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Variation of Xantphos-Based Ligands in the Palladium-Catalyzed Reaction of Aryl Halides with Ureas

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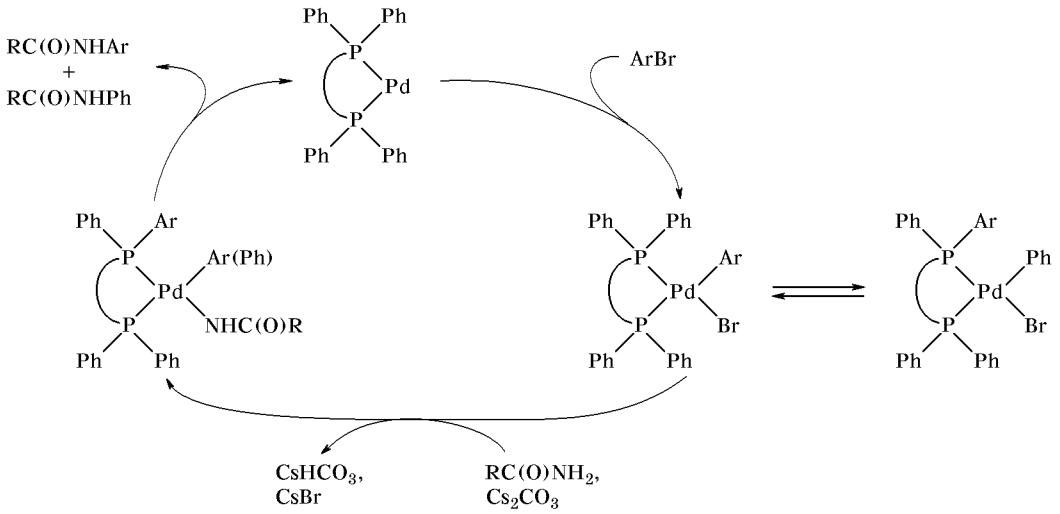
Abstract—A series of Xantphos-based ligands containing various substituents in the diphenylphosphino groups were synthesized, and their effect on the product yield and ratio in the palladium-catalyzed arylation of ureas with nonactivated aryl halides was studied. The arylation of urea and phenylurea in the presence of $Pd_2(dba)_3$–$CHCl_3$, 3,5-$(CF_3)_2$Xantphos, and Cs_2CO_3 in dioxane at 100°C gave the corresponding *N*,*N*′-diarylureas in 62–98% yield.

Arylureas are widely used as medicines [1], pesticides [1], and receptors for selective binding of anions [2] and in the synthesis of polymeric materials [3]. Arylureas are usually prepared by reactions of arylamines with isocyanates or carbonyl chloride [1]. Alternative routes include catalytic reductive carbonylation of nitroarenes [4] and oxidative carbonylation of amines [5]. Most of these procedures utilize ecologically hazardous and toxic reagents.

In the recent years, palladium-catalyzed arylation of amines (Buchwald–Hartwig reaction) [6] has become a convenient and effective method of building up C–N bonds. The scope of application of this procedure was extended to include amides [7–10], sulfonamides [8, 9], and ureas [11], which can be subjected to arylation under mild conditions with conservation of other functional groups. Xantphos [8–11] turned out to be the most efficient ligand for such palladium-catalyzed reactions. However, the use of Xantphos is generally limited to reactions with activated aryl halides. Analogous reactions with nonactivated substrates are difficult to accomplish. As a rule, large amounts of the catalyst are necessary, and the product yields are poor [8–11]. In many cases, especially when aryl halide contains donor substituents (e.g., methoxy group), the reaction fails to occur [8, 10]. The same applies to the arylation of ureas, which was studied by us previously: In the reactions

Scheme 1.



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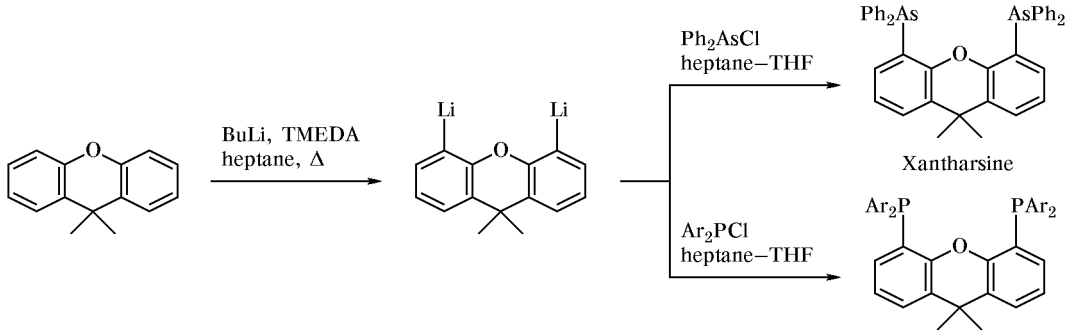
Scheme 2.



Ar = *o*-MeC_6H_4 (*o*-MeXantphos), *p*-$MeOC_6H_4$ (*p*-MeOXantphos), Ph (Xantphos), 3,5-$(CF_3)_2C_6H_3$ [3,5-$(CF_3)_2$Xantphos], C_6F_5 (FluoroXantphos).

with activated aryl halides, the corresponding *N*,*N*′-diarylureas are formed in high yelds, while the arylation of urea with *p*-bromotoluene under analogous conditions is characterized by incomplete conversion and low yield of the target product and is accompanied by formation of phenyl-substituted ureas [11]. Buchwald *et al.* [12] recently showed that copper complexes in the presence of diamine ligands effectively catalyze arylation of amides with aryl bromides (including nonactivated ones). However, we failed to effect arylation of urea under the same conditions.

Scheme 1 shows the catalytic cycle in the arylation reaction. Oxidative addition of even nonactivated aryl bromides to palladium(0) complex occurs under very mild conditions. In the presence of Xantphos, the amination of phenyl bromide can be performed at room temperature [13]. On the other hand, arylation of amides with nonactivated aryl bromides requires considerably more severe conditions (100°C) [8–11]. Therefore, the limiting stage in the reaction with nonactivated aryl bromides is either transmetalation or reductive elimination. In fact, increase in the donor power of substituent in the aryl group is known to hamper reductive elimination with formation of C–N bond [14]. Moreover, a considerable deceleration of stages following the oxidative addition could give rise to a variety of side processes. One of such processes is exchange between the aryl group attached to palladium and phenyl group of the phosphine ligand in the complex Pd(L–L)(Ar)Br [15]. The subsequent transmetalation and reductive elimination leads to formation of *N*-phenyl derivatives. The contribution of the exchange process increases in parallel with the donor power of the aryl group (Ar) [15]. Therefore, problems concerning formation of *N*-phenyl compounds as by-products and deactivation of the catalyst become especially important in the reactions of amides and ureas with nonactivated aryl bromides. Taking into account that the rate of reductive elimination rises as the electron density on the palladium atom decreases [16] and as the size of the ligand increases [17], we anticipated that bulky phosphine ligands having electron-acceptor substituents should favor the process.

Table 1. Synthesis of Xantphos-based ligands

Run no.	Ligand (L)	Temperature, °C second stage)	Yield, %
1	*p*-MeOXantphos	–20	34
2	3,5-$(CF_3)_2$Xantphos	0	7
3	3,5-$(CF_3)_2$Xantphos	–60	30
4	FluoroXantphos	–20	[a]
5	FluoroXantphos	–90	12
6	Xantharsine	–65	53

[a] Mixture of products.

We have synthesized a series of ligands with different electronic and steric parameters on the basis of Xantphos which is the most efficient ligand for palladium-catalyzed amidation of aryl halides [8–11]. Steric and electronic parameters of the ligands were varied via introduction of acceptor and donor substituents into different positions of the phenyl rings and via replacement of phosphorus by arsenic. Ligands L were synthesized by metalation of 9,9-dimethylxanthene and subsequent addition of diaryl(chloro)phosphine or chloro(diphenyl)arsine at reduced temperature as shown in Scheme 2.

