Turkish Journal of Chemistry

Volume 39 | Number 6 Article 11

1-1-2015

Synthesis of new thiol-derivatized aminophosphines and their catalytic activities in C--C coupling reactions

NERMİN BİRİCİK

NERMİN MERİÇ

CEZMİ KAYAN

ZEYNEP ÖZGEN

SEVİL ŞEKER AZİZOĞLU

See next page for additional authors

Synthesis of new thiol-derivatized aminophosphines and their catalytic activities in C--C coupling reactions

Authors
NERMİN BİRİCİK, NERMİN MERİÇ, CEZMİ KAYAN, ZEYNEP ÖZGEN, SEVİL ŞEKER AZİZOĞLU, and BAHATTİN GÜMGÜM

Turkish Journal of Chemistry

http://journals.tubitak.gov.tr/chem/

Research Article

Turk J Chem
(2015) 39: 1257 – 1264

doi:10.3906/kim-1505-91

Synthesis of new thiol-derivatized aminophosphines and their catalytic activities in C–C coupling reactions

Nermin BİRİCİK*, Nermin MERİÇ, Cezmi KAYAN, Zeynep ÖZGEN, Sevil ŞEKER AZİZOĞLU, Bahattin GÜMGÜM
Department of Chemistry, Faculty of Science, Dicle University, Diyarbakır, Turkey

Received: 26.05.2015 • **Accepted/Published Online:** 03.08.2015 • **Printed:** 25.12.2015

Abstract: A series of new aminophosphines [Ph_2PHN-C_6H_4-R, where R = *o*-SH (**4a**), *m*-SH (**4b**) **or** *p*-SH (**4c**)] were readily synthesized from cheap starting materials by the phosphorylation reaction of *o*, *m*, and *p*-aminothiophenols with Ph_2PCl in the presence of triethyl amine. The new compounds were characterized by NMR and IR spectroscopy and microanalysis. In addition, aminophosphine ligands–palladium systems were investigated as precatalysts in C–C coupling reactions. Compounds **4b** and **4c** were proved to be excellent catalysts for Suzuki and Heck cross-coupling reactions.

Key words: Aminophosphine, synthesis, catalysis, palladium, Suzuki–Heck

1. Introduction

The development of novel ligands remains the most attractive area in the field of transition metal-catalyzed reactions. Accordingly, in the past few years many efforts have been devoted to developing new catalytic systems.[1–4] Aminophosphine ligands and their complexes play a key role in the development of valuable compounds with these catalytic systems. Their catalytic applications are an area of growing interest and they are virtually considered as all key types of ligands encountered in organometallic chemistry.[5–9] Transition metal catalyzed cross-coupling reactions leading to the formation of carbon–carbon and carbon–heteroatom bonds are important in organic synthesis. Of these, the square-planar palladium complexes have received considerable attention.[10–14] The palladium-catalyzed reactions of aryl chlorides with both arylboronic acid (Suzuki reaction) and alkenes (Heck reaction) are the most common methods for C–C bond formation and hence have attracted much current interest.[15–18] The square-planar palladium complexes of aminophosphine ligands are an important class of compounds in this manner; they have trivalent phosphorus with a general formula of R-NH–PPh_2 or R-N(PPh_2) and consequently they can be distinguished in terms of number of direct phosphorus–nitrogen bonds (Figure 1).[19]

The aminophosphines and diphosphinoamines can be prepared from commercially available amines via the classical phosphorylation reaction or aminolysis of chlorophosphines.[20,21] The reaction usually takes place in the presence of a base and the final aminophosphine or diphosphinoamine product can be easily separated and isolated in high yields.

*Correspondence: nbiricik@dicle.edu.tr

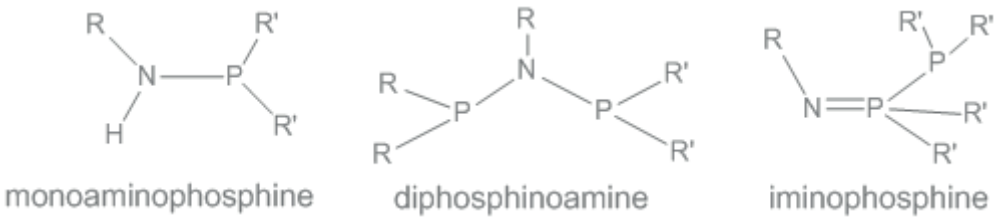


Figure.

