JOC Article

P(*i*-BuNCH$_2$CH$_2$)$_3$N: An Effective Ligand in the Palladium-Catalyzed Amination of Aryl Bromides and Iodides

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It is shown that the bicyclic triaminophosphine P(*i*-BuNCH$_2$CH$_2$)$_3$N serves as an effective ligand for the palladium-catalyzed amination of a wide array of aryl bromides and iodides. Other bicyclic or acyclic triaminophosphines, even those of similar basicity and/or bulk, were inferior.

Introduction

Palladium-catalyzed amination reactions are fundamentally important organic transformations that have received tremendous attention over the past few years.[1] Elegant work by Hartwig,[2] Buchwald,[3] and others[4] has led to significant improvements in amination methodology since its discovery by Migita and co-workers in 1983.[5] Most of the reported methods employ electron-rich phosphine ligands,[6] possessing either a ferrocene[7] or a biphenyl backbone,[8] or bulky nucleophilic N-heterocyclic carbenes (sometimes referred to as "phosphine mimics").[4a,c,9] Chelating phosphines such as 1,1′-bis(diphenylphosphino)ferrocene (DPPF)[2a] and 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (BINAP)[3b,10] have been demonstrated to exhibit improved catalytic activity in this type of transformation. Although room-temperature amination reactions are known,[8] the range of substrate combinations that can be employed at this temperature are rather limited, whereas reactions performed at 80 °C or higher accommodate a wide variety of substrates.

Although triaminophosphines, and particularly P(NMe$_2$)$_3$, have often been used to ligate transition metals, to the best of our knowledge there have been no reports of the use of such ligands in Pd-catalyzed amination chemistry. This may be partly due to the diminished electron-donating capability of acyclic triaminophosphines compared with trialkylphosphines, as was recently rationalized by Woollins.[11] The reduced Lewis basicity of triaminophosphines is believed to arise from differences in the geometries of their nitrogens. X-ray crystal structures of free tris(dialkylamino)phosphines and their transition metal complexes[12,13] reveal that phosphorus bears two nearly planar nitrogens and one pyramidal nitrogen. While the two planar nitrogens are capable of donating electron density to phosphorus via their unhybridized lone pairs (which are roughly perpendicular to the phosphorus lone pair) the pyramidal nitrogen simply acts as an electron-withdrawing atom since its more sp^3-hybridized lone pair is oriented anti to the phosphorus lone pair.

As part of our own effort to understand and exploit the stereoelectronic properties of tris(dialkylamino)phosphines, we reasoned that by rendering the backbone of the triaminophosphine quite rigid in a bicyclic framework in which all three nitrogens would be geometrically and conformationally very similar[14] to the two planar elec-

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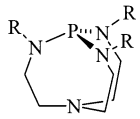
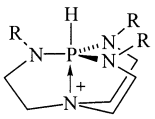
tron-donating nitrogens in tris(dialkylamino)phosphines, we could significantly enhance the basicity of such phosphines and thus facilitate oxidative addition to the metal. Furthermore, the electronic and steric influences in such ligands could be easily tailored by introducing suitable organic substituents at each PN_3 nitrogen to impart the desired steric bulk which could assist in the reductive elimination step. In addition to these advantages possessed by pro-azaphosphatranes of types **1a**−**6a**, such bicyclic systems also feature the potential for



1a R = Me
2a R = Et
3a R = *i*-Pr
4a R = *i*-Bu
5a R = *neo*-Pent
6a R = 4-Pyridyl

