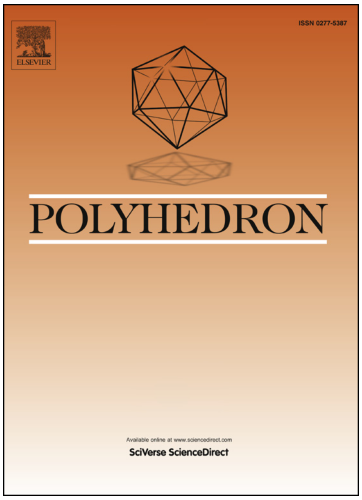


Synthesis, characterization and structural study of a phosphonium salt containing the $[Pd_2Br_6]^{2-}$ ion and its application as a novel, efficient and renewable heterogeneous catalyst for amination of aryl halides and the Stille cross-coupling reaction

Ali Naghipour, Arash Ghorbani-Choghamarani, Fateme Heidarizadi, Behrouz Notash

PII: S0277-5387(15)00746-9
DOI: http://dx.doi.org/10.1016/j.poly.2015.11.051
Reference: POLY 11697

To appear in: *Polyhedron*

Received Date: 20 October 2015
Accepted Date: 28 November 2015

Please cite this article as: A. Naghipour, A. Ghorbani-Choghamarani, F. Heidarizadi, B. Notash, Synthesis, characterization and structural study of a phosphonium salt containing the $[Pd_2Br_6]^{2-}$ ion and its application as a novel, efficient and renewable heterogeneous catalyst for amination of aryl halides and the Stille cross-coupling reaction, *Polyhedron* (2015), doi: http://dx.doi.org/10.1016/j.poly.2015.11.051

Synthesis, characterization and structural study of a phosphonium salt containing the $[Pd_2Br_6]^{2-}$ ion and its application as a novel, efficient and renewable heterogeneous catalyst for amination of aryl halides and the Stille cross-coupling reaction

Ali Naghipour[a*], *Arash Ghorbani-Choghamarani*[a], *Fateme Heidarizadi*[a], *Behrouz Notash*[b]

[a] *Department of Chemistry, Faculty of Science, Ilam University, Ilam, Iran.*
[b] *Department of Chemistry, Shahid Beheshti University, Tehran, Iran.*

Abstract

In this study palladium(II) acetate reacts with a phosphonium salt, $[Ph_3PCH_2C_6H_4CH_2Br]Br$, to give $[Ph_3PCH_2C_6H_4CH_2OC(O)CH_3]_2[Pd_2Br_6]$. Characterization of the obtained compound was performed by elemental analysis, IR, ^{1}H, ^{31}P, ^{13}C NMR and X-ray crystallography. It was found that this compound can act as an efficient catalyst for amination of aryl halides to afford primary amines and satisfactory results were obtained. It has also been successfully employed in the catalytic Stille cross-coupling reaction. The catalyst is easily recoverable and reusable without significant loss of its catalytic activity.

Keywords: Phosphonium salt, Palladium(II), Amination, C-C coupling.

1. Introduction

Aniline is one of the most important intermediates in many different kinds of applications, such as producing agrochemicals, pigments and dyes, pharmaceuticals, rubber processing chemicals and isocyanates, etc. [1,2]. Hence continuous efforts towards finding more efficient catalytic reactions under mild conditions, with high turnover numbers and fast reaction rates are being pursued for the preparation of aniline and its derivatives.

One of the routes for the synthesis of aniline is the reaction of aryl halide with ammonia in the presence of various transition-metal catalysts; however there are many problems in the direct utilization of ammonia, which can displace the ligand bound to the metal center causing the formation of a catalytically non-reactive species [3-5]. Ammonia, as well, has the tendency to form amido bridges with some catalysts, giving stable structures [6,7]. In addition, the resultant primary aniline is more active than ammonia, leading to diaryl amines. Because of these problems, the amination of aryl halides to produce primary aryl amines has been less studied, while many studies have been done on the production of secondary and tertiary amines [8-18].

In many studies, at the beginning of the reactions, ammonia equivalents, including (di)allylamine, ^{t}buthylcarbamate, imines and sulfoximines, are utilized for the conversion of

---

[*] Address correspondence to A. Naghipour, Department of Chemistry, Faculty of Science, Ilam University, P.O. Box 69315516, Ilam, Iran; Tel/Fax: +98 841 2227022; E-mail address: Naghipour2002@yahoo.com

aryl halides into the corresponding primary aryl amines, and finally deprotection is done [19]. Despite these problems, the use of ammonia as an *N*-nucleophile is still the most desired approach due to its low cost and availability [20-29].

Indeed, many researches have accomplished the amination of aryl halides in aqueous ammonia, but they mostly confronted some constraints, including needing a nitrogen or argon atmosphere, toxic solvents such as toluene, high temperatures and pressures, special equipment and materials like autoclaves, dry ice, etc. [30,31]. Recently, phosphonium salts have attracted considerable attention as effective catalysts for a range of organic reactions, including oxidation, polymerization, cross-coupling reactions [32,33]. Previously it has been demonstrated that certain phosphines are suitable ligands for palladium-catalyzed C–C, C–N, and C–O bond forming reactions [34-36], however, to the best of our knowledge, phosphonium salts have not been examined for the amination of aryl halides with aqueous ammonia. Thus, in continuation of our previous works on catalytic reactions [37,38], herein, in order to obtain primary amines, aqueous ammonia is utilized successfully as an environmentally friendly direct nitrogen source under air atmosphere and solvent free conditions. Furthermore we report the catalytic activity of this phosphonium compound for carbon-carbon bond formation by the Stille cross-coupling reaction using triphenyltin chloride (Ph_3SnCl) under green medium to obtain biphenyl derivatives. Biphenyl derivatives have wide range of activities, such as antimicrobial, antifungal, anti-proliferative, anti-diabetic, immunosuppressant, analgesic, anti-inflammatory, etc [39]. Biphenyl derivatives are also used as precursors for the synthesis of oligo(*p*-phenylene)s that have been extensively studied in the domain of artificial ion channels [40]. Palladium-catalyzed substitution and addition reactions involving organotin compounds have been used by many research groups throughout the world for synthetic purposes [41]. This is essentially due to the stability of the organotin reagents in air and moisture and their compatibility with various functional groups.

