These results suggest that the reaction using Filtrate 1 or 2 without Pd/C would be mediated by a sort of leached (homogeneous) palladium species.

The distinct difference between the Suzuki–Miyaura reaction, in which we mentioned that the palladium leaching was not observed, and the present aromatic amination is the use or non-use of the dppf ligand. We suspected that dppf might dissolve a small amount of active palladium species out from the 10% Pd/C by forming a kind of Pd-dppf complex. Pretreatment of the 10% Pd/C and dppf in boiling CPME and subsequent filtration afforded Filtrate 3 (entry 4).

Table 10. Can leached-palladium can be adsorbed in the carbon support again?



Entry	Filtrate Preparation			Product	
	Filtrate X	Filter (Y μm)	Reagents	R	Yield [%][a]
1	Filtrate 1	0.45 μm	10% Pd/C (4 mol%), dppf (6 mol), NaO-*t*-Bu (4 mmol), CPME (2 mL)	H	72
2	Filtrate 2	0.20 μm	Filtrate 1	H	72
3	Filtrate 2[b]			Cl	79
4	Filtrate 3	0.20 μm	10% Pd/C (4 mol%), dppf (6 mol%), CPME (2 mL)	H	67
5	Filtrate 3[c]			H	5
6	Filtrate 4	0.20 μm	10% Pd/C (4 mol%), NaO-*t*-Bu (4 mmol), CPME (2 mL)	H	0
7	Filtrate 5	0.20 μm	10% Pd/C (4 mol%), CPME (2 mL)	H	0
8	Filtrate 6	0.20 μm	Filtrate 3 (2 mL),[d] Norit (20 mg)	H	trace

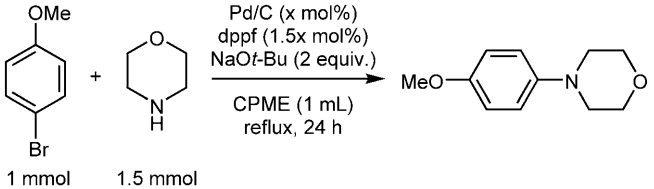
[a] Isolated yield.
[b] Prepared by the same procedure as that for entry 2.
[c] Prepared by the same procedure as that for entry 4. The amination was carried out without the further addition of dppf.
[d] Prepared from 10% Pd/C (6 mol%), dppf (9 mol%), and CPME (3 mL).

Similarly, Filtrates 4 and 5 were prepared without dppf by heating 10% Pd/C and NaO-*t*-Bu (entry 6), and only Pd/C in CPME (entry 7), respectively. The *N*-phenylation of morpholine using either Filtrate 2 or 3 proceeded to give the corresponding *N*-phenylmorphorine in approximately 70% yields (entries 2 and 4), while Filtrates 4 and 5 did not promote the reaction (entries 6 and 7). It is rational to consider that an interaction (coordination) of dppf with palladium metal of the Pd/C during the pretreatment would cause elution of the palladium species from 10% Pd/C to CPME and the resulting "Pd-dppf complex" would catalyze the phenylation. Although we anticipated that the further addition of dppf to Filtrate 3 was not necessary since the existing "Pd-dppf complex" would catalyze the reaction, no addition of dppf to the phenylation system drastically impeded the reaction progress (entry 5). The eluted palladium complex probably would not be stable without the further addition of dppf.

We then investigated if the leached palladium can be adsorbed in the carbon support again (Table 10).[12b] The suspension of the activated carbon (Norit) in Filtrate 3 was refluxed for 1 h and then passed through a 0.20 μm membrane filter to give Filtrate 6 (entry 8). The cross-coupling reaction without Pd/C in the resulting Filtrate 6 gave only a trace amount of product, presumably because a sufficient amount of the active palladium catalyst was not present in the reaction media. These results strongly suggest that the leached palladium could be redeposited onto the activated carbon.

When *5%* Pd/C (4 mol%) was used for the *N*-(4-methoxy)phenylation of morpholine (doubling the carbon support amount), the yield of the product was significantly reduced to 39% (Table 11, entry 2), in comparison to that when using 4 mol% of *10%* Pd/C (72%, entry 1). On the other hand, higher loadings of nickel metal of Ni/C reduced the catalyst activity

Table 11. Effect of doubling the carbon support amount.



Entry	Pd/C (mol%)	Yield [%]
1	10 Pd/C (4 mol%)	72
2	5% Pd/C (4 mol%)	39

based on larger nickel particles.[12b] For the present study using Pd/C, some other distribution phenomenon[25] or decreased metal adsorption might results in higher catalytic activity with the higher loading.