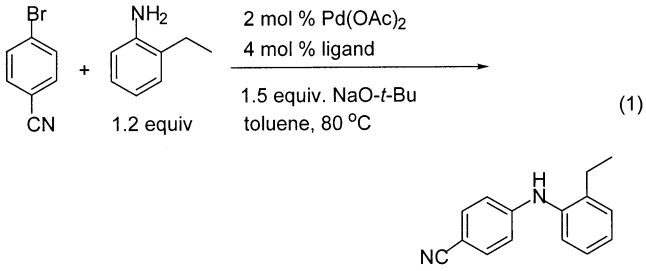


1b R = Me
2b R = Et
3b R = *i*-Pr
4b R = *i*-Bu
5b R = *neo*-Pent
6b R = 4-Pyridyl

basicity enhancement via transannulation of the bridgehead nitrogen's lone pair to the phosphorus as in **1b**−**6b**[15] some of which we recently showed possess pK_a values of approximately 33 in acetonitrile.[16] Compounds of type **1** have proven to be exceedingly useful nonionic bases and catalysts for a variety of useful transformations during the last 10 years.[17] Herein we show that commercially available **4a** is an excellent ligand in the palladium-catalyzed aminations of aryl bromides and iodides.

Results and Discussion

For our optimization studies, we selected the $Pd(OAc)_2$/L-catalyzed amination of 4-bromobenzonitrile with 2-ethylaniline in toluene as a model reaction (reaction 1). Initial reactions with **1a** and **2a** as ligands were disappointing, providing only a trace amount of N-arylated product (Table 1, entries 1 and 2). Since ligand steric hindrance can improve catalytic performance,[18] the more



(1)

TABLE 1. Screening of Triaminophosphine Ligands for the Reaction Shown in Eq 1[a]

entry	ligand	yield (%)[b]	entry	ligand	yield (%)[b]
1	**1a**	15	6	**6a**	0
2	**2a**	5	7	$P(NMe_2)_3$	10[c]
3	**3a**	0	8	$P(NEt_2)_3$	11[c]
4	**4a**	97	9	$P[N(i\text{-}Bu)_2]_3$	15[c]
5	**5a**	30			

[a] Control experiments show that either in the absence of a Pd source or in the absence of the bicyclic triaminophosphine ligand **4**, no reaction was observed. [b] Isolated yields (average of two runs). [c] 15% of hydrodehalogenated arene was isolated.

bulky bicyclic triaminophosphines **3a** and **4a** were employed in this reaction. Although ligand **3a** was not effective, it was gratifying to find that, with **4a** (a colorless liquid), the desired amination product was isolated in 97% yield (Table 1, entry 4). Interestingly, further increases in ligand steric hindrance (**5a** and **6a**) proved ineffective (Table 1, entries 5 and 6). The inefficiency of ligand **3a** might be due to the fact that it does not provide sufficient steric bulk since the Me groups on the *i*-Pr substituents are turned outward and away when the Pd is coordinated to phosphorus, a conformation that is also present in the solid-state structure of the free ligand and its protonated form.[14] Although **5a** could be assumed to be at least as efficient as **4a**, if not more so, it appears that, after a point achieved in **4a**, additional steric hindrance becomes detrimental to catalyst activity. Thus, **4a** presumably possesses a unique balance of stereoelectronic influences that optimize activity of the catalyst system. As expected, the relatively electron-poor acyclic triaminophosphine ligands $P(NR_2)_3$ (R = Me, Et, *i*-Bu) gave very poor yields with incomplete conversion (Table 1, entries 7−9).

The best results were obtained in aminations performed at 80 °C in toluene using NaO-*t*-Bu[19] as a base and a catalyst system generated in situ from 2 mol % $Pd(OAc)_2$ and 4 mol % of **4a**. With optimized conditions in hand, the scope of this catalytic process was examined with various aryl bromides and iodides, and the results are summarized in Tables 2 and 3, respectively. As seen in Table 2, the Pd/**4a** catalyst system efficiently catalyzed the cross-coupling reaction of electronically diverse aryl bromides with a variety of amines. Thus, electron-poor (e.g., 4-bromobenzonitrile), electron-neutral (e.g., 4-*tert*-butylbromobenzene), and electron-rich (e.g., 4-bromoanisole) aryl bromides coupled smoothly with various anilines (primary and secondary) to afford the N-arylated products in excellent yields (Table 2, entries 3, 7, 8, 17, and 18). Secondary cyclic amines were also efficiently arylated. For example, morpholine and pyrrolidine reacted with 4-bromobenzonitrile to give the desired products in high yields (Table 2, entries 1 and 2). Similarly, piperidine coupled with 4-*tert*-butylbromobenzene and 4-bromoanisole in good to excellent yields (Table 2, entries 9 and 19). It may be noted that the piperidine coupling reaction gave a large amount of reduced side products with a very active Pd/BINAP catalyst system.[10]

