SHORT COMMUNICATION

EurJOC European Journal of Organic Chemistry

DOI: 10.1002/ejoc.201300710

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

Nataliya Kostenko,[a] Cecilia Ericsson,[a] Magnus Engqvist,[a] Susana Villa Gonzalez,[b] and Annette Bayer*[a]

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

A new Negishi-type cross-coupling of 2-bromophosphinine has been developed. The new method expands the scope of palladium-catalyzed 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.

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 phosphorus-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 1960s.[2] Although phosphinines 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] Because of their unusual properties, the application of functionalized phosphinines as ligands in homogeneous catalysis has received considerable interest.[1b,1c,4]

The most successful strategies for the synthesis of complex phosphinine-containing structures are based on pyrylium 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–10e,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, functionalizable phosphinine building block when a phosphinine-2-carboxaldehyde was transformed into an alkene through 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 phosphanes, e.g. triphenylphosphane or tri-2-furylphosphane, 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)-catalyzed 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 by 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(diphenylphosphanyl)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

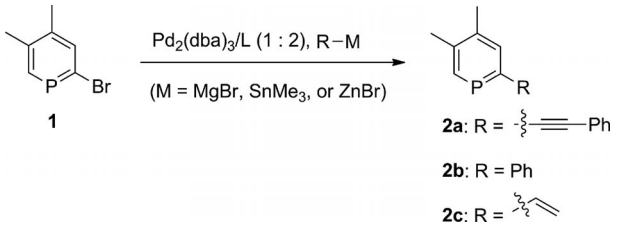
[a] Department of Chemistry, University of Tromsø, 9037 Tromsø, Norway,
E-mail: annette.bayer@uit.no
http://uit.no
[b] Department of Chemistry, NTNU, Trondheim, Norway

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.201300710.

© 2013 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

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 spectroscopy revealed a competition between reaction at phosphorus (δ_P = 64.05 ppm) and the halogen (δ_P = 183.66 ppm), which occurs in approximately equal amounts.

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	41
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.

Initial results employing organozinc reagents in the coupling with 2-bromophosphinine **1** were promising. 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 on 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 concentration ≈ 0.4 M in THF), prepared by 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 concentration ≈ 0.6 M in THF/nBu$_2$O) prepared by quenching a solution of phenyllithium with 1.2–1.5 equiv. excess of $ZnBr_2$, complete conversion was observed at a ratio of 1:2 within 24 h 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.

The influence of the ligand on the coupling reaction with phenylzinc 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 by using method B. The reaction mixtures were analyzed by ^{31}P NMR spectroscopy, and consumption of starting material and conversion to product were determined. Four ligands **3**, **4**, **6**, and **7** (Figure 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 h by ^{31}P NMR spectroscopy. 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).

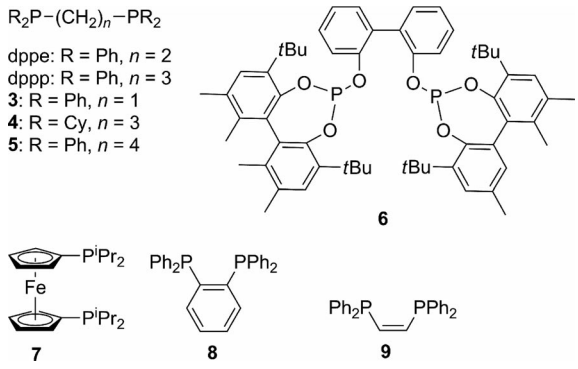


Figure 1. Ligands.

Conclusions

We have achieved a novel palladium-catalyzed Negishi-coupling with 2-bromophosphinine. The new protocol can be used to couple alkynyl-, phenyl-, and vinylzinc bromides. With dppe as ligand, the isolated yields (30–40%) were at a similar level as comparable coupling reactions employing more reactive polybromophosphinines[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

 © 2013 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

oven-dried glassware and dry solvents. THF, pentane, and *p*-xylene were distilled from Na/benzophenone and dichloromethane 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(diphenylphosphanyl)ethane (dppe) and 1,2-bis(diphenylphosphanyl)propane (dppp), **3**–**5** and **7**–**9** were commercially available from Sigma Aldrich. Ligand **6** was received from Strem. All commercially 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 a Model Varian 7000e FTIR Spectrometer. NMR spectra were recorded with an Oxford Varian 400 spectrometer operating at 400 MHz (^{1}H), 100.64 MHz (^{13}C), and 161.9 MHz (^{31}P). The coupling constants (J) are given in Hz. ^{1}H and ^{13}C chemical shifts (δ) are reported in ppm relative to the residual peak[19] of the NMR solvent. ^{1}H and ^{13}C chemical shifts were assigned 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 a MAT95XL Thermo-Finnigan instrument in EI-mode. Samples were introduced with a direct injection probe without pre-chromatographic treatment; source temperature 180 °C, probe temperature lower than 20 °C.

