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# Heterogeneous Aromatic Amination of Aryl Halides with Arylamines in Water with PS-PEG Resin-Supported Palladium Complexes

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**Abstract:** Catalytic aromatic amination is achieved in water under heterogeneous conditions by the use of immobilized palladium complexes coordinated with the amphiphilic polystyrene-poly-(ethylene glycol) resin-supported di(*tert*-butyl)phosphine ligand. Aromatic amination of aryl halides with diphenylamine and N,N-double arylation of anilines with bromobenzene were found to proceed in water with broad substrate tolerance to give the triarylamines in high yield with high recycla-

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bility of the polymeric catalyst beads. Very little palladium leached from the polymeric catalyst under the waterbased reaction conditions to provide a green and clean (metal-uncontaminated) protocol for the preparation of triarylamines, including the optoelectronically active N,N,N',N'-tetraaryl-1,1'-biphenyl-4,4'-diamines (TPDs).

# Introduction

Since the discoveries of Buchwald and Hartwig that the coupling of aryl halides and various amines can be catalyzed by palladium complexes, the catalytic amination of aryl halides, the so-called Buchwald-Hartwig reaction, has intrigued synthetic chemists, and is generally recognized as one of the most powerful methods for preparing a variety of arylamines.<sup>[1]</sup> However, in spite of increasing concern for the environment and the safety of chemical processes, only scattered interest has been given to the heterogeneous- and aqueous-switching of catalytic amination, which would provide a green alternative to the Buchwald-Hartwig reaction.<sup>[2,3]</sup> Arylamines have generated considerable interest owing to their presence in a number of biologically as well as electronically active compounds. Efficient removal of the metal complexes from the reaction mixture of the catalytic amination process would allow not only the recovery of

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costly noble-metal species but also the production of arylamines uncontaminated by metal species to provide clean compounds with improved biological and electronic utility.

We have recently developed amphiphilic polystyrenepoly(ethylene glycol) (PS-PEG) resin-supported transition metal catalysts<sup>[4]</sup> which promote various catalytic transformations smoothly in water under heterogeneous conditions, including palladium-catalyzed arylation (Suzuki-Miyaura coupling), alkenylation (Heck reaction), alkynylation (Sonogashira coupling), carbonylation of aryl halides,  $\pi$ -allylic substitution (Tsuji-Trost reaction), and cyclization of 1,6envnes. If the aromatic amination could be achieved in water with readily recoverable immobilized catalysts, the transformation would represent what may be considered an ideal amination process. Here we report the development of an environmentally benign and safe heterogeneous catalytic system for palladium-promoted amination of aryl halides, which is carried out in water with a readily recyclable immobilized catalyst to achieve the clean (metal uncontaminated) synthesis of triarylamines, such as optoelectronically active N,N,N',N'-tetraphenyl-1,1'-biphenyl-4,4'-diamine (TPD) derivatives

## **Results and Discussion**<sup>[5]</sup>

### Design and Preparation of PS-PEG Resin-Supported Trialkylphosphine-Palladium Complexes

It has been well-documented that the aromatic amination is efficiently catalyzed by palladium complexes of sterically

1788

hindered alkylphosphine ligands, for example,  $RP(t-C_4H_9)_2$ and  $RP(cyclo-C_6H_{11})_2$ , and a variety of alkylphosphine ligands have been designed and prepared for driving the amination catalysis, representative examples of which are shown in Figure 1.<sup>[6-9]</sup>

The amination is generally carried out in toluene with heating in the presence of a strong alkoxide base, such as *t*BuONa, under homogeneous conditions. Buchwald reported an isolated example of aromatic amination in water in 2003, by use of 2-{di(cyclohexyl)phosphino}-2',4',6'-tri(isopropyl)biphenyl (Figure 1, compound **D**),<sup>[8]</sup> and pioneering



Figure 1. Representative examples of phosphine ligands for the Buch-wald-Hartwig amination.

