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Regio- and Stereoselective Hydrophosphination Reactions of Alkynes with Phosphine−Boranes: Access to Stereodefined Vinylphosphine Derivatives

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Received March 17, 2003

Vinylphosphine−borane complexes are easily synthesized by regio- and stereoselective hydrophosphination of terminal alkynes with use of secondary phosphine−boranes as hydrophosphinating agent. The regioselectivity of the reaction is efficiently controlled by the choice of the activation process: thermal or metal catalyst activation. The vinylphosphine derivatives are purified by chromatography on silica gel. Scalability of the process is demonstrated on a gram scale. This simple route should promote the use of vinylphosphines as building blocks for organic and organometallic chemistry.

Introduction

The addition of phosphorus−hydrogen bonds to unsaturated carbon linkages is, in terms of synthetic value and atom economy, a very promising process for the construction of carbon−phosphorus bonds. Compared to the addition of other heteroatom hydrogen bonds (e.g., hydrosilylation,[1] hydroboration,[2] hydrostannation,[3]...), hydrophosphination has been much less studied.[4] Several published strategies, although not without merit, are limited to the addition of a P−H bond to activated species such as carbonyl derivatives,[5] imines,[6] or Michael acceptors.[7] Efficient P−H additions to unactivated species (alkenes, alkynes, allenes) are comparatively rather rare and mainly proceed with diphenylphosphine-oxides,[8a−c] phosphonate,[8c−e] or phosphite derivatives[8a,9] as hydrophosphinating agents. With free phosphines, addition onto alkynes has been achieved under basic,[10−12] radical,[13,14] or thermal activation.[15] However, since severe conditions are most of the time required,[10,11a,13−15] a mixture of products is often obtained, resulting in moderate yields.[10a,11b−c,12,13] The feasibility of the catalytic hydrophosphination of alkynes via a metal-catalyzed P−H bond activation has been shown in a few recent reports. Particularly, organolanthanide complexes are able to promote either an intramolecular[16] or an intermolecular[17] hydrophosphination−cyclization process. Palladium and nickel were also used to perform the addition

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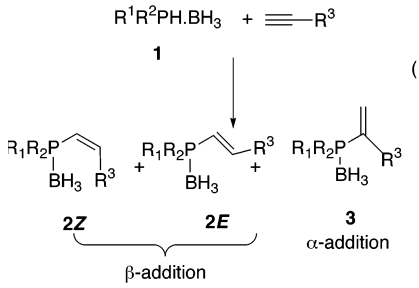
10.1021/jo030096q CCC: $25.00
Published on Web 08/05/2003

of diphenylphosphine to alkynes.[18] Despite their interests, all these methodologies suffer from lack of generality (diphenylphosphine is often the only source of phosphorus[10a,b,11,12,13b,c,17,18]) and from low to moderate selectivities.[11,12,13a,16,18] Consequently, an easy and rather general process allowing the conversion of inexpensive alkynes into the desired vinyl-phosphines in good yields and with high selectivities still represents a challenging and highly desirable transformation.

In a preceding contribution, we reported the synthesis of various functionalized secondary and tertiary phosphines by hydrophosphination of activated alkenes using phosphine−boranes as hydrophosphinating agents.[19,20] The P−H addition was performed under very mild conditions (room temperature and the absence of catalyst) because of the borane-induced activation of the P−H bond. The phosphine derivatives thus prepared were easily purified by chromatography on silica gel in air. The deprotection was performed by simple treatment of the borane complex with a Lewis base (DABCO).[21] Unfortunately, similar reactions with "nonactivated" unsaturated substrates proved to be inefficient. We were nevertheless able to overcome this problem using an activation source. The present contribution describes the hydrophosphination reaction of alkynes under thermal or metal catalyst activation using secondary phosphine−boranes as hydrophosphinating agents. Observations on factors affecting the scope and the regio- and the stereoselectivity of this transformation are discussed.

Results and Discussion

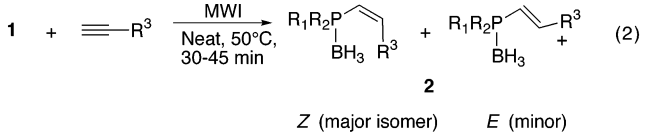
We examined the reaction of secondary phosphine−boranes **1** with terminal alkynes. The addition is expected to afford 2 types of alkenylphosphines via addition of the phosphorus atom either to the terminal carbon of the alkyne (*β*-addition leading to compound **2** with a *Z* or *E* stereochemistry) or to the internal carbon (α-addition leading to compound **3**) (eq 1). Interestingly, from a



synthetic point of view, we were able to control the regioselectivity of the process by using two different activation processes. Under thermal activation, only the *β*-adduct is obtained (anti-Markovnikov addition) and with palladium catalyst activation, the α-adduct is obtained (Markovnikov addition).

Thermal Activation. We first examined the reaction of diphenylphosphine−borane with a simple alkyne (e.g. 1-octyne) as a basis for our initial model. The protocol was then extended to various alkynes and secondary phosphine−boranes.

Diphenylphosphine−borane was added to an excess of octyne (i.e. the minimum to dissolve the solid phosphine) in the absence of catalyst. The mixture was then heated under microwave irradiation (MWI) at 50 °C (eq 2). The



(2)

2a : R^1 = Ph, R^2 = Ph, R^3 = n-C_6H_{13},

2b : R^1 = Ph, R^2 = Ph, R^3 = Ph,

2c : R^1 = Ph, R^2 = Ph, R^3 = $(CH_2)_2OH$

2d : R^1 = Ph, R^2 = Ph, R^3 = CH_2OCH_3

2e : R^1 = Me, R^2 = Ph, R^3 = n-C_6H_{13},

2f : R^1 = tBu, R^2 = Ph, R^3 = n-C_6H_{13}

use of microwave activation was found to be the best to achieve a fast and efficient reaction, the yields from the oil bath reaction being lower. Remarkably, use of a nitrogen atmosphere was not required owing to the reduced reaction time. After 30 min, the ^{31}P NMR spectrum confirmed a complete disappearance of the starting materials. Analysis of the crude product by ^1H NMR indicated that the phosphorus atom had attacked the terminal carbon atom of octyne (*β*-addition) with a very high regioselectivity leading to vinylphosphine complex **2a**. No trace of the other regioisomer (α-adduct) could be detected. As far as stereochemistry is concerned, the *Z* isomer was obtained as the major isomer with a high stereoselectivty (*Z*/*E* ratio higher than 95/5). Purification by column chromatography through silica gel (toluene) afforded pure (*Z*)-1-(diphenylphosphine−borane)-oct-1-ene **2a** in good yield as a colorless oil (Table 1, entry 1). The Z configuration was evidenced by the coupling constant of vinylic protons (J = 12,3 Hz).