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

4,5-Dimethyl-2(2-phenylethynyl)phosphinine (2a) through Stille Coupling: To a stirred solution of trimethyl(2-phenylethynyl)stannane (551 mg, 2.08 mmol, 1.3 equiv.) with $Pd_2(dba)_3$ (80 mg, 0.08 mmol, 10 mol-% in Pd), and dppe (64 mg, 0.16 mmol, 10 mol-%) in *p*-xylene (2.5 mL) was added a solution of 2-bromophosphinine **1** (325 mg, 1.6 mmol, 1 equiv.) in *p*-xylene (2.5 mL) at room temperature. The reaction mixture was heated at reflux at 110 °C for 1.5 h while stirring. The solvent was then evaporated in vacuo. The resulting deep brown oily residue was dissolved in dichloromethane (2–3 mL), Celite (1 g) 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 unreacted **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 Hz, 3 H, 4-CH_3), 2.43 (d, $^4J_{P,H}$ = 2.0 Hz, 3 H, 5-CH_3), 7.32–7.38 (m, 3 H, *meta*-, *para*-C_6H_5), 7.53–7.56 (m, 2 H, *ortho*-C_6H_5), 7.87 (d, $^3J_{P,H}$ = 4.6 Hz, 1 H, 3-H), 8.45 (d, $^2J_{P,H}$ = 38.9 Hz, 1 H, 6-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 22.3 [d, ^4J(P,C) = 2.5 Hz, 4-*C*H$_3$], 23.5 (d, $^3J_{P,C}$ = 3.7 Hz, 5-*C*H$_3$), 91.5 (d, $^2J_{P,C}$ = 29.1 Hz, –*C*≡C–C_6H_5), 95.1 (d, $^3J_{P,C}$ = 6.7 Hz, ≡*C*–C_6H_5), 123.7 (d, $J_{P,C}$ = 3.3 Hz, *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 Hz, *ortho*-C_6H_5), 139.5 (d, $^2J_{P,C}$ = 15.8 Hz, C-4), 140.3 (d, $^2J_{P,C}$ = 12.0 Hz, C-3), 142.7 (d, $^3J_{P,C}$ = 15.8 Hz, C-5), 147.7 (d, $^1J_{P,C}$ = 42.7 Hz, C-2), 155.2 (d, $^1J_{P,C}$ = 52.1 Hz, 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: $\tilde{\nu}$ = 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) cm^{-1}. 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 heated at reflux at 70 °C for 1.5 h. Yield: 53%.

