Palladium-Catalyzed Amination of Aryl Bromides Utilizing Arene−Chromium Complexes as Ligands

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The arene−chromium complexes of *o*-diphenylphosphino α-phenylethylamine or α-phenylethyl methyl ether derivatives were examined with regard to their activity as ligands for palladium(0)-catalyzed aryl amination of aryl bromides with a variety of amines. Both steric and electronic factors were found to be significant for the efficient palladium-catalyzed aryl amination reactions. Modulation of the inductive capacity of the arylphosphine atom was achieved by photoinduced ligand exchange of one carbonyl of the chromium tripode in the presence of electron-donating triphenylphosphine or phosphite. Among these arene−chromium ligands, the use of the monophosphine- or monophosphite-(dicarbonyl)chromium of *N*,*N*-dimethyl α-(*o*-diphenylphosphino)phenylethylamine and methyl α-(*o*-diphenylphosphino)phenylethyl ether produced the palladium(0)-catalyzed aryl amination products with cyclic amines or acyclic secondary amines in high yields; the corresponding strong electron-withdrawing tricarbonylchromium complex resulted in a modest yield of the aryl amination.

Introduction

The recent development in the palladium-catalyzed amination of aryl halides or triflates documented by Buchwald and Hartwig, independently, has been shown to be a general method for the formation of aromatic carbon−nitrogen bonds.[1] The mild conditions in the palladium-catalyzed aryl amination offer considerable advantages over the classical methods, which require either activated molecules or severe reaction conditions. In the palladium-catalyzed aryl amination, the stereo and electronic effects of the employed palladium ligands and the bite angle of the chelating ligands are significant factors for efficient coupling reactions.[2] In general terms, modestly hindered and electron-rich aryl phosphine ligands have been used for efficient palladium(0)-catalyzed aryl amination reactions. Thus, the monophosphine ligand P(*o*-tolyl)$_3$ or bisphosphine ligands BINAP and DPPF lead to efficient coupling of various amines with aryl bromides.[1,3] The ferrocenyl derived ligands PPFA and PPF−OMe have been also employed for the palladium(0)-catalyzed coupling of acyclic secondary amines with bromobenzene.[4] Toward further development of the palladium-catalyzed aryl aminations, we have explored the reactivity of different ligands and studied the effect of their structures on the outcome of amine coupling. For this purpose, we chose to use chromium-complexed chelating arene ligands due to their easy preparation and availability for further structural modification. Furthermore, these arene−chromium complexes would be expected to be useful as the chiral ligands for palladium-catalyzed asymmetric reactions. Herein, we wish to report that the palladium complexes derived from chromium-complexed arenes possessing diphenylphosphine on the ring and a dimethylamine or methoxyl group at the benzylic position are highly effective for the aryl amination reaction with both acyclic and cyclic secondary amines.

Results and Discussion

While arene−chromium complexes have been widely employed for stoichiometrically asymmetric reactions based on the characteristic properties of electron-withdrawing ability and the steric bulkiness of the tricarbonylchromium fragment,[5] there have been few

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(4) (a) Marcoux, J.-F.; Wagaw, S.; Buchwald, S. L. *J. Org. Chem.* **1997**, *62*, 1568−1569. (b) Wolfe, J. P.; Buchwald, S. L. *Tetrahedron Lett.* **1997**, *38*, 6359−6362.

(5) For some reviews see: (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; pp 922−940. (b) Solladié-Cavallo, A. In *Advances in Metal-Organic Chemistry*; Liebeskind, L. S., Ed.; JAI Press: Greenwich, CT, 1989; Vol. 1, pp 99−133. (c) Davies, S. G.; Coote, S. J.; Goodfellow, C. L. In *Advances in Metal-Organic Chemistry*; Liebeskind, L. S., Ed.; JAI Press: Greenwich, CT, 1991; Vol. 2, pp 1−57. (d) Uemura, M. In *Advances in Metal-Organic Chemistry*; Liebeskind, L. S., Ed.; JAI Press: Greenwich, CT, 1991; Vol. 2, pp 195−245.

(6) Uemura, M.; Miyake, R.; Nakayama, K.; Shiro, M.; Hayashi, Y. *J. Org. Chem.* **1993**, *58*, 1238−1244.