Encouraged by these results, the microwave reaction was applied to other alkynes exemplifying that the hydrophosphination process is quite general (eq 2). As demonstrated in Table 1, both aliphatic (entry 1) and oxygen-functionalized alkynes (entries 3 and 4) reacted with diphenylphosphine−borane to afford the corresponding adducts by regioselective attack of the phosphorus atom on the terminal carbon atom of the triple bond. With oxygen-containing alkynes (entries 3 and 4), the hydrophosphination required a prolonged reaction time (an additional 15 min) leading to the desired product together with a small amount of the decomplexed precursor, which oxidizes slowly in the reaction media. An exceptional behavior was observed with phenylacetylene (entry 2), which polymerizes in the reaction conditions. As exemplified by runs 5 and 6, alkylarylphosphine−boranes were also used. If methylphenylphosphine−borane (entry 5) was as reactive as diphenylphosphine−borane, *tert*-butylphenylphosphine−borane (entry 6) was

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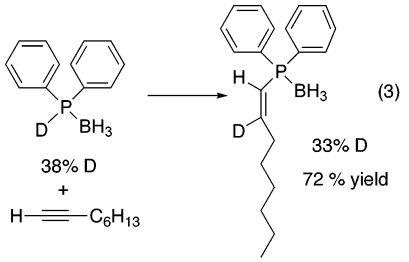
TABLE 1. Reaction Conditions, Yields, and Stereoselectivity for Microwave-Induced Hydrophosphination of Alkynesby Phosphine−Boranes 1

entry	$R^1R^2PH.BH_3$	$R^3C{\equiv}C-H$	time[a] (temp)[b]	compd	yield (%)[c]	*Z*/*E* ratio
1	$R^1 = R^2 = Ph$	$R^3 = n\text{-}C_6H_{13}$	30 (50)	**2a**	76	>95/5
2	$R^1 = R^2 = Ph$	$R^3 = Ph$	30 (50)	**2b**	0	
3	$R^1 = R^2 = Ph$	$R^3 = (CH_2)_2OH$	45 (50)	**2c**	49	>95/5
4	$R^1 = R^2 = Ph$	$R^3 = CH_2OCH_3$	45 (50)	**2d**	33	>95/5
5	$R^1 = Ph$, $R^2 = Me$	$R^3 = n\text{-}C_6H_{13}$	45 (70)	**2e**	82	80/20
6	$R^1 = Ph$, $R^2 = t$Bu	$R^3 = n\text{-}C_6H_{13}$	45 (80)	**2f**	49	70/30

[a] Time in min. [b] Temperature in °C. [c] After purification by column chromatography.

less reactive. This low reactivity is presumably due to the steric effect of the *tert*-butyl group. With both alkylphenylphosphine−boranes, the reaction proceeds again with an excellent regioselectivity (anti-Markovnikov type) but with a slightly lower stereoselectivity [*Z*/*E* ratio = 70/30 (entry 6) for R^2 = *tert*-butyl and 80/20 (entry 5) for R^2 = methyl].

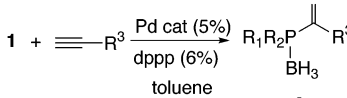
Hydrophosphination reactions were also performed with deuterated phosphine−borane complexes ($Ph_2PH{\cdot}BD_3$ and $Ph_2PD{\cdot}BH_3$). From these experiments, confirmation was made that hydroboration did not compete with hydrophosphination. Reactions involving $Ph_2PH{\cdot}BD_3$ did not show any incorporation of deuterium in the alkene moiety of the vinylphosphine derivatives, indicating that the boron hydrogens are not transferred. With $Ph_2PD{\cdot}BH_3$ (D content 38%) and oct-1-yne, adduct **2a**, in which the deuterium content at the C-2 position was 33%, was obtained in good yield (eq 3). Deuterium incorporation did not occur at the other sp_2 carbon of **2a** in good agreement with the observed regioselectivity.



(3)

Metal-Catalyzed Activation. Diphenylphosphine−borane and octyne (1.1 equiv) were reacted under nitrogen in the presence of a palladium(0) catalyst (5 mol %). Among the various investigated conditions (temperature, catalyst, ...), we found that hydrophosphination of octyne proceeded cleanly at 50 °C to give vinylic phosphine−borane **3a** in good yield when the catalytic system used was composed of tris(dibenzylideneacetone)dipalladium [$Pd_2(dba)_3$] and 1,3-bis(diphenylphosphino)propane (dppp). A brief variation of solvents showed that toluene was the most suited media. Under these conditions, only the α-adduct was obtained. No trace of the *β*-isomer was detected by NMR analysis of the crude product, indicating that the phosphorus atom attacks the internal carbon atom of octyne with a very high regioselectivity (eq 4). The pure vinylphosphine−borane **3a** was obtained as a colorless oil after purification by column chromatography through silica gel (toluene).

Palladium catalyst is essential for the addition process since no reaction occurs in its absence. In the first trials, the catalytic system used was composed of 5% of $Pd_2(dba)_3$ and 10% of dppp. In general, Pd(0) complexes such



(4)

3

3a: R^1 = Ph, R^2 = Ph, R^3 = n-C_6H_{13},
3b: R^1 = Ph, R^2 = Ph, R^3 = Ph,
3c: R^1 = Ph, R^2 = Ph, R^3 = $(CH_2)_2OH$
3d: R^1 = Ph, R^2 = Ph, R^3 = CH_2OCH_3
3e: R^1 = Ph, R^2 = Me, R^3 = n-C_6H_{13}
3f: R^1 = Ph, R^2 = Ph, R^3 = c-C_6H_{10},
3g: R^1 = Ph, R^2 = Me, R^3 = Ph

as tetrakis(triphenylphosphine)palladium ($Pd(PPh_3)_4$), $Pd_2(dba)_3$ with various bis-phosphines (dppp, binap), or readily reducible Pd(II) species such as palladium acetate [$Pd(OAc)_2$] with various phosphines are effective in promoting the hydrophosphination reaction. The efficiency of $Pd(OAc)_2$ reflects the ability to form the active Pd(0) in the media starting from a Pd(II). It should be noticed that the amount of catalyst could be lowered to 4% without any loss in activity. However, the catalyst loading has not been optimized. Whatever the catalyst used, only the α-adduct is formed, indicating that the regioselectivity is independent of the nature of the catalyst. Gram scale reaction gave the same high yield and the same selectivity.