2a through Negishi Coupling: To a stirred solution of phenylacetylene (542 mg, 0.58 mL, 5.31 mmol, 2 equiv.) in THF (2.6 mL) was added dropwise at –78 °C *n*-butyllithium (3.32 mL of a 1.6 M solution) in hexane. The pale yellow solution became cloudy white. Zinc bromide (1.44 g, 6.37 mmol, 2.4 equiv.) in THF (2.4 mL) was then added to the reaction mixture at –50 °C. The solution became colorless. It was left to stir at low temperature for 15 min, again cooled to –60 °C, and then added to a solution of 2-bromophosphinine **1** (539 mg, 2.67 mmol, 1 equiv.), Pd_2dba_3 (61 mg, 0.066 mmol, 5 mol-% in Pd), and dppe (53 mg, 0.133 mmol, 5 mol-%) in THF (1.5 mL) while stirring. The reaction mixture was warmed up to room temperature and then was heated at reflux at 50 °C for 24 h. The solvent was then removed under reduced pressure, which resulted in a deep green oily residue. The residue was dissolved in CH_2Cl_2 (approximately 15–20 mL) and filtered through 1–1.5 cm pad of Celite. Celite (2 g) 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. Isolation by column chromatography was performed with a pentane/CH_2Cl_2 (9:1) eluent mixture and gave a by-product, 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 equiv.), 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 THF (1.2 mL) was added at –30 °C a 0.5 M solution of phenylzinc bromide in THF (6.27 mL, 3.1 mmol, 4.0 equiv.). The resulting mixture was then heated overnight at 40 °C. After analysis with ^{31}P NMR spectroscopy, which indicated the total disappearance of the starting material, Celite (1 g) 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 a colorless, air-sensitive oil. Yield: 64 mg (41%). ^{1}H NMR ($CDCl_3$): δ = 2.44 (d, $^5J_{P,H}$ = 3.6 Hz, 3 H, 4-CH_3), 2.47 (d, $^5J_{P,H}$ = 1.5 Hz, 3 H, 5-CH_3), 7.34–7.38 (m, 1 H, *para*-C_6H_5), 7,42–7.46 (m, 2 H, *meta*-C_6H_5), 7,63–7.66 (m, 2 H, *ortho*-C_6H_5), 7.88 (d, $^3J_{P,H}$ = 5.5 Hz, 1 H, 3-H), 8.51 (d, $^2J_{P,H}$ = 38.8 Hz, 1 H, 6-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 22.8 (d, $^4J_{P,C}$ = 2.2 Hz, 4-*C*H$_3$), 23.3 (d, $^3J_{P,C}$ = 3.6 Hz, 5-C*H*$_3$), 127.5 (d, $^3J_{P,C}$ = 12.4 Hz, *ortho*-C_6H_5), 127.6 (d, $^5J_{P,C}$ = 1.8 Hz, *para*-C_6H_5), 129.0 (s, *meta*-C_6H_5), 136.3 (d, $^2J_{P,C}$ = 12.5 Hz, C-3), 139.7 (d, $^3J_{P,C}$ = 16.6 Hz, C-4), 142.3 (d, $^2J_{P,C}$ = 15.7 Hz, C-5), 143.8 (d, $^2J_{P,C}$ = 23.0 Hz, *ipso*-C_6H_5), 155.0 (d, $^1J_{P,C}$ = 49.8 Hz, C-6), 168.7 (d, $^1J_{P,C}$ = 47.6 Hz, 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: $\tilde{\nu}$ = 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) cm^{-1}. HRMS: calcd. for $C_{13}H_{13}P$ 200.0749; found 200.0745.

Method B: To a 1.8 M phenyllithium solution in dibutyl ether (2.63 mL, 5.15 mmol, 2.0 equiv.) was added a solution of zinc bromide (1.44 g, 6.29 mmol, 2.4 equiv.) in THF (2.5 mL) while stirring at –50 °C. The reaction mixture was stirred in a cooling bath for 30 min and then added to a stirred solution of 2-bromophosphinine **1** (532 mg, 2.58 mmol, 1 equiv.), Pd_2dba_3 (59 mg,

 © 2013 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

0.065 mmol, 5 mol-% in Pd), and dppp (53 mg, 0.129 mmol, 5 mol-%) in THF (2.2 mL) at –50 °C. The reaction mixture was warmed up to room temperature, and then it was heated at 50 °C for 24 h while stirring. After monitoring by ^{31}P NMR spectroscopy, 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 equiv.) was added THF (7.3 mL) and subsequently a solution of zinc bromide (1.39 g, 6.17 mmol, 2.4 equiv.) in THF (2.3 mL) at –50 °C. The reaction mixture became cloudy white and was stirred at low temperature for 30 min. The prepared solution was then added to a stirred solution of 2-bromophosphinine **1** (522 mg, 2.57 mmol, 1 equiv.), Pd_2dba_3 (59 mg, 0.064 mmol, 5 mol-% in Pd), and dppe (51 mg, 0.129 mmol, 5 mol-%) in THF (2.2 mL) at –50 °C. The reaction mixture was warmed up to room temperature while stirring, and then it was heated at 50 °C for 24 h. **2c** was isolated as described for **2b** (obtained through Negishi coupling) as a yellow, air-sensitive oil. Yield: 116 mg (30%). ^{1}H NMR ($CDCl_3$): δ = 2.37 (d, $^5J_{P,H}$ = 3.6 Hz, 3 H, 4-CH_3), 2.42 (d, $^5J_{P,H}$ = 1.7 Hz, 3 H, 5-CH_3), 5.21 (br. d, J = 10.7 Hz, 1 H, vinyl-CH_2, *cis*), 5.96 (ddd, $^3J_{H,H}$ = 17.4, $^4J_{P,H}$ = 3.5, $^2J_{H,H}$ = 1.0 Hz, 1 H, vinyl-CH_2, *trans*), 6.98 (dt, $^3J_{H,H}$ = 17.4, $^3J_{H,H}$ = 11.0, $^3J_{H,P}$ = 11.0 Hz, 1 H, vinyl-C*H*), 7.67 (d, $^3J_{P,H}$ = 5.9 Hz, 1 H, 3-H), 8.43 (d, $^2J_{P,H}$ = 38.4 Hz, 1 H, 6-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 22.4 (d, $^4J_{P,C}$ = 2.4 Hz, 4-*C*H$_3$), 23.1 (d, $^3J_{P,C}$ = 3.8 Hz, 5-*C*H$_3$), 113.6 (d, $^3J_{P,C}$ = 22.8 Hz, vinyl-*C*H$_2$), 135.2 (d, $^2J_{P,C}$ = 13.5 Hz, C-3), 139.3 (d, $^2J_{P,C}$ = 17.3 Hz, C-4), 139.6 (d, $^2J_{P,C}$ = 28.7 Hz, vinyl-*C*H), 142.6 (d, $^3J_{P,C}$ = 16.3 Hz, C-5), 154.6 (d, $^1J_{P,C}$ = 48.5 Hz, C-6), 164.3 (d, $^1J_{P,C}$ = 45.1 Hz, C-2) ppm. ^{31}P NMR ($CDCl_3$): δ = 183.8 ppm; ([D$_6$]THF): δ = 184.4 ppm. IR: $\tilde{\nu}$ = 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) cm^{-1}. HRMS: calcd. for $C_9H_{11}P$ 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 are presented.

