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Highly Efficient Ligands for the Palladium-Assisted Double N-Arylation of Primary Amines for One-Sep Construction of Carbazoles

Yibo Zhou^a and John G. Verkade^{a,*}

^a Department of Chemistry, Gilman Hall, Iowa State University, Ames, IA 50011, U.S.A. Fax: (+1)-515-294-0105; phone: (+1)-515-294-5023; e-mail: jverkade@iastate.edu

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Abstract: A highly efficient one-pot synthesis of carbazoles via palladium-catalyzed double N-arylation of primary amines with 2,2'-dihalobiphenyls is described using a catalyst system comprised of tris-(dibenzylideneacetone)dipalladium(0) (Pd_2dba_3) and the proazaphosphatrane P(i-BuNCH₂CH₂)₃N (8) or its derivative $(t-Bu)_2 P = N - P(i BuNCH_2CH_2$)₃N (9a) as the ligand. The process is effective for double N-arylation of 2,2'-biphenyl dibromide, diiodide, and even dichloride with a variety of primary amines including neutral, electronrich, electron-deficient, and sterically hindered anilines as well as aliphatic amines.

Keywords: biaryls; carbazoles; C–N coupling; heterocycles; palladium

Carbazole alkaloids possess a wide range of biological behaviors including antitumor, psychotropic, anti-inflammatory, antihistaminic and antibiotic activities.^[1] Carbazole derivatives are also widely useful owing to their photorefractive, photoconductive, hole-transporting, and light-emitting properties.^[2] The unique importance of these organic materials has attracted considerable interest in the efficient synthesis of carbazoles,^[3] and although many useful syntheses have been developed, there are few examples of the efficient construction of carbazoles in a single step under mild conditions. The Pd(0)-catalyzed intramolecular C-H activation of 2-amino-2'-halodiphenyl^[4] and the Pd(II)-mediated oxidative cyclization of diarylamines^[5] have been reported to be useful methods for constructing carbazoles, but only moderate yields were generally obtained. Very recently, Nozaki^[6] and Chida^[7] independently utilized biphenyls possessing Br, I or OTf functionalities (5 in Scheme 1) for the



Scheme 1. Pd-catalyzed double *N*-arlyation of primary amines with 2,2'-dihalobiphenyls.

Pd-catalyzed double arylation of primary amines (6 in Scheme 1) to synthesize 7 in this Scheme. Their approach was an important extension of the Buchwald-Hartwig *N*-arylation reaction,^[8] and it proved to be an excellent protocol for construction of a variety of substituted carbazoles in one-step. This novel method led to the successful synthesis of the carbazole-based natural products mukonine^[6a] and murrastifoline.^[7] However, these methodologies are generally plagued by the requirement for high catalyst loadings and harsh reaction conditions. Typically, 10-20 mol% of Pd catalyst and 30 mol% of a phosphine ligand $[(t-Bu)_3P^{[6]}]$ dialkylphosphinobiaryls $1-3^{[6]}$ or Xantphos $4^{[7]}$] were employed at 80-120°C, despite the observation that these ligands have been reported to be excellent for N-arylation.^[9,10] In addition, low yields were reported when aliphatic primary amines (such as benzylamine or *n*-octylamine) were employed as the substrate. Furthermore, no examples involving the less reactive substrate dichlorobiphenyl have been reported.

Previous work from our group has established that the commercially available proazaphosphatrane $\mathbf{8}^{[11]}$ bearing isobutyl groups on the PN₃ nitrogens and its derivative $(t-Bu)_2P-N=P(i-BuNCH_2CH_2)_3N$ $9a^{[12]}$



(Scheme 1, both first synthesized in our laboratories) are highly effective ligands for several palladium-catalyzed cross-coupling reactions of aryl bromides, iodides and chlorides, such as Suzuki^[12,13], Stille^[14], α -arylation^[15] and Buchwald-Hartwig amination reactions.^[16] We have suggested that the unusually high activity of 8 and 9a as supporting ligands in Pd-catalyzed coupling reactions is due primarily to their steric bulk and the uniquely electron-rich nature of their trivalent phosphorus atoms stemming from the geometrically favorable arrangement of the three sp^2 nitrogens contributing their unhybridized p electron lone pair density to the phosphorus and the possibly temporary $N \rightarrow P$ transannulation donating the bridgehead nitrogen's lone pair to the phosphorus in the proazaphosphatrane framework in each of these molecules.^[12,17]