work on the heterogeneous-switching of aromatic amination using an immobilized phosphine-palladium complex (ligand **E**. Figure 1) in 2001.<sup>[10–12]</sup> However, to the best of our knowledge, no catalyst system has yet been developed to accomplish the heterogeneous- and aqueous-switching of the amination in one system. As a result, we decided to prepare the palladium complexes co-ordinatively anchored onto the amphiphilic polystyrene-poly(ethylene glycol) copolymer (PS-PEG)<sup>[13]</sup> resin-supported bulky alkylphosphines, that is,  $PS-PEG-OCH_2CH_2P(t-C_4H_9)_2$  (1) and PS-PEG- $OCH_2CH_2P(cyclo-C_6H_{11})_2$  (2), as possible water-compatible polymeric ligands, for aromatic amination catalysis.<sup>[14,15]</sup> PS-PEG-OCH<sub>2</sub>CH<sub>2</sub>P(t-C<sub>4</sub>H<sub>9</sub>)<sub>2</sub> (1) was readily prepared via the nucleophilic substitution of PS-PEG-Br<sup>[16]</sup> with lithium di(tert-butyl)phosphide (Scheme 1). The structural studies on the resin-supported phosphine 1 were performed by gelphase  ${}^{31}P{}^{1}H$  NMR spectroscopy where a narrow singlet at  $\delta = +19.7$  ppm was observed to demonstrate the incorporation of the di(tert-butyl)phosphine unit onto the resin. The ICP-atomic emission spectroscopy (AES) analysis demonstrated the loading value of the phosphine unit to be 0.21

#### Abstract in Japanese:

両親媒性 PS-PEG レジン担持ジェブチルホスフィン-パラジウム錯体を開発した。同高分 子錯体は水中で芳香族ハライドとアリールアミン類のカップリング反応を触媒し対応する トリアリールアミン類を高効率で与えた。触媒は単純な濾過作業によって簡便に除去され 容易に回収再利用された。生成物へのパラジウムの漏出は確認されず,電子材料として期 待されるトリアリールアミン類のクリーン合成が違成された。



Scheme 1. Preparation of the PS-PEG resin-supported phosphines.

 $mol g^{-1,[17]}$  PS-PEG-OCH<sub>2</sub>CH<sub>2</sub>P(*cyclo*-C<sub>6</sub>H<sub>11</sub>)<sub>2</sub> (**2**, loading value = 0.21 mmol g<sup>-1</sup>) was also prepared by a similar method.

### Aquacatalytic Amination of Bromobenzene with Diphenyl-Amine using PS-PEG Resin-Supported Trialkylphosphine– Palladium Complexes

Condition screening: With the amphiphilic PS-PEG resinsupported bulky alkylphosphine ligands 1 and 2 in hand, we began to explore the catalytic ability of the palladium complexes of the resin-supported, steric-hindered alkylphosphines for the Buchwald-Hartwig amination in water. Considering the utility of the products as electroactive materials, we decided to study the catalytic aromatic amination with diarylamines affording triarylamines. In contrast to the vast amount of research on aromatic amination with alkylamines, only scant attention has been focused on aromatic amination with diarylamines, which is thus still a major challenge even with homogeneous catalysts.<sup>[18]</sup> In addition, a clean synthesis of triarylamines with little metal contamination would be a welcome process owing to their potential optoelectronic properties.<sup>[19]</sup> The reaction conditions were initially screened for the coupling of bromobenzene (3A) with diphenylamine (4) to afford triphenylamine (5A) with the palladium complexes by mixing the polymeric phosphines 1 or 2, and the palladium reagent,  $[PdCl(\eta^3-C_3H_5)]_2$ ,  $[Pd(dba)_2]$ , or [Pd- $(OAc)_2$ , in an appropriate ratio prior to their catalytic use. Thus, the reaction of **3A** with **4** (1.5 equiv to **3A**) was performed with a palladium complex of PS-PEG resin-supported phosphine in aqueous KOH solution under reflux for 24 h. It is also noteworthy that the aromatic amination took place with KOH as a base in water, whereas an alkoxide base (e.g., tBuONa) is frequently required to promote the reaction under the standard homogeneous conditions in an organic solvent. The hydrophobic organic substrates must diffuse into the hydrophobic polystyrene matrix in water to provide a highly *self-concentrated* reaction sphere where the coupling reaction releasing KBr into the aqueous phase should be significantly accelerated to reduce the initial molar concentration in the polymer matrix. After being cooled, the mixture was filtered, and the catalyst beads were rinsed with EtOAc to extract the organic products. The extract was concentrated in vacuo to give crystals of triphenylamine (5A) whose chemical purity was determined by NMR and GC analysis to be >95% without any chromatographic purification. The recovered polymer beads were re-