Acknowledgments

The authors gratefully acknowledge the financial support from the Research Council of Norway (grant number 165850/V30) and the University of Tromsø for a scholarship to N. K.

[1] a) F. Mathey, P. Le Floch in *Sci. Synth.*, *Vol. 15* (Ed.: D. S. C. Black), Georg Thieme Verlag, Stuttgart, **2004**, pp. 1097–1155; b) C. Müller, D. Vogt, *Dalton Trans.* **2007**, 5505–5523; c) C. Müller, D. Vogt, *C. R. Chim.* **2010**, *13*, 1127–1143; d) C. Müller, L. E. E. Broeckx, I. de Krom, J. J. M. Weemers, *Eur. J. Inorg. Chem.* **2013**, 187–202.

[2] a) G. Märkl, *Angew. Chem.* **1966**, *78*, 905; *Angew. Chem. Int. Ed. Engl.* **1966**, *5*, 846–847; b) A. J. Ashe, *J. Am. Chem. Soc.* **1971**, *93*, 3293–3295.

[3] a) P. D. Burrow, A. J. Ashe, D. J. Bellville, K. D. Jordan, *J. Am. Chem. Soc.* **1982**, *104*, 425–429; b) L. Nyulaszi, T. Veszpremi, *J. Phys. Chem.* **1996**, *100*, 6456–6462; c) L. Nyulaszi, *Chem. Rev.* **2001**, *101*, 1229–1246; d) A. Modelli, B. Hajgato, J. F. Nixon, L. Nyulaszi, *J. Phys. Chem. A* **2004**, *108*, 7440–7447.

[4] a) P. Le Floch, *Coord. Chem. Rev.* **2006**, *250*, 627–681; b) N. Mézailles, P. Le Floch, *Curr. Org. Chem.* **2006**, *10*, 3–25; c) L. Kollár, G. Keglevich, *Chem. Rev.* **2010**, *110*, 4257–4302; d) C. Müller, D. Vogt in *Phosphinine-based ligands in homogeneous catalysis: state of the art and future perspectives*, *Vol. 37* (Eds.: L. Peruzzini, M. Gonsalvi), Springer, **2011**, pp. 151–181.

[5] a) B. Breit, R. Winde, T. Mackewitz, R. Paciello, K. Harms, *Chem. Eur. J.* **2001**, *7*, 3106–3121; b) C. Müller, L. G. López, H. Kooijman, A. L. Spek, D. Vogt, *Tetrahedron Lett.* **2006**, *47*, 2017–2020; c) C. Müller, D. Wasserberg, J. J. M. Weemers, E. A. Pidko, S. Hoffmann, M. Lutz, A. L. Spek, S. C. J. Meskers, R. A. J. Janssen, R. A. van Santen, D. Vogt, *Chem. Eur. J.* **2007**, *13*, 4548–4559; d) C. Müller, E. A. Pidko, D. Totev, M. Lutz, A. L. Spek, R. A. van Santen, D. Vogt, *Dalton Trans.* **2007**, 5372–5375; e) C. Müller, Z. Freixa, M. Lutz, A. L. Spek, D. Vogt, P. W. N. M. van Leeuwen, *Organometallics* **2008**, *27*, 834–838; f) C. Müller, E. A. Pidko, A. J. P. M. Staring, M. Lutz, A. L. Spek, R. A. van Santen, D. Vogt, *Chem. Eur. J.* **2008**, *14*, 4899–4905; g) C. Müller, E. A. Pidko, M. Lutz, A. L. Spek, D. Vogt, *Chem. Eur. J.* **2008**, *14*, 8803–8807; h) J. R. Bell, A. Franken, C. M. Garner, *Tetrahedron* **2009**, *65*, 9368–9372; i) N. A. van der Velde, H. T. Korbitz, C. M. Garner, *Tetrahedron Lett.* **2012**, *53*, 5742–5744.