The ligand yields in the reaction of metalated dimethylxanthene with diaryl(chloro)phosphine having electron-acceptor groups (F or CF_3) strongly depended on the temperature (Table 1, run nos. 2–5). When

Table 2. Palladium-catalyzed reaction of urea with *p*-bromotoluene in the presence of Xantphos-based ligands

Run no.	Ligand (L)	Pd, mol %	Time, h	Conversion, %	Yield, %		
					A	**B**	**C**
1	*p*-MeOXantphos	4	2.5	34	–	–	–
			24	47	8	4	–
2	Xantphos	4	20	62	7	10	5
3	3,5-$(CF_3)_2$Xantphos	4	2.5	100	62	8	–
4	*o*-MeXantphos	4	20	9	–	–	–
5	FluoroXantphos	2.5	20	5	–	–	–
6	Xantharsine	2.5	20	8	–	–	–

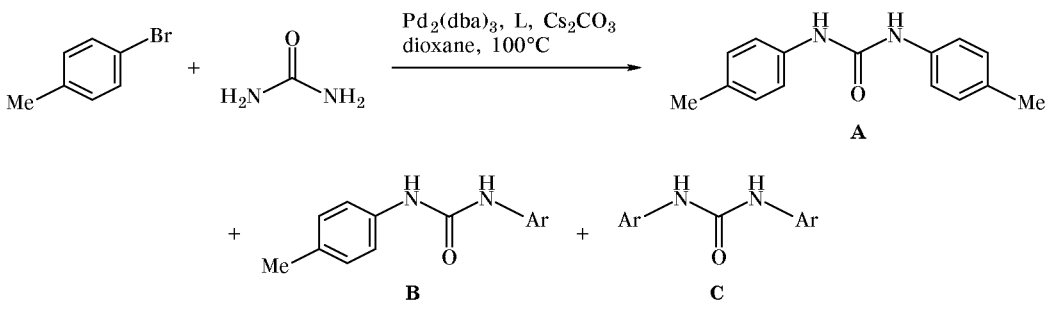
chlorobis(pentafluorophenyl)phosphine was added to dilithium derivative of 9,9-dimethylxanthene at –20°C, a complex mixture of products was obtained (run no. 4), from which we failed to isolate FluoroXantphos. The latter was isolated in a poor yield when the reaction was carried out at –90°C (run no. 5). Likewise, the yield of 3,5-$(CF_3)_2$Xantphos considerably increased when the phosphine was added at lower temperature (run nos. 2, 3).

We examined the efficiency of the prepared ligands in the reaction of *p*-bromotoluene with urea. In the presence of Xantphos, the conversion was incomplete, and the yield of *N*,*N*′-di-*p*-tolylurea was low (Table 2, run no. 2). As catalyst precursor we used $Pd_2(dba)_3 \cdot CHCl_3$, the palladium-to-ligand ratio was equal to 1.5, and Cs_2CO_3 was added as a base. The reactions were carried out in dioxane at 100°C (Table 2, Scheme 3).

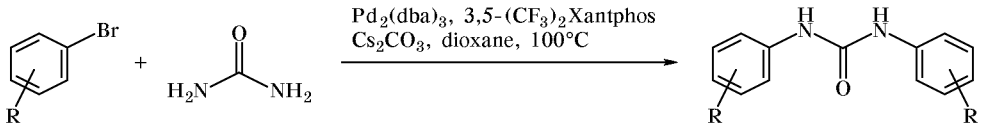
The data in Table 2 show (run nos. 1–3) that the conversion and product yields strongly depend on the electronic properties of the phosphine ligand. The conversion increases in going from donor *p*-MeOXantphos to Xantphos, and it reaches 100% in the presence of acceptor 3,5-$(CF_3)_2$Xantphos; moreover, in the latter case, the formation of by-products **B** and **C** is considerably suppressed. The yields of *N*,*N*′-di-*p*-tolylurea obtained with the use of *p*-MeOXantphos and Xantphos are almost similar (7–8%; run nos. 1, 2). Addition of 3,5-(CF_3)2Xantphos as ligand increases the yield of **A** to 62%, the conversion of *p*-bromotoluene being complete (run no. 3). Unexpected results were obtained with ligands having bulky aryl substituents. In the reactions with both donor *o*-MeXantphos and acceptor FluoroXantphos, the conversion was lower than 10%. Inefficiency of *o*-MeXantphos in the arylation of amides was also noted by Buchwald [9]. On the other hand, similar results were obtained with *o*-MeXantphos and Xantphos in the arylation of amines [18]. Replacement of the phosphorus atom in Xantphos by arsenic did not increase the efficiency (run no. 6). Thus, our experiments on ligand variation showed that 3,5-$(CF_3)_2$Xantphos is the only ligand efficient in the arylation of urea with *p*-bromotoluene. Therefore, it was used in the arylation of urea with nonactivated and weakly activated aryl halides (Table 3, Scheme 4).

The results showed that 3,5-$(CF_3)_2$Xantphos is clearly suprior to Xantphos. It ensures successful arylation of urea with nonactivated aryl bromides, and the yields of the corresponding *N*,*N*′-diarylureas attain 61–98% (Table 3, run nos. 1, 3, 5, 7, 9, 10). *ortho*-Substituted aryl bromides react much more readily than the *para* isomers (yield 80–98%; run nos. 1, 3,

Scheme 3.

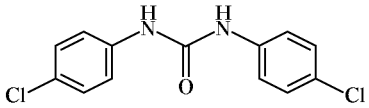
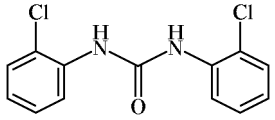
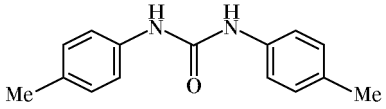
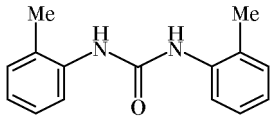
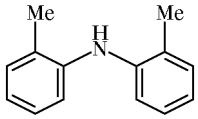
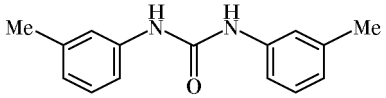
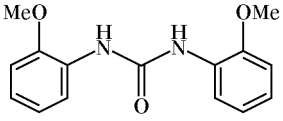


Scheme 4.



5, 7, 10). In the reaction of urea with *o*-bromochlorobenzene in the presence of Xantphos, a considerable amount of *o*,*o*′-dichlorodiphenylamine (35%) was formed in addition to the major product, *N*,*N*′-bis(*o*-chlorophenyl)urea (57%, run no. 4), whereas di-*o*-tolylamine was the only product (77%) in the reaction with *o*-bromotoluene (run no. 8); i.e., in the latter case replacement of the ligand changes the reaction direction. It should also be noted that the arylation of urea with *p*-bromochlorobenzene and *p*-bromotoluene

Table 3. Palladium-catalyzed arylation of urea with nonactivated aryl halides in the presence of 3,5-$(CF_3)_2$Xantphos and Xantphos

Run no.	Aryl halide	Ligand (L)	Pd, mol %	Time, h	Product	Conversion, %	Yield, %
1	*p*-ClC_6H_4Br	3,5-$(CF_3)_2$Xantphos	2	2		100	81
2	»	Xantphos	4	10		100	64
3	*o*-ClC_6H_4Br	3,5-$(CF_3)_2$Xantphos	1	5		100	91
4	»	Xantphos	4	11		100	57
5	*p*-MeC_6H_4Br	3,5-$(CF_3)_2$Xantphos	4	2.5		100	62
6	»	Xantphos	4	20		62	7
7	*o*-MeC_6H_4Br	3,5-$(CF_3)_2$Xantphos	1	4		100	98
8	*o*-MeC_6H_4Br	Xantphos	4	36		94	77[a]
9	*m*-MeC_6H_4Br	3,5-$(CF_3)_2$Xantphos	2	4		100	71
10	*o*-$MeOC_6H_4Br$	3,5-$(CF_3)_2$Xantphos	3	4		100	80
11	*p*-$MeOC_6H_4Br$	3,5-$(CF_3)_2$Xantphos	2.5	2	–	29	–[b]
12	»	3,5-$(CF_3)_2$Xantphos	4	4.5	–	15	–
13	*o*-$Me_2NC_6H_4Br$	3,5-$(CF_3)_2$Xantphos	4	5	–	27	–

[a] No *N*,*N*′-di-*o*-tolylurea was formed.

[b] Sodium *tert*-butoxide was used as a base.

in the presence of 3,5-$(CF_3)_2$Xantphos requires a smaller amount of the catalyst and gives greater yields of the products, as compared to Xantphos (run nos. 1, 2, 5–6).