The Pd/**4a** catalyst system was also effective for primary aliphatic amines that were branched at the α

(14) An X-ray structural study of **3a** showed that the bonding environment around the PN_3 nitrogen is rather planar, the sum of angles being 354.9, 356.6, and 357.5° (Wroblewski, A. E.; Pinkas, J.; Verkade, J. G. *Main Group Chem.* **1995**, *1*, 69).

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(19) Weaker bases such as Cs_2CO_3, CsF, K_3PO_4, K_2CO_3, and NaOH failed to promote coupling.

TABLE 2. Palladium/4a-Catalyzed Amination of Aryl Bromides[a]

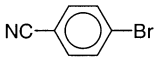
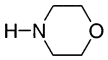
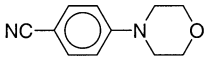
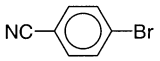
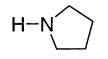
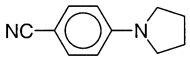
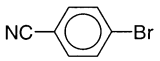
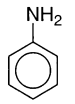
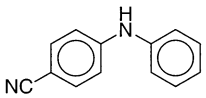
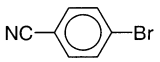
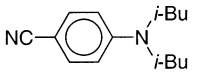
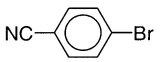
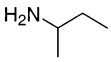
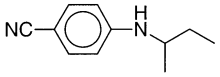
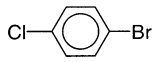
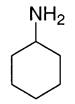
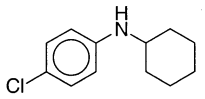
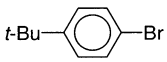
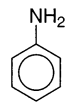
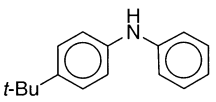
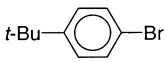
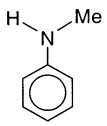
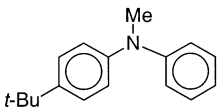
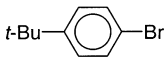
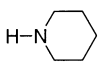
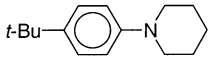
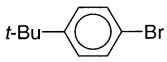
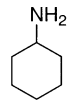
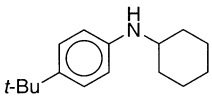
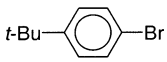
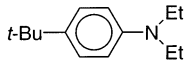
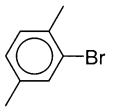
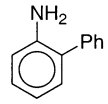
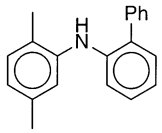
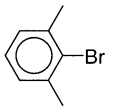
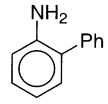
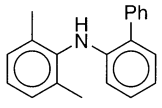
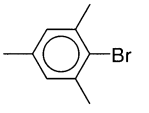
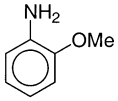
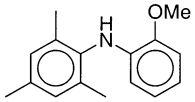
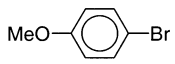
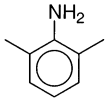
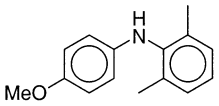
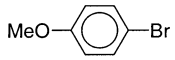
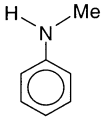
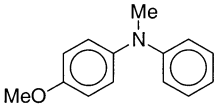
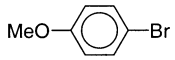
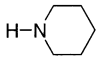
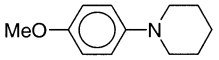
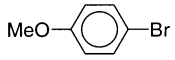
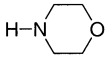
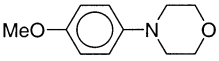
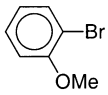
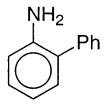
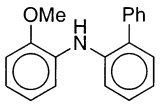
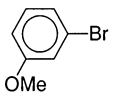
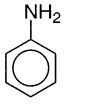
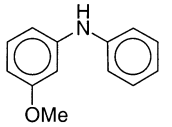
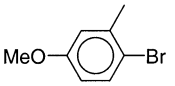
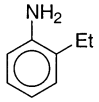
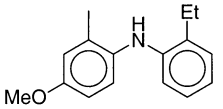
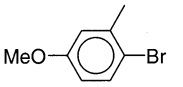
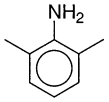
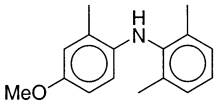
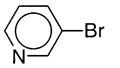
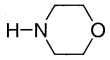
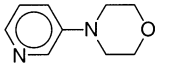
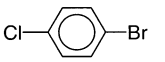
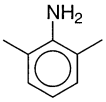
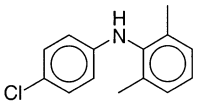
entry	aryl bromide	amine	product	yield (%)[b]
1				99
2				96
3				99
4		$(i\text{-Bu})_2NH$		70[c]
5				65[c]
6				70
7				99
8				93
9				82
10				88
11		Et_2NH		57[c]
12				99
13				94
14				99
15				99
16				84[d]