[6] a) N. Avarvari, P. Le Floch, F. Mathey, *J. Am. Chem. Soc.* **1996**, *118*, 11978–11979; b) N. Avarvari, P. Le Floch, L. Ricard, F. Mathey, *Organometallics* **1997**, *16*, 4089–4098; c) N. Mézailles, N. Avarvari, L. Ricard, F. Mathey, P. Le Floch, *Inorg. Chem.* **1998**, *37*, 5313–5316; d) N. Avarvari, N. Mézailles, L. Ricard, P. Le Floch, F. Mathey, *Science* **1998**, *280*, 1587–1589; e) N. Avarvari, N. Maigrot, L. Ricard, F. Mathey, P. Le Floch, *Chem. Eur. J.* **1999**, *5*, 2109–2118; f) X. Sava, N. Mézailles, N. Maigrot, F. Nief, L. Ricard, F. Mathey, P. Le Floch, *Organometallics* **1999**, *18*, 4205–4215; g) U. Rhörig, N. Mézailles, N. Maigrot, L. Ricard, F. Mathey, P. Le Floch, *Eur. J. Inorg. Chem.* **2000**, 2565–2571; h) N. Mézailles, N. Maigrot, S. Hamon, L. Ricard, F. Mathey, P. Le Floch, *J. Org. Chem.* **2001**, *66*, 1054–1056.

[7] P. Le Floch, D. Carmichael, F. Mathey, *Bull. Soc. Chim. Fr.* **1992**, *129*, 291–294.

[8] K. Waschbusch, P. Le Floch, F. Mathey, *Organometallics* **1996**, *15*, 1597–1603.

[9] D. Carmichael, P. Le Floch, H. G. Trauner, F. Mathey, *Chem. Commun.* **1996**, 971–971.

[10] a) P. Le Floch, D. Carmichael, F. Mathey, *Organometallics* **1991**, *10*, 2432–2436; b) P. Le Floch, D. Carmichael, L. Ricard, F. Mathey, A. Jutand, C. Amatore, *Organometallics* **1992**, *11*, 2475–2479; c) H. T. Teunissen, F. Bickelhaupt, *Tetrahedron Lett.* **1992**, *33*, 3537–3538; d) H. T. Teunissen, F. Bickelhaupt, *Phosphorus Sulfur Silicon Relat. Elem.* **1993**, *76*, 335–338; e) H. T. Teunissen, F. Bickelhaupt, *Organometallics* **1996**, *15*, 794–801.

[11] H. T. Teunissen, F. Bickelhaupt, *Organometallics* **1996**, *15*, 802–808.

[12] P. Rosa, P. Le Floch, L. Ricard, F. Mathey, *J. Am. Chem. Soc.* **1997**, *119*, 9417–9423.

[13] Y. L. Mao, F. Mathey, *Org. Lett.* **2012**, *14*, 1162–1163.

[14] a) P. Le Floch, D. Carmichael, L. Ricard, F. Mathey, *J. Am. Chem. Soc.* **1993**, *115*, 10665–10670; b) H. Trauner, P. Le Floch, J. M. Lefour, L. Ricard, F. Mathey, *Synthesis* **1995**, 717–726.

[15] J. W. Labadie, J. K. Stille, *J. Am. Chem. Soc.* **1983**, *105*, 6129–6137.

[16] N. Fey, J. N. Harvey, G. C. Lloyd-Jones, P. Murray, A. G. Orpen, R. Osborne, M. Purdie, *Organometallics* **2008**, *27*, 1372–1383.

[17] G. K. Anderson, G. J. Lumetta, *J. Organomet. Chem.* **1985**, *295*, 257–264.

[18] D. C. a. F. M. P. Le Floch in *Synthetic Methods of Organometallic and Inorganic Chemistry*, *Vol. 3*, Georg Thieme Verlag, Stuttgart, **1996**, pp. 167–171.

[19] H. E. Gottlieb, V. Kotlyar, A. Nudelman, *J. Org. Chem.* **1997**, *62*, 7512–7515.

Received: May 16, 2013
Published Online: June 21, 2013

 © 2013 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim