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Synthesis of *N*-aryl-aza-crown ethers via Pd-catalyzed amination reactions of aryl chlorides with aza-crown ethers

Sameer Urgaonkar and John G. Verkade*

Department of Chemistry, 1275 Gilman Hall, Iowa State University, Ames, IA 50011, USA

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Abstract—The $Pd_2(dba)_3$/P(*i*-$BuNCH_2CH_2)_3N$ (**1**) catalyst system effectively catalyzes the coupling of aza-crown ethers with electronically diverse aryl chlorides, affording *N*-aryl-aza-crown ethers in good yields. The $Pd_2(dba)_3$/P(*i*-$BuNCH_2)_3CMe$ (**2**) catalyst system containing the more constrained bicyclic triaminophosphine is useful for aryl chlorides possessing base-sensitive ester, nitro, and nitrile functional groups.

1. Introduction

The chemistry of *N*-aryl-aza-crown ether derivatives is attracting significant interest because of the utility of these compounds in synthesizing fluoroionophores in which, for example, a fluorescent aryl moiety is covalently linked to the nitrogen of an aza-crown ether.[1] These molecules can serve as sensitive and selective sensors of cations by binding them in the crown ether, thereby modifying the intensity and/or the energy of the signal of the fluorophore. Pyridine-functionalized aza-crown ethers have also been used as a scaffold for self-assembly in supramolecular chemistry.[2] Traditional approaches to the preparation of *N*-aryl-aza-crown ethers include nucleophilic aromatic substitution of activated aryl halides with aza-crown ethers under high pressure conditions,[3] or manipulation of functional groups on aniline precursors.[4] However, these approaches suffer from one or more of the following problems that impede accessibility to this important class of compounds: stringent conditions, multiple step syntheses, low yields, and limited substrate scope.

In recent years, palladium-catalyzed Buchwald–Hartwig amination reactions of aryl halides with amines have emerged as a method of choice for C–N bond forming processes.[5–7] In this respect, Witulski et al.[8] have developed a Pd/PPh_3 and a Pd/P(*o*-tol)$_3$ catalyst system for the coupling of aryl and heteroaryl bromides with aza-crown ethers. However, this method was limited to electron-poor aryl and heteroaryl bromides. Interestingly, the use of P(*t*-Bu)$_3$,[7] a popular ligand for Pd-catalyzed amination reactions, gave inferior results probably because of its steric bulk.

An improvement to the above protocol was described by Zhang and Buchwald[9] who achieved cross-coupling of aryl bromides with aza-crown ethers using a catalyst system comprised of $Pd_2(dba)_3$ and biphenyl-based monophosphine ligands with NaO-*t*-Bu as the base. Although electronically diverse and also *ortho*-substituted aryl bromides could be employed in these reactions, limitations still existed. For example, the authors noted that poor yields of *N*-aryl-aza-crown ethers were obtained when weak bases such as Cs_2CO_3 or K_3PO_4 were used in place of NaO-*t*-Bu, thus precluding the introduction of various base-sensitive functional groups into the aryl substrate. A particularly important apparent limitation was that no examples employing aryl chlorides as the coupling partner were reported. Aryl chlorides are cheaper and are available in wider diversity than bromides or iodides, and their applicability in coupling with aza-crown ethers would constitute a significant advance, especially since aza-crown ethers are currently quite expensive. We report here a general and efficient method for the synthesis of *N*-aryl-aza-crown ethers via a palladium-catalyzed amination reaction of aryl chlorides that occurs in the presence of bicyclic triaminophosphine ligands **1** and **2**.