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cycled for amination under the same conditions without any further purification or additional charge of palladium. Representative results are summarized in Table 1, along with the recovered polymeric complexes. When the reaction was carried out in refluxing 20 M aqueous KOH with the polymeric complex prepared from **1** and di( $\mu$ -chloro)bis( $\eta^3$ -allyl)dipalladium(II) ([PdCl( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>)]<sub>2</sub>) (P/Pd=1:1), the desired Ph<sub>3</sub>N (**5A**) was obtained in 87% yield (Table 1, entry 1) (conver-

Table 1. Screening of the reaction conditions forming  $Ph_3N$  (5A) by the reaction of PhBr (3A) and  $Ph_2NH$  (4a) in water with polymeric palladium complexes.<sup>[a]</sup>

3/		PO (O) PF 1 or 2 [Pd] aq. KOH, reflux	3₂ → ◯> 5A	
entry	Pd source (mol% of Pd)	Polymeric phosphine	P/Pd	yield [%] <sup>[b]</sup>
1	$[PdCl(\eta^{3}-C_{3}H_{5})]_{2}(5.0)$	1	1:1	87
2	$[PdCl(\eta^3-C_3H_5)]_2$ (5.0)	2	1:1	3
3	$[PdCl(\eta^3-C_3H_5)]_2$ (5.0)	1	1:1	57
4	$[PdCl(\eta^{3}-C_{3}H_{5})]_{2}$ (2.5)	1	1:1	51
5	$Pd(OAc)_{2}$ (5.0)	1	1:1	82
6 <sup>[c]</sup>	$Pd(dba)_2$ (5.0)	1	1:1	96
7	$[PdCl(\eta^{3}-C_{3}H_{5})]_{2}$ (5.0)	1	2:1	87
8 <sup>[d]</sup>	$[PdCl(\eta^{3}-C_{3}H_{5})]_{2}(5.0)$	1	2:1	92
9	$[PdCl(\eta^{3}-C_{3}H_{5})]_{2}$ (5.0)	2	2:1	<2
10 <sup>[d]</sup>	recycled catalyst beads from	n entry 1 (3rd re	euse)	74
11 <sup>[d]</sup>	recycled catalyst beads from	n entry 7 (3rd re	euse)	90
12 <sup>[d]</sup>	recycled catalyst beads from	n entry 11 (5th r	euse)	91

[a] All reactions were carried out in refluxing aqueous KOH (20 M). The ratio of **3A** (mol)/**4** (mol)/H<sub>2</sub>O (L) = 1.0:1.5:2.0, unless otherwise noted. [b] Yields of isolated product based on **3A** (entries 1–7, and 9) or **4** (entries 8, and 10–12). [c] During the reaction, the polymeric palladium complex decomposed (palladium black precipitated out inside the polymer matrix). [d] The ratio of **3A** (mol)/**4** (mol)/H<sub>2</sub>O (L) = 1.5:1.0:2.0.