In the present study, a new type of amino phosphine ligand was synthesized and employed in Pd-catalyzed Suzuki and Heck coupling reactions.[22,23] In continuation of our studies on aminophosphines,[24,25] we decided to prepare a series of aminophosphines possessing SH substituents on an aryl ring and explore their chemistry and catalytic functions in Suzuki and Heck cross-coupling reactions.

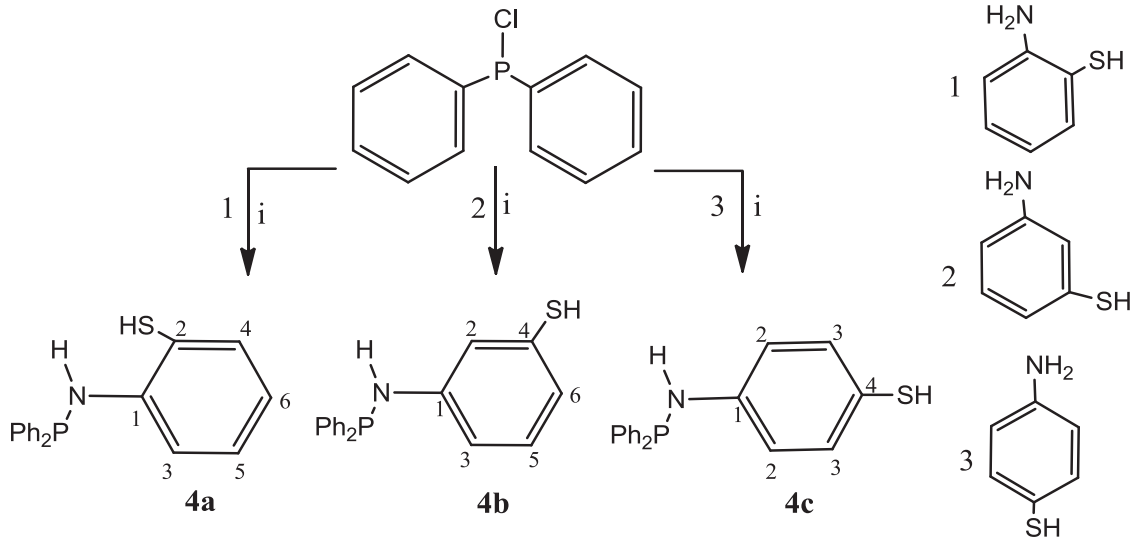
2. Results and discussion

Aminolysis of chlorophosphines or phosphorylation of an aromatic amine is an efficient method for preparing aminophosphines with a general formula of $R_2PN(H)R'$ or $(R_2P)_2NR'$.[19,20,26] The outcome of the phosphorylation reaction is influenced by the amine, the nature of the auxiliary base, and the solvent.[19,27] As shown in Scheme 1, we investigated the phosphorylation reactions of aniline derivatives possessing a thiol group with Ph_2PCl in the presence of Et_3N (molar ratio 1:2:2 and 1:3:3) in THF affording new (phosphino)amine ligands Ph_2PHN-C_6H_4-R [R = ***o***-SH (**4a**), ***m***-SH (**4b**), ***p***-SH (**4c**)]. The formation of a P–S bond is also possible in these reactions. However, under the present conditions, we did not observe the formation of products with a P–S bond since we did not observe the characteristic P–S bond shift at 100–200 ppm in the ^{31}P NMR spectra. The reaction of aminothiophenols with Ph_2PCl with a molar ratio of 1:3:3 gave mixtures containing P–N–P and P–N–H while with a 1:1:1 ratio (Ph_2P–NHR) was found as the main product observed by ^{31}P NMR spectroscopy at 30–37 ppm. ^{31}P-$\{^1H\}$ NMR investigation of the reaction mixtures showed that all reactions were completed after 1 h to give the anticipated products, aminophosphines **4a**–**c**. No formation of iminobiphosphine species (Ph_2P-PPh_2=NC_6H_4-R, where R = ***o***-SH, ***m***-SH, ***p***-SH) was observed. However, the method cannot be generalized for all anilines as earlier results showed that iminobiphosphines are formed as the major product with some aniline derivatives.[28] Additionally, the choice of solvent is also very important in determining the outcome of the reaction. All compounds (**4a**–**c**) were isolated in good yields and fully characterized by elemental analysis, and ^1H, ^{13}C-$\{^1H\}$, ^{31}P-$\{^1H\}$ NMR, and IR spectroscopy consistent with earlier studies.[29]

Although compounds **4b** and **4c** are very stable in air and in organic solvents, compound **4a** is somehow unstable in ambient air and in solution. It is stable in air for only 2 days and then decomposes completely.