Our recent explorations in palladium-catalyzed cross coupling reactions have established that electron-rich and commercially available proazaphosphatrane **1** (Fig. 1), first synthesized in our laboratories, serves as an excellent ligand

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* Corresponding author. Tel.: +1 515 2945023; fax: +1 515 2940105; e-mail: jverkade@iastate.edu

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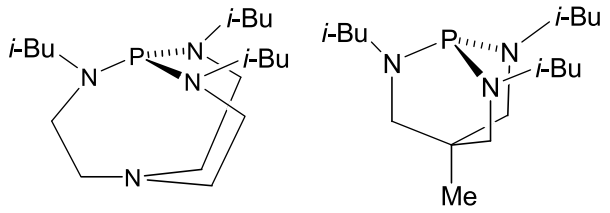


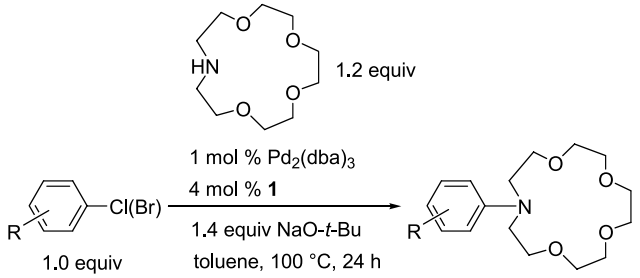
1 2

Figure 1. Bicyclic triaminophosphine ligands.

in Suzuki,[10] Buchwald–Hartwig amination,[11] Stille,[12] and *alpha*-arylation[13] reactions. Notoriously unreactive aryl chlorides can also be employed in these transformations. We have also developed a new bicyclic triaminophosphine ligand **2** (Fig. 1) for which we have demonstrated utility in Buchwald–Hartwig amination reactions.[14] It was noted that ligand **2** is especially useful for substrates with functionalities that require a weak base such as Cs_2CO_3.

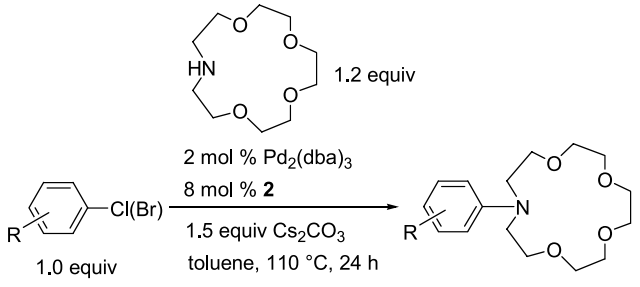
2. Results and discussion

We initially investigated the coupling of commercially available 1-aza-15-crown-5 with aryl chlorides. After brief experimentation, we established that a variety of aryl chlorides can be coupled with 1-aza-15-crown-5 using 1 mol% $Pd_2(dba)_3$ and 4 mol% ligand **1** in toluene at 100 °C (Scheme 1) in the presence of NaO-*t*-Bu as the base.



Scheme 1. Conditions for $Pd_2(dba)_3$/**1**-catalyzed synthesis of *N*-aryl-aza-crown ethers.

Not surprisingly, aryl chlorides possessing an ester, nitro or nitrile group did not fare well in this approach. For these substrates, however, conditions developed by us utilizing **2** as the ligand in the presence of the mild base Cs_2CO_3 proved to be gratifyingly efficacious (Scheme 2).



Scheme 2. Conditions for $Pd_2(dba)_3$/**2**-catalyzed synthesis of *N*-aryl-aza-crown ethers possessing base-sensitive functional groups.

The potential and scope of this methodology is illustrated in Table 1 by the reaction of a variety of aryl chlorides and bromides with 1-aza-15-crown-5. It is seen in this table that electronically diverse aryl chlorides as well as bromides can be coupled successfully in good to excellent yields with the aza-crown ether. Using the $Pd_2(dba)_3$/**1** catalyst system (2 mol% Pd), electron-poor 4-chlorobenzotrifluoride afforded the desired product in 86% yield (entry 1). Electron-neutral 4-chlorotoluene also reacted efficiently (80% product yield, entry 5). Electron-rich 4-chloroanisole, a more challenging substrate, also functioned as a substrate, providing the desired *N*-aryl-aza-crown ether in moderate yield (50%, entry 7). The *meta*-substituted aryl chloride, 3-chloroanisole also coupled, giving a 66% product yield (entry 6). Notably, 2-chloropyridine and less reactive 3-chloropyridine were also successfully coupled (entries 8 and 9). The coupling shown in entry 9 is particularly impressive, because to date, no catalyst system has been reported for the coupling of 3-halopyridines with aza-crown ethers. Under these conditions, electron-neutral and electron-rich aryl bromides also participated in the process (entries 11–13).