Table 2 (Continued)

entry	aryl bromide	amine	product	yield (%)[b]
17				97
18				91
19				92
20				95
21				93
22				96
23				96
24				98
25				89
26				90

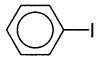
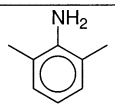
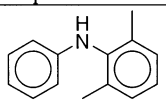
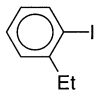
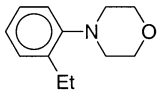
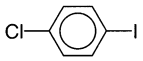
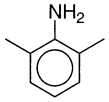
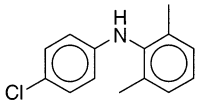
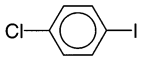
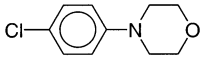
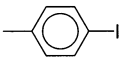
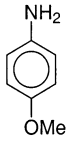
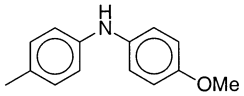
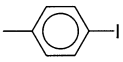
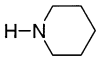
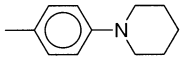
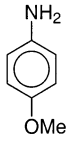
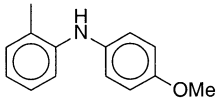
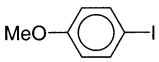
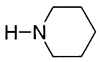
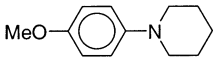
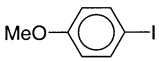
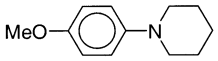
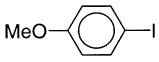
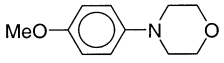
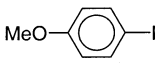
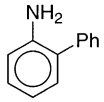
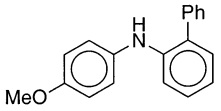
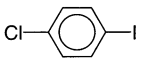
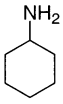
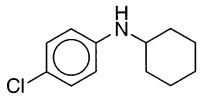
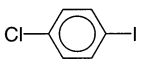
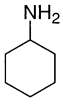
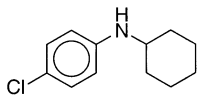
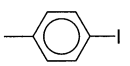
[a] Reaction conditions: 1.0 mmol of aryl bromide, 1.2 mmol of amine, 1.5 mmol of NaO-*t*-Bu, 2.0 mol % $Pd/(OAc)_2$, 4.0 mol % **4a**, 5 mL of toluene, 80 °C, 9−15 h. Reaction times have not been minimized. [b] Isolated yields (average of two runs). [c] 5.0 mol % $Pd(OAc)_2$ was used. [d] 3.0 mol % $Pd(OAc)_2$ was used.