We envisioned the possibility that the steric bulk and electron-richness of 8 and 9 might also function well in facilitating Pd-catalyzed double N-arylation of primary amines with 2,2'-dihalobiphenyls for a onepot synthesis of carbazoles (Scheme 1). Thus we first examined the reaction of 2,2'-dibromobiphenyl 5a with aniline 6a for screening purposes (Table 1). A control experiment confirmed the need for a ligand (entry 1). Both 8 and 9a proved to be effective ligands. Nearly quantitative yields of the carbazole 7a were obtained with 0.125 mol% of Pd₂dba₃ and 0.5 mol% of ligand 8 or 9a in the presence of 3.0 equiv. of NaO-t-Bu in toluene at 80°C for 1 hour (entries 3, 5). Even at room temperature, the reaction gave rise to 7a in 98% yield in the presence of 0.5 mol% of Pd₂dba₃ and 2 mol% of ligand 9a (entry 7). The less sterically bulky analogous ligands 9b and 9c gave 52% and 87% isolated yields of 7a, respectively (entries 9, and 10). Ligand 8 appears to be more efficient than 9a when catalyst loadings were decreased to 0.05 mol% of Pd₂dba₃ and 0.2 mol% of ligand (entries 4 and 6). The use of Cs_2CO_3 as the base failed to provide carbazole 7a (entry 8).

Thus, the reactions of biphenyl dibromide 5a with substituted anilines and aliphatic amines 6 were examined using the two catalyst systems Pd₂dba₃/8 and

Table 1. The double *N*-arylation of aniline **6a** with 2,2'-dibromobiphenyl **5a**.^[a]



Entry	Pd ₂ dba ₃ (mol%)	Ligand	Temp. [°C]	Time [h]	Yield [%] ^[b]
1	2.5	_	100	24	<2
2	0.25	8	80	1	98
3	0.125	8	80	1	98
4	0.05	8	80	24	67
5	0.125	9a	80	1	98
6	0.05	9a	80	24	10
7	0.5	9a	25	24	98
8	0.5	9a	80	24	$< 2^{[c]}$
9	0.25	9b	80	24	52
10	0.25	9c	80	24	87

 Pd₂dba₃:ligand=1:4, 0.5 mmol of 5a, 0.6 mmol of aniline, 1.5 mmol of NaO-t-Bu in 3 mL of toluene.

^[b] Isolated yields (average of 2 runs).

[c] Cs₂CO₃ (3.0 equiv.) was used as the base in place of NaO-t-Bu.

Pd₂dba₃/9a in the presence of NaO-t-Bu as a base. As is evident from Table 2, a variety of anilines possessing electron-neutral and electron-rich (entries 1-8), as well as sterically bulky groups (entries 6-11) were efficiently coupled with 5a, affording the desired carbazoles in excellent yields using both catalyst systems. Even the sterically encumbered 2,6-diisopropylaniline 6g successfully coupled with 5a to afford impressive yields (92-96%) of 7g with both catalyst systems (entries 9 and 10). Anilines with F or Cl functional groups also produced carbazoles in excellent yields (entries 12-16). Generally, the use of ligand 8 required lower catalyst loadings and shorter reaction times than 9a for the reaction to proceed to completion. However, the reactions of aliphatic primary amines and anilines with electron-withdrawing groups were more challenging for 8, providing only poor yields (50-60%) of carbazoles even when a higher catalyst loading of 8 was employed (entries 17 and 18).

It is noteworthy that at least 40-fold (and in some cases 80-fold) lower catalyst loadings and much shorter reaction times are needed in our protocol than with the Pd₂dba₃/(*t*-Bu)₃P, Pd₂dba₃/dialkylphosphinebiaryls **1–3**, and Pd₂dba₃/Xanthphos **4** catalyst systems reported by Nozaki^[6] and Chida,^[7] respectively. For example, **7a** and **7b** were synthesized using 5 mol% of Pd₂dba₃ and 20 mol% of (*t*-Bu)₃P at 80 °C for 24 h whereby 86% and 92% of desired carbazoles were obtained, respectively.^[6a] Using 10 mol% of Pd₂dba₃ and 30 mol% of **1** at 120 °C for 24 h, produced an
 Table 2. The double *N*-arylation of anilines 6 with 2,2'-dibromobiphenyl 5a.^[a]



b : R = <i>p</i> -MeOC ₆ H ₄	f: R = 2,6-(CH ₃) ₂ C ₆ H ₃	j: R = <i>p</i> -ClC ₆ H₄
$c: R = o-MeOC_6H_4$	g : R = 2,6-(<i>i</i> -Pr) ₂ C ₆ H ₃	k : R = <i>m</i> -ClC ₆ H ₄
d : $R = p - MeC_6H_4$	h: R = 1-naphthyl	I: $R = m - NO_2C_6H_4$
e : R = 2,4-(CH ₃) ₂ C ₆ H ₃	i: R = <i>p</i> -FC ₆ H₄	m : R = <i>n</i> -octyl

