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Palladium-Catalyzed Synthesis of Triarylamines from Aryl Halides and Diarylamines

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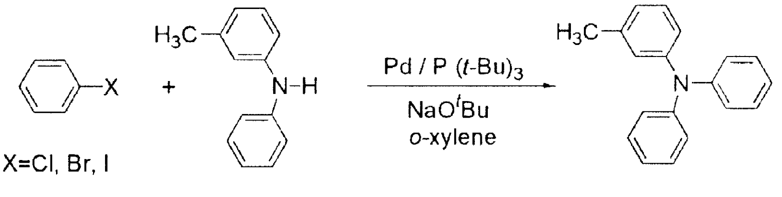
Abstract : Various triarylamines can be readily prepared in excellent yields by palladium-catalyzed cross-coupling reaction of aryl halides and diarylamines. The amination reaction takes place rapidly by using the catalyst combination of $Pd(OAc)_2$ and a bulky and electron-rich ligand, $P(t\text{-}Bu)_3$. © 1998 Elsevier Science Ltd. All rights reserved.

Recently, extensive research has been directed to the development of new triarylamines as hole-transport materials for organic electroluminescent (EL) display devices.[1] The common reactions that generate triarylamines are Ullmann couplings of aryl iodides and diarylamines with a stoichiometric amount of copper.[2] Unfortunately, Ullmann reactions involve high temperatures and generally give low or moderate yields. Waste water containing a large amount of a copper compound produced in the reactions also restricts application of the reactions on an industrial scale. Recently, Buchwald and Hartwig independently reported the catalytic amination reactions of aryl bromides or aryl iodides with palladium complexes with phosphine ligands, such as $P(o\text{-tolyl})_3$, BINAP, and DPPF.[3] However, until now there has been no report on catalytic amination reactions between aryl halides and diarylamines with palladium catalysts to prepare triarylamines.[4] Our efforts have been directed toward the development of facile and general synthetic methods of triarylamines with palladium catalysts. Here we report our results on a selective and reactive catalyst combination of palladium and $P(t\text{-}Bu)_3$ for the synthesis of various triarylamines.



Effects of phosphine ligands on the reactivity were examined in the palladium-catalyzed amination reaction of bromobenzene (1 equiv.) with N-(3-methylphenyl)aniline (1 equiv.) in the presence of NaO^tBu (1.2 equiv.) and $Pd(OAc)_2$ (0.025mol%) and phosphine (0.10mol%) in o-xylene solvent at 120℃ for 3 h.

The catalyst combinations of $Pd(OAc)_2$ and aryl phosphines, such as $P(o\text{-tolyl})_3$, BINAP, and PPh_3, gave

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low yields of N-(3-methylphenyl)diphenylamine (entries 3, 4, and 5 in Table 1).

Table 1 Influence of phosphine ligands on the synthesis of N-(3-methylphenyl)diphenylamine

Entry	Phosphine	Yield of 3[a] (mol%)	Corn Angle[b] (deg.)
1	$P(t\text{-}Bu)_3$	>99	182
2	PCy_3[c]	46	170
3	PPh_3	19	145
4	BINAP	18	---
5	$P(o\text{-}tolyl)_3$	5	194
6	$P(n\text{-}Bu)_3$	0	132

Conditions: Solvent; *o*-xylene, Aryl halide conc. 0.7mol/l
Bromobenzene / N-(3-methylphenyl)aniline / NaO^tBu = 1:1:1.2
Pd(OAc)2 0.025mol%, Phosphine/Pd=4:1
Temperature 120℃ (3h)
[a] Determined by GC with standard.
[b] Tolman's steric parameter.[5]
[c] Cy = cyclohexyl

A catalyst with a sterically small phosphine, $P(n\text{-}Bu)_3$, did not provide any products (entry 6). On the other hand, a catalyst combination with a bulky alkyl phosphine, PCy_3, showed moderate reactivity (entry 2).

It is particularly noteworthy that the reaction with a Pd and sterically more bulky $P(t\text{-}Bu)_3$ ligand was completed in 3h without producing any other products except the desired triarylamine (entry 1). The reaction rate in the amination reaction was reported to be determined at the reductive elimination step of arylamine from a palladium amide complex in the catalytic cycle.[6] The effects of phosphine ligands on the reactivity of the catalyst are assumed to influence the reductive elimination step. Since $P(t\text{-}Bu)_3$ is known for its electron-donating property, electron-rich and bulky ligands may accelerate elimination.