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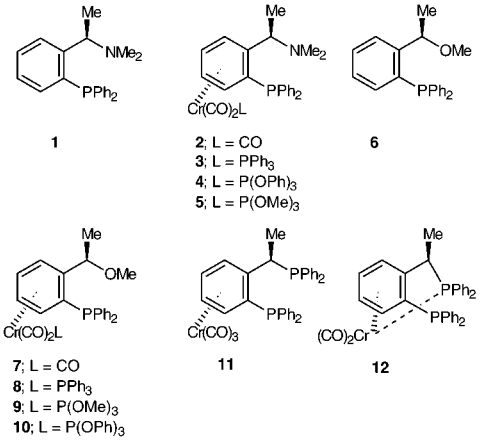
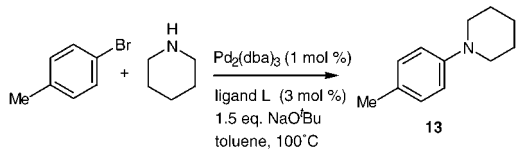


Figure 1. Arene ligands for palladium(0)-catalyzed aryl amination.

examples of their use as the ligand of catalytic reactions[6−11] compared with the number for ferrocenyl compounds. The electronic and steric tuning of the arene−chromium complexes could be easily modified by the introduction of an appropriate functional group on the arene ring or side chain or ligand exchange of the chromium tripode. With the objective of expanding this emerging class of new catalysts, we became interested in exploiting the electronic properties of arene−chromium carbonyl complexes, especially the ability to tune electronic parameters of the arene by selection of appropriate tripod ligands.[12] Modulation of the electronic parameters via ligand substitution of the chromium tripode would be a key feature for controlling the electron density of an aryl phosphine group. The chromium and chromium-free arene ligands employed in this palladium-catalyzed aryl amination are shown in Figure 1, and the tricarbonylchromium ligands **2** and **7** were easily prepared by regioselective lithiation of tricarbonylchromium-complexed *N*,*N*-dimethyl α-phenylethylamine and α-phenylethyl methoxymethyl ether followed by quenching with chlorodiphenylphosphine in a racemic or an enantiomerically active form.[13,14] Tricarbonylchromium-complexed bisdiphenylphosphino compound **11** was prepared by the previously reported procedure.[8] The corresponding dicarbonyl-monophosphines or -monophosphite complexes, **3**, **4**, **5**, **8**, **9**, and **10**, were prepared from **2** and **7** by a photolytic ligand exchange reaction in the presence of the corresponding phosphine or phosphite reagent.[6,7] However, photolysis of the bisdiphenylphosphino complex **11** produced a chelated dicarbonyl(diphenylphosphine)-chromium complex **12** even in the presence of triphenylphosphine, and the structure was determined by X-ray analysis.[15]

Table 1. Ligand Effect for Palladium(0)-Catalyzed Amination of 4-Bromotoluene with Piperidine



ligand	yield **13** (%)	ligand	yield **13** (%)
1	41	**7**	23
2	49	**8**	48
3	72	**9**	65
4	62	**10**	57
5	68	**11**	34
6	34	**12**	40

We initially examined the ability of the chromium-complexed arene ligands for the palladium(0)-catalyzed coupling of aryl bromide with a cyclic amine (Table 1). The reaction optimization was conducted on 4-bromotoluene and piperidine in the presence of 1.5 equiv of NaO^{t}Bu and a combination of 1.0 mol % of Pd(dba)$_2$ and 3.0 mol % of the arene ligand in toluene at 100 °C for 5 h. Use of optically pure (−)-tricarbonyl[*N*,*N*-dimethyl α-(*o*-diphenylphosphinophenyl)ethylamine]chromium (**2**) as the ligand resulted in 49% yield of *N*-(*p*-methylphenyl)-piperidine. The corresponding chromium-free aminophosphine ligand **1** gave a moderate 41% yield of the coupling product. However, an electron-donating monophosphine or monophosphite dicarbonyl chromium complex instead of tricarbonylchromium ligands increased the yield of the amination product remarkably under same conditions. Thus, (−)-monotriphenylphosphine-(dicarbonyl)chromium, (−)-monotrimethyl phosphite(dicarbonyl)chromium, and (−)-monotriphenyl phosphite-(dicarbonyl)chromium complexes of aminophosphine ligands **3**, **4**, and **5** produced the coupling product in 72, 62, and 68% yields, respectively. These results showed that both steric and electronic factors of the arene chromiun ligands are significant for efficient palladium-catalyzed aryl amination reactions. While the electron density of the aryl phosphine atom of the ligand **2** was reduced due to the strong electron-withdrawing ability of the tricarbonylchromium fragment, the corresponding monophosphine or monophosphite dicarbonyl chromium ligands **3**, **4**, and **5** became more electron rich. It is interesting that these chromium complexes ligands are effective for the palladium-catalyzed aryl aminations despite the large difference in the bite angle of P−Pd−N(or O) of chromium-complexed palladium catalysts compared with those of the ferrocenyl ligands, PPF or PPF−OMe.[2,16] Also, the presence of the corresponding benzylic oxygen analogues instead of the nitrogen atom indicated a similar behavior for the palladium-catalyzed amination. Thus, use of the racemic tricarbonyl[methyl α-(*o*-diphenylphosphino)phenylethyl ether]chromium (**7**) gave the amination product in only 23% yield, while the corresponding electron-donating ligands **8**, **9**, and **10** increased the amination product to 48%, 65%, and 57% yields, respectively. These data demonstrate that the