Thus the use of 3,5-$(CF_3)_2$Xantphos as ligand allowed us to effect successful reactions of urea with nonactivated and weakly activated substrates which afforded much less satisfactory yields of diarylureas in the presence of Xantphos. However, the scope of application of 3,5-$(CF_3)_2$Xantphos is also limited: the reaction of urea with *p*-bromoanisole even with 2.5 mol % of the catalyst was characterized by a low conversion (run no. 11) which we failed to improve by the use of a stronger base, *t*-BuONa instead of Cs_2CO_3 (run no. 12). Under analogous conditions, the conversion of *o*-bromoanisole was 100%, and the yield of *N*,*N*′-bis(*o*-methoxyphenyl)urea was 80% (run no. 10). *o*-Bromo-*N*,*N*-dimethylaniline did not react with urea (run no. 13).

We showed in [11] that arylation of phenylurea with activated aryl bromides in the presence of Xantphos leads to unsymmetrically substituted *N*-aryl-*N*′-phenylureas in high yields. The reaction is accompanied by formation of the corresponding symmetric *N*,*N*′-diarylureas and *N*,*N*′-diphenylurea via disproportionation of the major product. The fraction of symmetric ureas increases with time. Insofar as reactions of ureas with nonactivated aryl halides are fairly slow, it seemed impossible to obtain under analogous conditions unsymmtrically substituded *N*-aryl-*N*′-phenylureas having donor groups in the aryl fragment. However, using 3,5-$(CF_3)_2$Xantphos as ligand, we succedeed in synthesizing such products in fairly high yields (Scheme 5, Table 4; run nos. 1–3, 5, 7, 8). In order to minimize the contribution of side processes,

Scheme 5.

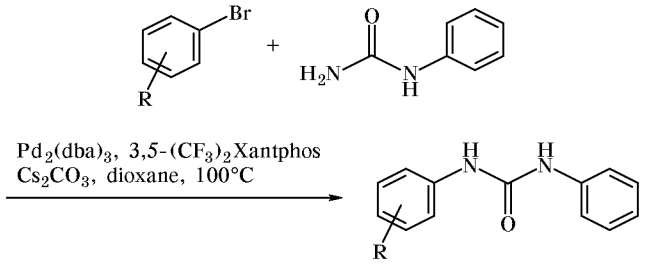
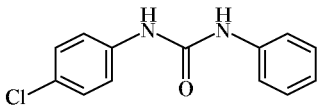
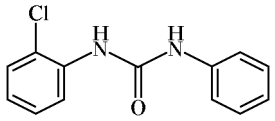
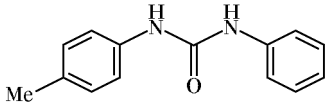
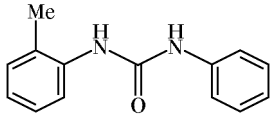
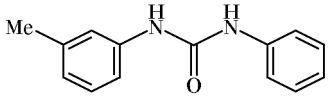
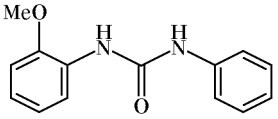
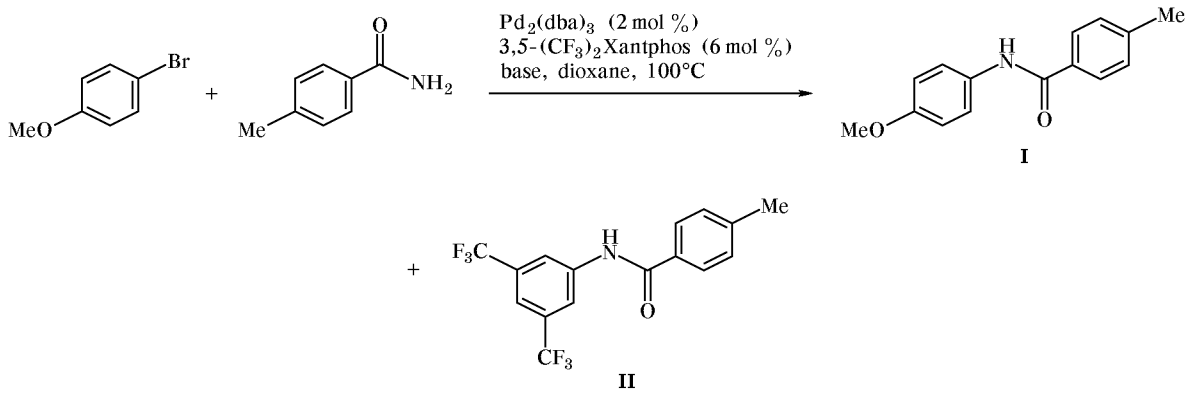


Table 4. Palladium-catalyzed arylation of phenylurea with nonactivated aryl halides in the presence of 3,5-$(CF_3)_2$-Xantphos and Xantphos as ligand (L)

Run no.	Aryl halide	Ligand (L)	Pd, mol %	Time, h	Product	Conversion, %	Yield, %
1	ClC_6H_4Br	3,5-$(CF_3)_2$Xantphos	2	1		100	72
2	*o*-ClC_6H_4Br	3,5-$(CF_3)_2$Xantphos	1	1		100	95
3	MeC_6H_4Br	3,5-$(CF_3)_2$Xantphos	3.5	1		100	80
4	»	Xantphos	4	1.5		63	37
5	*o*-MeC_6H_4Br	3,5-$(CF_3)_2$Xantphos	2.5	1		100	95
6	»	Xantphos	4	1.5		30	18
7	*m*-MeC_6H_4Br	3,5-$(CF_3)_2$Xantphos	2	1		100	81
8	*o*-$MeOC_6H_4Br$	3,5-$(CF_3)_2$Xantphos	4	1		100	91

Scheme 6.



the reaction time was shortened by increasing the amount of the catalyst. As in the reactions with urea, *ortho*-substituted aryl halides turned out to be more reactive substrates (run nos. 2, 5, 8). For comparison, the conversion and yield in the reaction of phenylurea with *o*-bromotoluene using Xantphos as ligand were lower (run no. 6). In addition, *o*-bromotoluene was less reactive than *p*-bromotoluene (run nos. 4, 6).

It is known that arylation of amides with strongly deactivated aryl halides (like *p*-bromoanisole) in the presence of Xantphos gives no acceptable yields of the corresponding *N*-aryl derivatives [8, 10]. Therefore, it was interesting to examine the arylation of amides using 3,5-$(CF_3)_2$Xantphos as ligand. For this purpose, *p*-bromoanisole was brought into reaction with *p*-methylbenzamide in the presence of 2 mol % of $Pd_2(dba)_3 \cdot CHCl_3$ and 6 mol % of the ligand in dioxane at 100°C (Scheme 6, Table 5). We did not succeed in attaining complete conversion of the initial aryl halide. However, the data in Table 3 (run nos. 11, 12) and Table 5 (run nos. 1, 2) indicate that the arylation of *p*-methylbenzamide occurs more readily than the arylation of urea. In both cases, a considerable amount of the aryl–aryl exchange product, *N*-[3,5-bis-(trifluoromethyl)phenyl]-4-methylbenzamide, was formed (run nos. 1, 2). When the reaction was carried in the presence of a stronger base (*t*-BuONa) and in a more polar solvent, the yield and conversion were reduced (run nos. 3, 4).

EXPERIMENTAL

Cesium carbonate was dried at 150–200°C under reduced pressure. Dioxane, tetrahydrofuran, and dimethylacetamide were dried and purified by standard procedures. Dioxane and THF were stored over potassium diphenylketyl in an evacuated vessel. The complex $Pd_2(dba)_3 \cdot CHCl_3$ [19], Xantphos [20], and *o*-TolXantphos [18] were synthesized by known methods. Aryl halides were purified by distillation or recrystallization prior to use.

The ^1H, ^{19}F, and ^{31}P NMR spectra were recorded on a Varian VXR-400 spectrometer at 400, 376, and 161.90 MHz, respectively; the chemical shifts were measured relative to signals of residual protons in the deuterated solvent (^1H), C_6F_6 (^{19}F, δ_F –162.9 ppm relative to $CFCl_3$), and 85% H_3PO_4 (^{31}P, external reference). GLC analysis was performed on an Agat-9

Table 5. Palladium-catalyzed arylation of *p*-methylbenzamide with *p*-bromoanisole in the presence of 3,5-$(CF_3)_2$-Xantphos as ligand

Run no.	Base	Solvent	Time, h	Conversion, %	Yield, %	
					I	**II**
1	Cs_2CO_3	Dioxane	2.5	51	–	–
			8	73	37	18
2	K_3PO_4	Dioxane	26.5	75	35	19
3	*t*-BuONa	Dioxane	21	41	21	–
4	Cs_2CO_3	DMA	8.5	42	–	–

chromatograph equipped with a flame-ionization detector; 2.5-m × 5-mm column packed with OV-17 on Inerton Super (160–200 μm); carrier gas nitrogen. The mass spectra (electron impact, 70 eV) were run on Kratos MS-30 and Kratos MS-890 instruments. Taking into account considerable discrepancies in the published melting points of some *N*,*N*′-diarylureas, only analytical data are given below for the products.