position. For instance, cyclohexylamine reacted with 4-*tert*-butylbromobenzene to produce the N-arylated product in 89% yield (Table 2, entry 10). Moreover, sterically hindered 2-bromotoluene reacted cleanly with cyclohexylamine (Table 2, entry 16). A slightly lower yield was obtained with electron-poor 4-bromochlorobenzene (Table 2, entry 6). A catalyst loading of 5 mol % allowed the reaction of 4-bromobenzonitrile with *sec*-butylamine (Table 2, entry 5). However, the reaction of long-chain primary alkylamines such as *n*-hexylamine with aryl bromides usually gave less than 50% yield of the desired product even when greater quantities of catalyst and/or longer reaction times were employed. The main side products were the diarylated amine, which may be attributed to the formation of a catalytically inactive bis(primary amine)palladium(II) complex,[20] and the hydrodehalogenated arene, resulting from β-hydride elimination. Reactions of acyclic secondary amines with aryl bromides also occurred (in moderate yields) although they required the use of 5 mol % $Pd(OAc)_2$. Thus, 4-bromobenzonitrile and 4-*tert*-butylbromobenzene reacted with diisobutylamine and diethylamine, respectively, to form the corresponding N-aryl product (Table 2, entries 4 and 11, respectively).

Steric hindrance on either coupling partner was well tolerated, often giving the desired product in almost quantitative yield. For example, mono and di-*ortho*-substituted aryl bromides reacted with 2-aminobiphenyl to give excellent yields of the desired product (Table 2, entries 12 and 13). Particularly noteworthy is the reaction of 2-bromomesitylene with 2,6-dimethylaniline, which afforded the tetra-*ortho*-substituted arylamine product in 99% isolated yield (Table 2, entry 15). With DPEphos (bis[2-(diphenylphosphino)phenyl] ether), *rac*-BINAP, or

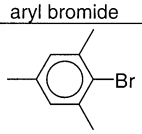
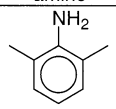
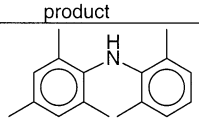
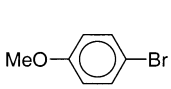
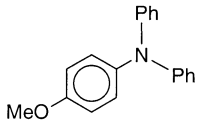
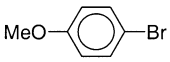
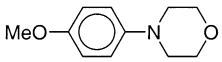
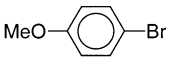
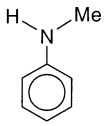
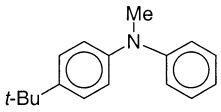
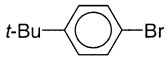
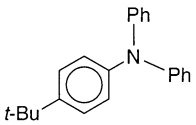
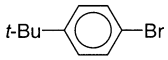
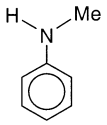
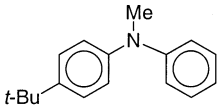
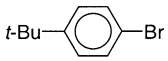
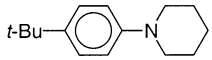
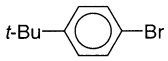
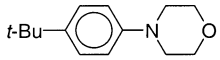
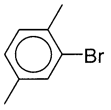
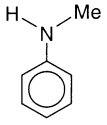
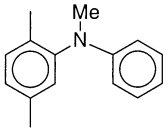
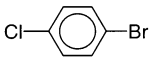
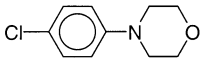
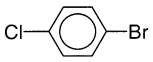
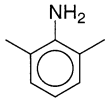
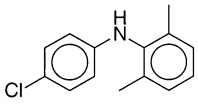
(20) Widenhoefer, R. A.; Buchwald, S. L. *Organometallics* **1996**, *15*, 3534.