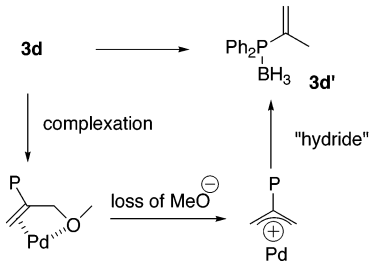
This Pd-catalyzed hydrophosphination was readily applicable to other terminal alkynes, thus proving the generality of the methodology. As demonstrated in Table 2, aliphatic (entry 1), aromatic terminal alkynes (entry 2), as well as derivatives bearing oxygen functionalities (entries 3 and 4), reacted efficiently with $Ph_2PH{\cdot}BH_3$ affording the corresponding adducts (colorless or pale yellow oils) in reasonable to good yields with the same high regioselectivity (eq 3). However, the rate of the reaction was significantly slower when methylpropargyl ether (entry 4) was used instead of oct-1-yne (entry 1). Interestingly, under the reaction conditions used, an olefinic bond is less reactive with respect to hydrophosphination. Indeed, 1-ethynylcyclohexene (entry 6) underwent selective addition at the triple bond. Secondary *P*-alkylarylphosphine−borane derivatives could also be used as hydrophosphinating agents (entries 5 and 7). Good yields and excellent regioselectivity were obtained although the rate of the reaction was somewhat lower than that observed with diphenylphosphine−borane and octyne (entry 1). Low amounts of side-products were sometimes observed depending on the nature of the catalyst. When $Pd(PPh_3)_4$ was used, a ^{31}P NMR signal at 22 ppm corresponding to triphenylphosphine−borane was detected, indicating a slow borane exchange between

TABLE 2. Reaction Conditions and Yields for Metal-Catalyzed Hydrophosphination of Alkynes by Phosphine−Boranes 1

entry	$R^1R^2PH.BH_3$	$R^3C{\equiv}C-H$	time[b] (temp)[c]	Pd source (%) ligand (%)	compd	yield (%)[a]
1	$R^1 = R^2 = Ph$	$R^3 = n\text{-}C_6H_{13}$	10 (40)	$Pd(OAc)_2$(5%) dppp (10%)	**3a**	84
2	$R^1 = R^2 = Ph$	$R^3 = Ph$	15 (50)	$Pd(PPh_3)$ (5%)	**3b**	49
3	$R^1 = R^2 = Ph$	$R^3 = (CH_2)_2OH$	15 (50)	$Pd(OAc)_2$ (4%) binap[d](8%)	**3c**	71
4	$R^1 = R^2 = Ph$	$R^3 = CH_2OCH_3$	50 (50)	$Pd_2(dba)_3$ (5%) dppp (6%)	**3d**	73
5	$R^1 = Ph$, $R^2 = Me$	$R^3 = n\text{-}C_6H_{13}$	35 (50)	$Pd(OAc)_2$ (5%) dppp (10%)	**3e**	85
6	$R^1 = R^2 = Ph$	$R^3 = c\text{-}C_6H_9$	14 (50)	$Pd(OAc)_2$ (5%) Binap (10%)	**3f**	60
7	$R^1 = Ph$, $R^2 = Me$	$R^3 = Ph$	14 (50)	$Pd(OAc)_2$ (5%) bdpp[e](10%)	**3g**	53

[a] After purification by column chromatography. [b] Time in hours. [c] Temperature in °C. [d] *rac*-2,2′-Bis(diphenylphosphino)-1,1′-binaphthyl. [e] 2,4-Bis(diphenylphosphino)pentane.

SCHEME 1. Proposed Mechanism for the Formation of 3d′



the starting phosphine−borane and the weakly coordinated PPh_3. With $Pd_2(dba)_3$, the ^{31}P NMR signal observed at 16 ppm is consistent with the hydrophosphination adduct of dba. To avoid these side-products, it was found more reliable to use, when it was possible, palladium acetate [$Pd(OAc)_2$] with a bidentate phosphine such as 1,3-bis(diphenylphosphino)propane (dppp). The most efficient catalyst for each alkyne is indicated in Table 2.

With methylpropargyl ether (entry 4), the formation of a side-product was observed. After isolation, spectral identification revealed the formation of 1-diphenylphosphine−borane−prop-1-ene **3d′** (Scheme 1). This compound may be formed by methanol elimination from the vinylic adduct since its formation occurs only after that of **3d**. It is possible that palladium plays an important role in this transformation by complexing **3d** and favoring the formation of a π-allylpalladium complex. The final product could be obtained by attack of a hydride, which might come from the borane or from a palladium-hydride source (Scheme 1).

Conclusion

We have successfully demonstrated that hydrophosphination of simple alkynes with secondary phosphine−borane reagents can provide a facile route for the construction of vinylphosphine derivatives. These compounds, which belong to a class of interest as ligand building blocks for homogeneous catalysis,[22] are much less readily available than the corresponding arylphosphines. The hydrophosphination reactions are performed under mild conditions and proceed with an excellent regio- and stereocontrol allowing the selective preparation of either the α-adduct (metal catalyzed reaction) or the *Z*-*β*-adduct (thermal activation) in gram scale. The purification of the vinylphosphine derivatives is easily performed by chromatography on silica gel. Further explorations of the scope, selectivity, and mechanism, as well as synthetic applications of this methodology, are currently underway.

Experimental Section

Caution: Phosphines are highly oxidizable and potentially toxic molecules. All reactions should be carried out in a well-ventilated hood.

Typical Procedure for Thermally Induced Hydrophosphination Reactions. The phosphine−borane and the alkyne were placed in a quartz reaction vessel. The reactor was submitted to microwave irradiation and let cool to room temperature. The crude product was then purified by silica gel column chromatography.

Analytical Data for Products 2a−f Described in Table 1: (*Z*)-1-(Boranatodiphenylphosphino)-oct-1-ene 2a. A 0.50-mmol (100 mg) sample of diphenylphosphine−borane was dissolved in 2.50 mmol (370 μL) of oct-1-yne and submitted to microwave irradiation for 0.5 h at 50 °C. The crude product was purified by column chromatography with toluene as eluent (R_f 0.80). After evaporation of the solvent, 118 mg (76%) of a colorless oily product was obtained (*Z*/*E* ratio greater than 95/5). ^{31}P NMR (121 MHz, $CDCl_3$) δ 8.4 ($^1J_{PB}$ = 56 Hz). ^1H NMR (300 MHz, $CDCl_3$) δ 7.75 (m, 4H), 7.50 (m, 6H), 6.65 (ddt, $^3J_{HPtrans}$ = 36.3 Hz, $^3J_{HHcis}$ = 12.3 Hz, $^3J_{HH}$ = 7.7 Hz, 1H), 6.00 (ddt, $^2J_{HP}$ = 12.2 Hz, $^3J_{HHcis}$ = 12.2 Hz, $^3J_{HH}$ = 1.5 Hz, 1H), 2.25 (m, 2H), 1.35 (m, 2H), 1.20 (m, 6H), 1.00 (qm, $^1J_{BH}$ = 95 Hz, 3H), 0.90 (t, $^3J_{HH}$ = 6.7 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.4 (ddm, $^1J_{CH}$ = 153 Hz, $^2J_{CP}$ = 4.3 Hz), 132.3 (ddm, $^1J_{CH}$ = 158 Hz, $^2J_{CP}$ = 9.6 Hz), 131.1 (dm, $^1J_{CP}$ = 58 Hz), 131.0 (dtdm, $^1J_{CH}$ = 157 Hz. $^2J_{CH}$ = 8.1 Hz, $^4J_{CP}$ = 2.4 Hz), 128.8 (ddm, $^1J_{CH}$ = 161 Hz, $^3J_{CP}$ = 10.2 Hz), 118.4 (ddm, $^1J_{CH}$ = 158 Hz, $^1J_{CP}$ = 55.6 Hz), 31.6 (tm, $^1J_{CH}$ = 125 Hz), 31.5 (tdm, $^1J_{CH}$ = 125 Hz, $^3J_{CP}$ = 7.8 Hz), 28.8 (tm, $^1J_{CH}$ = 125 Hz), 28.6 (tdm, $^1J_{CH}$ = 125 Hz, $^4J_{CP}$ = 1.2 Hz), 22.5 (tm, $^1J_{CH}$ = 125 Hz), 14.1 (qm, $^1J_{CH}$ = 125 Hz). ^{11}B NMR (128 MHz, $CDCl_3$) δ −34.0 (qd, $^1J_{BH}$ = 95 Hz, $^1J_{BP}$ = 56 Hz). HRMS calcd for $C_{20}H_{25}P$ ([M − BH_3]$^{+\bullet}$) 296.1694, found 296.1699. Anal. Calcd for $C_{20}H_{28}BP$: C, 77.43; H, 9.10. Found: C, 77.40; H, 9.35.