We investigated the reactivities of aryl halides in the reactions with N-(3-methylphenyl)aniline in the presence of the combination of $Pd(OAc)_2$ and $P(t\text{-}Bu)_3$. Complete conversion of N-(3-methylphenyl)aniline in the reactions with bromobenzene and iodobenzene was obtained in 3h at 100℃, whereas the reaction with an equimolecular amount of chlorobenzene was considerably slower even at higher reaction temperature 130℃ (entry 7 in Table 2). The low reactivity of aryl chlorides in the palladium-catalyzed carbon-carbon bond formation reactions known as the "Heck reaction" is commonly observed.[7] However, when a large excess amount of chlorobenzene against N-(3-methylphenyl)aniline was used, the amination reaction completed in 3h at 130℃ (entry 8). This result shows that, in the amination reaction, concentration of aryl halide greatly influences the reaction rate.

Table 2 Reactivity of Aryl halides in the synthesis of N-(3-methylphenyl)diphenylamine

Entry	Aryl halide	Condition	Temp. (℃)	Time (hr)	Yield of 3[a] (mol%)
7	Chlorobenzene	A	130	5	58
8	Chlorobenzene	B	130	3	>99
9	Bromobenzene	A	100	3	>99
10	Iodobenzene	A	100	3	98

Condition A: Aryl halide/ N-(3-metylphenyl)aniline/ NaO^tBu=1:1:1.2,
Solvent; *o*-xylene, Aryl halide conc. 0.7mol/l, $Pd(OAc)_2$ 0.025mol%, $P(t\text{-}Bu)_3$/Pd=4:1
Condition B: Aryl halide/ N-(3-metylphenyl)aniline/ NaO^tBu=2:1:1.2
Solvent; *o*-xylene, Aryl halide conc. 8.0mol/l, $Pd(OAc)_2$ 0.025mol%, $P(t\text{-}Bu)_3$/Pd=4:1
[a] Determined by GC with standard.

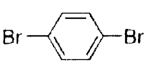
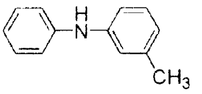
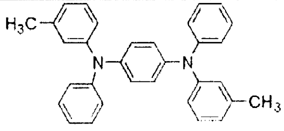
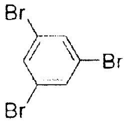
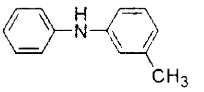
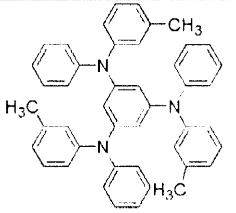
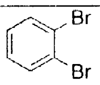
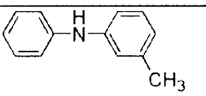
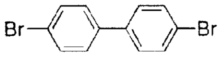
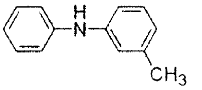
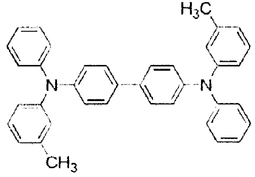
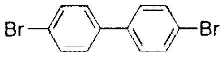
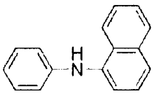
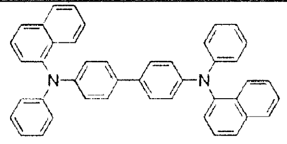
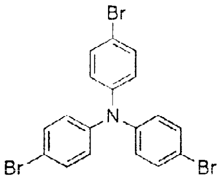
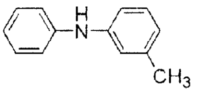
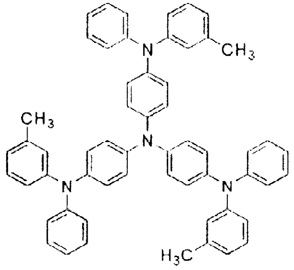
We also examined the amination reactions of polybrominated aromatic compounds with the combination catalyst of $Pd(OAc)_2$ and $P(t\text{-}Bu)_3$, since many triarylamines developed for hole-transport materials have more than two triarylamine moieties.

1,4-Dibromobenzene and

1,3,5-Tribromobenzene gave the corresponding desired products in high isolated yields (entries 11 and 12 in Table 3). We confirmed the reactions were completed and did not detect any side products by gas chromatography. The decrease of the yields is thought to be attributed to loss in the isolating process, including recrystallization. On the other hand, 1,2-dibromobenzene did not give any products and was recovered after the reaction (entry 13).

Amination reactions of 4,4'-dibromobiphenyl and tris(4-bromophenyl)amine gave the targeted diamines and tetraamine, respectively, in excellent isolated yields over 90% (entries 14, 15, and 16).