TABLE 3. Palladium/4a-catalyzed Amination of Aryl Iodides[a]

entry	aryl iodide	amine	product	yield (%)[b]
1				94
2				94
3				72[c]
4				89
5				90
6				78
7				95
8				56
9				75[d]
10				79
11				75[d]
12				43
13				51[e]
14				59[e]
15				62[e]

[a] Reaction conditions: 1.0 mmol of aryl iodide, 1.2 mmol of amine, 1.5 mmol of NaO-*t*-Bu, 2.0 mol % of $Pd(OAc)_2$, 4.0 mol % of ligand **4a**, 5 mL of toluene, 80 °C, 9−12 h. Reaction times have not been minimized. [b] Isolated yields (average of two runs). [c] 10% of hydrodehalogenated arene was isolated. [d] 2.0 mol % of $Pd_2(dba)_3$ was used instead of $Pd(OAc)_2$. [e] 4.0 mol % of $Pd(OAc)_2$ was employed.

TABLE 4. Amination of Aryl Bromides Using Pd/4a at Low Catalyst Loading[a]

entry	aryl bromide	amine	product	yield (%)[b]
1				94
2		Ph_2NH		95
3				93
4				91
5		Ph_2NH		96
6				94
7				92
8				99
9				61
10				50
11				87

[a] 0.5 mol % $Pd(OAc)_2$; 1 mol % ligand **4a**. [b] Isolated yields.

DPPF as a ligand,[21] the analogous reaction involving 2-bromo-*m*-xylene and 2,6-diisopropylaniline required much higher catalyst loading (5 mol % Pd) and a reaction temperature of 100 °C (20 °C higher than that reported in the present work).

Our protocol was equally effective for aryl bromides possessing substituents at various positions (Table 2, entries 21−24). The reaction of an heteroaryl bromide with morpholine also proceeded well (Table 2, entry 25).

Next, we investigated amination reactions of extensively used and easy obtainable aryl iodides (Table 3). With the $Pd(OAc)_2$/**4a** catalyst system, electronically neutral aryl iodides readily combined with anilines (Table 3, entries 1, 5, and 7) and secondary cyclic amines (Table 3, entries 2 and 6). Slightly lower yields of arylamines were achieved with electron-deficient aryl iodides (Table 3, entry 3) owing to formation of reduced arene side products. Electron-rich aryl iodides were also suitable substrates (Table 3, entries 10 and 11). Although $Pd(OAc)_2$ was used as a palladium source for most reactions, reactions of electron-rich aryl iodides usually proceeded well when $Pd_2(dba)_3$ was employed (Table 3, compare entries 8 and 9). The reaction of aryl iodides with primary aliphatic amines and acyclic secondary amines did not

(21) Sadighi, J. P.; Harris, M. C.; Buchwald, S. L. *Tetrahedron Lett.* **1998**, *39*, 5327.

proceed to completion even with higher catalyst loading (5 mol % Pd) and longer reaction times. However, cyclohexylamine did react with aryl iodides although in moderate yields (Table 3, entries 12−15) when a slightly higher catalyst loading (4 mol % Pd) was employed to permit the reaction to go to completion. In general (as can be seen from Tables 2 and 3) aryl iodides provided lower yields of the arylamine product compared with their bromide counterparts, the former being more prone to β-hydride elimination leading to formation of hydrodehalogenation product.

We also carried out amination reactions at a low catalyst loading (0.5 mol % Pd, Table 4),[22] and most of these reactions were complete in <22 h. The sterically hindered arylamine in entry 1 was formed in excellent yield (94%). Secondary cyclic amines were generally also efficiently arylated, often giving improved results over those obtained using either Pd/BINAP or Buchwald's catalyst sytem. For example, the reaction of 1-bromo-4-*tert*-butylbenzene with piperidine using 0.5 mol % Pd/**4a** afforded the desired product in 92% yield while Buchwald's catalyst system utilizing (*o*-biphenyl)PCy_2 as a ligand with 0.5 mol % Pd gave an 86% yield.[8] Similarly, the aforementioned substrate and morpholine were coupled in 99% isolated yield using 0.5 mol % Pd/**4a** while the Pd/BINAP catalyst system gave a 93% yield when the reaction was run neat.[10] Additionally, *N*-methylaniline, which is often a problematic substrate for the Pd/BINAP catalyst system, was also cleanly arylated (Table 4).