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(11) Jones, G. B.; Heaton, S. B.; Chapman, B. J.; Guzel, M. *Tetrahedron Asymmetry* **1997**, *8*, 3625−3635.
(12) Jones, G. G.; Chapman, B. J.; Mathews, J. E. *J. Org. Chem.* **1998**, *63*, 2928−2938.
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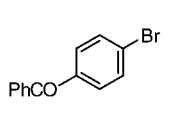
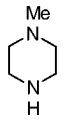
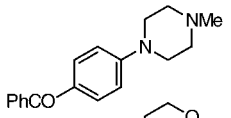
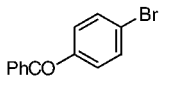
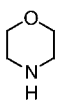
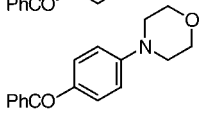
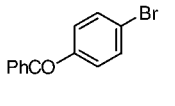
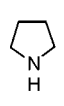
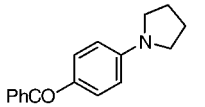
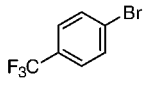
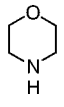
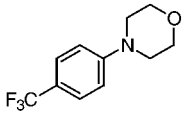
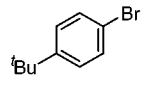
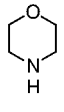
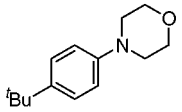
(14) Blagg, J.; Davies, S. G.; Goodfellow, C. L.; Sutton, K. H. *J. Chem. Soc., Perkin Trans. 1* **1987**, 1805−1811.
(15) Crystal structure data: formula, $C_{34}H_{28}O_2P_2Cr$; fw; 582.54; triclinic; space group *P*1 (no. 1); a = 9.031(3) Å; b = 10.489(3) Å; c = 8.551(4) Å; α = 98.96(3)°; β = 112.44(3)°; γ = 83.67(3)°; V = 738.4(5) Å^3; Z = 1; D_{calc} = 1.310 g cm^{-3}; final R = 0.037; R_w = 0.044.

Table 2. Palladium(0)-Catalyzed Amination of Aryl Bromides with Cyclic Amines by a Combination of $Pd(dba)_2$ and Ligand 3[a]

	Aryl Bromide	Amine	Product	Yield (%)
1				91
2				87
3				77
4				95
5				63

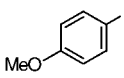
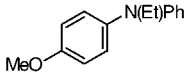
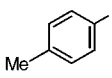
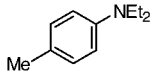
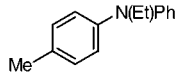
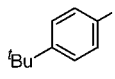
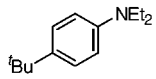
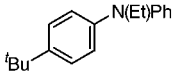
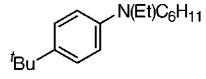
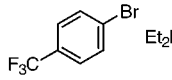
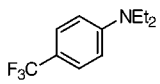
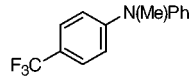
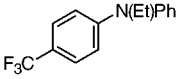
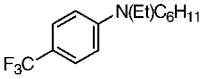
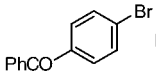
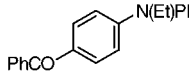
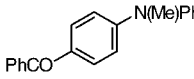
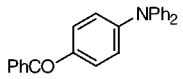
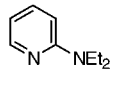
[a] Reactions were conducted with 1.0 mol % $Pd(dba)_2$, 3.0 mol % ligand **3**, and 1.5 equiv of $NaOBu^t$ in toluene at 100 °C for 5 h.

