SHORT COMMUNICATION

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Palladium(0)-Catalysed Cross-Couplings of 2-Bromophosphinine

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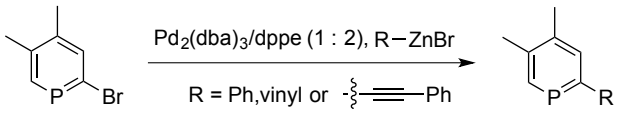
A new Negishi type cross-coupling of 2-bromophosphinine has been developed. The new method expands the scope of palladium-catalysed couplings to monobromophosphinines, which have been considered as poor substrates so far. Moreover, aryl-, alkenyl- and alkynylzinc bromides were found to be effective coupling partners.



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Introduction

Transition metal catalysis is a powerful tool in organic synthesis as illustrated by the wealth of reactions that rely on the activation by metal complexes. The ligand on the metal is a crucial component in this chemistry as it controls the reactivity of the catalyst towards specific substrate classes and the stereochemistry of the process. As such, the development of new ligand systems that impose novel and unique reactivity/selectivity profiles is a major goal of the field. Phosphinines[1], the higher homologues of pyridines, are planar, aromatic phosphorous-containing heterocycles with unique electronic, steric and coordination properties, which make them attractive scaffolds for ligand development. The first reports of $1\lambda^3$-phosphinines, appeared in the late 1960`s.[2] Although they are isoelectronic to pyridines, they exhibit quite different electronic properties. Spectroscopic and theoretical investigations indicate that phosphinines are better π-acceptor ligands, but less σ-donating, than pyridines.[3] Due to their unusual properties, the application of functionalized phosphinines as ligands in homogenous catalysis has received considerable interest.[1b, c, 4]

The most successful strategies for the synthesis of complex phosphinine-containing structures are based on pyryllium salts[5] or 1,3,2-diazaphosphinines[6] as precursors. Alternatively, a number of methods for the functionalization of preformed phosphinines[1a] are known, such as direct bromination[7], phosphination[8], ethylation[9] and transformations of 2-metallated phosphinines (M = Li[10], Mg[7], Zn[10c-e, 11] and Zr[1a, 12]). A major limitation of these methods is the lack of versatility with respect to the groups that can be introduced. However, Mao and Mathey recently introduced an interesting, functionalisable phosphinine building block when a phosphinine-2-carboxaldehyde was transformed into an alkene via a Wittig reaction.[13] In 1993, Le Floch *et al*. described the palladium(0)-catalyzed cross-coupling with organotin reagents.[14] They were able to couple polybromophosphinines with trimethyltin derivatives of furan, *N*-methylpyrrole, thiophene and phenylacetylene using $Pd(dba)_2$ and monodentate phosphines e. g. triphenylphosphine or tri-2-furylphosphine as the catalyst system. However, they discovered that mono- and dibromophosphinines were much poorer substrates for the Stille coupling. For example, the alkynylation of monobromophosphinines with trimethyl(2-phenylethynyl)stannane could not be achieved. Clearly, the incorporation of the phosphinine core into more complex structures still remains a synthetic challenge.

During our efforts to explore phosphinines as potential ligands in catalysis, we sought to broaden the scope of palladium(0)-catalysed functionalization of 2-bromophosphinines. Herein, we show that the previously described Stille type cross-coupling of organotin reagents can be extended to monobromophosphinines. More importantly, we present our preliminary results on the development of a Negishi type cross-coupling of organozinc reagents with 2-bromophosphinine which greatly increases the substituent diversity introduced via the coupling reaction.