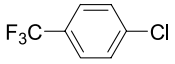
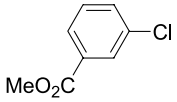
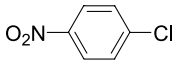
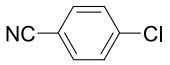
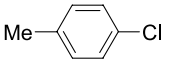
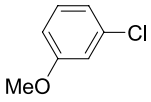
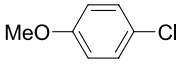
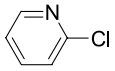
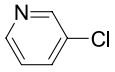
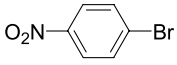
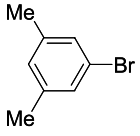
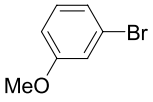
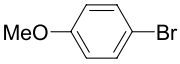
As mentioned earlier, the $Pd_2(dba)_3$/**2** catalyst system in the presence of the weak base Cs_2CO_3 was employed (4 mol% Pd) for substrates with base-sensitive functional groups. Thus, methyl-3-chlorobenzoate (73%, entry 2), 4-chloronitrobenzene (81%, entry 3), 4-chlorobenzonitrile (56%, entry 4), and 4-bromonitrobenzene (87%, entry 10) were all aminated under our standard conditions. For the reaction of 4-bromonitrobenzene, however, 2 mol% of Pd was sufficient for the coupling to occur in high yield.

Although ligands **1** and **2** are slightly air- and moisture-sensitive, they can be easily handled without the need for a glove-box using standard Schlenk techniques. Because of the moisture sensitivity of NaO-*t*-Bu and Cs_2CO_3, these reagents were stored and weighed inside the glove-box. However, we have established that the weighing of the aforementioned reagents inside the glove-box is not an absolute requirement. Thus when a sample of one of these reagents was taken from material stored inside the glove-box and weighed outside the glove-box with manipulations carried out using Schlenk techniques, amination reactions proceeded with almost equal efficiency (see parenthesized yields in entries 3, 6, and 11 of Table 1). The same procedure was also applied to other ingredients, that is, $Pd_2(dba)_3$, aryl chloride, toluene, and aza-crown ether.

The present methodology is not without its limitations, however. For example, *ortho*-substituted aryl chlorides did not couple with 1-aza-15-crown-5 to an appreciable extent and *ortho*-substituted aryl bromides provided only trace amounts of products.

We have also applied a biphenyl based aminophosphine ligand **3** (Buchwald's ligand) to synthesize the target compounds from aryl chlorides (Table 2). Using the protocol of Buchwald [i.e., 1 mol% of $Pd_2(dba)_3$ and 6 mol% of **3** (3L/Pd)], 4-chloroanisole and 4-chlorotoluene efficiently reacted with 1-aza-15-crown-5, affording the desired products in 61% (entry 1, Table 2) and 79% yields (entry 2, Table 2), respectively. However, when aryl chlorides with functional groups such as nitro and ester

Table 1. $Pd_2(dba)_3$/**1** or **2**-catalyzed synthesis of *N*-aryl-aza-crown ethers from aryl chlorides

Entry	Aryl halide	Ligand	mol% Pd	Base	Yield (%)[a]
1		**1**	2	NaO-*t*-Bu	80[b]
2		**2**	4	Cs_2CO_3	73[c]
3		**2**	4	Cs_2CO_3	81[c] (79)[d]
4		**2**	4	Cs_2CO_3	56[c]
5		**1**	2	NaO-*t*-Bu	80[b]
6		**1**	2	NaO-*t*-Bu	66[b] (61)[d]
7		**1**	2	NaO-*t*-Bu	50[b]
8		**1**	2	NaO-*t*-Bu	76[b]
9		**1**	2	NaO-*t*-Bu	51[b]
10		**2**	2	Cs_2CO_3	87[c]
11		**1**	2	NaO-*t*-Bu	82[b] (81)[d]
12		**1**	2	NaO-*t*-Bu	68[b]
13		**1**	2	NaO-*t*-Bu	60[b]

[a] Isolated yields (average of two runs).
[b] For reaction conditions, see Scheme 1.
[c] For reaction conditions, see Scheme 2.
[d] Yields in parenthesis refer to the same reaction performed without the use of glove-box (see text).