^{31}P-$\{^1H\}$ NMR spectra of compounds **4a**–**c** showed one singlet with a chemical shift of around 30–37 ppm for each, a significantly high field from chlorodiphenylphosphine. In their ^{31}P-$\{^1H\}$ NMR spectra, the chemical shifts of **4a**–**c** were 34.59, 30.67, and 36.71 ppm, respectively, which are similar and within the expected range of other reported structurally similar compounds.[30–33] Broad signals at around 3.60–4.10 ppm in their ^1H NMR spectra are attributed to NH + SH protons. For compound **4b**, no coupling is detected between the SH and the NH protons. IR spectra of **4a**–**c** contain absorptions at 744–738 cm^{-1} corresponding to the P–N–H bonds, bands between 2338 and 2570 cm^{-1} that are characteristic of S–H bonds, and vibrations between 3313 and 3336 cm^{-1}, ascribed to N–H bonds. A comparison of IR spectra of **4a**–**c** indicates the importance of the position of the thiol group. The typical S–H band in the IR spectrum of **4a** is around 200 cm^{-1} lower than that

of **4b**–**c**. The reason for the lower S–H band frequency for this compound may be associated with the possible intramolecular hydrogen bond formation.



Scheme. The phosphorylation of a series of aminothiophenols with chlorodiphenylphosphine: i) THF, Et_3N, 0 °C.

3. Catalysis

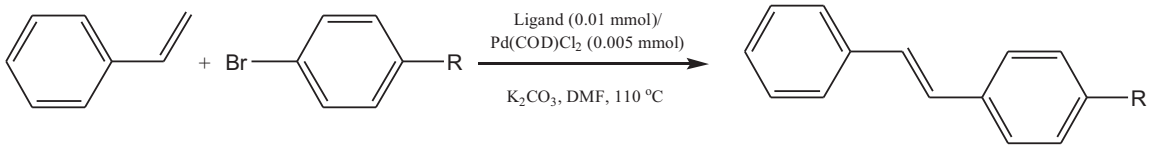
The palladium-catalyzed carbon–carbon bond forming reactions developed by Heck, Negishi, and Suzuki have had a large impact on synthetic organic chemistry and found many applications in target-oriented synthesis.[34,35] The cross-coupling of alkyl boronic acids with alkyl halides, known as the Suzuki reaction, is an efficient and less toxic method to form a carbon–carbon bond.[36–39] In a real catalytic process, the palladium complexes are thought to be reduced to zero-valent palladium, which in many cases are nanosized particles that can directly interact with the substrate.[40,41] The catalytic activities of the complexes depend largely on the ability of the ligands to activate and stabilize the zero-valent palladium nanoparticles. For this purpose, many palladium complexes are prepared using bulky phosphine ligands. Although the compounds **4a**–**c** are structurally very similar, they showed different catalytic activities in C–C coupling reactions. Higher yields of stilbene were obtained with **4b** and **4c** as compared with the other previously reported palladium-bis(phosphino)amine complexes.[42,43]

3.1. Heck reaction

The Heck reaction is a powerful and efficient method for C–C bond formation in the presence of a palladium catalyst to form a new alkene; it is strongly influenced by the choice of the solvent and base, as well as the reaction temperature. Thus we studied the effect of the reaction temperature, solvent, and Cs_2CO_3, K_2CO_3, and K_3PO_4 as a base in the reactions. Use of 0.01 mol of ligand (**4a**–**c**) and 2 equiv of K_2CO_3 in DMF (1:1) at 110 °C led to the best conversion with a period of 48 h with **4a**, 2 h with **4b**, and 2.5 h with **4c**. The longer reaction times to achieve high yield for catalyst **4a** may be attributed to the steric hindrance of *ortho*-substitution. We initially evaluated the catalytic activity of ligands for the coupling of 4-bromoacetophenone with styrene (Table 1, entries 1–3). Under the optimum reaction conditions, a wide range of aryl bromides bearing electron-donating or electron-withdrawing groups were reacted with styrene, affording the coupled

products in high yields by **4b** and **4c** (Table 1). As expected, the yields of the coupling product in reactions of aryl bromides with electron-withdrawing substituents are higher than those with electron-releasing substituents. Enhancements in activity, although less significant, are also observed when employing 4-bromobenzaldehyde instead of 4-bromoacetophenone (Table 1, entries 4–6).