Conclusions

In summary, we have established a practical method for the aromatic amination of aryl bromides or aryl chlorides using Pd/C as a catalyst to synthesize di- and triarylamines. The catalyst could be recovered and reused at least until the fourth cycle without any loss in catalytic activity. The reaction would proceed through a "release and capture" process in the reaction media and only a trace amount of released palladium would be the active catalyst species. Our protocol requires only commercially available reagents and would be a practical and economical system.

Experimental Section

General Remarks

All other reagents were purchased from commercial sources and used without further purification. Analytical thin-layer chromatography (TLC) was carried out on pre-coated Silica gel 60 F-254 plates (32–63 μm particle size). Pd/C was obtained from N.E. Chemcat Co. and Aldrich. Chemcat The TLC plates were visualized with UV light (254 nm). The membrane filters (0.20 and 0.45 μm Millex®-LH) were purchased from the Millipore Corporation, Bedford, MA. Flash column chromatography was performed with silica gel 60 (40–63 μm particle size, Merck & Co., Inc.) or Silica gel 60N (100–210 μm, Kanto Chemical Co., Inc.). The ^{1}H NMR and ^{13}C NMR spectra were recorded by a JEOL JNM EX-400 spectrometer or JEOL JNM AL-400 spectrometer (400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR). Chemical shifts (δ) are expressed in ppm and are internally referenced (0.00 ppm for TMS for ^{1}H NMR and 77.0 ppm for $CDCl_3$ for ^{13}C NMR). Electron impact (EI) and fast-atom bombardment (FAB) mass spectra were taken using a JEOL JMS-SX 102 A instrument. The mass spectra and high-resolution mass spectra were obtained in the Mass Spectrometry Laboratory at the Gifu Pharmaceutical University.

General Procedure for the Coupling between Amines and Aryl Halides (Table 4 and Table 5)

To a test tube with a stir bar were added the aryl halide (1.0 mmol), amine (1.5 mmol), NaO-*t*-Bu (144 mg, 1.5 mmol), 10% Pd/C (21.3 mg, 0.02 mmol), dppf (16.6 mg, 0.03 mmol), and CPME (1 mL) and then the system was sealed with a septum. The air inside was replaced with argon by three vacuum/argon cycles. The test tube was placed on an organic reactor, Chemi Station (EYELA, Tokyo Rikakikai Co., Ltd., Tokyo, Japan) or Chemist Plaza (Shibata Scientific Technology Ltd., Tokyo, Japan), and the mixture was heated to reflux (120 °C outer temperature). After 24 h, the test tube was cooled to room temperature and removed from the reaction apparatus, and Et_2O (20 mL) and H_2O (20 mL) were then added. The mixture was filtered through a 0.45 μm membrane filter and the layers were separated. The organic layer was washed with brine (10 mL), dried ($MgSO_4$), filtered, and concentrated under vacuum. The residue was purified by flash column chromatography on silica gel.

General Procedure for Triarylamine Synthesis from Aniline Derivatives (Table 6)

To a test tube with a stir bar were added an aniline derivative (1.0 mmol), aryl halide (2.5 mmol), NaO-*t*-Bu (240 mg, 2.5 mmol), 10% Pd/C (21.3 mg, 0.02 mmol), dppf (16.6 mg, 0.03 mmol), and mesitylene (1 mL), then the tube was connected to a Dimroth condenser. The system was sealed with a septum and the air inside was replaced with argon by three vacuum/argon cycles. The mixture was stirred at reflux (bath temperature, 180 °C). After 24 h, the test tube was cooled to room temperature and removed from the condenser, then Et_2O (20 mL) and H_2O (20 mL) were added. The mixture was filtered through a 0.45 μm membrane filter and the layers were separated. The organic layer was washed with brine (10 mL), dried ($MgSO_4$), filtered, and concentrated under vacuum. The residue was purified by flash column chromatography on silica gel.

General Procedure for Triarylamine Synthesis from Diphenylamine (Table 7)

To a test tube with a stir bar were added diphenylamine (169 mg, 1.0 mmol), aryl halide (1.5 mmol), NaO-*t*-Bu (144 mg, 1.5 mmol), 10% Pd/C (21.3 mg, 0.02 mmol), dppf (16.6 mg, 0.03 mmol), and mesitylene (1 mL), then the tube was connected to a Dimroth condenser. The system was sealed with a septum and the air inside was replaced with argon by three vacuum/argon cycles. The mixture was stirred at reflux (bath temperature, 180 °C). After 24 h, the test tube was cooled to room temperature and removed from the condenser, then Et_2O (20 mL) and H_2O (20 mL) were added. The mixture was filtered through a 0.45 μm membrane filter and the layers were separated. The organic layer was washed with brine (10 mL), dried ($MgSO_4$), filtered, and concentrated under vacuum. The residue was purified by flash column chromatography on silica gel.

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