sion of 4 = 100%, isolated yield of 5A = 87%, purity of 5A = >95%). The polymeric palladium complex generated from the PS-PEG-(dicyclohexyl)phosphine 2 hardly catalyzed the amination to give only 3% yield of 5A under otherwise similar conditions (entry 2). The chemical yield of 5A decreased as the concentration of palladium or base decreased (entries 3 and 4). A polymeric complex prepared from [Pd(OAc)<sub>2</sub>] exhibited a slightly lower catalytic performance than that prepared from  $[PdCl(\eta^3-C_3H_5)]_2$  (entry 1 vs 5). While palladium dibenzylideneacetone  $[Pd(dba)_2]$  was found to be a good Pd source, affording a high yield of 5A, as compared to  $[PdCl(\eta^3-C_3H_5)]_2$ , the polymeric complex prepared with [Pd(dba)<sub>2</sub>] decomposed during the reaction (entry 6). When the amination was examined with the palladium complex prepared by mixing the polymeric ligand 1 and  $[PdCl(\eta^3-C_3H_5)]_2$  in a ratio of P/Pd=2:1, **5A** was obtained in 87% yield of isolated product (entry 7; yield based on 3A). When the reaction was carried out with 3A and 4 in a ratio of 1.5:1.0, i.e., the inverse substrate ratio of entry 7, the amination proceeded smoothly as in entry 7, to give 5 A in 92% yield (entry 8; yield based on 4). Thus, the

ratio of the reaction substrates (halide/amine) is optional. A polymeric complex of **2** (P/Pd=2:1) again showed little catalytic activity for the amination (entry 9). The role of the Psubstituents (*tert*-butyl vs *cyclo*-hexyl) is not clear yet, but it has been reported that [alkyl(tBu)<sub>2</sub>P] (Figure 1, **A**, **B**, or **C**) or [aryl(*cyclo*-Hex)<sub>2</sub>P] (Figure 1, **D** or **E**) can be used as an effective ligands for the Buchwald–Hartwig aromatic amination under the standard homogeneous conditions.

Next, we examined the recyclability of the catalyst beads and found that the stability of the polymeric catalyst significantly increased with a complexation ratio of P/Pd=2:1 (Table 1, entries 10-12), though the initial catalytic activity was not affected by the complexation ratio of phosphine to palladium (entry 1 vs 7). Thus, the catalyst beads prepared in a P/Pd ratio of 1:1 were recovered from a first run (entry 1) and subjected to several recycling runs through repetition of the standard manipulation (reaction and workup). Catalytic activity decreased as the recycling was repeated, resulting in a 74% yield of 5A in a third recycling run. The polymeric catalyst prepared in a P/Pd ratio of 2:1 was also recovered from the first run (entry 7) and reused to demonstrate its high recyclability. Thus, under similar conditions, the third and fifth reuses showed high catalytic performance affording 5A in 90% and 91% yield, respectively (entries 11 and 12).<sup>[20]</sup>

Structural studies on the polymeric palladium complexes generated by mixing the polymeric phosphine **1** and [PdCl- $(\eta^3-C_3H_5)$ ]<sub>2</sub> in ratios of 1:1 and 2:1 (P/Pd) were conducted with gel-phase <sup>31</sup>P{<sup>1</sup>H} NMR and ICP-AES analyses (Figure 2). Formation of the palladium complexes [PdCl( $\eta^3$ -



Figure 2. Proposed structures of the polymeric palladium complexes.