2. Experimental

2.1. Materials and physical measurements

All reactants and solvents were obtained from Merck, Aldrich and Fluka Chemical Companies and were used without further purification. Melting points were measured on a Stuart SMP_3 apparatus. IR spectra (in the range 4000-400 cm^{-1}) were recorded on a Shimadzu 435-U-04 spectrophotometer and samples were prepared as KBr pellets. NMR spectra (^1H, ^{31}P and ^{13}C NMR) were recorded on a 400 MHz Bruker spectrometer in $CDCl_3$ or DMSO-d_6 as the solvent at room temperature. Elemental analysis was carried out with a CHNS-O Costech ECS 4010 analyzer. Thin-layer chromatography (TLC) was performed using Merck silica gel 60 F254 precoated plates (0.25 mm) and visualized by a UV fluorescence lamp.

2.2. X-ray crystallography

Crystal data of compound **1** were collected using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) on a STOE IPDS-2T diffractometer at 120(2) K. The molecular structure was solved by direct methods and then refined by full-matrix least-squares on F^2 using the X-STEP32 crystallographic software package [42]. All hydrogen atoms were added in their geometrically idealized positions. Non-hydrogen atoms were refined with anisotropic thermal parameters. Cell constants and orientation matrices were obtained by least-squares refinement of diffraction data from 13453 unique reflections.

2.3. Synthesis of bis(2-bromomethylbenzyl)triphenylphosphonium hexabromodipalladate(II) $[Ph_3PCH_2C_6H_4CH_2OC(O)CH_3]_2[Pd_2Br_6]$:

To a solution of 1,2-bis(bromomethyl)benzene (0.263 g, 1 mmol) in benzene (2 mL), a solution of triphenylphosphine (PPh_3) (0.262 g, 1 mmol) in benzene (2 mL) was added and the resulting mixture was stirred for 4 h at room temperature. The separated solid was filtered off and washed with diethyl ether (10 mL) to give $[Ph_3PCH_2C_6H_4CH_2Br]Br$ as a white powder. Yield: 0.446 g (85%). M.p. 180 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 4.27 (s, 2H, CH_2Br), 5.48 (d, 2H, CH_2P, J= 15.01 Hz), 6.95-7.72 (m, 19H, Ph). $^{13}C\{^1H\}$ NMR (75.45 MHz, DMSO, ppm) δ: 30.41 (d, CH_2P, J = 46.04 Hz), 45.60 (s, CH_2Br), 117.67 (d, C-P), 128.01, 128.13, 128.44, 128.50, 129.18, 129.22, 130.07, 130.24, 131,53, 131,60, 131.71, 131.78, 134.26, 134.39, 134.90, 134.94 (C, PPh_3). $^{31}P\{^1H\}$ NMR (121.50 MHz, DMSO, ppm) δ: 23.66.

The prepared (2-bromomethylbenzyl)triphenylphosphonium bromide (0.526 g, 1 mmol) was dissolved in 5 mL of ethanol. Then palladium(II) acetate (0.224 g, 1 mmol) in 5 mL of ethanol was added to this solution and the mixture was stirred at room temperature. After 3 hours, the product was filtered off and washed with diethyl ether (10 mL) to yield $[Ph_3PCH_2C_6H_4CH_2OC(O)CH_3]_2[Pd_2Br_6]$ as a brown powder. Yield: 0.46 g (60 %). M.p. 268 ˚C. IR (υ, cm^{-1}): 1432 (CH_2-P), 1106-1160 (C-O). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 4.29 (s, 2H, CH_2O), 5.13 (d, 2H, CH_2P, J = 15.1 Hz), 6.97-7.93 (m, Ph). ^{13}C NMR (75.45 MHz, DMSO, ppm) δ: 16.9 (s, CH_3 (acetate group)), 25.4 (d, CH_2P, J = 37 Hz), 55.5 (s, CH_2O), 117.1-137.9 (Ph), 170.0 (s, C=O). $^{31}P\{^1H\}$ NMR (121.50 MHz, DMSO, ppm) δ: 22.6. Anal. Calc. for $C_{28}H_{26}O_2P$, $0.5(Br_6Pd_2)$: C, 43.57; H, 3.37. Found: C, 44.05; H, 3.65%.

2.4. General procedure for amination of aryl halides:

To a solution of the aryl halide (1 mmol) and ammonium hydroxide (28%) (1 mL, 0.003 mmol), 0.005 g (0.003 mmol) of $[Ph_3PCH_2C_6H_4CH_2OC(O)CH_3]_2[Pd_2Br_6]$ as a catalyst were added and the reaction mixture was stirred at 60 ˚C for an appropriate time. The progress of the reaction was followed by TLC. After completion of the reaction, the product was extracted with ethyl acetate (3 × 10 mL). The combined ethyl acetate extracts were dried over anhydrous sodium sulfate (1.5 g), filtered and evaporated to give the pure product. The products were characterized by a comparison of their spectral (^{1}H NMR and IR) and physical data with those of authentic samples.

