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Palladium-Catalyzed C−P Coupling Reactions between Vinyl Triflates and Phosphine−Boranes: Efficient Access to Vinylphosphine−Boranes

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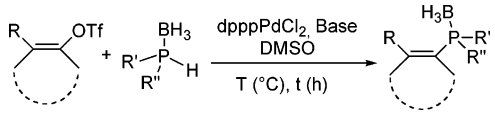

Vinylphosphine−borane complexes are easily synthesized by palladium-catalyzed C−P cross-coupling of vinyl triflates with secondary phosphine−boranes. This method allows the synthesis of phosphine derivatives not always easily accessible by other approaches. The vinylphosphine derivatives are purified by chromatography on silica gel. The versatility of the method is proved by using various triflates and diaryl-, dialkyl- and alkylarylphosphine−borane precursors. Chiral enantiopure phosphine−boranes are synthesized from chiral triflates.

Vinylphosphines play an important role in organophosphorus chemistry as synthetic intermediates for the preparation of polyphosphines and ligands for organometallic catalysis.[1] They can be used directly or after transformations of the C=C bond. The main methods to access vinylphosphines[2] are reaction between halophosphines and vinylic organometallic species, catalytic carbon−phosphorus cross-coupling reactions, and hydrophosphination of alkynes, i.e., the addition of a P−H bond to a carbon−carbon triple bond. From an economical and ecological point of view as well as for tolerance toward functional groups, hydrophosphination is by far the most attractive methodology.[3] However, the preparation, by this methodology, of compounds such as vinylphosphines containing cycles is precluded by the absence of five- or six-membered ring alkynes. Moreover, addition of phosphines to alkynes bearing bulky substituents is difficult to perform, and regioselectivity is beyond control since the addition only occurs to the less hindered sp carbon, whatever the activation source.[1a,4] Having interest in the formation of a C−P bond using the convenient phosphine−borane derivatives,[5] we also experienced difficulties in the synthesis of bulky phosphines using the hydrophosphination methodology. Following our goal to provide a general and efficient access to vinylphosphine derivatives, we decided to overcome this difficulty. Reaction between halophosphines and vinylic organometallic species suffering from a lack of tolerance toward functional groups, we turned our attention to C−P cross-coupling reactions. Only limited protocols involving vinylic substrates are reported in the literature.[6] They mainly involve the commercially available diphenylphosphine, and high temperatures are often required to ensure a reasonable conversion (typical conditions with unactivated substrates and diphenylphosphine are toluene, 110 °C,[6b] or benzene, 90 °C,[6g] ...). Different vinylic coupling partners may be used as an electrophilic source, but the most useful are vinyl triflates since they are easily accessible from numerous ketones. Furthermore, triflate derivatives are known to be more reactive than their bromide and chloride counterparts in the oxidative addition step.[7] Only the iodide compounds are more reactive, but their low availability precludes their use. A brief look at the literature showed that there was no successful example of coupling between secondary phosphine−borane complexes and unactivated vinyl triflates.[8] We report in this paper a general, efficient, and easy method to process the coupling between secondary phosphine−boranes having various electronic and steric properties and cyclic or acyclic vinyl triflates.

We first worked on the catalytic coupling of two acyclic triflate derivatives leading to products that we could not prepare using the hydrophosphination reaction.[5g] The bulky 3,3-dimethylbut-1-en-2-yl trifluoromethanesulfonate was prepared

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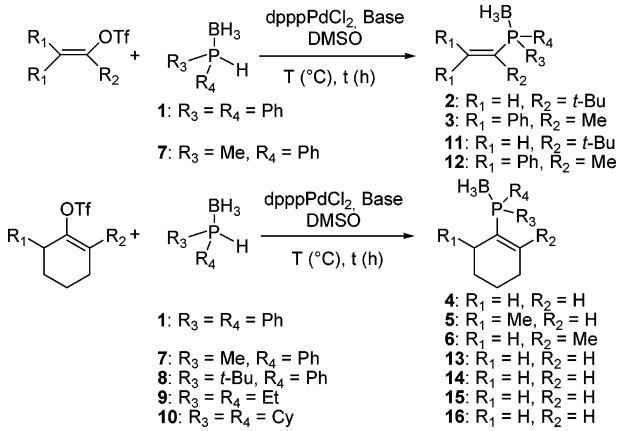
SCHEME 1