Table 1. Heck coupling reactions of aryl bromides with styrene[a].



Entry	R	Ligand (L)	Yield (%)[b]	TOF (h^{-1})[d]
1	$COCH_3$	**4a**	42 (91)[c]	-
2	$COCH_3$	**4b**	96	48
3	$COCH_3$	**4c**	95	38
4	CHO	**4a**	40 (89)[c]	-
5	CHO	**4b**	93	47
6	CHO	**4c**	91	36
7	H	**4a**	28 (75)[c]	-
8	H	**4b**	81	41
9	H	**4c**	78	31
10	OCH_3	**4a**	15 (60) [c]	-
11	OCH_3	**4b**	58	29
12	OCH_3	**4c**	56	22
13	CH_3	**4a**	19 (66) [c]	-
14	CH_3	**4b**	72	36
15	CH_3	**4c**	68	27

[a] Reaction conditions: 1.0 mmol of R-C_6H_4Br-*p*, 1.5 mmol of styrene, 2.0 mmol of K_2CO_3, 0.01 mmol of **4a–c** ligands, 0.005 mmol of Pd(COD)Cl_2, DMF (15 mL); [b] Purity of compounds was checked by ^{1}H NMR and yields are based on aryl bromide, all reactions were monitored by GC, temperature 110 °C, 24 h for **4a**; 2 h for **4b**; 2.5 for **4c**; [c] temperature 110 °C, 48 h for **4a;** [d] TOF = (mol product/mol Cat) × h^{-1}.

3.2. Suzuki coupling reaction

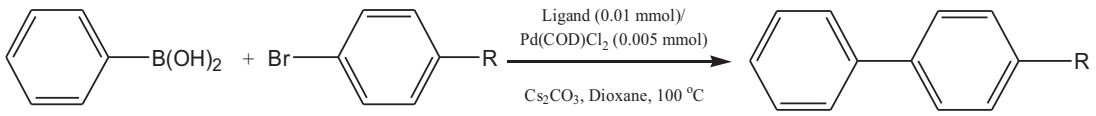
Compounds **4a–c** were tested in a standard Suzuki reaction for the synthesis of biphenyl, and the results are summarized in Table 2. From this table, it is evident that the ligands are an active catalyst for Suzuki cross-coupling for a range of aryl halides with phenyl boronic acid in dioxane. The product yields are dependent on the position of the thiol substituent in aminophosphine ligands. *ortho*-Isomer **4a** does not show good catalytic activity in the Suzuki reaction at 100 °C in dioxane and 24 h, except at 100 °C and 72 h in the presence of 0.01 mol% of ligand, 0.005 mmol Pd(COD)Cl_2, and 2.0 mmol Cs_2CO_3 (Table 2, entries 1, 4, 7, 10, 13). The best results were obtained at 72 h by **4a** under the conditions described below (Table 2, entry 1, 4, 7, 10, 13). On the other hand, compounds **4b** and **4c** were excellent catalysts for Suzuki cross-coupling reactions (Table 2).

4. Conclusion

A series of new phosphinoamines were prepared and obtained in good yields, which were then characterized by NMR, IR, and microanalysis. These ligands form a new aminophosphine ligand–palladium system that could be

applied as an efficient catalyst for Suzuki and Heck reactions. In these application reactions, in situ generated catalytic species show different activities for C–C coupling reactions. Among the ligands, **4b** and **4c** have higher activity compared with **4a** in both Suzuki and Heck cross-coupling reactions. Very low catalyst loadings and short reaction times are required for the quantitative coupling.

Table 2. Suzuki coupling reactions of aryl bromides with phenylboronic acid [a].