2.5. General procedure for the Stille cross-coupling reaction

A mixture of the aryl halide (1 mmol), Ph_3SnCl (0.4 mmol), K_2CO_3 (1.5 mmol), 0.005 g of $[Ph_3PCH_2C_6H_4CH_2OC(O)CH_3]_2[Pd_2Br_6]$ (0.003 mmol) as a catalyst and 1 mL polyethylene glycol (PEG) as the solvent was heated at 90 ˚C for an appropriate time. After completion of the reaction, based on TLC, the mixture was cooled to room temperature. The reaction mixture was added to water (10 mL), filtered (to remove the catalyst) and extracted three times with diethyl ether (3 × 5 mL). The combined diethyl ether extracts were dried over anhydrous sodium sulfate (1.5 g), filtered and evaporated to give the pure product. The products were characterized by a comparison of their spectral (^{1}H-NMR and IR) and physical data with those of authentic samples.

2.6. General procedure for the recovery of the catalyst

In both catalytic reactions, after completion of the reaction based on TLC, the reaction mixture was cooled to room temperature. Then water (5 mL) and the organic phase of the reaction (5 mL), ethyl acetate in the amination reaction or diethyl ether in the Stille cross-coupling reaction, were added and the mixture was filtered off to separate the catalyst. The catalyst was dried at 100 ˚C and directly used for the repeated reactions.

2.7. Representative NMR and IR data

Aniline: ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ_H: 7.27-7.21 (m, 2H), 6.88-6.84 (tt, J = 7.2, 1 Hz, 1H), 6.78-6.76 (m, 2H), 3.65 (s, 2H). IR (υ, cm^{-1}): 3433, 3376, 3298, 3189, 2969, 2916, 1852, 1719, 1633, 1604, 1578, 1508, 1456, 1379, 1298, 1274, 1214, 1164, 1116, 1021, 1004, 874, 862, 811, 779, 742, 722, 703, 572, 552, 488.

4-Nitroaniline: ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 8.12-8.10 (d, J = 9.2 Hz, 2H), 6.67-6.65 (d, J = 8.8 Hz, 2H), 4.43 (br, 2H). IR (υ, cm^{-1}): 3419, 3391, 3096, 3061, 2958, 2927, 2856, 1921, 1733, 1600, 1568, 1515, 1472, 1436, 1398, 1356, 1344, 1306, 1276, 1173, 1120, 1106, 1066, 1011, 958, 853, 839, 738, 723, 693, 675, 620, 541, 522.

4-Cyanoaniline: ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 7.65-7.68 (m, 2H), 7.54-7.58 (m, 2H), 4.26 (br, 2H). IR (υ, cm^{-1}): 3085, 3032, 2965, 2929, 2860, 2288, 2221, 1915, 1728, 1655, 1580, 1475, 1397, 1277, 1176, 1121, 1066, 1010, 960, 823, 767, 746, 722, 699, 540, 430.

4-Cyano-1,1'-biphenyl: ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 7.78-7.76 (m, 2H), 7.72-7.68 (m, 2H), 7.65-7.62 (m, 2H), 7.53-7.49 (m, 2H), 7.49-7.45 (m, 1H). IR (υ, cm^{-1}): 3433, 3066, 2922, 2351, 2218, 1929, 1637, 1596, 1475, 1398, 1275, 1110, 953, 843, 767, 693, 559, 512.

4-Nitro-1,1'-biphenyl: ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 8.32 (d, J = 8.8 Hz, 2H), 7.78 (d, J = 8.8 Hz, 2H), 7.66-7.64 (m, 2H), 7.56-7.50 (m, 2H), 7.50-7.46 (m, 1H). IR (υ, cm^{-1}): 3447, 3074, 2926, 2840, 1920, 1672, 1591, 1513, 1397, 1344, 1103, 926, 851, 738, 692, 530, 468.

4-Methoxy-1,1'-biphenyl: ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 7.55-7.60 (m, 4H), 7.43-7.47 (m, 2H), 7.32-7.36 (m, 1H), 7.02 (m, 2H), 3.86 (s, 3H). IR (υ, cm^{-1}): 3061, 2997, 2926, 2844, 1600, 1524, 1482, 1280, 1248, 1191, 1032, 688.

3. Results and discussion

3.1. Synthesis of the catalyst

Initially, (2-methylacetatobenzyl)triphenylphosphonium hexabromodipalladate(II) (**1**) was synthesized by the treatment of 1,2-bis(bromomethyl)benzene with PPh_3 in benzene as a solvent, yielding the corresponding phosphonium salt as the exclusive product, as only the monophosphonium salts are insoluble in benzene (their diphosphonium derivatives are dissolved in benzene). Subsequently, the reaction of the phosphonium bromide with palladium(II) acetate in a molar ratio of 1:1 in ethanol at room temperature for 3 h led to the formation of **1** as a brown solid, as shown in Scheme 1. The observed sharp and singlet peak at δ 22.591 ppm in the ^{31}P NMR spectrum confirmed the purity of the product.