Table 3 Synthesis of various triarylamines from aryl polyhalides and diarylamines

Entry	Aryl polybromide	Diarylamine	Product	Isolated Yield[a] (mol%)
11				80
12				77
13				No Reaction
14				91
15				92
16				92

Conditions: Solvent; *o*-xylene, Aryl halide conc. 0.7mol/l, $Pd(OAc)_2$ 0.025mol%(based on Br atom), $P(t\text{-}Bu)_3/Pd=4:1$ Br atom/ Diarylamine/ $NaO^tBu=1:1:1.2$, Temperature 120°C (3h)

[a] Products were isolated by recrystallization with MeOH/THF.

In summery, we have demonstrated that a P(t-Bu)$_3$-palladium complex catalyzed amination reaction of aryl halides is a convenient synthetic method for triarylamines which can be utilized as hole-transport materials for organic electroluminescent displays.

References and Notes

1) For example,

a) Inaba, H. ; Yonemoto, Y. ; Wakimoto, T. ; Imai, K. ; Shirota, Y. *Mol. Cryst. Liq. Cryst.* **1996**, *280*, 1331. b) Adachi, C. ; Nagami, K. ; Tamoto, N. *Appl. Phys. Lett.* **1995**, *60*, 2679. c) Shirota, Y. ;Kuwabara, Y. ; Inada, H. ; Wakimoto, T. ; Nakada, H. ; Yonemoto, Y. ; Kawami, S. ; Imai, K. *Appl. Phys. Lett.* **1994**, *65*, 807. d) Kuwabara, Y. ; Ogawa, H. ; Inada, H. ; Noma, N. ; Shirota, Y. *Adv.Mater.* **1994**, *6*, 677. e) Tang, C. W. ; Van Slylke, S. A. ; Chen, C. H. *J. Appl. Phys.* **1989**, *65*, 3610. f) Adachi, C. ; Tokito, S. ; Tsutsui, T. ; Saito, S. *Jpn. J. Appl. Phys.* **1988**, *27*, L269.
g) Tang, C. W ; Van Slylke, S. A. *Appl. Phys. Lett.* **1987**, *51*, 913.

2) For example,

a) Shirota, Y. ; Kobata, T. ; Noma, N. *Chem. Lett.* **1989**, 1145. b)USP 4,588,666

3) a) Driver, M .S. ; Hartwig J. F. *J. Am. Chem. Soc.* **1996**, *118*, 7217. b) Wolfe, J. P. ; Wagaw, S. ; Buchwald, S. L. *J. Am. Chem. Soc.* **1996**, *118*, 7215. c) Wolfe, J. P. ; Buchwald, S. L. *J. Org. Chem.* **1996**, *61*, 1133. d) Guran, A. S. ; Rennels, R. A. ; Buchwald, S. L. *Angew. Chem. Int. Ed. Engl.* ***1995***, *34*, 1348. e) Louie, J. ; Hartwig, J. F. *Tetrahedron Lett.* ***1995***, *36*, 3609.

4) After submission of this manuscript, two reports about triarylamines synthesis from aryl halides and diarylamines or anilines using Pd-aromatic phosphine catalyst were published as shown below, however our catalytic system has much high catalytic activity compared with the reported systems.

a) Louie, J. ; Hartwig, J. F. *J. Am. Chem. Soc.* **1997**, *119*, 11695. b) Thayumanavan,S. ; Barlow, S. ; Marder, S. R. *Chem. Mater.* **1997**, *9*, 3231.

5) Tolman, C. A. *Chem. Rev.* **1977**, *177*, 313.

6) a) Hartwig, J. F. ; Richards, S. ; Baranano, D ; Paul, F. *J. Am. Chem. Soc.* **1996**, *118*, 3626.
b) Baranano, D. ; Hartwig, J. F. *J. Am. Chem. Soc.* **1995**, *117*, 2937.

7) Grushin, V. V. ; Alper, H. *Chem. Rev.* **1994**, *94*, 1047.

8) **Typical procedure**

Pd(OAc)$_2$ (0.025mol%) and P(t-Bu)$_3$ (0.10mol%) (Phosphine/Pd=4:1) were added to the suspension of aryl halide (40mmol), diarylamine (40mmol) and NaO^{t}Bu (48mmol) in *o*-xylene (60ml) in N$_2$ atmosphere. The mixture was heated for 3h at 120℃. Subsequently, it was cooled to room temperature. H$_2$O (60ml) was added to it, and the organic layer was separated. Yield was determined by GC with standard. Products were isolated by recrystallization with MeOH/THF. Pd/P(t-Bu)$_3$ catalyst can be prepared from Pd(OAc)$_2$/P(t-Bu)$_3$ *in situ* or before the reaction.