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(*Z*)-4-(Boranatodiphenylphosphino)-but-3-Enol 2c. A 0.5-mmol (100 mg) sample of diphenylphosphine−borane was dissolved in 2.50 mmol (190 μL) of 4-butynol and submitted to microwave irradiation for 0.75 h at 50 °C. The crude product was purified by column chromatography with dichloromethane−methanol 97−3 as eluent (R_f 0.50). After evaporation of the solvent 66 mg (49%) of a colorless oily product was obtained (*Z*/*E* ratio greater than 95/5). ^{31}P NMR (121 MHz, $CDCl_3$) δ 8.5 (m). ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.60 (m, 4H), 7.40 (m, 6H), 6.65 (ddt, $^3J_{HPtrans}$ = 36.3 Hz, $^3J_{HHcis}$ = 12.3 Hz, $^3J_{HH}$ = 7.7 Hz, 1H), 6.05 (ddt, $^2J_{HP}$ = 11 Hz, $^3J_{HHcis}$ = 11 Hz, $^3J_{HH}$ = 1.4 Hz, 1H), 3.60 (t, $^3J_{HH}$ = 6.2 Hz, 2H), 2.45 (m, 2H), 2.35 (s, 1H), 1.00 (qm, $^1J_{BH}$ = 100 Hz, 3H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 150.0 (ddm, $^1J_{CH}$ = 154 Hz, $^2J_{CP}$ = 4.3 Hz), 132.6 (ddm, $^1J_{CH}$ = 163 Hz, $^2J_{CP}$ = 9.8 Hz), 131.5 (ddm, $^1J_{CH}$ = 161 Hz, $^4J_{CP}$ = 2.0 Hz), 131.1 (ddm, $^1J_{CP}$ = 58.7 Hz), 129.3 (ddm, $^1J_{CH}$ = 163 Hz, $^3J_{CP}$ = 10.2 Hz), 121.3 (ddm, $^1J_{CH}$ = 153 Hz, $^1J_{CP}$ = 55.0 Hz), 61.6 (t, $^1J_{CH}$ = 144 Hz), 34.9 (td, $^1J_{CH}$ = 145 Hz, $^3J_{CP}$ = 7.4 Hz). ^{11}B NMR (128 MHz, $CDCl_3$) δ −34.5 (m). HRMS calcd for $C_{16}H_{17}OP$ ($[M - BH_3]^{+\bullet}$) 256.1017, found 256.1025.

(*Z*)-1-(Boranatodiphenylphosphino)-3-methoxypropene 2d. A 1-mmol (200 mg) sample of diphenylphosphine−borane was dissolved in 5 mmol (422 μL) of methylpropargyl ether and submitted to microwave irradiation for 0.75 h at 50 °C. The crude product was purified by column chromatography with dichloromethane as eluent (R_f 0.50). After evaporation of the solvent 81 mg (33%) of a colorless oily product was obtained (*Z*/*E* ratio greater than 95/5). ^{31}P NMR (101 MHz, $CDCl_3$) δ 9.4 (m). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (m, 4H), 7.45 (m, 6H), 6.70 (ddt, $^3J_{HPtrans}$ = 36.2 Hz, $^3J_{HHcis}$ = 13.0 Hz, $^3J_{HH}$ = 6.0 Hz, 1H), 6.15 (ddt, $^3J_{HHcis}$ = 12.9 Hz, $^2J_{HP}$ = 9.9 Hz, $^4J_{HH}$ = 1.8 Hz, 1H), 4.10 (ddd, $^3J_{HH}$ = 5.9 Hz, $^4J_{HP}$ = 2.2 Hz, $^4J_{HH}$ = 2.2 Hz, 2H), 3.20 (s, 3H), 1.00 (qm, $^1J_{BH}$ = 100 Hz, 3H). ^{13}C NMR (63 MHz, $CDCl_3$) δ 149.5 (d, $^2J_{CP}$ = 3.1 Hz), 132.6 (d, $^2J_{CP}$ = 9.4 Hz), 131.6 (d, $^4J_{CP}$ = 2.5 Hz), 130.6 (d, $^1J_{CP}$ = 58.5 Hz), 129.3 (d, $^3J_{CP}$ = 10.7 Hz), 120.9 (d, $^1J_{CP}$ = 53.5 Hz), 70.4 (d, $^3J_{CP}$ = 6.9 Hz), 58.9 (s). ^{11}B NMR (128 MHz, $CDCl_3$) δ −34.2 (m). HRMS calcd for $C_{16}H_{17}OP$ ($[M - BH_3]^{+\bullet}$) 256.1017, found 256.0981.