(P/Pd = 1:1)[PdCl(n<sup>3</sup>- $C_{3}H_{5}$  (phosphine)] and  $C_3H_5$ )(phosphine)<sub>2</sub>]Cl (P/Pd=2:1) was achieved by mixing  $[PdCl(\eta^3-C_3H_5)]_2$  and an appropriate molar equivalent of the phosphine 1 in dichloromethane at ambient temperature for 60 min. Upon conversion of the polymeric phosphine 1 to the palladium-phosphine complexes  $[PdCl(\eta^3 C_3H_5$ )(phosphine)] (P/Pd = 1:1) $[Pd(\eta^3$ and  $C_3H_5$ )(phosphine)<sub>2</sub>]Cl (P/Pd=2:1), the phosphorus signals shifted downfield to +54.4 ppm and +54.8 ppm, respectively. Thus, the reaction progress with 1 (P/Pd=1:1) was conveniently monitored by gel-phase <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy of the resin beads dispersed in [D]chloroform. After the complexation was completed, it was noted that a narrow singlet observed at  $\delta = +19.7$  ppm in the starting phosphine 1 had disappeared and been replaced by a new resonance at  $\delta = +54.4$  ppm. The remarkably low field shift demonstrates that the phosphino group of 1 coordinates to palladium forming a  $\pi$ -allylpalladium-phosphine complex on the amphiphilic solid support. Using similar procedures, we prepared a palladium-bis(phosphine) complex by mixing [PdCl- $(\eta^3-C_3H_5)]_2$  and 2 molar equivalents of the phosphine 1 (vs the palladium) where a new narrow singlet resonance at  $\delta =$ +54.8 ppm had appeared. ICP-AES analysis of the palladium-phosphine complexes 1-Pd (P/Pd=1:1) and 1-Pd (P/ Pd=2:1) showed the ratio of phosphorus, palladium, and chlorine to be 0.9:1.0:1.0 and 1.9:1.0:1.1, demonstrating that their structures are  $[PdCl(\eta^3-C_3H_5)(phosphine)]$  (P/Pd=1:1) and [PdCl(η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>)(phosphine)<sub>2</sub>]Cl (P/Pd=2:1), respectively, as depicted in Figure 2. The high recyclability of the palladium complex, prepared with 2 molar equivalents of the polymeric phosphine 1 (vs the palladium) (Table 1, entries 10 and 11), can be attributed to the chelating coordination by the two phosphino groups.

It is also noteworthy that little palladium residue was contaminated in the coupling product **5A** when the procedure in entry 8 of Table 1 was employed. Thus, ICP-AES analysis revealed that the palladium species that leached from the polymeric catalyst to contaminate the 1st crop crystals of Ph<sub>3</sub>N (**5A**; from ethyl acetate-hexane) was lower than the detection limit of ICP-AES analysis. The standard homogeneous amination conditions and usual post treatment (organic-aqueous extraction, filtration, solidification, recrystallization) gave crystals of **5A** infected with 0.071 % of palladium (Table 2, conditions B).

Consequently, the catalytic conditions employed in entry 8 of Table 1 were identified as the best system to achieve both heterogeneous- and aqueous-switching of the aromatic amination with high catalytic and recycling performance, which should realize a green and clean preparation of triarylamines with only negligible metal contamination.

#### Synthesis of a Variety of Triarylamines by Aquacatalytic Amination of Haloarenes with Anilines

Amination of various haloarenes: The heterogeneous aquacatalytic amination was examined with a variety of haloarenes under the reaction conditions identified above (see, Table 1, entry 8) and exhibited wide substrate tolerance (Scheme 2). Thus, the amination catalysis with phenyl chloride and iodide proceeded in water as smoothly as that with



Scheme 2. Amination of various haloarenes.

Table 2. Comparative studies on the amination product 5A by heterogeneous and homogeneous aromatic amination of 3A with 4.<sup>[a]</sup>

Br 3A	+ HN $4$ $5A$	
	conditions A <sup>[a]</sup>	conditions B <sup>[b]</sup>
		(homogeneous conditions)
yield (%) of isolated 1st crop crystals <sup>[c]</sup>	74	73
chemical purity (%) <sup>[d]</sup>	>99	97
contaminating value (%) of Pd <sup>[e]</sup>	< 0.01	0.071

[a] Conditions A: According to the conditions employed in Table 1, entry 8. The reaction scale = 5.2 mmol (Ph<sub>2</sub>NH). [b] Conditions B: The reaction was carried out with [Pd(dba)<sub>2</sub>] (5 mol% Pd),  $tBu_3P$  (10 mol%), and tBuONa (1.1 equiv) in 1,4-dioxane at 100°C for 3 h (100% conversion). The reaction scale = 5.2 mmol (Ph<sub>2</sub>NH). The ratio of **3 A** (mol)/**4** (mol)/solvent (L)=1.5:1.0:2.0. [c] Recrystallized from EtOAc/hexane. [d] Determined by GC titration with [(4-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>N] as an internal standard. [e] Determined by ICP-AES analysis.