9,9-Dimethyl-4,5-bis[bis(4-methoxyphenyl)phosphino]xanthene (*p*-MeOXantphos). A 1.69 M solution of butyllithium in petroleum ether (bp 65–68°C), 3.8 ml (6.42 mmol) was added with stirring at room temperature under argon to a solution of 0.545 g (2.591 mmol) of 9,9-dimethylxanthene and 0.77 g (1 ml, 6.62 mmol) of TMEDA. The mixture turned dark red. It was heated for 50 min under reflux (on a water bath) and cooled to 0°C, and a solution of 1.80 g (6.44 mmol) of chlorobis(4-methoxyphenyl)-phosphine [21] in 8 ml of THF was added dropwise with stirring over a period of 20 min. The mixture was allowed to warm up to room temperature, stirred for 14 h, diluted with 80 ml of methylene chloride, washed with two portions of water, dried over $MgSO_4$, and evaporated. The residue was washed with petroleum ether and subjected to column chromatography on silica gel (40–63 μm, Fluka), using in succession benzene, benzene–CH_2Cl_2, and CH_2Cl_2 as eluent. The white solid thus isolated was additionally purified by reprecipitation from methylene chloride with petroleum ether. Yield 630 mg (35%), white crystals, mp 219–222°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 7.38 d (2H, *J* = 7.6 Hz), 7.08 m (8H), 6.94 t (2H, *J* = 7.6 Hz), 6.74 d (8H, *J* = 8.4 Hz), 6.53 d (2H, *J* = 7.7 Hz), 3.78 s (12H), 1.63 s (6H). ^{31}P–{^{1}H} NMR spectrum ($CDCl_3$): δ_P –20.27 ppm. Mass spectrum, *m*/*z* (I_{rel}, %): 698 (100) $[M]^{+\cdot}$. Found, %: C 74.10; H 5.76. $C_{43}H_{40}O_5P_2$. Calculated, %: C 73.92; H 5.77. The other ligands were synthesized by a similar procedure.

9,9-Dimethyl-4,5-bis{bis[bis(3,5-trifluoromethyl)-phenyl]phosphino}xanthene [3,5-$(CF_3)_2$Xantphos] (Table 1, run no. 2) was synthesized using 0.390 g (1.85 mmol) of 9,9-dimethylxanthene, 2.75 ml (4.67 mmol) of a 1.69 M solution of BuLi, and 0.7 ml (0.54 g, 4.63 mmol) of TMEDA. A solution of 2.28 g (4.62 mmol) of bis[3,5-bis(trifluoromethyl)phenyl]-chlorophosphine [21] was added at 0°C. After appropriate treatment, the residue (a viscous material) was purified by column chromatography using petroleum ether (bp 65–68°C)–diethyl ether (first 20 : 1 and then 10 : 1) as eluent. The isolated white solid was recrystallized from methanol. Yield 154 mg (7%), mp 164–165°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 7.88 s (4H), 7.61 s (8H), 7.57 d (2H, *J* = 7.7 Hz), 7.12 t (2H, *J* = 7.7 Hz), 6.40 d (2H, *J* = 7.7 Hz), 3.78 s (12H), 1.67 s (6H). ^{31}P–{^{1}H} NMR spectrum ($CDCl_3$): δ_P –14.36 ppm. Mass spectrum, *m*/*z* (I_{rel}, %): 1122 $[M]^+$. Found, %: C 50.22; H 2.03. $C_{47}H_{24}F_{24}OP_2$. Calculated, %: C 50.29; H 2.15.

9,9-Dimethyl-4,5-bis{bis[bis(3,5-trifluoromethyl)-phenyl]phosphino}xanthene [3,5-$(CF_3)_2$Xantphos] (Table 1, run no. 3) was synthesized using 0.390 g (1.85 mmol) of 9,9-dimethylxanthene, 2.75 ml (4.67 mmol) of a 1.69 M solution of butyllithium in petroleum ether, and 0.7 ml (0.54 g, 4.63 mmol) of TMEDA. Bis[3,5-bis(trifluoromethyl)phenyl]chlorophosphine [21], 2.28 g (4.62 mmol) was added at –65°C. White crystals, yield 755 mg (30%).

9,9-Dimethyl-4,5-bis[bis(pentafluorophenyl)-phosphino]xanthene (FluoroXantphos) (Table 1, run no. 5). The synthesis was performed using 0.425 g (2.02 mmol) of 9,9-dimethylxanthene, 2.8 ml (5.04 mmol) of a 1.8 M solution of butyllithium in petroleum ether, and 0.76 ml (0.58 g, 5.03 mmol) of TMEDA. Chlorobis(pentafluorophenyl)phosphine [22], 2 g (5 mmol) was added at –90°C over a period of 10 min, the mixture was allowed to warm up to room temperature, stirred for 16 h, diluted with 120 ml of chloroform, washed with three portions of a solution of potassium chloride, dried over $MgSO_4$, and evaporated. The residue was subjected to column chromatography using as eluent ethyl acetate–petroleum ether (bp 65–68°C), first 1 : 40 and then 1 : 20. The product was additionally purified by recrystallization from methanol. White crystals, yield 234 mg (12%), mp 227–229°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 7.54 d (2H, *J* = 7.6 Hz), 7.09 t (2H, *J* = 7.6 Hz), 6.72 m (2H), 1.70 s (6H). ^{31}P–{^{1}H} NMR spectrum ($CDCl_3$): δ_P –58.3 ppm. ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: –131.22 m (8F), –150.34 t (4F, *J* = 20.7 Hz), –161.18 t (8F, *J* = 20.7 Hz). Mass spectrum, *m*/*z* (I_{rel}, %): 938 (5) $[M]^+$, 923 (100) $[M - CH_3]$. Found, %: C 49.92; H 1.41. $C_{39}H_{12}F_{20}OP_2$. Calculated, %: C 49.90; H 1.29.

9,9-Dimethyl-4,5-bis(diphenylarsino)xanthene (Xantharsine) was synthesized using 0.670 mg (3.18 mmol) of 9,9-dimethylxanthene, 4.5 ml (8.10 mmol) of a 1.8 M solution of butyllithium in petroleum ether, and 1.19 ml (0.92 g, 7.9 mmol) of TMEDA. Chloro(diphenyl)arsine, 2.1 g (7.94 mmol), was added at –60°C over a period of 30 min. The mixture was allowed to warm up to room temperature, stirred for 17 h, diluted with 100 ml of methylene chloride, washed with two portions of water, dried over $MgSO_4$, and evaporated. The residue was washed with petroleum ether and recrystallized from *i*-PrOH–

$CHCl_3$ (5 : 1). Yield 1.116 g (52%). White crystals, mp 209–211°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 7.38 d (2H, *J* = 7.6 Hz), 7.21 m (20H), 6.93 t (2H, *J* = 7.6 Hz), 6.66 d (2H, *J* = 7.6 Hz), 1.63 s (6H). ^{13}C–{^{1}H} NMR spectrum ($CDCl_3$), δ_C, ppm: 152.35, 139.65, 133.90, 132.34, 129.82, 128.32, 128.00, 126.35, 123.60, 34.54, 31.99. Mass spectrum, *m/z* (I_{rel}, %): 666 (100) $[M]^+$, 651 (71) $[M - CH_3]$, 589 (39) $[M - C_6H_5]$, 422 (22) $[M - CH_3 - Ph_2As]$, 345 (18) $[M - CH_3 - Ph_2As - C_6H_5]$. Found, %: C 69.91; H 5.11. $C_{39}H_{32}As_2O$. Calculated, %: C 70.28; H 4.84.

9,9-Dimethyl-4,5-bis[diphenylphosphino]xanthene (Xantphos) was synthesized by the procedure reported in [20]. mp 229–230°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 7.41 d (2H, *J* = 7.7 Hz), 7.15–7.30 m (20H), 6.96 t (2H, *J* = 7.7 Hz), 6.55 d (2H, *J* 7.7 = Hz), 1.66 s (6H). ^{31}P–{^{1}H} NMR spectrum ($CDCl_3$): δ_P –17.5 ppm.