It appears that the catalytic system comprising $Pd(OAc)_2$ and ligand **4a** is the most effective catalyst reported to date for the reaction of sterically hindered arylbromides and anilines. Moreover, the scope of Pd/**4a** catalyst system exceeds (for the examples discussed above) or generally equals that of Pd/BINAP, Pd/(*o*-biphenyl)PCy_2, or Pd/(*o*-biphenyl)P(*t*-Bu)$_2$.

Because arylamines are industrially important synthetic targets, a crucial requirement for viability of an industrial process to synthesize them using palladium technology is ligand cost. In this regard it is worth mentioning that **4a** at $50.50/5 g is cheaper than racemic BINAP, P(*t*-Bu)$_3$ and (*o*-biphenyl)PCy_2, or (*o*-biphenyl)P(*t*-Bu)$_2$ by almost a factor of 2, 3, and 5, respectively.[23]

In summary, we have demonstrated that ligand **4a** functions uncommonly efficiently in amination reactions. Various aryl bromides and iodides were readily coupled with a range of amines, including primary and secondary anilines, cyclic secondary amines, primary amines branched at the α position, and (with limited success) acyclic secondary amines. Good to excellent yields were obtained with the vast majority of substrate combinations. Several salutary features of **4a** are (a) commercial availability, (b) optimum steric effects provided by the *i*-butyl groups, and (c) electron-richness of the phosphorus arising from the donating capability of all three virtually planar nitrogens adjacent to the phosphorus, as well as the possibility for augmented basicity of the phosphorus arising from transannular bonding between the bridgehead nitrogen and the phosphorus atom. Both of these basicity-enhancing stereoelectronic influences are lacking in acyclic triaminophosphines, which we have shown behave poorly under our reaction conditions. Finally, we believe that the comparatively very low price of ligand **4a**, compared with other phosphine ligands usually employed in amination reactions, enhances its appeal. An exploration of aryl chloride aminations using our approach is underway.

Experimental Section

General Experimental Conditions. All reactions were performed under an atmosphere of argon in oven-dried glassware. Toluene was collected from a solvent purification system and stored over 4 Å molecular sieves. ^{1}H and ^{13}C NMR spectra were recorded at 300 and 75.5 MHz, respectively, unless otherwise noted. Thin-layer chromatography (TLC) was performed using commercially prepared 60 mesh silica gel plates visualized with short-wavelength UV light (254 nm). Silica gel 60 (9385, 230−400 mesh) was used for column chromatography. Melting points were determined in unsealed capillary tubes and are uncorrected. The reported yields are isolated yields and are the average of two runs. All commercially available reagents were used as received. Ligands **1a**−**6a** were prepared according to our previously reported procedures[15] (although ligands **1a**, **3a**, and **4a** are commercially available from Aldrich).

General Procedure for Aminating Aryl Bromides and Iodides. An oven-dried Schlenk flask equipped with a magnetic stirring bar was charged with $Pd(OAc)_2$ (2 mol %) and NaO-*t*-Bu (1.5 mmol) inside a nitrogen-filled glovebox. The flask was capped with a rubber septum and removed from the glovebox. Aryl halide (1.0 mmol), amine (1.2 mmol), and toluene (5 mL) were then successively added. The flask was placed in an 80 °C oil bath, and the reaction mixture was stirred until the starting material had been completely consumed as judged by TLC. The mixture was cooled to room temperature and adsorbed onto silica gel. The crude product was purified by column chromatography. The presence of hydrodehalogenated product in some of the preparations was verified by TLC using authentic samples for comparison.