phenyl bromide under the same conditions to afford triphenylamine (5A) in 75% and 89% yield, respectively. Electronwithdrawing and electron-donating aromatic substituents, such as CF<sub>3</sub>, CH<sub>3</sub>, OCH<sub>3</sub>, N- $(CH_3)_2$ , and Ph groups, were tolerated under similar conditions to give the corresponding triarylamines 5B-5J in good to excellent yield. The catalytic efficiency of the amination was strongly affected by substituents at the ortho position of the bromoarenes. Thus, the amination

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of *ortho*-tolyl bromide (**3D**) gave 44% yield of **5D**, whereas that of *meta*- and *para*-tolyl bromides (**3E** and **3F**) afforded the corresponding **5E** and **5F** in 88% and 95% yield, respectively. A similar steric effect was also observed with 1- and 2-bromonaphthalene (**3K** and **3L**), where the desired triarylamines **5K** and **5L** were obtained in 20% and 87% yield, respectively. The heteroaromatic halide **3M** also underwent amination in water under similar conditions to give diphenyl(pyridyl)amine 5M in 71% yield (Scheme 2).

Double arylation of various anilines: Considering the lack of commercially available diarylamine derivatives ( $Ar_2NH$ ), the double arylation of primary anilines with haloarenes should offer a practical alternative synthetic route to various triarylamines (Scheme 3). The double arylation was ach-



Scheme 3. Double arylation of various anilines.

ieved by the aquacatalytic amination with 3 mol equivalents of bromobenzene with the aniline **6**. Thus, when the arylation of anilines bearing 2-trifluoromethyl, 2-methyl, 3methyl, and 4-methyl substituents (**6a-d**) was carried out with the palladium complex of PS-PEG resin-supported di(*tert*-butyl)phosphine ligand **1** in water in the presence of KOH, the arylation took place twice successively on the nitrogen of the aniline substrates to give the corresponding triarylamines **7a**, **7b**, **7c**, and **7d** in 85%, 86%, 83%, and 87% yield of isolated product, respectively, where 2.5 mol% of palladium was enough to promote the double arylation compared to the reactive bromo residue (5 mol% to aniline).

Steric hinderance of the amino groups influenced the efficiency of the double arylation more than electronic factors. Thus, when the double arylation was examined with 2-methoxyaniline (6 f) under similar conditions, the second N-arvlation was significantly retarded to give 34% yield of the double arylated compound 7f along with 43% of the Nmonoarylated compound 7 f'. The double N-arylation took place successfully with the electron-rich anilines 6g and 6h to afford the N,N-diphenylanilines 7g and 7h in 85% and 92% yield, respectively. The reaction of the aniline substrates 6i and 6j, bearing the sterically demanding 2-morpholino and 2-tert-butyl groups, respectively, with bromobenzene resulted in the formation of the monoarylation products 7i' and 7i' in high yield (Scheme 3). These observations prompted us to examine the stepwise introduction of different N-aryl groups on the nitrogen of anilines. Thus, 4-(dimethylamino)aniline (6h) reacted with 1 equiv of 4-bromobiphenyl (3L) under the N-arylation conditions in water to give N-naphth-2-ylaniline which was subsequently treated with 4-bromotoluene (3F, 1 equiv) to give N-biphen-4-yl-N-(4-methoxy)phenyltol-4-ylamine (8) in 70% vield (Scheme 4).



Scheme 4. Stepwise N-arylation with different aryl groups.