9,9-Dimethyl-4,5-bis[bis(2-methylphenyl)phosphino]xanthene (*o*-TolXantphos) was synthesized by the procedure reported in [18]. mp 229–230°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 7.42 d (2H, *J* = 7.6 Hz), 7.20–7.06 m (8H), 7.00–6.91 m (6H), 6.67 d (4H, *J* = 7.6 Hz), 6.47 d (2H, *J* = 7.6 Hz), 2.26 s (12H), 1.68 s (6H). 31P–{^{1}H} NMR spectrum ($CDCl_3$): δ_P –32.43 ppm.

General procedure for arylation of urea. A reactor was filled with argon and charged with 0.65 mmol of urea, 1.4 mmol of Cs_2CO_3, 0.5–2 mol % ($0.5–2\times10^{-2}$ mmol) of $Pd_2(dba)_3\cdot CHCl_3$, and 1.5–6 mol % ($1.5–6\times10^{-2}$ mmol) of 3,5-$(CF_3)_2$Xantphos or Xantphos, and a solution of 1 mmol of aryl bromide and 0.2 mmol of 1,2,4,5-tetramethylbenzene (internal standard) in 4 ml of dioxane saturated with argon were added in a stream of argon. The mixture was degassed by triple freezing–evacuation–defrosting procedure, and the reactor was filled with argon. The mixture was stirred at 100°C. The progress of the reaction was monitored by GLC and TLC (Silufol UV-254 plates). When the reaction was complete, the mixture was diluted with 30 ml of ethyl acetate and filtered. The filtrate was evaporated, and the residue was subjected to chromatography on silica gel (40–100 μm) using ethyl acetate–petroleum ether (bp 65–68°C) as eluent.

The ligands were varied following the above procedure for arylation of urea; 0.6 mmol of *p*-bromotoluene, 0.36 mmol of urea, 0.84 mmol of Cs_2CO_3, 1.2×10^{-2} mmol of $Pd_2(dba)_3\cdot CHCl_3$ (4 mol % of Pd), 3.6×10^{-2} mmol of ligand, and 15 mg of 1,2,4,5-tetramethylbenzene (internal standard) in 3 ml of dioxane were used. The mixture was heated with stirring under argon over a period indicated in Table 2. The conversion with respect to the initial aryl halide was determined by GLC.

***N,N′*-Di-*p*-chlorophenylurea.** *In the presence of 3,5-$(CF_3)_2$Xantphos.* From 115 mg (0.6 mmol) of *p*-bromochlorobenzene, 23 mg (0.36 mmol) of urea, 285 mg (0.85 mmol) of Cs_2CO_3, 6.2 mg (0.006 mmol) of $Pd_2(dba)_3\cdot CHCl_3$, and 20.2 mg (0.018 mmol) of 3,5-$(CF_3)_2$Xantphos in 3 ml of dioxane we obtained 69 mg (81%) of a white solid. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 8.84 s (2H), 7.47 d (4H, *J* = 8.8 Hz), 7.32 d (4H, *J* = 8.8 Hz). Found, %: C 55.63; H 3.62; N 9.58. $C_{13}H_{10}Cl_2N_2O$. Calculated, %: C 55.54; H 3.59; N 9.96.

***N,N′*-Di-*p*-chlorophenylurea.** *In the presence of Xantphos.* From 190 mg (0.99 mmol) of *p*-chlorobromobenzene, 39 mg (0.65 mmol) of urea, 450 mg (1.38 mmol) of Cs_2CO_3, 20.46 mg (0.0198 mmol) of $Pd_2(dba)_3\cdot CHCl_3$, and 32.97 mg (0.057 mmol) of Xantphos in 3 ml of dioxane we obtained 110 mg (79%) of a white solid which contained (according to the ^{1}H NMR and mass spectral data), ~14% of *N*-*p*-chlorophenyl-*N′*-phenylurea. Mass spectrum, *m/z* (I_{rel}, %): 280 (10) $[p\text{-}ClC_6H_4NHC(O)NHC_6H_4Cl\text{-}p]^{+\cdot}$, 246 (1.7) $[p\text{-}ClC_6H_4NHC(O)NHC_6H_5]^{+\cdot}$, 153 (23) $[p\text{-}ClC_6H_4NCO]^{+\cdot}$, 127 (100) $[p\text{-}ClC_6H_4NH_2]^{+\cdot}$. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 8.84 s (2H), 7.47 d (4H, *J* = 8.9 Hz), 7.32 d (4H, *J* = 8.9 Hz) [11]. Recrystallization from ethanol gave 89 mg (64%) of a solid with mp >300°C; published data: mp 292–294°C [23], 303–305°C [24], 318°C [25].

***N,N′*-Di-*o*-chlorophenylurea.** *In the presence of 3,5-$(CF_3)_2$Xantphos.* From 114 mg (0.59 mmol) of *o*-bromochlorobenzene, 21 mg (0.35 mmol) of urea, 285 mg (0.85 mmol) of Cs_2CO_3, 3.1 mg (0.003 mmol) of $Pd_2(dba)_3\cdot CHCl_3$, and 10.1 mg (0.009 mmol) of 3,5-$(CF_3)_2$Xantphos in 3 ml of dioxane we obtained 77 mg (81%) of a white solid. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 9.03 s (2H), 8.07 d (2H, *J* = 8.0 Hz), 7.47 d (2H, *J* = 8.0 Hz), 7.30 d.d (2H, *J* = 7.7, 8.0 Hz), 7.06 d.d (2H, *J* = 7.7, 8.0 Hz). Found, %: C 55.53; H 3.53; N 9.75. $C_{13}H_{10}Cl_2N_2O$. Calculated, %: C 55.54; H 3.59; N 9.96.

***N,N′*-Di-*o*-chlorophenylurea.** *In the presence of Xantphos.* From 191 mg (1 mmol) of *o*-bromochlorobenzene, 36 mg (0.6 mmol) of urea, 460 mg (1.41 mmol) of Cs_2CO_3, 15.5 mg (0.015 mmol) of $Pd_2(dba)_3\cdot CHCl_3$, and 26.1 mg (0.045 mmol) of 3,5-$(CF_3)_2$Xantphos in 4 ml of dioxane we obtained 80 mg (57%) of *N,N′*-di-*o*-chlorophenylurea as a pale yellow solid. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 9.03 s (2H), 8.07 d (2H, *J* = 8.0 Hz), 7.47 d (2H, *J* = 8.0 Hz), 7.30 d.d (2H, *J* = 7.7, 8.0 Hz), 7.06 d.d (2H, *J* = 7.7, 8.0 Hz). Also, 41 mg (35%) of *o,o′*-di-

chlorodiphenylamine was isolated as a colorless oily substance. ^{1}H NMR spectrum (acetone-d_6), δ, ppm: 7.44–7.48 m (2H), 7.22–7.29 m (4H), 6.97–7.20 m (2H), 6.71 s (1H).

***N*,*N*′-Di-*p*-tolylurea.** *In the presence of 3,5-$(CF_3)_2$-Xantphos.* From 102.9 mg (0.601 mmol) of *p*-bromotoluene, 22 mg (0.36 mmol) of urea, 280 mg (0.86 mmol) Cs_2CO_3, 12.6 mg (0.0122 mmol) of $Pd_2(dba)_3 \cdot CHCl_3$, and 40.4 mg (0.036 mmol) of 3,5-$(CF_3)_2$Xantphos in 3 ml of dioxane we obtained 44 mg (61%) of a white solid. ^{1}H NMR spectrum (acetone-d_6), δ, ppm: 8.02 s (2H), 6.83 d (4H, *J* = 8.3 Hz), 6.62 d (4H, *J* = 8.3 Hz), 2.87 s (6H). Found, %: C 74.79; H 6.84; N 11.61. $C_{15}H_{16}N_2O$. Calculated, %: C 74.97; H 6.71; N 11.66. Also, 8.4 mg of *N*-*p*-tolyl-*N*′-[3,5-bis(trifluoromethyl)phenyl]urea was isolated as by-product. ^{1}H NMR spectrum (acetone-d_6), δ, ppm (*J*, Hz): 8.71 s (1H), 8.27 s (1H), 8.19 s (2H), 7.58 s (1H), 7.41 d (2H, *J* = 8.1), 7.11 d (2H, *J* = 8.1), 2.27 s (3H). ^{19}F–{^{1}H} NMR spectrum (acetone-d_6): δ_F –61.9 ppm.