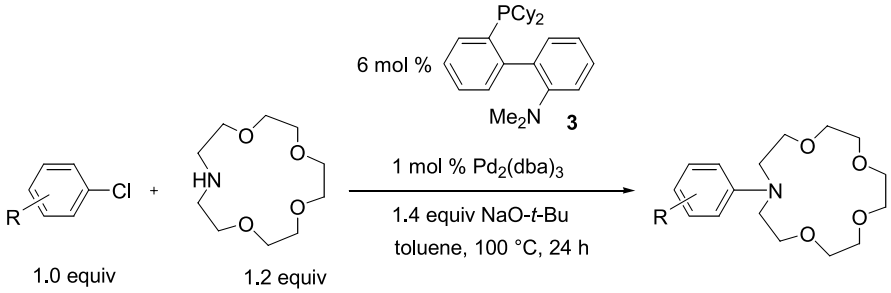
were employed in the presence of Cs_2CO_3 as the base, the corresponding products were obtained in only poor yields (entries 3 and 4, Table 2). As demonstrated above, the coupling of these substrates can be best carried out using ligand **2**.

We have extended our methodology based on the $Pd_2(dba)_3$/**1** catalyst system to the arylation of a second aza-crown ether, namely, 1-aza-18-crown-6 and the results are summarized in Table 3. Using unactivated and deactivated aryl chlorides, bromides, and iodides, yields obtained were in the range of 51–55% (entries 1–4). For an aryl iodide, only 1 mol% of Pd was used.

3. Conclusions

The synthesis of various *N*-aryl-aza-crown ethers was readily achieved via palladium-catalyzed amination of aryl chlorides, bromides, and iodides in which the catalyst system consists of $Pd_2(dba)_3$ and one of the bicyclic triaminophosphine ligands **1** or **2**, the choice depending on the nature of the aryl substrate. Using this approach, the reaction is tolerant of a variety of functional groups. To the best of our knowledge, our protocol is the first reported for coupling aryl chlorides with aza-crown ethers. We have also demonstrated the utility of Buchwald's ligand in the reactions involving aryl chlorides.

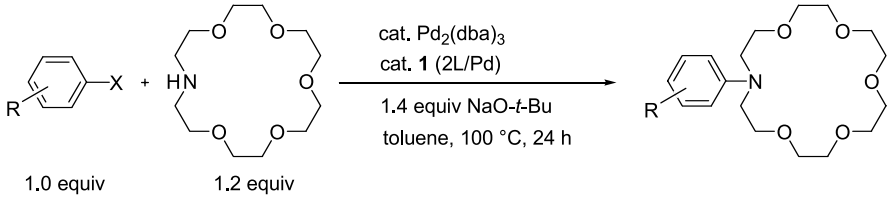
Table 2. Synthesis of *N*-aryl-aza-crown ethers from aryl chlorides using Buchwald's protocol

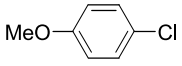
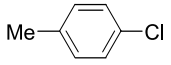
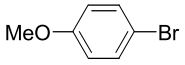
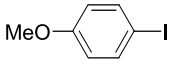


Entry	R	Yield (%)[a]
1	4-OMe	61
2	4-Me	79
3	4-NO_2	44[b,c]
4	3-CO_2Me	26[b,c]

[a] Isolated yields (average of two runs).
[b] 2 mol% of $Pd_2(dba)_3$ and 12 mol% of **3** were used.
[c] Cs_2CO_3 was used as the base.

Table 3. $Pd_2(dba)_3$/**1**-catalyzed coupling of aryl halides with 1-aza-18-crown-6



Entry	Aryl halide	mol% Pd	Yield (%)[a]
1		2	51
2		2	52
3		1.8	54
4		1	55

[a] Isolated yields (average of two runs).