1-(Boranatomethylphenylphosphino)-oct-1-ene 2e. A 0.40-mmol (55 μL) sample of methylphenylphosphine−borane was dissolved in 2.00 mmol (296 μL) of oct-1-yne and submitted to microwave irradiation for 0.75 h at 70 °C. The crude product was purified by column chromatography with toluene as eluent (R_f 0.65). After evaporation of the solvent 81 mg (82%) of a colorless oily product was obtained (*Z*/*E* ratio of 80/20). The two stereoisomers could not be separated. HRMS calcd for $C_{15}H_{26}BP$ ($[M]^{+\bullet}$) 248.1865, found 248.1842; HRMS calcd for $C_{15}H_{23}P$ ($[M - BH_3]^{+\bullet}$) 234.1537, found 234.1524. **(*Z*)-1-(Boranatomethylphenylphosphino)-oct-1-ene 2e.** ^{31}P NMR (101 MHz, $CDCl_3$) δ 0.0 (m). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (m, 2H), 7.45 (m, 3H), 6.50 (ddt, $^3J_{HPtrans}$ = 35.44 Hz, $^3J_{HHcis}$ = 12.21 Hz, $^3J_{HH}$ = 7.73 Hz 1H), 5.80 (ddt, $^2J_{HP}$ = 12.3 Hz, $^3J_{HHcis}$ = 12.3 Hz, $^4J_{HH}$ = 1.19 Hz, 1H), 2.20 (m, 2H), 1.60 (d, $^2J_{HP}$ = 10.13 Hz, 3H), 1.30 (m, 2H), 1.25 (m, 2H), 1.20 (m, 4H), 1.00 (qm, $^1J_{BH}$ = 97 Hz, 3H), 0.85 (t, $^3J_{HH}$ = 6.92 Hz, 3H). ^{13}C NMR (63 MHz, $CDCl_3$) δ 150.5 (d, $^2J_{CP}$ = 3.8 Hz), 129.8 (d, $^4J_{C-P}$ = 55.3 Hz), 129.4 (d, $^2J_{CP}$ = 9.4 Hz), 129.0 (d, $^4J_{CP}$ = 2.5 Hz), 126.8 (d, $^3J_{CP}$ = 10.1 Hz), 117.1 (d, $^1J_{CP}$ = 54.1 Hz), 29.6 (s), 29.2 (d, $^3J_{CP}$ = 8.1 Hz), 26.8 (s), 26.7 (s), 20.5 (s), 12.2 (d, $^1J_{CP}$ = 42.5 Hz), 12.0 (s). ^{11}B NMR (128 MHz, $CDCl_3$) δ −33.9 (qd, $^1J_{BH}$ = 97 Hz, $^1J_{BP}$ = 59 Hz). **(*E*)-1-(Boranatomethylphenylphosphino)-oct-1-ene 2e.** ^{31}P NMR (101 MHz, $CDCl_3$) δ 5.1 (m). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (m, 2H), 7.45 (m, 3H), 6.60 (ddt, $^3J_{HPcis}$ = 18.7 Hz, $^3J_{HHtrans}$ = 16.7 Hz, $^3J_{HH}$ = 6.58 Hz 1H), 5.90 (ddt, $^3J_{HHtrans}$ = 16.64 Hz, $^2J_{HP}$ = 12.66 Hz, $^4J_{HH}$ = 1.46 Hz, 1H), 2.20 (m, 2H), 1.60 (d, $^2J_{HP}$ = 10.13 Hz, 3H), 1.30 (m, 2H), 1.25 (m, 2H), 1.20 (m, 4H), 1.00 (qm, $^1J_{BH}$ = 100 Hz, 3H), 0.90 (t, $^3J_{HH}$ = 6.92 Hz, 3H). ^{13}C NMR (63 MHz, $CDCl_3$) δ 149.6 (d, $^2J_{CP}$ = 6.3 Hz), 129.2 (d, $^2J_{CP}$ = 9.4 Hz), 129.0 (d, $^1J_{CP}$ = 55 Hz), 128.9 (d, $^4J_{CP}$ = 3 Hz), 126.8 (d, $^3J_{CP}$ = 10.1 Hz), 117.5 (d, $^1J_{CP}$ = 56.0 Hz), 32.8 (d, $^3J_{CP}$ = 14.8 Hz), 29.6 (s), 26.8 (s), 25.0 (s), 20.5 (s), 12.0 (s), 10.2 (d, $^1J_{CP}$ = 41.1 Hz). ^{11}B NMR (128 MHz, $CDCl_3$) δ −35.9 (m).

1-(Boranato-*t*-butylphenylphosphino)-oct-1-ene 2f. A 0.50-mmol (98 mg) sample of *tert*-butylphenylphosphine−borane was dissolved in 2.50 mmol (283 μL) of oct-1-yne and submitted to microwave irradiation for 0.75 h at 80 °C. The crude product was purified by column chromatography with toluene as eluent (R_f 0.70). After evaporation of the solvent 71 mg (49%) of a colorless oily product was obtained (*Z*/*E* ratio of 70/30). The two stereoisomers could not be separated. HRMS calcd for $C_{18}H_{29}P$ ($[M - BH_3]^{+\bullet}$) 276.2007, found 276.2000. **(*Z*)-1-(Boranato-*tert*-butylphenylphosphino)oct-1-ene 2f.** ^{31}P NMR (121 MHz, $CDCl_3$) δ 23.0 (m). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (m, 2H), 7.40 (m, 3H), 6.60 (ddt, $^3J_{HPtrans}$ = 33.4 Hz, $^3J_{HHcis}$ = 12.5 Hz, $^3J_{HH}$ = 7.6 Hz, 1H), 5.95 (ddt, $^3J_{HHcis}$ = 12.3 Hz, $^2J_{HP}$ = 12.3 Hz, $^4J_{HH}$ = 1.0 Hz, 1H), 2.15 (m, 2H), 1.45 (m, 2H), 1.30 (m, 2H), 1.15 (d, $^2J_{HP}$ = 13.7 Hz, 9H), 1.10 (m, 4H), 1.00 (qm, $^1J_{BH}$ = 98 Hz, 3H), 0.80 (t, $^3J_{HH}$ = 7.1 Hz, 3H). ^{13}C NMR (63 MHz, $CDCl_3$) δ 152.0 (d, $^2J_{CP}$ = 2.5 Hz), 131.8 (d, $^2J_{CP}$ = 8.2 Hz), 129.1 (d, $^4J_{CP}$ = 2.5 Hz), 126.3 (d, $^1J_{CP}$ = 49 Hz), 126.2 (d, $^3J_{CP}$ = 10.1 Hz), 112.1 (d, $^1J_{CP}$ = 53.5 Hz), 30.1 (d, $^3J_{CP}$ = 6.4 Hz), 29.7 (d, $^2J_{CP}$ = 2 Hz), 27.2 (d, $^1J_{CP}$ = 36.0 Hz), 27.0 (s), 26.6 (s), 23.4 (d, $^4J_{CP}$ = 2.1 Hz), 20.7 (s), 12.2 (s). ^{11}B NMR (128 MHz, $CDCl_3$) δ −36.8 (qd, $^1J_{BH}$ = 98 Hz, $^1J_{BP}$ = 55 Hz).