Entry	R	Ligand (L)	Yield (%)[b]	TOF (h^{-1})[d]
1	$COCH_3$	**4a**	60 (91)[c]	-
2	$COCH_3$	**4b**	96	48
3	$COCH_3$	**4c**	96	48
4	CHO	**4a**	58 (89)[c]	-
5	CHO	**4b**	95	48
6	CHO	**4c**	96	48
7	H	**4a**	49 (80)[c]	-
8	H	**4b**	82	41
9	H	**4c**	89	45
10	OCH_3	**4a**	29 (59)[c]	-
11	OCH_3	**4b**	65	33
12	OCH_3	**4c**	67	34
13	CH_3	**4a**	38 (65)[c]	-
14	CH_3	**4b**	75	38
15	CH_3	**4c**	76	38

[a] Reaction conditions: 1.0 mmol of R-C_6H_4Br-*p*, 1.5 mmol of phenylboronic acid, 2.0 mmol of Cs_2CO_3 0.01 mmol of **4a**–**c** ligands, 0.005 mmol of Pd(COD)Cl_2, dioxane (15 mL); [b] Purity of compounds was checked by ^{1}H NMR and yields are based on aryl bromide, all reactions were monitored by GC, temperature 100 °C, 24 h for **4a**; 2.0 h for **4b** and **4c**; [c] temperature 100 °C, 72 h for **4a**; [d] TOF = (mol product/mol Cat) × h^{-1}.

5. Experimental

5.1. Materials and methods

Unless otherwise stated, all reactions were carried out under an atmosphere of argon using conventional Schlenk glassware, and solvents were dried using established procedures and distilled under argon immediately prior to use. Analytical grade and deuterated solvents were purchased from Merck. PPh_2Cl and *o*,*m*, .eps and*p*−aminothiophenol were purchased from Fluka and were used as received. The IR spectra were recorded on a Mattson 1000 ATI UNICAM FT-IR spectrometer as KBr pellets. ^{1}H NMR (400.1 MHz), ^{13}C NMR (100.6 MHz), and ^{31}P NMR spectra (162.0 MHz) were recorded on a Bruker AV400 spectrometer, with δ referenced to external TMS and 85% H_3PO_4. Elemental analysis was carried out on a Fisons EA 1108 CHNS-O instrument. Melting points were recorded by a Gallenkamp Model apparatus with open capillaries.

5.2. Synthesis and characterization of ligands

5.2.1. Synthesis of 4a

Chlorodiphenylphosphine (0.18 g, 0.79 mmol) was slowly added to a solution of 2-aminothiophenol (0.10 g, 0.79 mmol) and triethylamine (0.08 g, 0.79 mmol) in THF (25 mL) at 0 °C with vigorous stirring. The mixture was stirred at room temperature for 1 h, triethylammonium chloride was filtered off under argon, and the solvent was removed under reduced pressure. The residue was then washed with cold diethylether (2 × 15 mL) and dried in vacuo to produce a viscous oily compound **4a** (yield: 0.21 g, 85.9%); ^{1}H NMR ($CDCl_3$, ppm): δ 7.28–7.65 (m, 11H, aromatic protons), 7.13 (t, J= 7.6 Hz, 1 H, aromatic protons), 6.76 (d, J= 8.0 Hz, 1H, aromatic protons), 6.66 (t, J= 7.5 Hz, 1H, aromatic protons) 4.11 (br, 2H, NH + SH); ^{13}C{^{1}H} NMR ($CDCl_3$, ppm): δ 148.08 (C1-Ar), 138.03 (d, J= 25.2 Hz, i-carbons of $NHPPh_2$), 136.14 (d, J= 5.0 Hz, C2-Ar), 132.78 (d, J= 21.1 Hz, o-carbons of $NHPPh_2$), 129.78 (C3-Ar), 129.38 (s, p-carbons of $NHPPh_2$), 128.59 (d, J= 6.0 Hz, m-carbons of $NHPPh_2$), 118.90 (C4-Ar), 116.67 (d, J= 13.1 Hz, C5-Ar), 115.41 (C6-Ar); assignment was based on the ^{1}H–^{13}C HETCOR and ^{1}H–^{1}H COSY spectra; ^{31}P{^{1}H} NMR ($CDCl_3$, ppm): δ 34.59 (s). IR (KBr pellet in cm^{-1}).*epsv* 3313 (N–H), 3145, 3046 (aromatic C–H), 2338 (S–H), 1435 (P–Ph), 744 (P–NH); $C_{18}H_{16}NSP$ (mw: 309.37 g/mol): calcd. C, 69.88; H, 5.21; N, 4.53; found C, 69.10; H, 5.04; N, 4.12%.