Scheme 1 here

*3.2. X-ray crystallographic study of compound **1***

Suitable crystals of compound **1** were obtained by slow evaporation from a dichloromethane solution over several days and its structure was determined by single-crystal X-ray diffraction. The anion and cation moieties of the compound are shown in Fig. 1. Compound **1** crystallizes in the triclinic space group P-1 with two molecules in the unit cell. It can be seen from the ORTEP view of the compound that the geometry of the [Pd_2Br_6] moiety is nearly planar and the structure around the phosphorus atom is close to tetrahedral. The bromo group attached to CH_2 in the ligand structure is replaced by an acetate group in the final compound structure. Significant crystallographic data are summarized in Table 1 and some selected bond distances and angles are given in Table 2.

Figure 1 here
Table 1 here
Table 2 here

3.3. Catalytic study

3.3.1. Amination of aryl halides

To study the catalytic activity of the synthesized compound (**1**), the amination reaction of aryl halides was selected, a reaction that does not proceed in the absence of a catalyst. For this purpose, aqueous ammonia was used as the supplier of the amine group. Initially, heterogeneous catalyst optimization was carried out and the optimal amount was found to be 0.005 g (0.3 mol %). The reaction of iodobenzene with aqueous ammonia was then performed in various organic solvents and the results are shown in Table 3.

Table 3 here

Optimal conditions for the reaction determined are as follows: 1 mmol of aryl halide, 1 mL of aqueous ammonia and 0.005 g (0.3 mol%) of catalyst in solvent free conditions. To evaluate the efficiency of this method, various aryl halides were applied and the results are summarized in Table 4 (Scheme 2). The products were characterized by spectral techniques (^{1}H NMR and IR). As can be seen, the products were obtained in very good to excellent yields.

Scheme 2 here

Table 4 here

3.3.2. Stille cross-coupling reaction

Another reaction studied in this research was the Stille cross-coupling reaction. In order to determine the most appropriate reaction conditions and evaluate the catalytic efficiency of compound **1**, we studied the influence of the amount of compound **1**, solvent and temperature on the reaction times and yields. Thus, the reaction of iodobenzene, triphenyltin chloride and potassium carbonate in polyethylene glycol at 90 ˚C was selected as a model reaction and different amounts of catalyst were investigated. The results are illustrated in Table 5.

Table 5 here

According to Table 5, to prove the true effectiveness of the heterogeneous catalyst, the reaction without catalyst was performed. It was found that biphenyl was not made after 15 minutes of heating.

Before temperature and base optimization, it was necessary to choose a suitable solvent. For this purpose, several solvents, including water, N,N-dimethylformamide, ethanol and polyethylene glycol (PEG), were used. The results are shown in Table 6. Polyethylene glycol was chosen as the optimal solvent for the reaction. The reason for the PEG selection was the fact that this solvent is a green solvent. Furthermore it is cheaper than other organic solvents.

Table 6 here

Next the effect of temperature on the rate of the reaction was studied using the reaction of iodobenzene, triphenyltin chloride and potassium carbonate in the presence of the optimum quantity of catalyst (Table 7). It was observed that the reaction did not proceed at room temperature. At 90 ˚C, the reaction proceeded to give the corresponding product in good yield. A further increase in temperature to 100 ˚C had little effect on the rate of reaction. Therefore, we kept reaction temperature at 90 ˚C as the optimal temperature.

Table 7 here

Finally, optimization of base was performed in this study. According to Table 8, potassium carbonate could be selected as the optimum base among used bases.

Table 8 here

The best result was obtained with a 1:0.4:1.5 ratio of aryl halide:triphenyltin chloride: potassium carbonate with 0.005 g of catalyst at 90 ˚C.

The generality of this reaction was examined using several types of aryl halides, having electron donating and electron withdrawing groups (Scheme 3). In all cases, the corresponding products were obtained in good to excellent yield (Table 9). The products were characterized by spectral techniques (^{1}H NMR, ^{13}C NMR and IR).

Scheme 3 here

Table 9 here

As can be seen from Tables 4 and 9, the catalytic system worked exceedingly well in both reactions with a wide range of substrates under the optimized reaction conditions.

3.3.3. Recovery of the catalyst

The reusability of catalysts is an important advantage and makes them useful for commercial applications. For an investigation of the heterogeneous catalyst stability, the activity of the catalyst was tested for these reactions. The separated catalyst was reused over four consecutive runs in the amination reaction (column a) and synthesis of biaryl compounds (column b), demonstrating excellent recoverability and reusability. The results are presented in Fig. 2.

Figure 2 here

Conclusion

In this research, an efficient method was used for the amination of aryl halides by aqueous ammonia in the presence of a phosphonium salt containing palladium(II), which enables the direct synthesis of a number of primary amines with very good to excellent yields. This method requires neither a solvent nor a base, which are often used for similar catalytic amination reactions of aryl halides. Another advantage of this method is the ease of product separation. Moreover, a small amount of catalyst (0.3 mol%) is required and di- or triarylamine products were not observed in any reactions. Furthermore we demonstrated that this compound is an efficient catalyst for the Stille cross-coupling reaction using the commercially available and cheap reagent triphenyltin chloride. In addition, the reactions need not be performed under an inert or dry atmosphere. The catalyst showed high activity, and its reusability was examined for up to four consecutive cycles in both reactions.