Reaction of urea with *p*-bromotoluene in the presence of Xantphos. From 102 mg (0.60 mmol) of *p*-bromotoluene, 24 mg (0.40 mmol) of urea, 275 mg (0.84 mmol) of Cs_2CO_3, 12.8 mg (0.0124 mmol) of $Pd_2(dba)_3 \cdot CHCl_3$, and 21.05 mg (0.0364 mmol) of Xantphos in 2.5 ml of dioxane we obtained 16 mg (22%) of a light brown solid containing *N*,*N*′-diphenylurea, *N*-*p*-tolyl-*N*′-phenylurea, and *N*,*N*′-di-*p*-tolylurea at a ratio of 5.2 : 10.0 : 6.8 (calculated from the intensities of amide proton signals; their chemical shifts were in agreement with published data [26]). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 8.65 s [PhN**H**C(O)NHPh], 8.60 s [PhN**H**C(O)NHTol-*p*), 8.54 s [PhNHC(O)N**H**Tol-*p*], 8.48 s [*p*-TolNHC(O)-N**H**Tol-*p*], 8.40–8.47 m, 7.29–7.35 m, 7.23–7.29 m, 7.04–7.10 m, 6.92–6.99 m. Mass spectrum, *m*/*z* (I_{rel}, %): 240 (54) $[p\text{-TolNHC(O)NHTol-}p]^{+\cdot}$, 226 (72) $[\text{PhNHC(O)NHTol-}p]^{+\cdot}$, 212 (28) $[\text{PhNHC(O)-NHPh}]^{+\cdot}$, 133 (23) $[p\text{-TolNCO}]^{+\cdot}$, 119 (23) $[\text{PhNCO}]^{+\cdot}$, 107 (100) $[p\text{-TolNH}_2]^{+\cdot}$, 93 (98) $[\text{PhNH}_2]^{+\cdot}$.

***N*,*N*′-Di-*m*-tolylurea.** From 102 mg (0.600 mmol) of *m*-bromotoluene, 22 mg (0.36 mmol) of urea, 280 mg (0.86 mmol) of Cs_2CO_3, 6.4 mg (0.0062 mmol) of $Pd_2(dba)_3 \cdot CHCl_3$ and 20.2 mg (0.0018 mmol) of 3,5-$(CF_3)_2$Xantphos in 3 ml of dioxane we obtained 72 mg (71%) of a white solid. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 8.55 s (2H), 7.29 s (2H), 7.21 d (2H, *J* = 8.1 Hz), 7.14 d.d (2H, *J* = 7.4, 8.1 Hz), 6.87 d (2H, *J* = 7.4 Hz), 2.27 s (3H). Found, %: C 74.71; H 6.77; N 11.24. $C_{15}H_{16}N_2O$. Calculated, %: C 74.97; H 6.71; N 11.66.

***N*,*N*′-Di-*o*-tolylurea.** The reaction was performed with 257 mg (1.5 mmol) of *o*-bromotoluene, 54 mg (0.9 mmol) of urea, 680 mg (2.08 mmol) of Cs_2CO_3, 7.8 mg (0.0075 mmol) of $Pd_2(dba)_3 \cdot CHCl_3$, and 25.3 mg (0.00225 mmol) of 3,5-$(CF_3)_2$Xantphos in 3 ml of dioxane. The light grey solid was filtered off and dissolved in DMF, the solution was filtered, and the product was precipitated with water. Yield 177 mg (98%). White solid. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 8.28 s (2H), 7.79 d (2H, *J* = 8.0 Hz), 7.17 d (2J, *J* = 7.5 Hz), 7.13 d.d (2H, *J* = 7.5, 8.0 Hz), 6.94 t (2H, *J* = 7.5 Hz), 2.26 s (6H). Found, %: C 75.1; H 6.67; N 11.68. $C_{15}H_{16}N_2O$. Calculated, %: C 74.97; H 6.71; N 11.66.

Reaction of urea with *o*-bromotoluene in the presence of Xantphos. From 171 mg (1.0 mmol) of *o*-bromotoluene, 36 mg (0.6 mmol) of urea, 480 mg (1.5 mmol) of Cs_2CO_3, 20.6 mg (0.02 mmol) of $Pd_2(dba)_3 \cdot CHCl_3$, and 35.2 mg (0.06 mmol) of Xantphos in 4 ml of dioxane we obtained 77.2 mg (77%) of di-*o*-tolylamine as a white solid. ^{1}H NMR spectrum (acetone-d_6), δ, ppm: 7.17 d (2H, *J* = 7.4 Hz), 7.07 t (2H, *J* = 7.8 Hz), 6.86 t (2H, *J* = 7.4 Hz), 6.81 d (2H, *J* = 7.8 Hz), 6.06 s (1H), 2.23 s (6H). According to the ^{1}H NMR data, the product contained about 7% of impurities.

***N*,*N*′-Di(*o*-methoxyphenyl)urea.** From 112 mg (0.6 mmol) of *o*-bromoanisole, 22 mg (0.36 mmol) of urea, 270 mg (0.83 mmol) of Cs_2CO_3, 9.7 mg (0.0093 mmol) of $Pd_2(dba)_3 \cdot CHCl_3$, and 30.3 mg (0.027 mmol) of 3,5-$(CF_3)_2$Xantphos in 3 ml of dioxane we obtained 65 mg (80%) of a white solid. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 8.80 s (2H), 8.09 d (2H, *J* = 7.9 Hz), 6.99 d (2H, *J* = 7.9 Hz), 6.93 d.d (2H, *J* = 7.5, 7.8 Hz), 6.87 d.d (2H, *J* = 7.5, 7.8 Hz), 3.87 s (6H). Found, %: C 66.05; H 6.07; N 9.82. $C_{15}H_{16}N_2O_3$. Calculated, %: C 66.16; H 5.92; N 10.29.

General procedure for arylation of phenylurea. A reactor was filled with argon and charged with 0.6 mmol of phenylurea, 0.84 mmol of Cs_2CO_3, 1–2 mol % of $Pd_2(dba)_3 \cdot CHCl_3$, and 3–6 mol % of Xantphos or 3,5-$(CF_3)_2$Xantphos, and a solution of 0.6 mmol of aryl bromide in 3 ml of dioxane saturated with argon was added. The mixture was degassed by triple freezing–evacuation–defrosting procedure, and the reactor was filled with argon. The mixture was stirred at 100°C under argon, and the progress of the reaction was monitored by GLC and TLC (Silufol UV-254). When the reaction was complete, the mixture was cooled to room temperature, diluted with 30 ml of ethyl acetate, filtered, and evaporated. The residue was purified by chromatography on silica gel

(40–63 μm, Fluka) using ethyl acetate–petroleum ether (bp 65–68°C) as eluent.

***N*-*p*-Chlorophenyl-*N*′-phenylurea.** From 96 mg (0.5 mmol) of *p*-bromochlorobenzene, 68 mg (0.50 mmol) of phenylurea, 230 mg (0.70 mmol) of Cs_2CO_3, 5.3 mg (0.0051 mmol) of $Pd_2(dba)_3 \cdot CHCl_3$, and 17.1 mg (0.00152 mmol) of 3,5-$(CF_3)_2$Xantphos in 2.5 ml of dioxane we obtained 105 mg of a white solid. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 8.80 s (1H), 8.69 s (1H), 7.48 d (2H, *J* = 8.6 Hz), 7.44 d (2H, *J* = 8.0 Hz), 7.31 d (2H, *J* = 8.6 Hz), 7.27 t (2H, *J* = 7.4, *J* = 8.0 Hz), 6.97 d (1H, *J* = 7.4 Hz). According to the ^{1}H NMR data, the product also contained 8% of *N*,*N*′-diphenylurea and 8% of *N*,*N*′-di-*p*-chlorophenylurea (calculated from the intensities of the amide proton signals [11]).