Entry	RNH ₂	Pd_2dba_3 (mol%)	Ligand	Time [h]	Yield [%] ^[b]
1	6b	0.125	8	4	98
2	6b	0.125	9a	6	97
3	6c	0.125	8	4	97
4	6c	0.25 (0.125)	9a	24 (24)	98 (44)
5	6d	0.125	8	24	98
6	6e	0.125	8	15	99
7	6f	0.25	8	30	98
8	6f	0.50	9a	24	97
9	6g	0.50	8	24	96
10	6g	0.50	9a	48	92
11	6h	0.25	8	20	99
12	6i	0.125	8	2	98
13	6i	0.125	9a	1	99
14	6j	0.125	8	4	95
15	6j	0.125	9a	6	96
16	6k	0.125	8	4	97
17	61	5	8	40	60 ^[c]
18	6m	5	8	6	50 ^[d]

 Pd₂dba₃:ligand=1:4, 0.5 mmol of 5a, 0.6 mmol of aniline, 1.5 mmol of NaO-t-Bu in 3 mL of toluene at 80 °C.

^[b] Isolated yields (average of 2 runs).

[c] Cs₂CO₃ (3.0 equiv.) was used as the base in place of NaO-t-Bu.

^[d] The reaction went to completion but hydrodehalogenated byproducts and other uncharacterized products were observed.

85% yield of **7a**.^[7] By contrast, with our protocol in which 0.125 mol% of Pd_2dba_3 and 0.5 mol% of either ligand **8** or **9a** are used, carbazoles **7a** and **7b** are provided in 97–98% yields at 80°C in 1–6 h (Table 1, entries 3 and 5; Table 2, entries 1 and 2).

To improve the yields for aliphatic primary amines and electron-deficient anilines, we investigated their couplings with biphenyl diiodide **5b** in the presence of Pd₂dba₃ and the commercially available ligand **8** (Table 3). It is important to note that the *N*-alkylcarbazoles, which were prepared in poor yields under the conditions used by Nozaki^[6] and Chida,^[7] were obtained in good to excellent yields by employing diiodide **5b** as the substrate and the catalyst system Pd₂dba₃/**8** (entries 2 and 3).

Table 3. The double *N*-arylation of primary amines **6** with 2,2'-diiodobiphenyl **5b**.^[a]



Entry	RNH_2	$Pd_2dba_3 (mol\%)$	Time [h]	Yield [%] ^[b]
1	61	5	48	34 ^[c]
2	6m	0.5	40	94
3	6n	3	24	84 ^[d]

 Pd₂dba₃:ligand=1:4, 0.5 mmol of 5b, 0.6 mmol of aniline, 1.5 mmol of NaO-t-Bu in 3 mL of toluene at 80 °C.

^[b] Isolated yields.

 [c] Cs₂CO₃ (3.0 equiv) was used as the base in place of NaOt-Bu.

^[d] A 10% yield of the side product biphenyl was isolated.

Historically, aryl iodides have been less effective substrates for Pd-catalyzed C-N bond-forming amination processes than their bromide counter-parts because iodides are more prone to β-hydride elimination leading to formation of hydrodehalogenation products,^[18] even though they are more reactive in Pd-catalyzed C-C cross-coupling reactions.^[19] However, the double N-arylation of long-chain aliphatic primary amines such as *n*-octylamine **6m** with biphenyl diiodide 5b proceeded smoothly to give the desired carbazole product 7m in 94% isolated yield by using 5 mol% Pd₂dba₃ and 20 mol% ligand 8 (entry 2). By contrast, under the same conditions, the reaction of biphenyl dibromide 5a with 6m gave only a 50% yield of 7m. Although the reaction did proceed to completion, hydrodehalogenation side products and other uncharacterized compounds were detected by GC in the reaction mixture (Table 2, entry 18). Importantly, benzylamine 6n also successfully reacted with 5b to provide N-benzyl-protected carbazole product 7n in 84% yield (entry 3). The major side product for this reaction was the biphenyl (10%) that was generated by hydrodehalogenation of 5b. The formation of the N-benzyl-protected carbazole is significant since most known natural carbazole alkaloids possess a free N-H moiety.^[1] In the case of 3-nitroaniline **6**, biphenyl diiodide 5b again provided a poor yield of product (entry 1).