using Stang's method.[9] The reactions were performed with phosphine−borane complexes to ensure an easy handling of the phosphine derivatives and also to activate the *P*−*H* bond of the phosphine.[10] A preliminary screening of conditions allowed us to select dpppPdCl$_2$ as the source of palladium and a weak base such as K_2CO_3 to avoid the triflate hydrolysis.[11] The reactions were carried out in a polar solvent (DMSO) at 60 °C with a 1:1 phosphine **1**:triflate ratio. An almost complete conversion (90%) was observed after only 2.5 h. This can be explained by the fast oxidative addition of vinyl triflate to Pd(0) in polar coordinating solvents, which leads to cationic palladium species as already reported by Jutand.[12] To complete the conversion, the reaction time was extended to 4 h. Surprisingly, no improvement in the conversion was observed. Using a slight excess of triflate (1.1 equiv) proved no benefit for the conversion (90%). These results led us to reason that a partial hydrolysis of the triflate in the medium could be responsible for this incomplete conversion. To circumvent this problem, it was reported in the literature to add the triflate dropwise.[11b] This process being fastidious, we preferred to add a small excess of the triflate (0.1 equiv) after 1 h of reaction. Under these conditions, a complete conversion was obtained after 2.5 h, validating the hydrolysis hypothesis. The purification was easily performed by silica gel flash chromatography in air, affording phosphine−borane **2** in 71% yield (Scheme 1, Table 1, entry 1). The tetrasubstituted vinylphosphine **3**, again not accessible through a hydrophosphination process, since it does not bear any hydrogen on the double bond, was the next goal. The 1,1-diphenylprop-1-en-2-yl trifluoromethanesulfonate, synthesized from Wallace's procedure,[11a] was coupled with phosphine−borane **1** under the previously defined conditions. A complete conversion was obtained after 2.5 h, and phosphine **3** was isolated in 82% yield after purification (Scheme 1, Table 1, entry 3).

We then turned our attention to the formation of six-membered ring cyclic vinylphosphines. With cyclohexenyl triflate, under the optimized conditions described above, the coupling product **4** was obtained with a lower yield of 68% after purification (Scheme 1, Table 1, entry 5). Performing the reaction under microwave irradiation (MWI)[13] (DMSO, dppp-PdCl$_2$, K_2CO_3, 1.1 equiv of triflate) afforded a complete conversion to **4** after 15 min at 60 °C (Scheme 1, Table 1, entry 6). Due to the short reaction time (15 min), the slight excess of triflate (0.1 equiv) was directly added at the start of the reaction. After purification, the expected phosphine **4** was isolated in 71% yield, i.e., about the same yield as that obtained in an oil bath (68%), indicating that the loss in yield occurred during the purification process. On standing, **4** crystallized from diethyl ether, affording orange crystals which were suitable for X-ray analysis (see the Supporting Information (SI)).

Interestingly, dissymmetric ketones can lead to two different triflates via thermodynamic and kinetic enolates, thus offering the opportunity to prepare from the same substrate two different vinylphosphine derivatives, which is a real advantage over haloalkenes. To testify this possibility, we selected 2-methylcyclohexanone. Following published procedures, kinetic[14] and thermodynamic[15] triflates were independently prepared and then reacted with phosphine−borane **1** under previously reported conditions. Phosphine−boranes **5** issued from the kinetic enolate and **6** issued from its regioisomer were isolated respectively in 70% and 65% yields, confirming the validity of the method (Scheme 1, Table 1, entries 12 and 13).