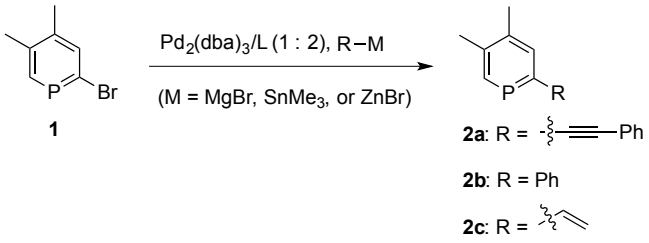
Results and Discussion

In order to find the optimal organometallic reagents for the coupling of 2-bromo-4,5-dimethylphosphinine **1**, the reactivity of organomagnesium, -tin and -zinc compounds (Table 1) was investigated. In a Stille type coupling utilizing $Pd_2(dba)_3$ and 1,2-bis(diphenylphosphino)ethane (dppe) (1:2) as the catalyst system with a catalyst loading of 10 mol % Pd/**1** at reflux in *p*-xylene or THF, an acetylenic tin compound performed well providing **2a** in 42 % and 53 % yield, respectively (Table 1, entry 1). Couplings with less reactive[15] vinyl- and phenyltin reagents could not be achieved under these conditions (Table 1, entry 2 and 3). Couplings with Grignard reagents gave a mixture of products. Analysis of the crude reaction mixture after coupling of 2-bromophosphinine **1** and phenylmagnesium bromide in THF at 40 °C by ^{31}P-NMR revealed a competition between reaction at phosphorus (δ_P = 64.05 ppm) and the halogen (δ_P = 183.66 ppm), occurring in approximately equal amounts.

Initial results employing organozinc reagents in the coupling with 2-bromophosphinine **1** were promising. Both alkynyl, aryl-

,and vinylzinc bromides were reactive in the desired coupling reaction (Table 1, entry 4—6). Negishi couplings were carried out with $Pd_2(dba)_3$/dppe (1:2) as catalyst system. The catalyst loading was 5 – 10 mol % Pd/**1**. ^{31}P NMR analysis of reaction mixtures was utilized to determine the conversion of starting material and provided valuable information about the reaction conditions. It was established that the phosphinine : RZnBr ratio necessary for complete conversion of the 2-bromophosphinine **1** was dependent on the method of preparation of the organozinc bromide reagent. When a commercially available phenylzinc bromide solution (final conc. ~0.4 M in THF), prepared by a reaction of phenylbromide with metallic zinc, was applied, a 1:4 ratio was necessary for complete conversion at 40 °C (method A). In case of a phenylzinc bromide solution (final conc. ~0.6 M in THF/nBu_2O) prepared by quenching a solution of phenyllithium with 1.2-1.5 equivalents excess of $ZnBr_2$, complete conversion was observed at a ratio of 1 : 2 within 24 hrs at 50 °C (method B). The coupling product 2-phenylphosphinine **2b** was isolated in 40 % yield independent of the source of the organozinc reagent (Table 1, entry 4). When the conditions of method B were applied to the alkynylation of **1** with phenylethynylzinc bromide, **2a** was obtained in 36 % yield (Table 1, entry 5). Alkenylation of **1** with vinylzinc bromide gave 2-vinylphosphinine **2c** in 30 % yield (Table 1, entry 6). The desired cross-coupling reactions were accompanied by homocoupling of the organotin reagent.

Table 1. Optimization of the Reaction Conditions and Reaction Scope

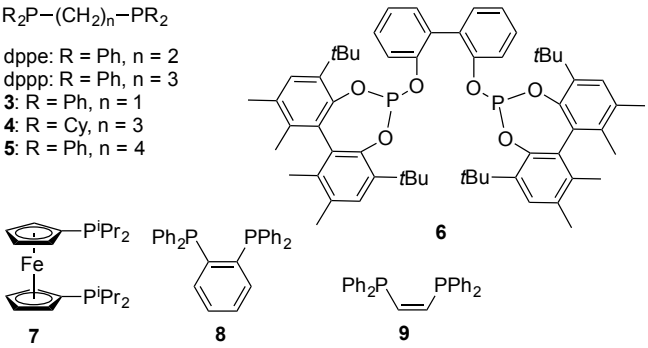


entry	M	R	ligand	product	% yield
1	$SnMe_3$	Ph	dppe	**2a**	42[a]/53[b]
2[a]	$SnMe_3$	Ph-	dppe	**2b**	0
3[a]	$SnMe_3$	Vinyl-	dppe	**2c**	0
4[c]	ZnBr	Ph	dppe	**2a**	36
5[d]	ZnBr	Ph-	dppe	**2b**	40
6[d]	ZnBr	Vinyl-	dppe	**2c**	30
7[d]	ZnBr	Ph-	dppp	**2b**	76
8[d]	ZnBr		**8**	**2b**	6

[a]Reaction conditions: THF, 70 °C, 1.5 h; [b]Reaction conditions: *p*-xylene, 110 °C, 1.5 h; [c]Reaction conditions: THF, 70 °C, 24 h; [d]Reaction conditions: THF, 50 °C, 24 h.