***N*-(*p*-Cyanophenyl)-2-ethylaniline**: white solid, mp 63−64 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43 (d, 2H, J = 7.9 Hz), 7.32 (d, 1H, J = 6.7 Hz), 7.25−7.19 (m, 3H), 6.77 (d, 2H, J = 8.8 Hz), 5.90 (s, 1H), 2.59 (q, 2H, J = 4.7 Hz), 1.20 (t, 3H, J = 6.3 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 149.9, 139.1, 137.5, 133.8, 129.7, 127.1, 126.1, 125.1, 120.3, 114.2, 100.5, 24.5, 14.5. Anal. Calcd for $C_{15}H_{14}N_2$: C, 81.08; H, 6.30; N, 12.61. Found: C, 81.00; H, 6.38; N, 12.27.

***N*,*N*-Diisobutyl-4-cyanoaniline**: white solid, mp 71−73 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43 (d, 2H, J = 9.0 Hz), 6.61 (d, 2H, J = 9.1 Hz), 3.21 (d, 4H, J = 7.4 Hz), 2.14−1.98 (m, 2H), 0.92 (d, 12H, J = 6.6 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 150.9, 133.6, 121.0, 112.0, 96.6, 60.1, 26.5, 20.4. Anal. Calcd for $C_{15}H_{22}N_2$: C, 78.26; H, 9.56; N, 12.17. Found: C, 78.10; H, 10.01; N, 12.25.

***N*-(*4-tert*-Butylphenyl)cyclohexylamine**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25−7.19 (m, 2H), 6.58−6.56 (m, 2H), 3.28−3.21 (m, 1H), 2.05 (d, 2H, J = 12.1 Hz), 1.80−1.65 (m, 3H), 1.41−1.15 (m, 15 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 145.2, 139.7, 126.2, 113.0, 52.1, 33.8, 31.8, 26.2, 25.2, 16.5. Anal. Calcd for $C_{16}H_{25}N$: C, 83.11; H, 10.82; N, 6.06. Found: C, 83.21; H, 10.56; N, 5.92.

2,5-Dimethyl-2′-phenyldiphenylamine: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51−7.35 (m, 5H), 6.77 (d, 1H, J = 2.57), 5.42 (s, 1H), 2.29 (s, 3H), 2.05 (s, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 141.4, 141.2, 139.3, 136.7, 130.84, 129.5, 129.1, 128.7, 127.6,

(22) The reaction of 1-chloro-4-iodobenzene with morpholine using the Pd/**4a** catalyst system (0.5 mol % Pd) gave an 85% yield of the desired product. The general protocol for the amination of aryl iodides using Pd/**4a** at such a low catalyst loading has not yet been fully scoped.

(23) Ligand **4a**: $50.50 (5 g, Aldrich). Racemic BINAP: $90.60 (5 g, Aldrich). P(*t*-Bu)$_3$: $148.00 (5 g, Aldrich). 2-(Di-*tert*-butylphosphino)-biphenyl or 2-(dicyclohexylphosphino)biphenyl: $99.00 (2 g, Strem).

126.1, 123.1, 120.3, 120.1, 116.8, 21.4, 17.6. Anal. Calcd for $C_{20}H_{19}N$: C, 87.91; H, 6.96; N, 5.13. Found: C, 87.88; H, 6.73; N, 5.38.

2,6-Dimethyl-2′-phenyldiphenylamine: white solid, mp 101−103 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63 (d, 2H, J = 7.3 Hz), 7.54 (t, 2H, J = 6.7 Hz), 7.43 (t, 1H, J = 7.0 Hz), 7.23 (d, 1H, J = 6.7 Hz), 7.16−7.12 (m, 4H), 6.85 (t, 1H, J = 7.0 Hz), 6.27 (d, 1H, J = 8.2 Hz), 5.32 (s, 1H), 2.23 (s, 6H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 143.3, 139.7, 138.4, 136.3, 130.4, 129.6, 129.1, 128.7, 128.6, 127.7, 127.5, 126.0, 117.9, 111.7, 18.5. Anal. Calcd for $C_{20}H_{19}N$: C, 87.91; H, 6.96; N, 5.13. Found: C, 87.79; H, 6.66; N, 5.45.

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Supporting Information Available: Spectra of previously unknown compounds and references for known compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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