Supplementary data

CCDC 1030177 contains the supplementary crystallographic data for compound **1**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

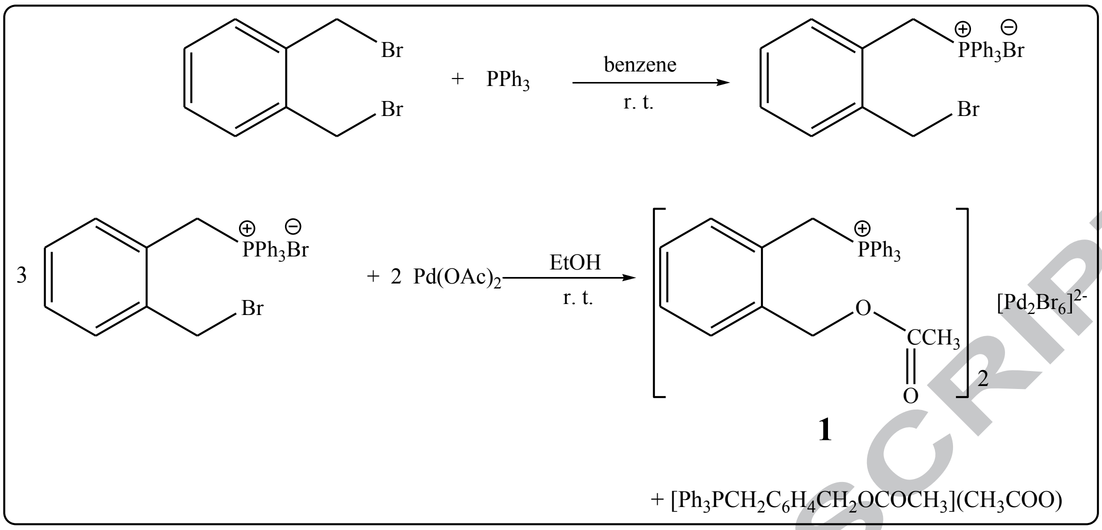
Acknowledgement

This work was supported by the research facilities of Ilam University, Ilam, Iran.

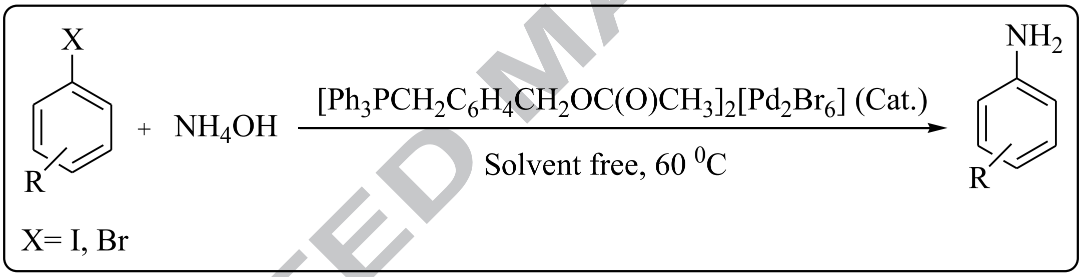
References

1. T. Kahl, K. W. Schröder, F. R. Lawrence, W. J. Marshall, H. Höke, R. Jäckh, *Aniline in Ullmann's Encyclopedia of Industrial Chemistry, John Wiley & Sons, New York*, 2007.
2. Lawrence S A. Amines: Synthesis, Properties and Application. Cambridge: Cambridge University Press, 2004.
3. R. A. Widenhoefer, S. L. Buchwald, Organometallics 15 (1996) 2755-2763.
4. R. A. Widenhoefer, S. L. Buchwald, Organometallics 15 (1996) 3534-3542.
5. F. Paul, J. Patt, J. F. Hartwig, Organometallics 14 (1995) 3030-3039.
6. S. Park, A. L. Rheingold, D. M. Roundhill, Organometallics 10 (1991) 615-623.
7. A. L. Casalnuovo, J. C. Calabrese, D. Milstein, Inorg. Chem. 26 (1987) 971-973.
8. Q. Shen, S. Shekhar, J. P. Stambuli, J. F. Hartwig, Angew. Chem. Int. Ed. 44 (2005) 1371-1375.
9. Q. Dai, W. Z. Gao, D. Liu, L. Kapes, X. M. Zhang, J. Org. Chem. 71 (2006) 3928-3934.
10. X. Xie, T. Y. Zhang, Z. G. Zhang, J. Org. Chem. 71 (2006) 6522-6529.
11. L. Ackermann, J. H. Spatz, C. J. Gschrei, R. Born, A. Althammer, Angew. Chem. Int. Ed. 45 (2006) 7627-7630.
12. N. Marion, E. C. Ecarnot, O. Navarro, D. Amoroso, A. Bell, S. P. Nolan, J. Org. Chem. 71 (2006) 3816-3821.
13. O. Navarro, N. Marion, J. Mei, S.P. Nolan, Chem. Eur. J. 12 (2006) 5142-5148.
14. K. W. Anderson, R. E. Tundel, T. Ikawa, R. A. Altman, S. L. Buchwald, Angew. Chem. Int. Ed. 45 (2006) 6523-6527.
15. Q. Shen, T. Ogata, J. F. Hartwig, J. Am. Chem. Soc. 130 (2008) 130, 6586-6596.
16. B. P. Fors, P. Krattiger, E. Strieter, S. L. Buchwald, Org. Lett. 10 (2008) 3505-3508.
17. M. R. Biscoe, B. P. Fors, S. L. Buchwald, J. Am. Chem. Soc. 130 (2008) 6686-6687.
18. B. P. Fors, D. A. Watson, M. R. Biscoe, S. L. Buchwald, J. Am. Chem. Soc. 130 (2008) 13552-13554.
19. D. Prim, J. M. Campagne, D. Joseph, B. Andrioletti, Tetrahedron 58 (2002) 2041-2075.
20. J. R. J. LeBlanc, S. Madhavan, R. E. Porter, P. Kellogg, *Encyclopedia of Chemical Technology*, *Wiley-Interscience*, 2nd Ed, New York, 1963.
21. J. R. Jennings, *Catalytic Ammonia Synthesis: Fundamentals and practice*, *Plenum Press*, New York, 1991.
22. T. Gross, A. M. Seayad, M. Ahmad, M. Beller, Org. Lett. 4 (2002) 2055-2058.
23. D. M. Roundhill, Chem. Rev. 92 (1992) 1-27.
24. B. Zimmermann, J. Herwig, M. Beller, Angew. Chem. Int. Ed. 38 (1999) 2372-2375.
25. T. Prinz, B. Driessen-Holscher, Chem. Eur. J. 5 (1999) 2069-2076.
26. T. Prinz, W. Keim, B. Driessen-Holscher, Angew. Chem. Int. Ed. Engl. 35 (1996) 1708-1710.
27. S. Ogo, K. Uehara, T. Abura, S. Fukuzumi, J. Am. Chem. Soc. 126 (2004) 3020-3021.
28. A. Martin, M. Kant, R. Jackstell, H. Klein, M. Beller, Chem. Ing. Tech. 79 (2007) 891-900.
29. H. Klein, R. Jackstell, M. Kant, A. Martin, M. Beller, Chem. Eng. Technol. 30 (2007) 721-725.
30. T. Maejima, Y. Shimoda, K. Nozaki, S. Mori, Y. Sawama, Y. Monguchi, H. Sajiki, Tetrahedron 68 (2012) 1712-1722.
31. P. Ji, J. H. Atherton, M. I. Page, J. Org. Chem. 77 (2012) 7471−7478.