Following our efforts to increase the availability of varied phosphines, representative alkylarylphosphine−boranes **7** and **8** and dialkylphosphine−boranes **9** and **10** having various steric and electronic properties were submitted to this C−P cross-coupling procedure. Methylphenylphosphine−borane (**7**), which is less reactive than diphenylphosphine−borane (**1**), due to the inductive donor effect of the methyl group, was reacted with both acyclic and cyclic triflates. As anticipated, an incomplete conversion was observed under the reported conditions (DMSO, K_2CO_3, 60 °C, 2.5 h). Various conditions were then tested. The best ones are as follows: 80 °C, 6 h, K_3PO_4, with a slight excess of triflate (0.2 equiv), leading to compounds **11**−**13** with yields between 71 and 87% (Scheme 1, Table 1, entries 2, 4, and 7). It is worth noting that when K_2CO_3 is used instead of K_3PO_4, the reaction is less clean and a small amount (13%) of degradation products is observed. On standing, compound **12** crystallized from diethyl ether, affording white crystals, which were suitable for X-ray analysis (see the SI). These results prompted us to extend the study to the electron-rich phosphine−boranes **8**−**10**. Precursors **8** and **9** were easily coupled with cyclohexenyl triflate in a conventional oil bath (K_2CO_3, 80 °C, 4 h), leading to **14** and **15** in 70% and 50% yield, respectively (Scheme 1, Table 1, entries 8 and 10). Previous studies in our laboratory having shown that the microwave activation was especially relevant when using electron-rich precursors,[5a,e,f] the process was applied to phosphine−boranes **8** and **10**. Compounds **14** and **16** were efficiently obtained in less than 1 h

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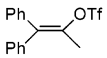
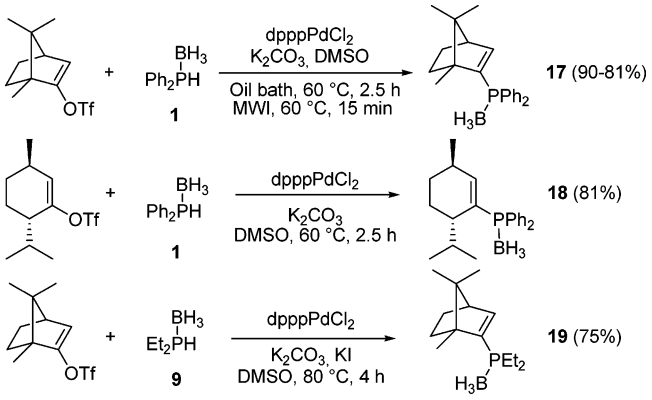
TABLE 1. C−P Cross-Coupling Reactions

Entry	Vinyltriflate	Phosphine -borane	Base	T (°C)	t	Activation	Isolated Yield (%)	Coupling product
1		**1**	K_2CO_3	60	2.5 h	Oil bath	71	**2**
2		**7**	K_3PO_4	80	6 h	Oil bath	72	**11**
3		**1**	K_2CO_3	60	2.5 h	Oil bath	82	**3**
4		**7**	K_3PO_4	80	6 h	Oil bath	87	**12**
5		**1**	K_2CO_3	60	2.5 h	Oil bath	68	**4**
6		**1**	K_2CO_3	60	15 min	MWI[a]	71	**4**
7		**7**	K_3PO_4	80	6 h	Oil bath	71	**13**
8		**8**	K_2CO_3	80	4 h	Oil bath	70	**14**
9		**8**	K_2CO_3	80	20 min	MWI[a]	77	**14**
10		**9**	K_2CO_3	80	4 h	Oil bath	50	**15**
11		**10**	K_2CO_3	80	55 min	MWI[a]	67	**16**
12		**1**	K_2CO_3	60	2.5 h	Oil bath	70	**5**
13		**1**	K_2CO_3	60	2.5 h	Oil bath	65	**6**

[a] MWI = microwave irradiation.

SCHEME 2



with reasonable yield, 77% and 67%, respectively (Scheme 1, Table 1, entries 9 and 11).

Finally, since using an enantiopure chiral triflate would lead to an enantiopure chiral phosphine, camphor[16] and menthol[17] triflates (easily available from the chiral pool) were reacted with **1** under the conditions previously defined (dpppPdCl$_2$, K_2CO_3, 2.5 h), leading to enantiopure **17** and **18** in respectively 90% and 81% yield (Scheme 2). MWI was also suitable, affording the enantiopure tertiary phosphine−borane **17** in 81% yield after only 15 min at 60 °C. On standing, compound **17** crystallized from diethyl ether, affording red crystals, which were suitable for X-ray analysis (see the SI). Camphor triflate was at last reacted with the electron-rich diethylphosphine−borane (**9**). The reaction was quite sluggish at 80 °C, and after 4 h, only 77% conversion was observed. To complete the reaction, potassium iodide (3 equiv) was added to the reaction mixture. This salt was reported to facilitate the reaction in the carbonylative coupling reaction between arylboronic acids and aryl triflates.[18] Under these conditions, a clean and complete conversion was obtained and phosphine−borane **19** was isolated satisfactorily in 75% yield after purification by flash chromatography in air.