The influence of the ligand on the coupling reaction with phenyl zinc bromide was also explored. As a selection tool for bidentate phosphorus(III) donor ligands we chose the score plot from the principal component analysis described by Fey *et al.*[16] All selected ligands were tested using method B. The reaction mixtures were analysed by ^{31}P-NMR and consumption of starting material and conversion to product were determined. Four ligands **3**, **4**, **6** and **7** (Fig. 1) were identified as commercially available ligands with significantly different properties than dppe. None of these ligands induced the coupling reaction of **1** and phenylzinc bromide. We continued the screening experiments with dppp and ligands **5**, **8** and **9,** which are closer to dppe in chemical space and thereby exhibit similar properties. No coupling was observed with ligands **5** and **9**. With dppp and **8** complete consumption of 2-bromophosphinine **1** was observed after 24 hrs by ^{31}P NMR. However, the isolated yields obtained from the coupling of **1** and phenylzinc bromide with dppp and ligand **8** were 76 % and 6 %, respectively (Table 1, entry 7 and 8).

Figure 1. Ligands



Conclusions

In conclusion, we have achieved a novel Palladium–catalyzed Negishi-coupling with 2-bromophosphine. The new protocol can be used to couple alkynyl-, phenyl- and vinyl zinc bromides. With dppe as ligand, the isolated yields (30—40%) were at a similar level as comparable coupling reactions employing more reactive polybromophosphinines[16b][14b] (40%). A better ligand for the transformation was identified by the aid of a score plot of the principal component analysis of bidentate ligands. With dppp as ligand, the isolated yield for the coupling of phenylzinc bromide with **1** improved to 76%. Our protocol for the Negishi-coupling of 2-bromophosphinines is a valuable new transformation allowing for the introduction of phosphinines into more complex structures.

Experimental Section

General Procedures. All oxygen-and/or water sensitive reactions were carried out under dry nitrogen using Schlenk techniques with oven-dried glassware and dry solvents. THF, pentane and p-xylene were distilled from Na/benzophenone and methylene chloride from P_2O_5 before use. Tris(dibenzylideneacetone)dipalladium(0) ($Pd_2(dba)_3$) was purchased from Alfa Aesar, zinc bromide (anhydrous), phenylacetylene, solutions of 1.6 M *n*-butyllithium in hexane, 1.0 M vinylmagnesium bromide in THF, 0.5 M phenylzinc bromide in THF, 1.8 M phenyllithium in di-*n*-butyl ether and the bidentate *P*,*P*-ligands 1,2-bis(diphenylphosphino)ethane (dppe), 1,2-bis(diphenylphosphino)propane (dppp), **3-5** and **7-9** were commercially available from Sigma Aldrich. Ligand **6** was received from Strem. All commercial available reagents were used as received except for phenylacetylene which was distilled under nitrogen prior to use. Starting materials were prepared according to literature methods: trimethyl(2-phenylethynyl)stannane[17] and 2-bromo-4,5-dimetylphosphinine.[18]

IR spectra were recorded with Model Varian 7000e FT-IR spectrometer.

NMR spectra were recorded at an Oxford Varian 400 spectrometer operating at 400 MHz (^1H), 100.64 MHz (^{13}C) and 161.9 MHz (^{31}P). The coupling constants (J) are given in Hz. ^1H and ^{13}C chemical shifts (δ) are reported in ppm relative to the residual peak[19] of the NMR solvent. ^1H and ^{13}C chemical shifts were assignment by 2D NMR experiments: H,H-COSY, HSQC and HMBC. ^{31}P NMR spectra were recorded using an insertion NMR tube filled with PPh_3 (δ = -5.4 ppm) solution in C_6D_6 as a reference.

Signal patterns are indicated as s (singlet), d (doublet), t (triplet), q (quartet) or m (multiplet).

The high and low resolution mass spectra were measured with MAT95XL Thermo-Finnigan instrument in EI-mode. Samples were introduced with direct injection probe without pre-chromatographic treatment, source temperature 180 °C, probe temperature lower than 20 °C.

The new phosphinines described in this work were sensitive to air and unstable upon standing.