Recently, significant progress has been made in the development of catalysts capable of utilizing unreactive aryl chlorides as substrates in Pd-catalyzed cross-coupling processes.^[9b,10a,16b,20] To the best of our knowledge, however, there are no reports of the use of biphenyl dichlorides for direct carbazole synthesis *via* a double *N*-arylation reaction of primary amines. Encouraged by our promising results with dibromide **5a**

and diiodide 5b, we further extended our approach to the use of biphenyl dichloride 5c as the substrate. Representative results are summarized in Table 4. The catalyst system Pd₂dba₃/9a proved to be superior to the $Pd_2dba_3/8$ system when 5c was the substrate (entries 1 and 11). As seen in Table 4, a catalyst system of 0.5 mol% Pd₂dba₃ and 2 mol% of 9a in combination with NaO-t-Bu as the base in toluene at 100°C allowed coupling of biphenyl dichloride 5c with a wide array of amines, including electron-poor, electron-neutral, and electron-rich examples, affording the desired carbazoles in excellent yields. Sterically hindered primary amines are also well tolerated, often giving the desired products in excellent yields (entries 3, 5–7). Surprisingly, the reactions of electrondeficient anilines 3-nitroaniline 61 and 4-trifluoromethylaniline 60 proceed to completion, giving good to excellent isolated yields of carbazole 71 (75%) and 70 (90%), respectively, when the Pd₂dba₃/9a catalyst system was employed and Cs₂CO₃ was used as the

Table 4. The double *N*-arylation of primary amines **6** with 2,2'-dichlorobiphenyl **5c**.^[a]

	CI	+ RNH ₂ + RNH ₂ + NaO- <i>t</i> - NaO- <i>t</i> - Tolue	Pa₃ → -Bu ne	N B	
Į	ōc	6a – g, i, l, m, o	7a –	g, i, l, m, o	
a : $R = C_6H_5$ b : $R = p$ -MeOC ₆ H ₄ c : $R = o$ -MeOC ₆ H ₄ d : $R = p$ -MeC ₆ H ₄		e: R = 2,4-(CH ₃) ₂ C f: R = 2,6-(CH ₃) ₂ C g: R = 2,6-(<i>i</i> -Pr) ₂ C i: R = <i>p</i> -FC ₆ H ₄	C ₆ H ₃ I: R ₆ H ₃ m : ∣ ₅H ₃ o : F	I: R = m -NO ₂ C ₆ H ₄ m: R = n -octyl o: R = p -CF ₃ -C ₆ H ₄	
Entry	RNH ₂	Pd ₂ dba ₃ (mol%)	Time [h]	Yield [%] ^[b]	
1	6a	0.50	24	95 (61) ^[c]	
2	6b	0.50	24	95	
3	6c	0.50	24	95	
4	6 d	0.50	24	94	
5	6e	0.50	24	94	
6	6f	0.50	30	92	
7	6g	0.50	30	94	
8	6i	0.50	24	95	
19	61	5	40	75 ^[d] (92) ^[e]	
10	6m	5	40	36	
11	60	5	24	90 ^[d] (88) ^[f]	

[a] Pd₂dba₃:ligand 9a=1:4, 0.5 mmol of 5c, 0.6 mmol of amine, 1.5 mmol of NaO-t-Bu in 3 mL of toluene at 100 °C.

^[b] Isolated yields (average of 2 runs).

- [c] 0.5 mol% Pd₂dba₃, 2 mol% ligand 8, 3.0 equiv. of NaO-t-Bu, 100 °C, 24 h. A 26% yield of monoarylation product was obtained.
- ^[d] Cs₂CO₃ (3.0 equiv.) was used as the base in place of NaO-t-Bu.
- ^[e] GC yield.
- ^[f] 5 mol% Pd₂dba₃, 20 mol% ligand 8, 3.0 equiv. of Cs₂CO₃, 100 °C, 3 days.

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base (entries 9 and 11). However, in contrast to the reaction of *n*-octylamine **6m** with diiodobiphenyl **5b** to afford a 94% yield of carbazole **7m** (Table 3, entry 2), the reaction of **6m** with dichlorobiphenyl **5c** was sluggish and provided only a low yield of **7m** (entry 10).

In conclusion, we have described two highly active catalyst systems consisting of a palladium source and the commercially available ligand 8 or its derivative 9a for a one-pot synthesis of carbazoles. Our process is effective for the double *N*-arylation of primary amines (including neutral, electron-rich, electron-deficient, and sterically hindered anilines and aliphatic amines) with biphenyl dibromide, diiodide, as well as dichloride. Our methodology employs the lowest palladium and ligand loadings reported to date for the synthesis of carbazoles, and our protocols operate in shorter reaction times compared with those in previous reports.

Experimental Section

General Procedure for the Double N-Arylation Reaction

Argon was bubbled into a mixture of Pd_2dba_3 , ligand (8 or 9), base (NaO-*t*-Bu or Cs₂CO₃, 1.5 mmol, 3.0 equiv.), 2,2'-dihalogenbiphenyl (5, 0.5 mmol), and amine (6, 0.6 mmol) in toluene (3 mL) for 5 min. The mixture was then heated at 80–100 °C for 1–40 h (see Tables) and after cooling, the mixture was filtered through a pad of silica gel (3 g, ethyl acetate). The filtrate was concentrated to give a residue, which was purified by column chromatography (silica gel, hexane/ ethyl acetate 100/1) to afford carbazole 7. Full experimental details and characterization data are given in the Supporting Information.

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