chromium complexation of amino phosphine ligands is essential to achieving high yield of the amination product and the exchange of one of the three carbonyls on the chromium fragment to the electron-donating phosphine or phosphite could be a more significant factor for the efficient palladium-catalyzed aryl aminations. Also, the monophosphine or monophosphite(dicarbonyl)chromium complexes of amino phosphine ligands **3**, **4**, and **5** showed slightly higher activity than the corresponding benzyl oxygen analogues **8**, **9**, and **10** for the palladium-catalyzed amination reaction. The tricarbonylchromium complex of bisphosphine compound **11** and the chelated monodentate diphenylphosphine(dicarbonyl)chromium complex **12** gave a modest yield of the amination product of *p*-bromotoluene with piperidine.[17]

We next studied the palladium-catalyzed amination of both electron-poor and electron-rich aryl bromides with other cyclic amines using arene−chromium complexes as the ligand. The amination of aryl bromides with cyclic amines was carried out under identical reaction conditions by a combination of 1.0 mol % of $Pd(dba)_2$ and 3.0 mol % of the arene ligand **3** in the presence of NaO^tBu in toluene (Table 2). These results demonstrate that the electron-poor aryl bromides gave the palladium-catalyzed amination products with cyclic amines in good yields, and the yield in the amination of the electron-rich arene was slightly decreased under the same reaction conditions.

These monophosphine(dicarbonyl)chromium complexed-arene compounds were found to be also effective ligands for palladium-catalyzed amination of aryl bromides with acyclic secondary amines (Table 3). Thus, both electron-poor and electron-rich aryl bromides produced the amination products with acyclic dialkylamines or aryl alkylamines in good yields. With electron-rich arenes, the monotriphenylphosphine(dicarbonyl)chromium of dimethylamino phosphine ligand **3** showed higher activity than the corresponding ether ligand **9** (entries 1 vs 2 and 5 vs 6). With the electron-poor aryl bromides, both chromium-complexed ligands possessing the dimethyl-

Table 3. Pallaium(0)-Catalyzed Amination of Aryl Bromides with Acyclic Amines by a Combination of $Pd(dba)_2$ and (Arene)chromium Ligand

	Aryl Bromide	Amine	Ligand	Product	Yield (%)
1		Ph(Et)NH	**3**		83
2			**9**		73
3		Et_2NH	**3**		89
4		Ph(Et)NH	**3**		83
5		Et_2NH	**3**		90
6			**9**		81
7		Ph(Et)NH	**3**		90
8		$C_6H_{11}(Et)NH$	**3**		82
9		Et_2NH	**3**		91
10		Ph(Me)NH	**3**		96
11			**8**		97
12			**9**		95
13		Ph(Et)NH	**3**		95
14		$C_6H_{11}(Et)NH$	**3**		70
15			**9**		71
16		Ph(Et)NH	**3**		91
17		Ph(Me)NH	**3**		92
18		Ph_2NH	**3**		53
19		Et_2NH	**3**		57

(16) For discussion about the bite angle that influences the rate of reductive elimination of a transition-metal complex, see ref 3 and the following: Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; pp 324−329.

(17) Surprisingly, the chelated monodentate ligand **12** produced the corresponding amine compound for the coupling reaction of *p*-benzoyl bromobenzene with morpholine in 88% yield.

amino or methoxy groups at the benzylic position, **3**, **8**, or **9**, resulted in a high yield of the amination products. It is noteworthy that this catalyst system of **3** and $Pd(dba)_2$ was also effective for the preparation of triarylamine by cross-coupling of aryl bromide with diarylamine (entry 18).[18] Bromopyridine was also coupled with diethylamine to produce α-diethylaminopyridine in 57% yield by using the amino ligand **3** (entry 19).

In conclusion, we have demonstrated that the arene−chromium complex is able to modulate the inductive capacity of the arylphosphine atom by substitution of the chromium tripode and regulate its ability as a ligand for the palladium-catalyzed aryl amination. Thus, the monotriphenylphosphine(dicarbonyl)chromium complex of *N*,*N*-dimethyl α-(*o*-diphenylphosphino)phenylethylamine **3** was found to be an efficient supporting ligand for the palladium-catalyzed amination of both electron-rich and -deficient aryl bromides with cyclic or acyclic secondary amines. We are currently investigating the scope of palladium-catalyzed aryl amination by the electronic modification of diarylphosphine, the application for asymmetric reaction using the optically active arene−chromium complexes as chiral ligands, and further extension of the reaction to the coupling of aryl bromides with ketone or alcohol compounds using the chromium-complexed arene ligands.