(*E*)-1-(Boranato-*tert*-butylphenylphosphino)oct-1-ene 2f. ^{31}P NMR (121 MHz, $CDCl_3$) δ 25.5 (m). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (m, 2H), 7.40 (m, 3H), 6.90 (ddt, $^3J_{HPcis}$ = 16.8 Hz, $^3J_{HHtrans}$ = 16.8 Hz, $^3J_{HH}$ = 6.7 Hz, 1H), 6.25 (ddt, $^3J_{HHtrans}$ = 16.6 Hz, $^2J_{HP}$ = 6.6 Hz, $^4J_{HH}$ = 1.0 Hz, 1H), 2.30 (m, 2H), 1.90 (m, 2H), 1.30 (m, 2H), 1.10 (d, $^2J_{HP}$ = 13.7 Hz, 9H), 1.10 (m, 4H), 1.00 (qm, $^1J_{BH}$ = 100 Hz, 3H), 0.90 (t, $^3J_{HH}$ = 7.1 Hz, 3H). ^{13}C NMR (63 MHz, $CDCl_3$) δ 153.5 (d, $^2J_{CP}$ = 9 Hz), 131.3 (d, $^2J_{CP}$ = 8.2 Hz), 129.0 (d, $^4J_{CP}$ = 2.5 Hz), 126.5 (d, $^1J_{CP}$ = 52.5 Hz), 126.3 (d, $^3J_{CP}$ = 10 Hz), 111.7 (d, $^1J_{CP}$ = 56.0 Hz), 29.7 (d, $^3J_{CP}$ = 5.0 Hz), 29.7 (d, $^2J_{CP}$ = 2 Hz), 27.6 (d, $^1J_{CP}$ = 35.3 Hz), 27.0 (s), 26.6 (s), 23.6 (d, $^4J_{CP}$ = 2.6 Hz), 20.7 (s), 12.2 (s). ^{11}B NMR (128 MHz, $CDCl_3$) δ −38.9 (m).

Typical Procedure for Palladium-Catalyzed Hydrophosphination of Alkynes. The reactions were carried out under a nitrogen atmosphere with use of the Schlenk technique. The metal source, the ligand, and half of the solvent were first introduced in the flask and the mixture was allowed to stir at room temperature for at least 10 min. The alkyne, the phosphine−borane, and the second half of the solvent were then added and the solution was heated at the corresponding temperature until completion.

Analytical Data for Products 3a−g Described in Table 2: 2-(Boranatodiphenylphosphino)oct-1-ene 3a. A mixture of 2.5 mmol (500 mg) of diphenylphosphine−borane, 2.75 mmol (407 μL) of oct-1-yne, 5 mol % of palladium acetate, and 10 mol % of dppp (1,3-bis(diphenylphosphino)propane) in 5.0 mL of toluene was stirred at 50 °C for 12 h. The crude product was purified by column chromatography with toluene as eluent (R_f 0.80). After evaporation of the solvent 650 mg (84%) of a colorless oily product was obtained. ^{31}P NMR (121 MHz, $CDCl_3$) δ 24.7 (q, $^1J_{PB}$ = 60 Hz). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55 (m, 4H), 7.40 (m, 6H), 5.80 (dd, $^3J_{HPtrans}$ = 36 Hz, $^2J_{HH}$ = 0.44 Hz, 1H), 5.35 (dd, $^3J_{HPcis}$ = 18 Hz, $^2J_{HH}$ = 0.8 Hz, 1H), 2.20 (m, 2H), 1.40 (quint, $^3J_{HH}$ = 7.4 Hz, 2H), 1.15 (m, 6H), 1.00 (qm, $^1J_{BH}$ = 91 Hz, 3H), 0.80 (t, $^3J_{HH}$ = 6.6 Hz, 3H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 140.0 (dm, $^1J_{CP}$ = 46 Hz), 132.1 (ddm, $^1J_{CH}$ = 163 Hz, $^2J_{CP}$ = 9.4 Hz), 130.2 (dtd, $^1J_{CH}$ = 160 Hz, J_{CH} = 7 Hz, $^4J_{CP}$ = 2.4 Hz), 127.7 (ddm, $^1J_{CH}$ = 162 Hz, $^3J_{CP}$ = 10.2 Hz), 127.5 (tdm, $^1J_{CH}$ = 156 Hz, $^2J_{CP}$ = 6.3 Hz), 126.9 (dm, $^1J_{CP}$ = 57 Hz), 31.8 (tdm, $^1J_{CH}$ = 127 Hz, $^2J_{CP}$ = 12.0 Hz), 30.5 (t, $^1J_{CH}$ = 126 Hz), 27.8 (tm, $^1J_{CH}$ = 127 Hz), 27.2 (td, $^1J_{CH}$ = 131 Hz, $^3J_{CP}$ = 5 Hz), 21.5 (tm, $^1J_{CH}$ = 124 Hz), 13.0 (qm, $^1J_{CH}$ = 123 Hz). ^{11}B NMR (128 MHz, $CDCl_3$) δ −35.6 (qd, $^1J_{BH}$ = 91 Hz, $^1J_{BP}$ = 60 Hz). HRMS calcd for $C_{20}H_{25}P$ ($[M - BH_3]^{+\bullet}$) 296.1694, found 296.1685.

1-(Boranatodiphenylphosphino)-1-phenylethene 3b. A mixture of 0.50 mmol (100 mg) of diphenylphosphine−borane, 0.55 mmol (62 μL) of phenylacetylene, 5 mol % of palladium acetate, and 10 mol % of dppp (1,3-bis(diphenylphosphino)-propane) in 1.0 mL of toluene was stirred at 50 °C for 15 h. The crude product was purified by column chromatography with toluene as eluent (R_f 0.65). After evaporation of the solvent 73 mg (49%) of a pale yellow solid product is obtained. ^{31}P NMR (121 MHz, $CDCl_3$) δ 24.0 ($^1J_{PB}$ = 57 Hz). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60 (m, 6H), 7.40 (m, 9H), 6.10 (dd, $^3J_{HPtrans}$ = 33.8 Hz, $^2J_{HH}$ = 0.9 Hz, 1H), 5.65 (dd, $^3J_{HPcis}$ = 16.9 Hz, $^2J_{HH}$ = 0.9 Hz, 1H), 1.00 (qm, $^1J_{BH}$ = 91 Hz, 3H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 140.7 (dm, $^1J_{CP}$ = 46.2 Hz), 137.4 (dm, $^2J_{CP}$ = 9.8 Hz), 132.3 (ddm, $^1J_{CH}$ = 163 Hz, $^2J_{CP}$ = 9.4 Hz), 131.8 (td, $^1J_{CH}$ = 159 Hz, $^2J_{CP}$ = 8.2 Hz), 130.3 (ddt, $^1J_{CH}$ = 160 Hz, $^4J_{CP}$ = 2.7 Hz), 127.7 (ddm, $^1J_{CH}$ = 150 Hz, $^3J_{CP}$ = 10.2 Hz), 127.2 (dm, $^1J_{CH}$ = 160 Hz), 127.1 (dm, $^1J_{CH}$ = 160 Hz), 127.1 (dm, $^1J_{CH}$ = 160 Hz), 127.0 (dm, $^1J_{CP}$ = 57 Hz). ^{11}B NMR (128 MHz, $CDCl_3$) δ −34.1 (qd, $^1J_{BH}$ = 91 Hz, $^1J_{BP}$ = 57 Hz). HRMS calcd for $C_{20}H_{17}P$ ([M − BH_3]$^{+\bullet}$) 288.1068, found 288.1076.