N,N-N'N'-Tetraarylphenylenediamines: Tetraarylphenylenediamines were prepared via successive amination of the two bromides of dibromobenzene or the successive double arylation of the two amino groups (quadruple arylation) of phenylenediamine. Diamination of 1,4-dibromobenzene (9) with 3 equiv of diphenylamine (4) took place in water in the presence of 5 mol% palladium of the polymeric 1-Pd complex (2.5 mol% to bromo residue) to give 55% yield of N,N,N',N'-tetraphenyl-*para*-phenylenediamine (10). N-Phenyl-N-*m*-tolylamine (11) also underwent the successive amination of 9 to give 12 in 47% yield. Likewise, 1,3-dibromobenzene (13) gave *meta*-phenylenediamine 14 in 55% yield under similar aquacatalytic conditions. N,N,N',N'-Tetraphenyl-*para*-phenylenediamine (**10**) was also prepared via quadruple arylation of phenylenediamine (**15**) with bromoarenes (**3**). Thus, the N,N,N'A-arylation of **15** was carried out with 6 mol equiv of **3A** in water under the arylation conditions to give a 75% yield of N,N,N',N'-tetraaryl-*para*phenylenediamine **10** (Scheme 5).



Scheme 5. Preparation of N,N-N'N'-tetraarylphenylenediamines through diamination.

N,N,N',N'-*Tetraaryl*-1,1'-biphenyl-4,4'-diamines (*TPD*): N,N,N',N'-Tetraphenyl-1,1'-biphenyl-4,4'-diamine derivatives (TPDs) are known as optoelectroactive organic materials owing to their hole-transport property.<sup>[21]</sup> Because of their utility in optoelectronic devices (e.g., EL devices), a costly purification process with sublimation is often required to provide TPDs with a high level of metal-uncontaminated purity. With a clean aromatic amination protocol in hand, we set about demonstrating its applicability for the preparation of TPD derivatives (Scheme 6).<sup>[22]</sup> The reaction of 4,4'dibromobiphenyl (**16**) with diphenylamine (**4**) was carried



Scheme 6. Preparation of N,N,N',N'-tetraaryl-1,1'-biphenyl-4,4'-diamines (TPD).

out with 5 mol% palladium of the polymeric 1-Pd complex (P/Pd=2:1) in aqueous KOH solution under reflux for 24 h. The aromatic amination took place successively at two of the bromo groups of 16 to give a 50% yield of the isolated N,N,N',N'-tetraphenyl-1,1'-biphenyl-4,4'-diamine (17). Little palladium was observed (lower than the detection limit of ICP-AES analysis) even in the crude product and analytically pure 17 was isolated by simple chromatographic purification or recrystallization. Amination of 16 with phenyl(metatolyl)amine (11) and naphthylphenylamine (19) gave N,N'diphenyl-N,N'-di(*meta*-tolyl)-1,1'-biphenyl-4,4'-diamine (18) N,N'-dinaphthyl-N,N'-diphenyl-1,1'-biphenyl-4,4'-diaand mine (20) in 33% and 59% yield, respectively. Triple amination of tribromobenzene (21) also proceeded under similar conditions, though the chemical yield of the desired triple amination product was moderate. Thus, amination of 21 with 4.5 mol equivalents of 4 was catalyzed by the polymeric complex 1-Pd (5 mol% to 21, 1.33 mol% to bromo residue) in water under similar conditions to give tris(4-diphenylaminophenyl)amine (22), a hole-transport material, in 25% yield (Scheme 7).

### Conclusions

The Buchwald–Hartwig amination was achieved in water under heterogeneous conditions by use of immobilized palladium complexes, coordinated with amphiphilic polystyrene–poly(ethylene glycol) resin-supported di(*tert*-butyl)phosphine ligand, which were designed and prepared with a



Scheme 7. Triple amination forming tris(4-diphenylaminophenyl)amine.

view toward using them in water. Aromatic amination of aryl halides with diphenylamine and N,N-double arylation of anilines with bromobenzene were found to proceed smoothly in water with broad substrate tolerance to give triarylamines in high yield with high recyclability of the polymeric catalyst beads. Since little palladium leached from the polymeric catalyst under the water-based reaction conditions, this method provides a green and clean (metal-uncontaminated) protocol for the preparation of triarylamines. The catalytic system was applied to successive amination of dibromoarenes and N,N,N'N'-quadruple arylation of phenylenediamine producing N,N,N'N'-tetraarylphenylenediamines. With the heterogeneous catalytic system, electroactive N,N,N',N'-tetraaryl-1,1'-biphenyl-4,4'-diamines (TPDs) were obtained without metal contamination.