Experimental Section

All reactions were carried out under an argon atmosphere. The tricarbonyl(*o*-diphenylphosphino arene)chromium ligands were prepared by trapping an intermediate *o*-lithiated complex of tricarbonyl(*N*,*N*-dimethyl α-phenylethylamine)chromium or tricarbonyl(methoxymethyl α-phenylethyl ether)chromium with chlorodiphenylphosphine according to the literature.[13,14] The ligand exchange of one carbonyl of the tricarbonyl fragment to the corresponding phosphine or phosphite ligand was achieved by irradiation with a high-pressure mercury lamp in the presence of the corresponding phosphine or phosphite reagents. Toluene was continuously refluxed and distilled from calcium hydride. Aryl bromides were purchased from commercial sources and were used without further purification.

(−)-Triphenylphosphine(dicarbonyl)[*N*,*N*-dimethyl α-(*o*-diphenylphosphinophenyl)ethylamine]chromium (3).[7] Typical procedure of ligand exchange of one of the three carbonyls on the chromium in the presence of a phosphine or phosphite reagent under photoirradiation is as follows. A solution of (−)-tricarbonyl[*N*,*N*-dimethyl α-(*o*-diphenylphosphinophenyl)ethylamine]chromium (2.0 g, 4.3 mmol) and triphenylphosphine (2.0 g, 8.5 mmol) in benzene (30 mL) was irradiated with a high-pressure mercury lamp under nitrogen at room temperature for 20 min. The precipitate was filtered off, and the filtrate was evaporated in vacuo. The residue was purified by silica gel column chromatography with hexane/ethyl acetate (10/1) to give 2.0 g (63%) of **3**: mp 151 °C; $[\alpha]^{22}_D$ −344 (*c* 0.58, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.85 (3 H, d, J = 7.0 Hz), 1.65 (6 H, s), 3.79 (1 H, m), 4.45−4.70 (4 H, m), 7.25−7.50 (25 H, m); IR ($CHCl_3$) 1970, 1890 cm^{-1}. Anal. Calcd for $C_{42}H_{39}O_2NP_2Cr$: C, 71.69; H, 5.30; N, 1.99. Found; C, 71.42; H, 5.30; N, 2.10.

(±)-Triphenylphosphine(dicarbonyl)[methyl α-(*o*-Diphenylphosphinophenyl)ethyl Ether]chromium (8): mp 188 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.28 (3 H, d, J = 6.3 Hz), 2.80 (3 H, s), 4.31−4.64 (4 H, m), 4.98 (1 H, t, J = 6.3 Hz), 7.26−7.48 (25 H, m); IR ($CHCl_3$) 1890, 1840 cm^{-1}. Anal. Calcd for $C_{41}H_{36}O_3P_2Cr$: C, 71.30; H, 5.27. Found; C, 71.11; H, 5.19.

(±)-Chelated Complex 12 (70% yield): mp 110 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.53 (3 H, dd, J = 7.9, 12.0 Hz) 3.84 (1 H, q, J = 7.9 Hz), 4.05 (1 H, t, J = 6.3 Hz), 4.82 (1 H, d, J = 6.3 Hz), 5.03 (1 H, d, J = 6.3 Hz), 5.51 (1 H, t, J = 6.3 Hz), 7.19−7.52 (18 H, m), 7.91−7.99 (2 H, m); ^{31}P NMR (162 MHz), δ −8.6 (s), 20.2 (s); IR ($CHCl_3$) 1970, 1900, 1840 cm^{-1}. Anal. Calcd for $C_{34}H_{28}O_2P_2Cr$: C, 70.04; H, 4.85. Found; C, 69.67; H, 4.88.