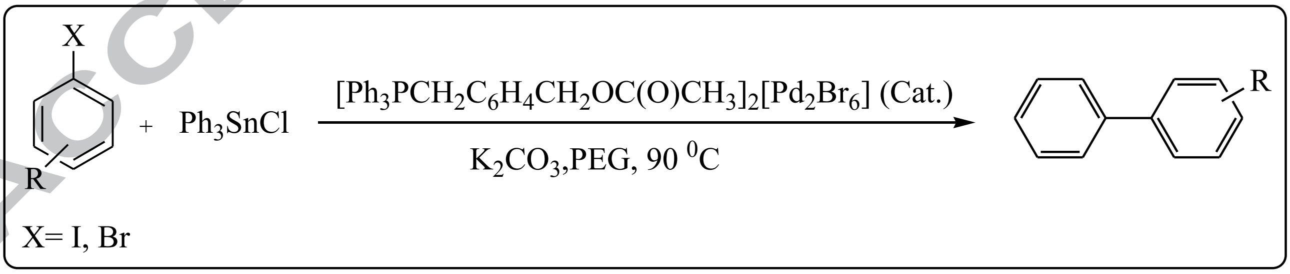
32. A. Naghipour, K. Badpa, Z. Hajighasemi, B. Notash, Polyhedron 87 (2015) 349-353.
33. C. J. Lee, C. N. Sheu, C. C. Tsai, Z. Z. Wu, W. Lin, Chem. Commun. 50 (2014) 5304-5306.
34. A. Tewari, M. Hein, A. Zapf, M. Beller, Tetrahedron 61 (2005) 9705–9709.
35. J. R. Gorlich, R. Schmutzler, Phosphorus, Sulfur, Silicon Relat. Elem. 102 (1995) 211-215.
36. A. Ghorbani-Choghamarani, F. Nikpour, F. Ghorbani, F. Havasi, RSC Adv. 5 (2015) 33212-33220.
37. A. Ghorbani-Choghamarani, G. Azadi, RSC Adv. 5 (2015) 9752-9758.
38. A. Ghorbani-Choghamarani, M. Norouzi, J. Mol. Catal. A-Chemical 395 (2014) 172-179.
39. Z. J. Jain, P. S. Gide, R. S. Kankate, Arabian Journal of Chemistry (2013) in press.
40. S. Litvinchuk, G. Bollot, J. Mareda, A. Som, D. Ronan, M. R. Shah, P. Perrottet, N. Sakai, S. Matile, J. Am. Chem. Soc. 126 (2004) 10067-10075.
41. R. Franzen, Can. J. Chem. 78 (2000) 957-962.
42. Stoe & Cie GmbH. *Crystallographic Package*, Version 1.07b, Darmstadt, Germany, 2000.
43. H. Xu, C. Wolf, Chem. Commun, 21 (2009) 3035-3037.
44. K. G. Thakur, K. S. Srinivas, K. Chiranjeevi, G. Sekar, Green Chem. 13 (2011) 2326-2329.
45. V. Dichiarante, M. Fagnoni, A. Albini, Chem. Commun. 28 (2006) 3001-3003.
46. R. Gupta, S. Sanotra, H. Nawaz Sheikh, B. Lal Kalsotra, J. Nano. Chem. 3 (2013) 1-9.
47. S. J. Hoseini, V. Heidari, H. Nasrabadi, J. Mol. Catal. A: Chem. 396 (2015) 90-95.
48. A. K. Sahoo, T. Oda, Y. Nakao, T. Hiyama, Adv. Synth. Catal. 346 (2004) 1715-1727.
49. http://www.sigmaaldrich.com



Scheme 1. Synthesis of $[Ph_3PCH_2C_6H_4CH_2OC(O)CH_3]_2[Pd_2Br_6]$



Scheme 2. Amination of various aryl halides in the presence of compound **1**.