5.2.2. Synthesis of 4b

Chlorodiphenylphosphine (0.17 g, 0.77 mmol) was slowly added to a solution of 3-aminothiophenol (0.10 g, 0.77 mmol) and triethylamine (0.08 g, 0.77 mmol) in THF (25 mL) at 0 °C with vigorous stirring. The mixture was stirred at room temperature for 1 h, triethylammonium chloride was filtered off under argon, and the solvent was removed under reduced pressure. The residue was then washed with cold diethylether (2 × 15 mL) and dried in vacuo to produce a viscous oily compound **4b** (yield: 0.20 g, 84.7%); ^{1}H NMR ($CDCl_3$, ppm): δ 7.40–7.65 (m, 10H, aromatic protons), 7.07 (t, J= 7.8 Hz, 1H, aromatic protons), 6.91 (d, J= 7.8 Hz, 1H, aromatic protons), 6.85 (d, J= 1.6 Hz, 1H, aromatic protons), 6.56 (m, 1H, aromatic protons), 3.66 (br, 2H, NH + SH); ^{13}C{^{1}H} NMR ($CDCl_3$, ppm): δ 146.92 (C1-Ar), 137.58 (d, J= 24.1 Hz, i-carbons of $NHPPh_2$), 132.75 (d, J= 21.1 Hz, o-carbons of $NHPPh_2$), 129.77 (C4-Ar), 129.31 (s, p-carbons of $NHPPh_2$ + C2-Ar), 128.60 (d, J= 7.0 Hz, m-carbons of $NHPPh_2$), 121.70 (d, J= 8.0 Hz, C3-Ar), 117.82 (d, J= 10.1 Hz, C6-Ar), 113. 89 (C5-Ar); assignment was based on the ^{1}H–^{13}C HETCOR and ^{1}H–^{1}H COSY spectra; ^{31}P{^{1}H} NMR ($CDCl_3$, ppm): δ 30.67 (s). IR (KBr pellet in cm^{-1}).*epsv* 3336 (N–H), 3057 (aromatic C–H), 2570 (S–H), 1435 (P–Ph), 744 (P–NH); $C_{18}H_{16}NSP$ (mw: 309.37 g/mol): calcd. C, 69.88; H, 5.21; N, 4.53; found C, 69.15; H, 5.09; N, 4.21%.

5.2.3. Synthesis of 4c

Chlorodiphenylphosphine (0.17 g, 0.78 mmol) was slowly added to a solution of 4-aminothiophenol (0.10 g, 0.78 mmol) and triethylamine (0.08 g, 0.78 mmol) in THF (25 mL) at 0 °C with vigorous stirring. The mixture was stirred at room temperature for 1 h, triethylammonium chloride was filtered off under argon, and the solvent was removed under reduced pressure. The residue was then washed with cold diethylether (2 × 15 mL) and dried in vacuo to produce an off-white solid compound **4c** (mp 67–68 °C; yield: 0.21 g, 88.1%); ^{1}H NMR ($CDCl_3$, ppm): δ 7.02–7.91 (m, 12H, aromatic protons), 6.50 (d, J= 8.4 Hz, 2H, aromatic protons), 3.69 (br, 2H, NH + SH); ^{13}C{^{1}H} NMR ($CDCl_3$, ppm): δ 146.38 (C1-Ar), 138.15 (d, J= 26.2 Hz, i-carbons

of $NHPPh_2$), 134.78 (C4-Ar), 134.73 (C2-Ar), 132.77 (d, J = 21.1 Hz, o-carbons of $NHPPh_2$), 129.16 (s, p-carbons of $NHPPh_2$), 128.50 (d, J = 6.0 Hz, m-carbons of $NHPPh_2$), 115.68 (C3-Ar); assignment was based on the ^1H–^{13}C HETCOR and ^1H–^1H COSY spectra; $^{31}P\{^1H\}$ NMR ($CDCl_3$, ppm): δ 36.71 (s). IR (KBr pellet in cm^{-1}).*epsv* 3278 (N–H) 3147, 3016 (aromatic C–H), 2532 (S–H), 1431 (P–Ph), 738 (P–NH); $C_{18}H_{16}NSP$ (mw: 309.37 g/mol): calcd. C, 69.88; H, 5.21; N, 4.53; found C, 69.21; H, 5.00; N, 4.09%