4,5-dimethyl-2(2-phenylethynyl)phosphinine 2a via *Stille coupling.* To a stirred solution of trimethyl(2-phenylethynyl)stannane (551 mg, 2.08 mmol, 1.3 eq) with $Pd_2(dba)_3$ (80 mg, 0.08 mmol, 10 mol % in Pd) and dppe (64 mg, 0.16 mmol, 10 mol %) in 2.5 ml of p-xylene was added a solution of 2-bromophosphinine **1** (325 mg, 1.6 mmol, 1 eq) in 2.5 ml of *p*-xylene at room temperature. The reaction mixture was refluxed at 110 °C for 1.5 h while stirring. Then solvent was evaporated *in vacuo*, a deep brown oily residue was dissolved in 2-3 ml of methylene chloride, 1 g of Celite was added and the solvent was removed completely under reduced pressure. The coated Celite was loaded onto the top of a silica gel packed column. A first fraction eluted with pentane gave non-reacted **1**, the second fraction eluted with pentane/CH_2Cl_2 (9:1) contained 1,4-diphenylbutadiyne resulting from homocoupling of the tin reagent and the third yielded product **2a** as a white powder sensitive to air. The separation of the homocoupled by-product from the phosphinine was challenging. Yield: 150 mg (42 %). ^{1}H NMR ($CDCl_3$): δ = 2.37 (d, $^5J_{P,H}$ = 3.4, 3H, 4-CH_3), 2.43 (d, $^4J_{P,H}$ = 2.0, 3H, 5-CH_3), 7.32-7.38 (m, 3H, *meta-, para*-C_6H_5), 7.53-7.56 (m, 2H, *ortho*-C_6H_5), 7.87 (d, $^3J_{P,H}$ = 4.6, 1H, 3-H), 8.45 (d, $^2J_{P,H}$ = 38.9, 1H, 6-H) ppm; ^{13}C NMR ($CDCl_3$): δ = 22.3 (d, $^4J_{P,C}$ = 2.5, 4–*C*H$_3$), 23.5 (d, $^3J_{P,C}$ = 3.7, 5–*C*H$_3$), 91.5 (d, $^2J_{P,C}$ = 29.1, –*C*≡C–C_6H_5), 95.1 (d, $^3J_{P,C}$ = 6.7, ≡*C*–C_6H_5), 123.7 (d, $J_{P,C}$ = 3.3, *ipso*-C_6H_5), 128.4 (s, *para*-C_6H_5), 128.5 (s, *meta*-C_6H_5), 131.7 (d, $J_{P,C}$ = 2.9, *ortho*-C_6H_5), 139.5 (d, $^2J_{P,C}$ = 15.8, C-4), 140.3 (d, $^2J_{P,C}$ = 12.0, C-3), 142.7 (d, $^3J_{P,C}$ = 15.8, C-5), 147.7 (d, $^1J_{P,C}$ = 42.7, C-2), 155.2 (d, $^1J_{P,C}$ = 52.1, C-6) ppm; ^{31}P NMR ($CDCl_3$): δ = 206.3 ppm; (C_6D_6): δ = 207.6 ppm, (pentane): δ = 211.4 ppm. IR, cm^{-1}: 3053 (vw), 2980 (vw), 2943 (vw), 2911 (vw), 2853 (vw), 1683 (vw), 1592 (w), 1547 (w), 1487 (m), 1442 (m), 1372 (w), 1331 (w), 1196 (w), 1133 (w), 1070 (w), 1015 (w), 757 (vs), 691 (s). HRMS calcd for $C_{15}H_{13}P$, 224.0749; found 224.0748.

Phenylethynylphosphinine **2a** could also be prepared according to the procedure above in THF refluxing at 70 °C for 1.5 h. Yield: 53 %.

2a via *Negishi coupling.* To a stirred solution of phenylacetylene (542 mg, 0.58 ml, 5.31 mmol, 2 eq) in 2.6 ml of THF was added dropwise at - 78°C 3.32 ml of a 1.6 M *n*-butyllithium solution in hexane. The pale yellow solution became white cloudy. Then zinc bromide (1.44 g, 6.37 mmol, 2.4 eq) in 2.4 ml of THF was added to the reaction mixture at –50 °C. The solution became colorless. It was left stirring at low temperature for 15 min then again was cooled down to - 60°C and added to a solution of 2-bromophosphinine **1** (539 mg, 2.67 mmol, 1 eq), Pd_2dba_3 (61 mg, 0.066 mmol, 5 mol % in Pd) and dppe (53 mg, 0.133 mmol, 5 mol %) in 1.5 ml of THF while stirring. The reaction mixture was allowed to warm up to room temperature and then was refluxed at 50 °C for 24 h. Then the solvent was removed under reduced pressure resulting in a deep green oily residue. The residue was dissolved in approx. 15-20 ml of CH_2Cl_2 and filtered through 1-1.5 cm pad of Celite. Celite (2g) was added to the filtrate and the solvent was removed *in vacuo*. The coated Celite was loaded onto the top of a silica gel packed column. The isolation by column chromatography was performed with pentane/CH_2Cl_2 (9:1) eluent mixture and gave a byproduct 1,4-diphenylbutadiyne in a first fraction and pure product **2a** in a second fraction. Yield: 214 mg (36 %).