***N*-*o*-Chlorophenyl-*N*′-phenylurea.** From 95 mg (0.49 mmol) of *o*-bromochlorobenzene, 68 mg (0.50 mmol) of phenylurea, 230 mg (0.70 mmol) of Cs_2CO_3, 2.6 mg (0.0025 mmol) of $Pd_2(dba)_3 \cdot CHCl_3$, and 8.6 mg (0.0076 mmol) of 3,5-$(CF_3)_2$Xantphos in 2.5 ml dioxane we obtained 116 mg (95%) of a white solid. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 9.39 s (1H), 8.27 s (1H), 8.16 d (1H, *J* = 8.2 Hz), 7.4–7.53 m (3H), 7.29 d.d (4H, *J* = 7.4, 8.2 Hz), 6.94–7.08 m (3H). Found, %: C 63.14; H 4.56; N 11.18. $C_{13}H_{11}ClN_2O$. Calculated, %: C 63.29; H 4.49; N 11.36.

***N*-Phenyl-*N*′-*p*-tolylurea.** From 106 mg (0.49 mmol) of *p*-bromotoluene, 82 mg (0.6 mmol) of phenylurea, 270 mg (0.83 mmol) of Cs_2CO_3, 10.9 mg (0.0025 mmol) of $Pd_2(dba)_3 \cdot CHCl_3$, and 35.9 mg (0.032 mmol) of 3,5-$(CF_3)_2$Xantphos in 3 ml of dioxane we obtained 108 mg (80%) of a white solid. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 8.86 s (1H), 8.80 s (1H), 7.69 d (2H, *J* = 8.0), 7.59 d (2H, *J* = 8.0 Hz), 7.52 t (2H, *J* = 7.7 Hz), 7.34 d (2H, *J* = 8.0 Hz), 7.21 t (1H, *J* = 7.4 Hz), 2.76 s (3H). Found, %: C 74.10; H 6.34; N 12.17. $C_{14}H_{14}N_2O$. Calculated, %: C 74.31; H 6.24; N 12.38.

Reaction of *p*-bromotoluene with phenylurea in the presence of Xantphos. From 104 mg (0.60 mmol) of *p*-bromotoluene, 82 mg (0.6 mmol) of phenylurea, 285 mg (0.87 mmol) of Cs_2CO_3, 12.6 mg (0.0025 mmol) of $Pd_2(dba)_3 \cdot CHCl_3$, and 21.3 mg (0.0368 mmol) of Xantphos in 3 ml of dioxane we obtained 75 mg of a light brown solid consisting of *N*-phenyl-*N*′-*p*-tolylurea and *N*,*N*′-diphenylurea at a ratio of 39 : 17 (calculated from the intensity ratio of the amide proton signals in the ^{1}H NMR spectrum; the chemical shifts were consistent with those given in [11, 26]). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 8.66 s [PhN**H**C(O)NHPh], 8.61 s [PhN**H**C(O)NHTol-*p*], 8.55 c [PhNHC(O)N**H**Tol-*p*], 7.39–7.53 m, 7.33 d (*J* = 8.2 Hz), 7.22–7.30 m, 7.07 d (*J* = 8.2 Hz), 6.91–7.00 m, 2.24 s.

***N*-Phenyl-*N*′-*m*-tolylurea.** From 103 mg (0.60 mmol) of *m*-bromotoluene, 81 mg (0.59 mmol) of phenylurea, 280 mg (0.86 mmol) of Cs_2CO_3, 7.74 mg (0.0075 mmol) of $Pd_2(dba)_3 \cdot CHCl_3$, and 25.2 mg (0.0224 mmol) of 3,5-$(CF_3)_2$Xantphos in 3 ml of dioxane we obtained 109 mg (81%) of a white solid. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 8.63 s (1H), 8.57 s (1H), 7.45 d (2H, *J* = 8.0 Hz), 7.18–7.33 m (4H), 7.15 t (1H, *J* = 7.7 Hz), 6.96 t (1H, *J* = 7.4 Hz), 6.78 d (1H, *J* = 7.4 Hz), 2.27 s (3H). Found, %: C 74.02; H 6.42; N 11.44. $C_{14}H_{14}N_2O$. Calculated, %: C 74.31; H 6.24; N 12.38.

***N*-Phenyl-*N*′-*o*-tolylurea.** From 104 mg (0.61 mmol) of *o*-bromotoluene, 81 mg (0.59 mmol) of phenylurea, 270 mg (0.83 mmol) of Cs_2CO_3, 7.8 mg (0.0075 mmol) of $Pd_2(dba)_3 \cdot CHCl_3$, and 25.5 mg (0.0227 mmol) of 3,5-$(CF_3)_2$Xantphos in 3 ml of dioxane we obtained 128 mg (95%) of a white solid. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 9.01 s (1H), 7.91 s (1H), 7.83 d (1H, *J* = 8.0 Hz), 7.45 d (2H, *J* = 7.7, 8.3 Hz), 7.27 t (2H, *J* = 8.0 Hz), 7.17 d (1H, *J* = 7.5 Hz), 7.12 d (1H, *J* = 7.7 Hz), 6.6 d (*J* = 7.4 Hz), 6.93 d (*J* = 7.4 Hz). Found, %: C 74.24; H 6.42; N 12.36. $C_{14}H_{14}N_2O$. Calculated, %: C 74.31; H 6.24; N 12.38.

***N*-(*o*-Methoxyphenyl)-*N*-phenylurea.** From 94 mg (0.50 mmol) of *o*-bromoanisole, 69 mg (0.50 mmol) of phenylurea, 225 mg (0.69 mmol) of Cs_2CO_3, 11 mg (0.0106 mmol) of $Pd_2(dba)_3 \cdot CHCl_3$, and 33.9 mg (0.0302 mmol) of 3,5-$(CF_3)_2$Xantphos in 2.5 ml of dioxane we obtained 111 mg (91%) of a white solid. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 9.3 s (1H), 8.22 s (1H), 8.12 d (1H, *J* = 7.8 Hz), 7.45 d (2H, *J* = 8.0 Hz), 7.27 d.d (2H, *J* = 7.8, 8.0 Hz), 6.85–7.04 m (4H), 3.87 s (3H). Found, %: C 69.24; H 5.85; N 11.27. $C_{14}H_{14}N_2O_2$. Calculated, %: C 69.41; H 5.82; N 11.56.

Reaction of *o*-bromotoluene with phenylurea in the presence of Xantphos. From 102 mg (0.59 mmol) of *o*-bromotoluene, 80 mg (0.59 mmol) of phenylurea, 270 mg (0.83 mmol) of Cs_2CO_3, 12.7 mg (0.0122 mmol) of $Pd_2(dba)_3 \cdot CHCl_3$, and 21.2 mg (0.0366 mmol) of Xantphos in 3 ml of dioxane we obtained 40 mg of a colorless solid consisting of *N*-phenyl-*N*′-*o*-tolylurea and *N*,*N*′-diphenylurea at a ratio of 19 : 10 (calculated from the intensity ratio of the amide proton signals in the ^{1}H NMR spectrum; the chemical shifts were consistent with those given in [11, 26]). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 9.01 s [PhN**H**C(O)NHTol-*o*], 8.66 s [PhN**H**-

C(O)NHPh], 7.91 s [PhNHC(O)N**H**Tol], 7.84 d (J = 7.4 Hz), 7.42–7.50 m, 7.33 d.d (J = 7.4, 8.6 Hz), 7.27 m, 7.10–7.20 m, 6.90–7.00 m, 2.24 s.

Arylation of *p*-methylbenzamide with *p*-bromoanisole. A reactor was filled with argon and charged with 0.4 mmol of *p*-methylbenzamide, 0.56 mmol of Cs_2CO_3, 4 mol % of $Pd_2(dba)_3 \cdot CHCl_3$, and 6 mol % of 3,5-$(CF_3)_2$Xantphos, and a solution of 0.4 mmol of *p*-bromoanisole in 3 ml of dioxane saturated with argon was added. The mixture was degassed by evacuation, the reactor was filled with argon, and the mixture was stirred at 100°C under argon, the progress of the reaction being monitored by GLC and TLC (Silufol UV-254). When the reaction was complete, the mixture was cooled to room temperature, diluted with 30 ml of ethyl acetate, filtered, and evaporated. The residue was subjected to chromatography on silica gel (40–63 μm, Fluka), using ethyl acetate–petroleum ether (bp 65–68°C) as eluent.