3-(Boranatodiphenylphosphino)but-4-enol 3c. Palladium acetate (45 mg, 4 mol %) and binap (249 mg, 8 mol %) in 5 mL of toluene were stirred at rt for 15 min. Then, toluene (5.0 mL), diphenylphosphine−borane (1 g, 5 mmol), and 3-butyn-1-ol (416 μL, 5.5 mmol) were added to the catalyst solution. The mixture was stirred for 15 h at 50 °C. After evaporation of the solvent, dichloromethane was added (3 mL) to precipitate binap, which was recovered by filtration. The filtrate was then reduced to 50% and the crude mixture was purified by column chromatography with dichloromethane as eluent (R_f 0.25). After evaporation of the solvent, 959 mg (71%) of a white solid was obtained. ^{31}P NMR (121 MHz, $CDCl_3$) δ 25.5 (m). ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.60 (m, 4H), 7.40 (m, 6H), 6.00 (d, $^3J_{HPtrans}$ = 34.6 Hz, 1H), 5.40 (d, $^3J_{HPcis}$ = 17.5 Hz, 1H), 3.70 (t, $^3J_{HH}$ = 6.5 Hz, 2H), 2.60 (s, 1H), 2.45 (dt, $^3J_{HP}$ = 11.1 Hz, $^2J_{HH}$ = 6.5 Hz, 2H), 1.00 (qm, $^1J_{BH}$ = 98 Hz, 3H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 136.5 (dm, $^1J_{CP}$ = 47 Hz), 132.1 (ddm, $^1J_{CH}$ = 163 Hz, $^2J_{CP}$ = 9.4 Hz), 130.4 (ddm, $^1J_{CH}$ = 161 Hz, $^4J_{CP}$ = 2.44 Hz), 129.9 (tdm, $^1J_{CH}$ = 160 Hz, $^2J_{CP}$ = 5.5 Hz), 127.8 (ddm, $^1J_{CH}$ = 163 Hz, $^3J_{CP}$ = 10.2 Hz), 126.4 (dm, $^1J_{CP}$ = 57.5 Hz), 59.9 (td, $^1J_{CH}$ = 146 Hz, $^3J_{CP}$ = 4.3 Hz), 35.1 (td, $^1J_{CH}$ = 145 Hz, $^2J_{CP}$ = 12.5 Hz). ^{11}B NMR (128 MHz, $CDCl_3$) δ −34.5 (q, $^1J_{BH}$ = 98 Hz). HRMS calcd for $C_{16}H_{17}$-OP ([M − BH_3]$^{+\bullet}$) 256.2793, found 256.1025. Anal. Calcd for $C_{16}H_{20}$BOP: C, 71.14; H, 7.46. Found C, 70.733; H, 7.26.

2-(Boranatodiphenylphosphino)-3-methoxypropene 3d. A mixture of 0.80 mmol (160 mg) of diphenylphosphine−borane, 1.20 mmol (101 μL) of methylpropargyl ether, 5 mol % of palladium dibenzylidene acetone [$Pd_2(dba)_3$], and 6 mol % of dppp (1,3-bis(diphenylphosphino)propane) in 1.6 mL of toluene was stirred at 50 °C for 15 h. The crude product was purified by column chromatography with toluene as eluent (R_f 0.50). After evaporation of the solvent 155 mg (73%) of a pale yellow oily product was obtained. ^{31}P NMR (121 MHz, $CDCl_3$) δ 20.2 (m). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60 (m, 4H), 7.45 (m, 6H), 6.15 (dtm, $^3J_{HPtrans}$ = 34.1 Hz, $^2J_{HH}$ = 1.5 Hz, 1H), 5.50 (dm, $^3J_{HPcis}$ = 17.7 Hz, 1H), 3.95 (dt, $^3J_{HP}$ = 5.2 Hz, $^4J_{HH}$ = 1.7 Hz, 2H), 3.20 (s, 3H), 1.00 (qm, $^1J_{BH}$ = 98 Hz, 3H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 137.5 (dm, $^1J_{CP}$ = 48.1 Hz), 133.4 (ddm, $^1J_{CH}$ = 164 Hz, $^2J_{CP}$ = 9.8 Hz), 131.6 (ddm, $^1J_{CH}$ = 162 Hz, $^4J_{CP}$ = 2.7 Hz), 129.5 (tdm, $^1J_{CH}$ = 158 Hz, $^2J_{CP}$ = 4.3 Hz), 129.0 (ddm, $^1J_{CH}$ = 162 Hz, $^3J_{CP}$ = 10.6 Hz), 127.6 (dm, $^1J_{CP}$ = 58.3 Hz), 72.1 (dm, $^2J_{CP}$ = 8.0 Hz), 58.7 (q, $^1J_{CH}$ = 143 Hz). HRMS calcd for $C_{16}H_{17}OP$ ([M − BH_3]$^{+\bullet}$) 256.2793, found 256.1018.

2-(Boranatodiphenylphosphino)-propene 3d′. ^{31}P NMR (121 MHz, $CDCl_3$) δ 24.5 (q, $^1J_{PB}$ = 56 Hz). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60 (m, 4H), 7.45 (m, 6H), 5.80 (dm, $^3J_{HPtrans}$ = 35.2 Hz, 1H), 5.30 (dm, $^3J_{HPcis}$ = 17.4 Hz, $^2J_{HH}$ = 1.0 Hz, 1H), 1.90 (dm, $^3J_{HP}$ = 10.4 Hz, 3H), 1.00 (qm, $^1J_{BH}$ = 95 H, 3H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 136.7 (dm, $^1J_{CP}$ = 48.5 Hz), 132.2 (ddm, $^1J_{CH}$ = 163 Hz, $^2J_{CP}$ = 9.4 Hz), 131.5 (ddm, $^1J_{CH}$ = 161 Hz, $^4J_{CP}$ = 2.9 Hz), 129.9 (tdm, $^1J_{CH}$ = 158 Hz, $^2J_{CP}$ = 7.8 Hz), 128.7 (ddm, $^1J_{CH}$ = 163 Hz, $^3J_{CP}$ = 9.8 Hz), 127.8 (dm, $^1J_{CP}$ = 57.1 Hz), 20.7 (qdm, $^1J_{CH}$ = 129 Hz, $^2J_{CP}$ = 12.3 Hz). ^{11}B NMR (128 MHz, $CDCl_3$) δ −35.8 (qd, $^1J_{BH}$ = 95 Hz, $^1J_{BP}$ = 56 Hz). HRMS calcd for $C_{15}H_{18}BP$ ([M]$^{+\bullet}$) 240.1239, found 240.1246. HRMS calcd for $C_{15}H_{15}P$ ([M − BH_3]$^{+\bullet}$) 226.0911, found 226.0908. Anal. Calcd for $C_{15}H_{18}BP$: C, 75.04; H, 7.56. Found: C, 74.62; H, 7.57.