### **Experimental Section**

**Preparation of PS-PEG-P**(*tert*-C<sub>4</sub>H<sub>9</sub>)<sub>2</sub> (1): *n*-Butyllithium (2.69 mol L<sup>-1</sup> in hexane, 0.47 mL, 1.25 mmol) was added to a mixture of di-*tert*-butylphosphine (1.83 g, 1.25 mmol) and THF (10 mL, three freeze-pump-thaw cycles) over 1 h and the mixture was stirred at  $-78^{\circ}$ C for 1 h under a nitrogen atmosphere. The reaction mixture was added to the TentaGel<sup>®</sup> S Br (2.01 g, 0.50 mmol of bromine residue) dispersed in THF (20 mL, three freeze-pump-thaw cycles) at  $-78^{\circ}$ C under a nitrogen atmosphere and the resulting mixture was stirred for 1 h. The reaction mixture was warmed to room temperature slowly (for 1 h) and stirred for an additional 1 h at ambient temperature. The mixture was filtered and washed with water (20 mL, 3 times), THF (20 mL, 3 times), and CH<sub>2</sub>Cl<sub>2</sub> (20 mL, 3 times). The residue was dried in vacuo for 18 h to give the polymer-supported ligand (1). <sup>31</sup>P NMR (400 MHz, CDCl<sub>3</sub>, 25°C):  $\delta = +19.7$ .

The loading amount of phosphine was analyzed by ICP-AES. The ligand (1) (19.7 mg) was treated with HNO<sub>3</sub> (20%, 3 mL) at 90 °C for 21 h and filtered. The filtrate was filled with pure water up to 50 mL and analyzed by ICP-AES to determine that the loading value of phosphine was  $0.21 \text{ mmol g}^{-1}$ .

**Preparation of 1-Pd complex (P/Pd = 2:1):** The polymer-supported ligand (1) (1.27 g, 0.32 mmol of phosphine residue) was mixed with di(μ-chloro)bis(η<sup>3</sup>-allyl)dipalladium(II) ([PdCl(η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>)]<sub>2</sub>) (30.2 mg, 0.17 mmol of Pd) in CH<sub>2</sub>Cl<sub>2</sub> (12.7 mL) at ambient temperature and shaken for 1 h under a nitrogen atmosphere. The mixture was filtered and the resulting resin beads were washed with CH<sub>2</sub>Cl<sub>2</sub> (12.7 mL, 3 times), dried in vacuo overnight to provide the **1**-Pd complex (1.33 g). <sup>31</sup>P NMR (400 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = +54.4.

Coupling of haloarenes with diarylamines: A typical procedure is given for the coupling of bromobenzene (3A) with diphenylamine (4) (Table 1, entry 8). A mixture of the catalyst (1-Pd complex (P/Pd=2:1), 0.015 mmol of Pd), bromobenzene (0.45 mmol), and diphenylamine (0.30 mmol) in 20 м KOH aqueous solution (0.6 mL) was shaken for 24 h under reflux conditions in a nitrogen atmosphere. After being cooled, the mixture was filtered, and the recovered resin beads were extracted with EtOAc (2 mL, 4 times). The combined extracts were dried over anhydrous  $Na_2SO_4$ . The solvent was evaporated to give crude crystals of triphenylamine (5A), which were evaluated for chemical purity and yield by NMR and GC analysis (Table 2). Analytically pure 5A was obtained by recrystallization from EtOAc/hexane. Triphenylamine (5A); CAS: 603–34–9; white crystals; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta = 7.23$  (t, J=7.0 Hz, 6H), 7.08 (d, J=8.0 Hz, 6H), 6.99 (t, J=7.0 Hz, 3H); <sup>13</sup>C NMR(125 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta = 147.8$ , 129.2, 124.1 122.6; MS  $(EI(+)): m/z 245 (M^+).$ 

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