4,5-dimethyl-2-phenylphosphinine *2b* (method A). To a stirred solution of 2-bromophosphinine **1** (159 mg, 0.78 mmol, 1 eq.), Pd_2dba_3 (17.9 mg, 0.020 mmol, 5 mol % in Pd) and dppe (15.6 mg, 0.039 mmol, 5.0 mol %) in 1.2 ml of THF was added at –30 °C a 0.5 M solution of phenylzinc bromide in THF (6.27 ml, 3.1 mmol, 4.0 eq). The resulting mixture was then heated overnight at 40 °C. After analysis with ^{31}P NMR indicating the total disappearance of the starting material, 1 g of Celite was added and the solvent was evaporated under reduced pressure. The resulting dark brown mixture was chromatographed. The product **2b** was eluted with pentane/CH_2Cl_2 (9:1) and isolated as colorless, air sensitive oil. Yield: 64 mg (41 %).

^{1}H NMR ($CDCl_3$): δ 2.44 (d, $^5J_{P,H}$ = 3.6, 3H, 4–CH_3), 2.47 (d, $^5J_{P,H}$ = 1.5, 3H, 5–CH_3), 7.34-7.38 (m, 1H, *para*-C_6H_5), 7,42-7.46 (m, 2H, *meta*-C_6H_5), 7,63-7.66 (m, 2H, *ortho*-C_6H_5), 7.88 (d, $^3J_{P,H}$ = 5.5, 1H, 3-H), 8.51 (d, $^2J_{P,H}$ = 38.8, 1H, 6-H) ppm; ^{13}C NMR ($CDCl_3$): δ = 22.8 (d, $^4J_{P,C}$ = 2.2, 4–*C*H$_3$), 23.3 (d, $^3J_{P,C}$ = 3.6, 5–C*H*$_3$), 127.5 (d, $^3J_{P,C}$ = 12.4, *ortho*-C_6H_5), 127.6 (d, $^5J_{P,C}$ = 1.8, *para*-C_6H_5), 129.0 (s, *meta*-C_6H_5), 136.3 (d, $^2J_{P,C}$ = 12.5, C-3), 139.7 (d, $^3J_{P,C}$ = 16.6, C-4), 142.3 (d, $^2J_{P,C}$ = 15.7, C-5), 143.8 (d, $^2J_{P,C}$ = 23.0, *ipso*-C_6H_5), 155.0 (d, $^1J_{P,C}$ = 49.8, C-6), 168.7 (d, $^1J_{P,C}$ = 47.6, C-2) ppm; ^{31}P NMR ($CDCl_3$/C_6D_6, PPh_3): δ = 183.8 ppm; (THF/C_6D_6, PPh_3): δ = 181.1 ppm. IR, cm^{-1}: 3057 (w), 3028 (w), 2974 (w), 2939 (w), 2916 (w), 2860 (w), 1945 (w), 1874 (w), 1801 (w), 1749 (w), 1685 (w), 1596 (w), 1483 (m), 1445 (m), 1431 (w), 1377 (w), 1322 (w), 1306 (w), 1270 (w), 1238 (w), 1190 (w), 1156 (w), 1119 (w); 1074 (w), 1030 (w), 1018 (w), 1009, (w), 773 (m), 736 (vs), 694 (vs).. HRMS calcd for C_{13} H_{13} P, 200.0749; found 200.0745.

***2b* (method B).** To a 1.8 M phenyllithium solution in dibutylether (2.63 ml, 5.15 mmol, 2.0 eq) was added a solution of zinc bromide (1.44 g, 6.29 mmol, 2.4 eq) in 2.5 ml of THF while stirring at –50 °C. The reaction mixture was stirred with cooling bath for 30 min and then added to a stirred solution of 2-bromophosphinine **1** (532 mg, 2.58 mmol, 1 eq), Pd_2dba_3 (59 mg, 0.065 mmol, 5 mol % in Pd) and dppp (53 mg, 0.129 mmol, 5 mol %) in 2.2 ml of THF at –50 °C. The reaction mixture was allowed to warm up to room temperature and then it was heated at 50°C for 24 h while stirring. After ^{31}P NMR control, which indicated the total disappearance of the starting material, the product **2b** was isolated as described above. Yield: 392 mg (76 %).