4. Experimental

4.1. General methods

$Pd_2(dba)_3$, NaO-*t*-Bu, and Cs_2CO_3 were purchased from Aldrich and used without further purification. Toluene was collected from a Grubbs type solvent purification system. All other reagents were commercially available and are used as received. Ligands **1**[15] and **2**[14] were prepared according to previously reported procedures, although **1** is commercially available from Aldrich and Strem Chemicals. For convenience, stock solutions of **1** and **2** in toluene (2 mM) were prepared and stored under argon outside the glove-box. All reactions were performed under an atmosphere of argon in oven-dried glassware. ^1H and ^{13}C NMR spectra were recorded at 300 and 75.5 MHz, respectively, unless otherwise noted. Elemental analyses were performed by Desert Analytics (Tucson, Arizona, USA). Mass spectra were recorded on a Kratos MS 50 instrument. The yields reported are isolated yields and are the average of two runs.

4.2. General procedure for the coupling of aryl halides with aza-crown ethers using the $Pd_2(dba)_3$/1 or $Pd_2(dba)_3$/2 catalyst system (Tables 1 and 3)

An oven-dried Schlenk flask equipped with a magnetic stirring bar was charged with $Pd_2(dba)_3$ (0.5–2 mol%, see Tables 1 and 3), an appropriate aza-crown ether (1.2 mmol), and NaO-*t*-Bu (1.4 mmol) or Cs_2CO_3 (1.5 mmol) inside a glovebox. If the aryl halide (1.0 mmol) was a solid, it was also added at this time. The flask was capped with a rubber septum and removed from the glove box. Ligand **1** or **2** (2–8 mol%) was then added via syringe from a stock solution

(2 mM in toluene). Aryl halide (if a liquid, 1.0 mmol) and toluene (3 mL) were then successively added via syringe. The reaction mixture was heated at the temperature indicated (see Tables 1 and 3) for 24 h. The mixture was then cooled to room temperature, adsorbed onto silica gel and then purified by column chromatography using initially 10% ethyl acetate/hexanes and then ethyl acetate as eluents.

4.3. General procedure for the coupling of aryl chlorides with 1-aza-15-crown-5 using Buchwald's catalyst system (Table 2)

Inside a glovebox, an oven-dried Schlenk flask equipped with a magnetic stirring bar was charged with $Pd_2(dba)_3$ (1 mol%), 1-aza-15-crown-5 (1.2 mmol), ligand **3** (6 mol%), and NaO-*t*-Bu (1.4 mmol). The flask was capped with a rubber septum and removed from the glove box. Then aryl chloride (1.0 mmol) and toluene (3 mL) were successively added via syringe and the reaction mixture was heated at 100 °C for 24 h. The mixture was cooled to room temperature, adsorbed onto silica gel and then purified by column chromatography using initially 10% ethyl acetate/hexanes, followed by ethyl acetate as eluents.

4.4. References for known compounds and spectroscopic data for unknown compounds

4.4.1. *N*-(4-Trifluoromethylphenyl)-1-aza-15-crown-5 (Table 1, entry 1). The ^1H and ^{13}C NMR spectra were in accordance with those described in the literature.[9]

4.4.2. *N*-(3-Carbomethoxyphenyl)-1-aza-15-crown-5 (Table 1, entry 2). ^1H NMR (300 MHz, $CDCl_3$): δ 7.30–7.19 (m, 3H), 6.85–6.82 (m, 1H), 3.86 (s, 3H), 3.76–3.58 (m, 20H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 167.9, 147.8, 131.3, 129.4, 117.0, 116.0, 112.3, 71.5, 70.4, 70.3, 68.6, 52.7, 52.2. HRMS *m/z* Calcd for $C_{18}H_{27}NO_6$: 353.18384. Found: 353.18430. Anal. Calcd for $C_{18}H_{27}NO_6$: C, 61.19; H, 7.65. Found: C, 61.34; H, 7.81.