To conclude, the catalyzed C−P cross-coupling reaction has been applied with success to a large variety of both phosphine−borane and triflate precursors, providing access to tertiary dialkyl-, alkylaryl-, and diarylvinylphosphines. Enantiopure phosphines were simply prepared by reacting enantiopure triflates derived from chiral ketones with secondary phosphine−boranes in the presence of a catalytic amount of palladium. The vinylphosphine derivatives thus prepared are easily purified by chromatography on silica gel. This efficient route complements the convenient methods available for the preparation of vinylphosphines, which are useful building blocks for organic and organometallic chemistry.

Experimental Section

Vinyl triflates[9,11a,14−17] and phosphine−borane **1**,[19] **7**,[20] **8**,[21] **9**,[22] and **10**[23] precursors were prepared according to literature procedures. All triflates were distilled under reduced pressure before use.

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C−P Cross-Coupling Reactions with Diphenylphosphine−borane (1). Method A: General Procedure for Oil-Bath Reactions. In a Schlenk tube, flushed under N_2, dpppPdCl$_2$ (5.6 mol %) is dissolved in DMSO. Vinyl triflate (1 equiv), K_2CO_3 (1.2 equiv), and phosphine−borane **1** (1 equiv) are introduced. The mixture is heated to 60 °C for 2.5 h, and vinyl triflate (0.1 equiv) is added after 1 h of reaction. After the resulting mixture was cooled to room temperature, BH_3·SMe_2 is added to complete boration of the product if a partial decomplexation has occurred during the reaction. The mixture is stirred for 30 min and hydrolyzed with degassed water. The aqueous layer is extracted with diethyl ether. The combined organic layers are dried over $MgSO_4$ and concentrated under reduced pressure. The crude product is then purified by silica gel column chromatography with toluene as the eluent.

Method B: General Procedure for Microwave Reactions. In a microwave reactor, dpppPdCl$_2$ (5.6 mol %), K_2CO_3 (1.2 equiv), and phosphine−borane **1** (1 equiv) are introduced, and the reactor is flushed under N_2. DMSO and vinyl triflate (1.1 equiv) are added. The mixture is irradiated for 15 min at 60 °C. After the mixture is cooled to room temperature, BH_3·SMe_2 is added to complete boration of the product if a partial decomplexation has occurred during the reaction. The mixture is stirred for 30 min and hydrolyzed with degassed water. The aqueous layer is extracted with diethyl ether. The combined organic layers are dried over $MgSO_4$ and concentrated under reduced pressure. The crude product is then purified by silica gel column chromatography with toluene as the eluent.

Synthesis of (3,3-Dimethylbut-1-en-2-yl)diphenylphosphine−borane (2). Method A. dpppPdCl$_2$ (25 mg, 0.04 mmol), DMSO (1.9 mL), 3,3-dimethylbut-1-en-2-yl trifluoromethanesulfonate (143 μL, 0.75 mmol), K_2CO_3 (125 mg, 0.9 mmol), diphenylphosphine−borane (**1**) (150 mg, 0.75 mmol), degassed water (1.5 mL), diethyl ether (3 × 2 mL). Yield: 71% (150 mg). Red powder. Mp: 66 °C. R_f = 0.72. ^{31}P NMR (161.9 MHz, $CDCl_3$): δ 23.1−21.8 (m). ^{1}H NMR (400.1 MHz, $CDCl_3$): δ 7.67−7.61 (m, 4H), 7.44−7.42 (m, 6H), 6.08 (d, 1H, $^3J_{HP}$ = 32.4 Hz), 5.17 (d, 1H, $^3J_{HP}$ = 16.8 Hz), 1.82−0.82 (m, 3H), 1.23 (s, 9H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 150.3 (d, $^1J_{CP}$ = 37.2 Hz), 133.1 (d, $^2J_{CP}$ = 9.2 Hz), 131.0 (d, $^4J_{CP}$ = 2.2 Hz), 129.7 (d, $^1J_{CP}$ = 57.7 Hz), 129.0 (d, $^2J_{CP}$ = 2.9 Hz), 128.6 (d, $^3J_{CP}$ = 10.1 Hz), 38.7 (d, $^2J_{CP}$ = 13.8 Hz), 30.9 (d, $^3J_{CP}$ = 3.4 Hz). ^{11}B NMR (128.4 MHz, $CDCl_3$): δ −30.2 to −35.5 (m). Anal. Calcd for $C_{18}H_{24}BP$ (282.2): C, 76.62; H, 8.57. Found: C, 76.25; H, 8.88.