6. General procedure for Heck coupling reaction

The aminophosphine ligands (**4a**–**4c**, 0.01 mmol), $Pd(COD)Cl_2$ (0.005 mmol), aryl bromide (1.0 mmol), styrene (1.5 mmol), base (2 mmol), and solvent (15 mL) were added to a Schlenk tube under argon atmosphere and the reaction was monitored at various conditions and parameters (temperature, time, base, etc.). After completion of the reaction, the mixture was cooled, extracted with ethyl acetate–hexane (1:5), filtered through a pad of silica gel with copious washing, concentrated, and purified using flash chromatography on silica gel. The purity of the compounds was checked immediately using GC and ^1H NMR. Yields are based on aryl halides.

7. General procedure for Suzuki cross-coupling reaction

The aminophosphine ligands (**4a**–**4c**, 0.01 mmol), $Pd(COD)Cl_2$ (0.005 mmol), aryl bromide (1.0 mmol), phenylboronic acid (1.5 mmol), base (2 mmol), and solvent (15 mL) were added to a Schlenk tube under argon atmosphere and the reaction was followed at various conditions and parameters (temperature, time, base, etc.). After completion of the reaction, the mixture was cooled, extracted with ethyl acetate–hexane (1:5), filtered through a pad of silica gel with copious washing, concentrated, and purified using flash chromatography on silica gel. The purity of the compounds was checked immediately using GC and ^1H NMR. Yields are based on aryl halides.

References

1. Dewana, A.; Buragohaina, Z.; Mondala, M.; Sarmaha, G.; Boraha, G.; Bora, U. *Appl. Organometal. Chem.* **2014**, *28*, 230–233.
2. Pongrácz, P.; Kostas, I. D.; Kollár, L. *J. Organomet. Chem.* **2013**, *723*, 149–153.
3. Priyaa, S.; Balakrishna, M. S.; Mobin, S. M.; McDonald, R. *J. Organomet. Chem.* **2003**, *688*, 227–235.
4. Dolinsky, M. C. B.; Lin, W. O.; Dias, M. L. *J. Mol. Catal. A: Chem.* **2006**, *258*, 267–274.
5. Ly, T. Q.; Woollins, J. D. *Coord. Chem. Rev.* **1998**, *176*, 451–481.
6. Fei, Z.; Dyson, P. J. *Coord. Chem. Rev.* **2005**, *249*, 2056–2074.
7. Ghisolfi, A.; Fliedel, C.; Rosa, V.; Monakhov, K. Y.; Braunstein, P. *Organometallics* **2014**, *33*, 2523–2534.
8. Nakajima, T.; Fukushima, Y.; Tsuji, M.; Hamada, N.; Kure, B.; Tanase, T. *Organometallics* **2013**, *32*, 7470–7477.
9. Cimarelli, C.; Fratoni, D.; Palmieri, G. *Tetrahedron: Asymmetry* **2009**, *20*, 2234–2239.
10. Saikia, B.; Boruah, P. R.; Ali, A. A.; Sarma, D. *Tetrahedron Lett.* **2015**, *6*, 633–635
11. Naik, S.; Kumaravel, M.; Mague, J. T.; Balakrishna, M. S. *Dalton Trans.* **2014**, *43*, 1082–1095.
12. Gaw, K. G.; Smith, M. B.; Wright, J. B.; Slawin, A. M. Z.; Coles, S. J.; Hursthouse, M. B.; Tizzard, G. J. *J. Organomet. Chem.* **2012**, *699*, 39–47.
13. Lamblin, M.; Nassar-Hardy, L.; Hierso, J. C.; Fouquet, E.; Felpin, F. X. *Adv. Synth. Catal.* **2010**, *352*, 33–79.
14. Bolliger, J. L.; Frech, C. M. *Adv. Synth. Catal.* **2010**, *352*, 1075–1080.