4.4.3. *N*-(4-Nitrophenyl)-1-aza-15-crown-5 (Table 1, entries 3 and 10). The ^1H and ^{13}C NMR spectra were in accordance with those described in the literature.[8a]

4.4.4. *N*-(4-Cyanophenyl)-1-aza-15-crown-5 (Table 1, entry 4). The ^1H and ^{13}C NMR spectra were in accordance with those described in the literature.[16]

4.4.5. *N*-(4-Methylphenyl)-1-aza-15-crown-5 (Table 1, entry 5 and Table 2, entry 2). The ^1H and ^{13}C NMR spectra were in accordance with those described in the literature.[17]

4.4.6. *N*-(3-Methoxyphenyl)-1-aza-15-crown-5 (Table 1, entries 6 and 12). The ^1H and ^{13}C NMR spectra were in accordance with those described in the literature.[9]

4.4.7. *N*-(4-Methoxyphenyl)-1-aza-15-crown-5 (Table 1, entries 7 and 13, and Table 2, entry 1). The ^1H and ^{13}C NMR spectra were in accordance with those described in the literature.[9]

4.4.8. *N*-(2-Pyridinyl)-1-aza-15-crown-5 (Table 1, entry 8). ^1H NMR (300 MHz, $CDCl_3$): δ 8.05 (d, J=3.5 Hz, 1H), 7.34 (t, J=7.1 Hz, 1H), 6.49–6.42 (m, 2H), 3.72–3.57 (m, 20H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 157.8, 148.0, 137.2, 111.6, 106.0, 71.4, 70.4, 70.2, 69.3, 51.2. HRMS *m/z* Calcd for $C_{15}H_{24}N_2O_4$: 296.17361. Found: 296.17410. Anal. Calcd for $C_{15}H_{24}N_2O_4$: C, 60.81; H, 8.11. Found: C, 60.67; H, 8.31.

4.4.9. *N*-(3-Pyridinyl)-1-aza-15-crown-5 (Table 1, entry 9). ^1H NMR (400 MHz, $CDCl_3$): δ 8.08–8.05 (m, 1H), 7.90 (d, J=4.3 Hz, 1H), 7.09–7.06 (m, 1H), 6.94–6.92 (m, 1H), 3.74–3.55 (m, 20H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.7, 137.3, 134.2, 123.8, 118.2, 71.5, 70.5, 70.2, 68.4, 52.5. HRMS *m/z* Calcd for $C_{15}H_{24}N_2O_4$: 296.17361. Found: 296.17410. Anal. Calcd for $C_{15}H_{24}N_2O_4$: C, 60.81; H, 8.11. Found: C, 60.98; H, 7.97.

4.4.10. *N*-(3,5-Dimethylphenyl)-1-aza-15-crown-5 (Table 1, entry 11). The ^1H and ^{13}C NMR spectra were in accordance with those described in the literature.[9]

4.4.11. *N*-(4-Methoxyphenyl)-1-aza-18-crown-6 (Table 3, entries 1, 3, and 4). ^1H NMR (300 MHz, $CDCl_3$): δ 6.82–6.70 (m, 4H), 3.74–3.56 (m, 27H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 151.8, 142.4, 115.1, 114.4, 71.03, 70.99, 70.8, 69.0, 56.0, 52.4. HRMS *m/z* Calcd for $C_{19}H_{31}NO_6$: 369.21514. Found: 369.21580. Anal. Calcd for $C_{19}H_{31}NO_6$: C, 61.79; H, 8.40. Found: C, 61.63; H, 8.33.

4.4.12. *N*-(4-Methylphenyl)-1-aza-18-crown-6 (Table 3, entry 2). ^1H NMR (300 MHz, $CDCl_3$): δ 7.02 (d, J=8.4 Hz, 2H), 6.62 (d, J=8.5 Hz, 2H), 3.70–3.56 (m, 24H), 2.23 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 146.0, 130.0, 125.2, 112.1, 71.1, 71.08, 71.0, 70.9, 69.1, 51.7, 20.4. HRMS *m/z* Calcd for $C_{19}H_{31}NO_5$: 353.22022. Found: 353.22100. Anal. Calcd for $C_{19}H_{31}NO_5$: C, 64.59; H, 8.78. Found: C, 64.67; H, 8.67.

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