Scheme 3. Synthesis of biaryls in the presence of $[Ph_3PCH_2C_6H_4CH_2OC(O)CH_3]_2[Pd_2Br_6]$

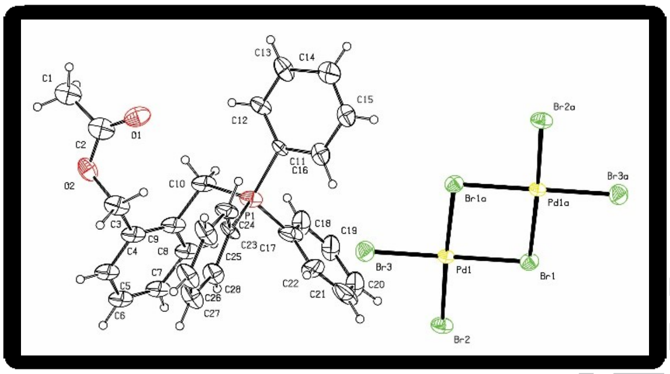


Figure 1. Asymmetric unit of $[Ph_3PCH_2C_6H_4CH_2OC(O)CH_3]_2[Pd_2Br_6]$

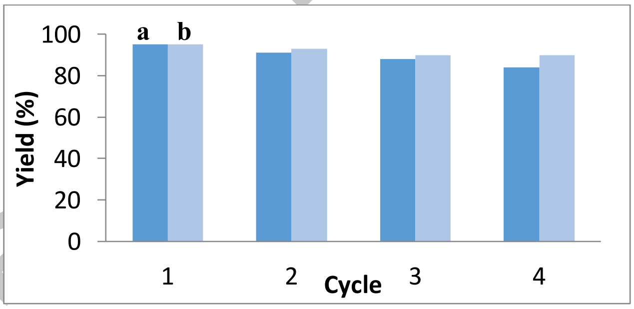


Figure 2. Reuse of the catalyst in the amination (a) and Stille cross-coupling (b) reactions.

Table 1
Crystal data and structure refinement for compound **1**.

Chemical formula	$C_{28}H_{26}O_2P$, 0.5(Br_6Pd_2)
Formula weight	771.56
Temperature (K)	120(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	P-1
a (Å)	10.392(2)
b (Å)	12.015(2)
c (Å)	13.601(3)
α (°)	72.65(3)
β (°)	71.58(3)
γ (°)	65.73(3)
Volume (Å^3)	1440.7(6)
Z	2
Absorption coefficient (mm^{-1})	4.883
Crystal size (mm^3)	0.15× 0.15×0.05
Crystal F(000)	752
Goodness-of-fit on F^2	0.907

Table 2
Selected bond distances and bond angles for compound 1.

Bond length (Å)		**Bond angles (deg.)**	
Pd(1)–Br(2)	2.410(3)	Br(3)-Pd(1)-B	92.66(11)
Pd(1)–Br(1)	2.449(3)	Br(3)-Pd(1)-B	90.32(10)
Pd(1)–Br(3)	2.386(3)	Br(2)-Pd(1)-B	175.05(11)
P(1)–C(23)	1.778(17)	C(23)-P(1)-C(	108.8(10)

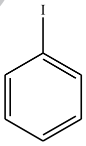
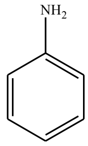
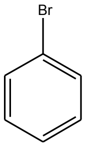
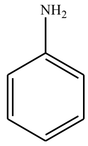
P(1)–C(17)	1.78(2)	C(17)-P(1)-C(	108.5(9)
P(1)–C(10)	1.801(17)	C(23)-P(1)-C(	109.5(9)
P(1)–C(11)	1.819(17)	C(2)-O(1)-C(2	116.7(18)
O(1)–C(2)	1.21(3)	P(1)-C(10)-H(	109.3
O(2)–C(2)	1.27(3)		
O(2)–C(3)	1.45(2)		
C(1)–C(2)	1.49(3)		

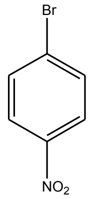
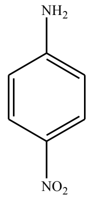
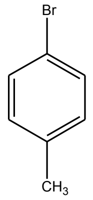
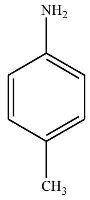
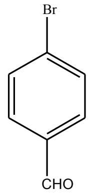
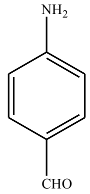
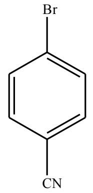
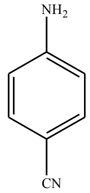
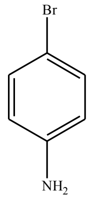
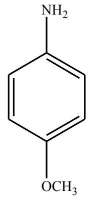
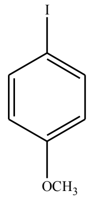
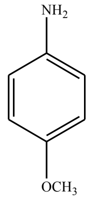
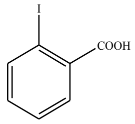
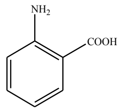
Table 3
Effect of solvent on amination of iodobenzene by aqueous ammonia.

Entry	**solvent**	**Time (h)**	**Yield (%)**
1	Water	7	61
2	N,N-Dimethylformamide	7	46
3	Ethanol	7	55
4	Solvent free	7	93

Reaction conditions: iodobenzene: 1 mmol, aqueous ammonia: 1 mL, catalyst: 0.005 g, at 60 ˚C, 7 h.