15. Bolliger, J. L.; Frech, C. M. *Chima* **2009**, *63*, 23–28.
16. Miyaruna, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457–2483.
17. Whitcombe, N. J.; Hii, K. K.; Gibson, S. E. *Tetrahedron* **2001**, *57*, 7449–7476.
18. Seechurn, C. C. C. J.; Kitching, M. O.; Colacot, T. J.; Snieckus, V. *Angew. Chem. Int. Ed.* **2012**, *51*, 5062–5085.
19. 9. Fei, Z.; Scopelliti, R.; Dyson, P. J. *Dalton Trans.* **2003**, 2772–2279.
20. Fei, Z.; Păunescu, E.; Ang, W. H.; Scopelliti, R.; Dyson, P. J. *Eur. J. Inorg. Chem.* **2014**, 1745–1750.
21. Biricik, N.; Durap, F.; Kayan, C.; Gümgüm, B. *Heteroatom Chem.* **2007**, *18*, 613–616.
22. Biricik, N.; Durap, F.; Gumgum, B; Fei, Z.; Scopelliti, R. *Trans. Met. Chem.* **2007**, *32*, 877–883.
23. Zhao, D.; Fei, Z.; Ang, W. H. *Cent. Eur. J. Chem.* **2008**, *6*, 93–98.
24. Biricik, N.; Kayan, C.; Gümgüm, B.; Fei, Z.; Scopelliti, R.; Dyson, P. J.; Gurbuz, N.; Ozdemir, I. *Inorg. Chim. Acta* **2010**, *363*, 1039–1047.
25. Kayan, C.; Biricik, N.; Aydemir, M.; Scopelliti, R. *Inorg. Chim. Acta* **2012**, *385*, 164–169.
26. Gaw, K. G.; Smith, M. B.; Slawin, A. M. Z. *New J. Chem.* **2000**, *24*, 429–435.
27. Fei, Z.; Scopellit, R.; Dyson, P. J. *Inorg. Chem.* **2003**, *42*, 2125–2130.
28. Fei, Z.; Biricik, N.; Scopelliti, R.; Dongbin, Z.; Dyson, P. J. *Inorg. Chem.* **2004**, *43*, 2228–2230.
29. Priya, S.; Balakrishna, M. S.; Mague, J. T. *J. Organomet. Chem.* **2003**, *679*, 116–124.
30. Gopalakrishnan, J. *Appl. Organomet. Chem.* **2009**, *23*, 291–318.
31. Ansell, J.; Wills, M. *Chem. Soc. Rev.* **2002**, *31*, 259–268.
32. Appleby, T.; Woollins, J. D. *Coord. Chem. Rev.* **2002**, *235*, 121–140.
33. Bichler, B.; Veiros, L. F.; Öztopcu, O.; Puchberger, M.; Mereiter, K.; Matsubara, K.; Kirchner, K. A. *Organometallics* **2011**, *30*, 5928–5942.
34. Rodriguez, M.; Zubiri, I.; Woollins, J. D. *Comment. Inorg. Chem.* **2003**, *24*, 189–252.
35. Ly, T. Q.; Woollins, J. D. *Coord. Chem. Rev* . **1998**, *176*, 451–481.
36. Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457–2483.
37. Johnson, B. F. G. *Top. Catal.* **2003**, *24*, 147–159.
38. Suzuki, A. *J. Organomet. Chem.* **1999**, *57*, 147–168.
39. Kotha, S.; Lahiri, K.; Kashninath, D. *Tetrahedron Lett.* **2002**, 9633–9695.
40. Migowski, P.; Dupont, J. *Chem. Eur. J.* **2006**, *13*, 32–39.
41. Fei, Z.; Geldbach, T. J.; Zhao, D.; Dyson, P. J. *Chem. Eur. J.* **2006**, *12*, 2122–2130.
42. Gümgüm, B.; Biricik, N.; Durap , F.; Özdemir, I.; Gürbüz, N.; Ang, W. H.; Dyson, P. J. *Appl. Organometal. Chem.* **2007**, *21*, 711–715.
43. Biricik, N.; Durap, F.; Kayan, C.; Gümgüm, B.; Gürbüz, N.; Özdemir, I.; Ang, W. H.; Fei, Z.; Scopelliti, R. *J. Organomet. Chem.* **2008**, *693*, 2693–2699.