C−P Cross-Coupling Reactions with Diethylphosphine−Borane (9). Synthesis of ((1*R*,4*R*)-1,7,7-trimethylbicyclo[2.2.1]-hept-2-en-2-yl)diethylphosphine−Borane (19). In a Schlenk tube, flushed under N_2, dpppPdCl$_2$ (19 mg, 0.03 mmol, 5.6 mol %) is dissolved in DMSO (1 mL). KI (288 mg, 1.73 mmol, 3 equiv), (1*R*,4*R*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-en-2-yl trifluoromethanesulfonate (125 μL, 0.58 mmol), K_2CO_3 (96 mg, 0.69 mmol, 1.2 equiv), and phosphine−borane **9** (60 μL, 0.58 mmol) are introduced. The mixture is heated to 80 °C for 4 h, and (1*R*,4*R*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-en-2-yl trifluoromethanesulfonate (13 μL, 0.06 mmol, 0.1 equiv) is added after 2 h of reaction. After the resulting mixture is cooled to room temperature, BH_3·SMe_2 is added to complete boration of the product if a partial decomplexation has occurred during the reaction. The mixture is stirred for 30 min and hydrolyzed with 0.5 mL of degassed water. The aqueous layer is extracted with diethyl ether (3 × 2 mL). The combined organic layers are dried over $MgSO_4$ and concentrated under reduced pressure. The crude product is then purified by silica gel column chromatography with toluene as the eluent (R_f = 0.61), giving a yellow powder (103 mg, 75%). Mp: 32 °C, $[\alpha]^{25}_D$ = −51.8 (*c* 0.695, $CHCl_3$). ^{31}P NMR (161.9 MHz, $CDCl_3$): δ 12.5 (q, $^1J_{PB}$ = 63.9 Hz). ^{1}H NMR (400.1 MHz, $CDCl_3$): δ 6.71 (dd, 1H, $^3J_{HP}$ = 9.6 Hz, $^3J_{HH}$ = 3.6 Hz), 2.52−2.46 (m, 1H), 1.96−1.86 (m, 1H), 1.86−1.67 (m, 4H), 1.65−1.56 (m, 1H), 1.27 (s, 3H), 1.27−1.18 (m, 1H), 1.14 (dt, 3H, $^3J_{HP}$ = 14.8 Hz, $^3J_{HH}$ = 7.6 Hz), 1.10 (dt, 3H, $^3J_{HP}$ = 14.4 Hz, $^3J_{HH}$ = 7.6 Hz), 1.04−0.95 (m, 1H), 0.83 (s, 3H), 0.82 (s, 3H), 0.53 (q, 3H, $^1J_{HB}$ = 94.6 Hz). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 150.7 (d, $^2J_{CP}$ = 5.2 Hz), 135.7 (d, $^1J_{CP}$ = 45.5 Hz), 57.7 (d, $^2J_{CP}$ = 3.3 Hz), 57.5 (d, $^3J_{CP}$ = 5.6 Hz), 53.2 (d, $^3J_{CP}$ = 9.6 Hz), 31.6 (s), 24.2 (d, $^4J_{CP}$ = 2.8 Hz), 19.6 (s), 19.2 (s), 17.1 (d, $^1J_{CP}$ = 37.8 Hz), 15.8 (d, $^1J_{CP}$ = 38.7 Hz), 13.1 (s), 7.1 (d, $^2J_{CP}$ = 3.3 Hz), 6.9 (s). ^{11}B NMR (128.4 MHz, $CDCl_3$): δ −37.4 (dq, $^1J_{BP}$ = 63.9 Hz, $^1J_{BH}$ = 94.6 Hz). Anal. Calcd for $C_{14}H_{28}BP$ (238.2): C, 70.60; H, 11.85. Found: C, 70.48; H, 12.23.

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Supporting Information Available: General experimental information, NMR data of **3**−**6** and **11**−**18**, NMR spectra of **2**−**6** and **11**−**19**, and X-ray data of **4**, **12**, and **17**. This material is available free of charge via the Internet at http://pubs.acs.org.

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