Arylation of *p*-methylbenzamide with *p*-bromoanisole in the presence of Cs_2CO_3. From 54.4 mg (0.4 mmol) of *p*-methylbenzamide, 73.2 mmol (0.39 mmol) of *p*-bromoanisole, 185 mg (0.56 mmol) of Cs_2CO_3, 8.3 mg (0.008 mmol) of $Pd_2(dba)_3 \cdot CHCl_3$, and 27.2 mg (0.0243 mmol) of 3,5-$(CF_3)_2$-Xantphos in 2 ml of dioxane we obtained 35 mg (37%) of *N*-*p*-methoxyphenyl-*p*-methylbenzamide as a white solid. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 9.37 s (1H), 7.88 d (2H, J = 8.3 Hz), 7.74 d (2H, J = 9.2 Hz), 7.29 d (2H, J = 8.3 Hz), 6.90 d (2H, J = 9.2 Hz), 3.78 s (3H), 2.38 s (3H). Found, %: C 74.24; H 6.12; N 6.07. $C_{15}H_{15}NO_2$. Calculated, %: C 74.59; H 6.22; N 5.80. In addition, 25 mg (18%) of *N*-[3,5-bis(trifluoromethyl)phenyl]-*p*-methylbenzamide was isolated as a light yellow solid, mp 159–160°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 10.03 s (1H), 8.56 s (2H), 7.97 d (2H, J = 8.3 Hz), 7.74 s (1H), 7.36 d (2H, J = 8.3 Hz), 2.41 s (3H).

Arylation of *p*-methylbenzamide with *p*-bromoanisole in the presence of K_3PO_4. From 92.3 mg (0.49 mmol) of *p*-methylbenzamide, 67.1 mmol (0.49 mmol) of *p*-bromoanisole, 160 mg (0.75 mmol) of K_3PO_4, 10.3 mg (0.01 mmol) of $Pd_2(dba)_3 \cdot CHCl_3$, and 27.2 mg (0.0299 mmol) of 3,5-$(CF_3)_2$Xantphos in 2.5 ml of dioxane we obtained 41 mg (35%) of *N*-(*p*-methoxyphenyl)-*p*-methylbenzamide as a white solid. In addition, 39 mg (19%) of *N*-[3,5-bis(trifluoromethyl)phenyl]-*p*-methylbenzamide was isolated as a light yellow solid.

Arylation of *p*-methylbenzamide with *p*-bromoanisole in the presence of sodium *tert*-butoxide. From 94 mg (0.50 mmol) of *p*-methylbenzamide, 67.3 mmol (0.49 mmol) of *p*-bromoanisole, 68 mg (0.71 mmol) of *t*-BuONa, 12.4 mg (0.012 mmol) of $Pd_2(dba)_3 \cdot CHCl_3$, and 34.3 mg (0.0306 mmol) of 3,5-$(CF_3)_2$Xantphos in 2.5 ml of dioxane we obtained 26 mg (21%) of *N*-(*p*-methoxyphenyl)-*p*-methylbenzamide as a white solid.

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REFERENCES

1. Vishnyakova, T.P., Golubeva, I.A., and Glebova, E.V. *Usp. Khim.,* 1985, vol. 54, p. 429; Vyshnyakova, T.P., Golubeva, I.A., and Glebova, E.V., *Russ. Chem. Rev. (Engl. Transl.),* 1985, vol. 54, p. 249.
2. Schmidtchen, F.P. and Berger, M., *Chem. Rev.* 1997, vol. 97, p. 1609.
3. Okaniwa, M., Takeuchi, K., Asai, M., and Ueda, M., *Macromolecules,* 2002, vol. 35, p. 6224; Okaniwa, M., Takeuchi K., Asai, M., and Ueda, M., *Macromolecules,* 2002, vol. 35, p. 6232.
4. Tafesh, A.M. and Weiguny, J., *Chem. Rev.,* 1996, vol. 96, p. 2035.
5. Mulla, S.A.R., Rode, C.V., Kelkar, A.A., and Gupte, S.P., *J. Mol. Catal. A: Chem.,* 1997, vol. 122, p. 103.
6. Wolfe, J.P., Wagaw, S., Marcoux, J.-F., and Buchwald, S.L., *Acc. Chem. Res.,* 1998, vol. 31, p. 805; Yang, B.H. and Buchwald, S.L., *J. Organomet. Chem.,* 1999, vol. 576, p. 125; Hartwig, J.F., *Angew. Chem., Int. Ed.,* 1998, vol. 37, p. 2046; Wolfe, J.P. and Buchwald, S.L., *J. Org. Chem.,* 2000, vol. 65, p. 1144; Wolfe, J.P., Tomori, H., Sadighi, J.P., Yin, J., and Buchwald, S.L., *J. Org. Chem.,* 2000, vol. 65, p. 1158.
7. Wolfe, J.P., Rennels, R.A., and Buchwald, S.L., *Tetrahedron,* 1996, vol. 52, p. 7525; He, F., Foxman, B.M., and Snider, B.B., *J. Am. Chem. Soc.,* 1998, vol. 120, p. 6417; Yang, B.H. and Buchwald, S.L. *Org. Lett.,* 1999, vol. 1, p. 35; Shakespeare, W.C., *Tetrahedron Lett.,* 1999, vol. 40, p. 2035; Hartwig, J.F., Kawatsura, M., Hauck, S.I., Shaughnessy, K.H., and Alcazar-Roman, L.M., *J. Org. Chem.,* 1999, vol. 64, p. 5575.
8. Yin, J. and Buchwald, S.L., *Org. Lett.,* 2000, vol. 2, p. 1101.
9. Yin, J. and Buchwald, S.L., *J. Am. Chem. Soc.,* 2002, vol. 124, p. 6043.
10. Cacchi, S., Fabrizi, G., Goggiamani, A., and Zappia, G., *Org. Lett.,* 2001, vol. 3, p. 2539; Browning, R.G., Mahmud, H., Badarinarayana, V., and Lovely, C.J., *Tetrahedron Lett.,* 2001, vol. 42, p. 7155.

11. Artamkina, G.A., Sergeev, A.G., and Beletskaya, I.P., *Tetrahedron Lett.,* 2001, vol. 42, p. 4381; Artamkina, G.A., Sergeev, A.G., and Beletskaya, I.P., *Russ. J. Org. Chem.,* 2002, vol. 38, p. 538.
12. Klapars, A., Huang, X., and Buchwald, S.L., *J. Am. Chem. Soc.,* 2002, vol. 124, p. 7421.
13. Guari, Y., van Strijdonck, G.P.F., Boele, M.D.K., Reek, J.N.H., Kamer, P.C.J., and Leeuwen, P.W.N.M., *Chem. Eur. J.,* 2001, vol. 7, p. 475.
14. Hartwig, J.F., *Acc. Chem. Res.,* 1998, vol. 31, p. 852.
15. Kong, K.-C. and Cheng, C.-H., *J. Am. Chem. Soc.,* 1991, vol. 113, p. 6313.
16. Collman, J.P., Hegedus, L.S., Norton, J.R., and Finke, R.G., *Principles and Applications of Organotransition Metal Chemistry,* Mill Valley, CA: University Science Books, 1987, p. 324.
17. Hartwig, J.F., Richards, S., Baranano, D., and Paul, F., *J. Am. Chem. Soc.,* 1996, vol. 118, p. 3626.
18. Haman, B.C. and Hartwig, J.F., *J. Am. Chem. Soc.,* 1998, vol. 120, p. 3694.
19. Ishii, Y., *Ann. N.Y. Acad. Sci.,* 1972, vol. 239, p. 114; Ukai, T., Kawazura, H., and Ishii, Y., *J. Organomet. Chem.,* 1974, vol. 65, p. 253.
20. Kranenburg, M., van der Burgt, Y.E.M., Kamer, P.C.J., amd van Leeuwen, P.W.N.M., *Organometallics,* 1995, vol. 14, p. 3081; Hillebrand, S., Bruckmann, J., and Kruger, M.W., *Tetrahedron Lett.,* 1995, vol. 36, p. 75.
21. Casalnuovo, A.L., Rajan Babu, T.V., Ayers, T.A., Warren, T.H., *J. Am. Chem. Soc.,* 1994, vol. 117, p. 9869.
22. Magnelli, D.D., Tesi, G., Lowe, J.U., and McQuistion, W.E., *Inorg. Chem.,* 1996, vol. 5, p. 457.
23. Peyron, L. and Peyron, J., *Bull. Soc. Chim. Fr.,* 1953, p. 846.
24. Dieck, H.A., Laine, R.M., and Heck, R.F., *J. Org. Chem.,* 1975, vol. 40, p. 2819.
25. Hoi, Ng.Ph.B., Xuong, Ng.D., and Suu, V.T., *J. Chem. Soc.,* 1958, p. 2815.
26. Miyahara, M., *Chem. Pharm. Bull.,* 1986, vol. 34, p. 1950.