Table 4
The amination of various aryl halides.

Entry	Aryl halide	Product	Yield[a] (%)	Time (h)	M. p. (˚C)
1			93	7	Colorless Oil [43]
2			90	15	Colorless Oil [43]

3			95	5	147-149 [44]
4			89	18	42-44 [43]
5			90	5	68-70 [43]
6			94	4	86-88 [45]
7			92	5	136-138 [46]
8			88	9	56-58 [44]
9			93	8	55-58 [44]
10			90	6	142-145 [43]

---

[a] Isolated Yield.

Reaction conditions: aryl halide: 1 mmol, aqueous ammonia: 1 mL, catalyst: 0.005 g, at 60 ˚C.

Table 5

Optimization of the amount of compound **1** for the synthesis of biphenyl.

Entry	Compound 1 (g)	Time (min)	Yield (%)
1	0.00	15	0
2	0.002	15	65
3	0.005	15	95
4	0.007	15	95

Reaction conditions: iodobenzene: 1 mmol, Ph_3SnCl: 0.4 mmol, K_2CO_3: 1.5 mmol, 1 mL PEG, at 90 ˚C, 15 min.

Table 6

Effect of solvent on the synthesis of biphenyl.

Entry	solvent	Time (min)	Yield (%)
1	Water	15	44
2	N,N-Dimethylformamide	15	86
3	Ethanol	15	79
4	PEG	15	93

Reaction conditions: iodobenzene: 1 mmol, Ph_3SnCl: 0.4 mmol, K_2CO_3: 1.5 mmol, at 90 ˚C, 15 min.

Table 7

The effect of temperature on the synthesis of biphenyl.

Temperature (˚C)	Compound 1 (g)	Time (min)	Yield (%)
25	0.005	15	0
60	0.005	15	55
90	0.005	15	95
100	0.005	15	95

Reaction conditions: iodobenzene: 1 mmol, Ph_3SnCl: 0.4 mmol, K_2CO_3: 1.5 mmol, 1 mL PEG, 15 min.

Table 8

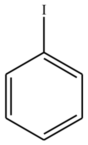
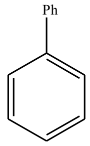
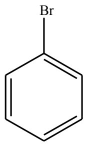
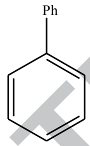
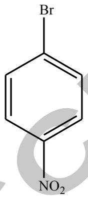
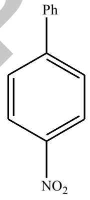
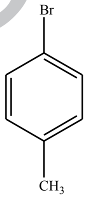
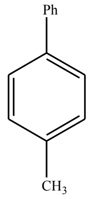
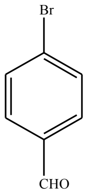
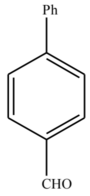
Optimization of base in the Stille cross-coupling reaction

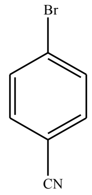
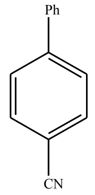
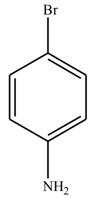
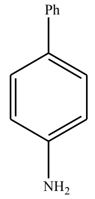
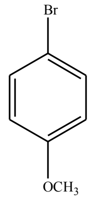
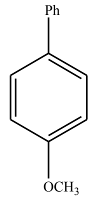
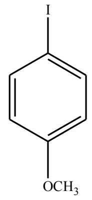
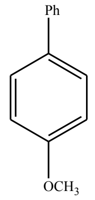
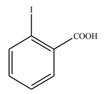
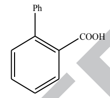
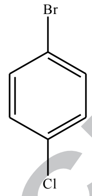
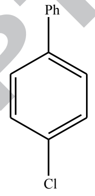
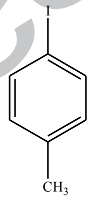
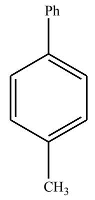
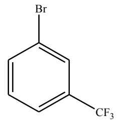
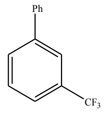
Base	**Time (min)**	**Yield (%)**
Potassium carbonate (K_2CO_3)	15	94
Potassium hydroxide (KOH)	15	90
Triethylamine (Et_3N)	15	65
Sodium bicarbonate ($NaHCO_3$)	15	75

Reaction conditions: iodobenzene: 1 mmol, Ph_3SnCl: 0.4 mmol, base: 1.5 mmol, 1 mL PEG, catalyst: 0.005 g, 15 min, at 90 °C.

Table 9

Stille cross-coupling for the synthesis of biaryls from aryl halides.

Entry	Aryl halide	Product	Yield[a] (%)	Time (min)	M. p. (°C)
1			95	10	61-63 [47]
2			93	15	62-64 [47]
3			96	8	109-111 [48]
4			92	35	42-44 [48]
5			95	10	56-58 [48]

6			94	8	82-84 [48]
7			90	40	49-51 [48]
8			91	25	82-84 [48]
9			93	15	82-84 [48]
10			92	15	116-119 [49]
11			95	10	75-77 [48]
12			94	25	43-44 [48]
13			91	15	Colorless Oil [48]

---

[a] Isolated Yield.

Reaction conditions: iodobenzene: 1 mmol, Ph_3SnCl: 0.4 mmol, K_2CO_3: 1.5 mmol, PEG: 1 mL, catalyst: 0.005 g, at 90 ˚C.

Graphical Abstract