2-(Boranatomethylphenylphosphino)oct-1-ene 3e. A mixture of 0.30 mmol (41 μL) of methylphenylphosphine−borane, 0.33 mmol (37.5 μL) of oct-1-yne, 5 mol % of palladium acetate, and 10 mol % of dppp (1,3-bis(diphenylphosphino)-propane) in 0.5 mL of toluene was stirred at 50 °C for 35 h. The crude product was purified by column chromatography with toluene as eluent (R_f 0.60). After evaporation of the solvent 63 mg (85%) of a colorless oily product was obtained. ^{31}P NMR (101 MHz, $CDCl_3$) δ 14.5 (q, $^1J_{PB}$ = 59 Hz). ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.60 (m, 2H), 7.40 (m, 3H), 5.75 (d, $^3J_{HPtrans}$ = 36.5 Hz, 1H), 5.70 (d, $^3J_{HPcis}$ = 18.5 Hz, 1H), 2.05 (m, 2H), 1.60 (d, $^2J_{HP}$ = 10.0 Hz, 3H), 1.35 (quint, $^3J_{HH}$ = 6.84 Hz, 2H), 1.20 (m, 6H), 0.80 (t, $^3J_{HH}$ = 6.72 Hz, 3H), 0.75 (qm, $^1J_{BH}$ = 97 Hz, 3H). ^{13}C NMR (63 MHz, $CDCl_3$) δ 140.2 (d, $^1J_{HP}$ = 45.3 Hz), 130.3 (d, $^3J_{HP}$ = 9.4 Hz), 129.7 (d, $^4J_{HP}$ = 2.0 Hz), 127.8 (d, $^1J_{HP}$ = 55.3 Hz), 127.3 (d, $^2J_{HP}$ = 9.4 Hz), 124.3 (d, $^2J_{HP}$ = 8.8 Hz), 30.7 (d, $^2J_{HP}$ = 10.1 Hz), 30.1 (s), 27.2 (s), 26.5 (d, $^3J_{HP}$ = 5.0 Hz), 21.0 (s), 12.5 (s), 8.8 (d, $^1J_{CP}$ = 39.6 Hz). ^{11}B NMR (128 MHz, $CDCl_3$) δ −35.5 (qd, $^1J_{BH}$ = 97 Hz, $^1J_{BP}$ = 59 Hz). HRMS calcd for $C_{15}H_{23}P$ ([M − BH_3]$^{+\bullet}$) 234.1537, found 234.1511.

1-(Boranatodiphenylphosphino)-1-(1-cyclohexenyl)-ethene 3f. A mixture of 1.0 mmol (200 mg) of diphenylphosphine−borane, 1.1 mmol (129.3 μL) of 1-ethynylcyclohexene, 5 mol % of palladium acetate, and 10 mol % of binap in 2.0 mL of toluene was stirred at 50 °C for 14 h. The crude product was purified by column chromatography with toluene as eluent (R_f 0.70). After evaporation of the solvent 182 mg (60%) of a pale yellow oily product was obtained. ^{31}P NMR (101 MHz, $CDCl_3$) δ 23.2 (m). ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.60 (m, 4H), 7.35 (m, 6H), 5.85 (d, $^3J_{HPtrans}$ = 34.3 Hz, 1H), 5.85 (m, 1H), 5.15 (d, $^3J_{HPcis}$ = 17.5 Hz, 1H), 2.00 (m, 2H), 1.90 (m, 2H), 1.45 (m, 2H), 1.35 (m, 2H), 1.00 (q, $^1J_{PB}$ = 97 Hz, 3H). ^{13}C NMR (63 MHz, $CDCl_3$) δ 142.6 (d, $^1J_{CP}$ = 45.9 Hz), 134.5 (d, $^2J_{CP}$ = 10.1 Hz), 133.6 (d, $^2J_{CP}$ = 10.1 Hz), 131.7 (d, $^3J_{CP}$ = 45.9 Hz), 131.5 (d, $^4J_{CP}$ = 2.5 Hz), 129.5 (d, $^1J_{CP}$ = 56.6 Hz), 129.0 (d, $^3J_{CP}$ = 10.1 Hz), 128.2 (d, $^2J_{CP}$ = 7.5 Hz), 28.3 (d, $^3J_{CP}$ = 3.8 Hz), 26.0 (s), 23.0 (s), 22.0 (s). HRMS calcd for $C_{20}H_{21}P$ ([M − BH_3]$^{+\bullet}$) 292.1380, found 292.1395.

1-(Boranatomethylphenylphosphino)-1-phenylethene 3g. A mixture of 0.25 mmol (34.5 μL) of methylphenylphosphine−borane, 0.275 mmol (30.2 μL) of 1-ethynylcyclohexene, 5 mol % of palladium acetate, and 10 mol % of bdpp (2,4-bis(diphenylphosphino)pentane) in 0.5 mL of toluene was stirred at 50 °C for 14 h. The crude product was purified by column chromatography with toluene as eluent (R_f 0.65). After evaporation of the solvent 32 mg (53%) of a pale yellow oily product was obtained. ^{31}P NMR (101 MHz, $CDCl_3$) δ 13.0 (q, $^1J_{PB}$ = 60 Hz). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (m, 2H), 7.45 (m, 3H), 7.25 (m, 2H), 7.10 (m, 3H), 6.20 (dd, $^3J_{HPcis}$ = 17.8 Hz, $^2J_{HH}$ = 0.9 Hz, 1H), 6.05 (dd, $^3J_{HPtrans}$ = 36.1 Hz, $^2J_{HH}$ = 0.9 Hz, 1H), 1.60 (d, $^2J_{HP}$ = 9.9 Hz, 3H), 1.00 (q, $^1J_{HB}$ = 95 Hz, 3H). ^{13}C NMR (63 MHz, $CDCl_3$) δ 142.6 (d, $^1J_{CP}$ = 44.7 Hz), 138.2 (d, $^2J_{CP}$ = 6.3 Hz), 132.1 (d, $^2J_{CP}$ = 9.4 Hz), 131.2 (s), 131.1 (s), 129.4 (d, $^1J_{CP}$ = 55.5 Hz), 128.8 (d, $^3J_{CP}$ = 10.1 Hz), 128.3 (s), 128.1 (d, $^4J_{CP}$ = 1.1 Hz), 127.9 (d, $^3J_{CP}$ = 3.4 Hz), 10.3 (d, $^1J_{CP}$ = 40.8 Hz). ^{11}B NMR (128 MHz, $CDCl_3$) δ −34.2 (qd, $^1J_{BH}$ = 95 Hz, $^1J_{BP}$ = 60 Hz).

Acknowledgment. The authors thank CNRS and le Conseil Régional de Basse Normandie for financial support. D.M. acknowledges the Ministry of Education

and Research for the award of a Ph.D. fellowship. The authors also thank Prof. J. Hamelin and Dr. J. P. Bazureau (SESO, Université de Rennes I) for the loan of the MWI device, Dr. P. Guenot (CRMPO, Rennes) for mass spectra, and Dr. J. M. Denis (SESO, Université de Rennes I) for fruitful discussions.

Supporting Information Available: General experimental details as well as ^{31}P, ^{1}H, and ^{13}C NMR spectra of new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

JO030096Q