Palladium-Catalyzed Aryl Amination. Typical procedure for the aryl amination is as follows. An oven-dried Schlenk tube was charged with *p*-bromotoluene (171 mg, 1.0 mmol), piperidine (128 mg, 1.50 mmol), NaO^tBu (144 mg, 1.50 mmol), $Pd_2(dba)_3$ (10.0 mg, 0.01 mmol), and the arene−chromium ligand **3** (21 mg, 0.03 mmol) and purged with argon. Toluene (2.50 mL) was added, and the reaction mixture was heated at 100 °C under argon for 5 h. The reaction mixture was filtered, and the filtrate was concentrated under reduced pressure. The crude product was purified by chromatography on silica gel with hexane/ethyl acetate (50/1) to give 127 mg (72%) of *N*-(*p*-methylphenyl)piperidine[1c] as a liquid: ^{1}H NMR ($CDCl_3$, 270 MHz) δ 1.56−1.73 (6 H, m), 2.27 (3 H, s), 3.09 (4 H, t, J = 5.6 Hz), 6.87 (2 H, d, J = 8.5 Hz), 7.06 (2 H, d, J = 8.5 Hz).

***N*-Ethyl-*N*-(*p*-trifluoromethylphenyl)aniline, as a Liquid:** ^{1}H NMR ($CDCl_3$, 270 MHz) δ 1.23 (3 H, t, J = 7.3 Hz), 3.78 (2 H, q, J = 7.3 Hz), 6.77 (2 H, d, J = 8.9 Hz), 7.15−7.23 (3 H, m), 7.35−7.41 (4 H, m); IR ($CHCl_3$) 1580, 1480, 1310 cm^{-1}; MS (relative intensity) *m*/*z* 265 (M^+, 83), 250 (100), 237 (41), 198 (66); HRMS calcd for $C_{15}H_{14}NF_3$ 265.1079, found 265.1087.

***N*-Ethyl-*N*-(*p*-methylphenyl)aniline:** ^{1}H NMR ($CDCl_3$, 270 MHz) δ 1.20 (3 H, t, J = 6.9 Hz), 2.32 (3 H, s), 3.74 (2 H, q, J = 6.9 Hz), 6.82−7.23 (9 H, m); IR ($CHCl_3$) 1580, 1480 cm^{-1}; MS (relative intensity) *m*/*z* 211 (M^+, 66), 196 (100), 167 (14), 113 (21).

***N*,*N*-Diethyl-*p*-trifluoromethylaniline:** ^{1}H NMR ($CDCl_3$, 270 MHz) δ 1.17 (6 H, t, J = 6.9 Hz), 3.38 (4 H, q, J = 6.9 Hz), 6.65 (2 H, d, J = 8.9 Hz), 7.41 (2 H, d, J = 8.9 Hz); IR ($CHCl_3$) 1520, 1310, 1260, 1110 cm^{-1}; MS (relative intensity) *m*/*z* 217 (M^+, 66), 202 (35), 187 (35), 174 (100); HRMS calcd for $C_{11}H_{14}NF_3$ 217.1078, found 217.1063.

***N*-Ethyl-*N*-(*p*-*t*-butylphenyl)cyclohexylamine:** ^{1}H NMR ($CDCl_3$, 270 MHz) δ 1.15 (6 H, t, J = 6.9 Hz), 1.28 (9 H, s), 1.31−1.85 (10 H, m), 3.25 (4 H, q, J = 6.9 Hz), 3.50−3.51 (1 H, m), 6.67 (2 H, d, J = 8.9 Hz), 7.23 (2 H, d, J = 8.9 Hz); IR ($CHCl_3$) 1600, 1500 cm^{-1}; MS (relative intensity) *m*/*z* 259 (M^+, 45), 230 (2), 216 (100), 202 (3), 176 (5).

***N*-(*p*-Benzoylphenyl)-*N*-methylaniline:** ^{1}H NMR ($CDCl_3$, 270 MHz) δ 3.38 (3 H, s), 6.78 (2 H, d, J = 8.9 Hz), 7.22−7.75 (12 H, m); IR ($CHCl_3$) 1630, 1580, 1490 cm^{-1}; MS (relative intensity) *m*/*z* 287 (M^+, 85), 273 (4), 210 (100), 196 (4), 181 (10); MS (relative intensity) *m*/*z* 301 (M^+, 63), 286 (100), 224 (5); HRMS calcd for $C_{20}H_{17}NO$ 287.1310, found 287.1307.

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Supporting Information Available: Physical data for some arene ligands and amination products and an ORTEP drawing including the atomic coordinates, thermal parameters, bond distances, bond angles, and thermal parameters for the compound **12** (30 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(18) Yamamoto, T.; Nishiyama, M.; Koie, Y. *Tetrahedron Lett.* **1998**, *39*, 2367−2370.