4,5-dimethyl-2-vinylphosphinine *2c*. To a stirred 1.0 M solution of vinylmagnesium bromide in THF (5.14 ml, 5.14 mmol, 2.0 eq) was added 7.3 ml of THF and subsequently a solution of zinc bromide (1.39 g, 6.17 mmol, 2.4 eq) in 2.3 ml of THF at –50 °C. The reaction mixture became white cloudy and was stirred at low temperature for 30 min. Then the prepared solution was added to a stirred solution of 2-bromophosphinine **1** (522 mg, 2.57 mmol, 1 eq.), Pd_2dba_3 (59 mg, 0.064 mmol, 5 mol % in Pd) and dppe (51 mg, 0.129 mmol, 5 mol %) in 2.2 ml of THF at –50 °C. The reaction mixture was allowed to warm up to room temperature while stirring and then it was heated at 50 °C for 24 h. **2c** was isolated as described for **2b** (via Negishi coupling) as yellow, air sensitive oil. Yield: 116 mg (30 %). ^{1}H NMR ($CDCl_3$): δ 2.37 (d, $^5J_{P,H}$ = 3.6, 3H, 4–CH_3), 2.42 (d, $^5J_{P,H}$ = 1.7, 3H, 5–CH_3), 5.21 (br d, J = 10.7, 1H, *vinyl*-CH_2, *cis*), 5.96 (ddd, $^3J_{H,H}$ = 17.4, $^4J_{P,H}$ = 3.5, $^2J_{H,H}$ = 1.0, 1H, *vinyl*-CH_2, *trans*), 6.98 (dt, $^3J_{H,H}$ = 17.4, $^3J_{H,H}$ = 11.0, $^3J_{H,P}$ = 11.0, 1H, *vinyl*-C*H*), 7.67 (d, $^3J_{P,H}$ = 5.9, 1H, 3-H), 8.43 (d, $^2J_{P,H}$ = 38.4, 1H, 6-H) ppm; ^{13}C NMR ($CDCl_3$): δ = 22.4 (d, $^4J_{P,C}$ = 2.4, 4–CH_3), 23.1 (d, $^3J_{P,C}$ = 3.8, 5–CH_3), 113.6 (d, $^3J_{P,C}$ = 22.8, *vinyl*-CH_2), 135.2 (d, $^2J_{P,C}$ = 13.5, C-3), 139.3 (d, $^2J_{P,C}$ = 17.3, C-4), 139.6 (d, $^2J_{P,C}$ = 28.7, *vinyl*-C*H*), 142.6 (d, $^3J_{P,C}$ = 16.3, C-5), 154.6 (d, $^1J_{P,C}$ = 48.5, C-6), 164.3 (d, $^1J_{P,C}$ = 45.1, C-2) ppm; ^{31}P NMR ($CDCl_3$): δ = 183.8 ppm; (THF-d_6): δ = 184.4 ppm. IR, cm^{-1}: 3123 (w), 3074 (w), 3049 (w), 2972 (w), 2938 (w), 2906 (w), 2844 (w), 2171 (w),1591 (w), 1569 (w), 1544 (w), 1485 (m), 1440 (m), 1371 (m), 1328 (w), 1194 (w), 1132 (w),1069 (w), 1014 (m), 755 (vs), 690 (vs). HRMS calcd for C_9 H_{11} P, 150.0593; found 150.0591.

Supporting Information (see footnote on the first page of this article): Copies of the ^{1}H NMR and ^{13}C NMR spectra of the products.

Acknowledgments

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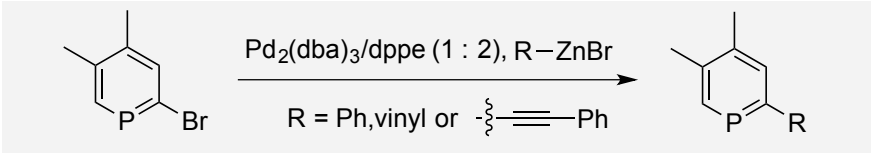

Phospinines are phosphor containing heterocycles with interesting properties. Here, the results for palladium-catalysed cross-couplings of bromo-phosphinine are described.

Coupling of various types of organozinc compounds can be achieved, providing a new, powerful option for functionalisation of phosphinines.

Nataliya Kostenko, Cecilia Ericson, Magnus Engqvist, Susana Villa Gonzalez and Annette Bayer* ……...
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Palladium(0)-Catalysed Cross-Couplings of 2-Bromophosphinine

Keywords: Phosphorus heterocycles / Phosphinines / Homogeneous catalysis / C–C coupling / Palladium