Metalation of 3,4-Dimethylphosphole–Boranes as a Potential Route to Functional Phospholes

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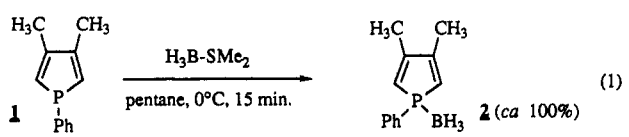
sec-Butyllithium selectively deprotonates one of the methyl groups of (1-phenyl-3,4-dimethylphosphole)–borane in THF at −80 °C to give an allylic anion. This delocalized anion reacts with electrophiles at either the α-endocyclic or γ-exocyclic positions. Protonation, deuteration, methylation, silylation, and stannylation take place at the α-position. The 2-(functional group)-3-methylene-4-methyl-2,3-dihydrophosphole–borane adducts thus formed have their functional groups *cis* to BH_3. Isomerization to the corresponding phospholes occurs in a basic medium. The reaction with ethyl acetate also takes place at the α-position, but the final product **11** results from the isomerization and self-reduction of the initial 2-acetyl 3-methylene derivative. Finally, the reaction with diethyl oxalate selectively occurs at the γ-position to give the α-keto ester **14**.

The recently described lithiation of a 2-bromophosphole represents, easily, the most general route to 2-(functional group)-phospholes.[1] However, this route suffers slightly from the low accessibility of 2-bromophospholes. While looking for alternative and, if possible, simpler syntheses of these 2-(functional group)-phospholes, our attention was caught by a report of Imamoto and co-workers describing the metalation and functionalization of methyldiphenylphosphine–borane.[2] Some time ago, we showed that the allylic metalation of 3,4-dimethylphosphole sulfides followed by interaction with selected electrophiles gives some 2-(functional group)-phosphole sulfides which can be reduced to the corresponding trivalent species.[3] Although this route is not general and gives low yields of the required products, it has the advantage that the starting phosphole sulfides are readily accessible. This led us to wonder if the allylic metalation of 3,4-dimethylphosphole–boranes might be a convenient alternative route to some 2-(functional group)-phospholes, taking into account the fact that decomplexation of $R_3P{\cdot}BH_3$ is, in any case, much easier than the reduction of $R_3P{=}S$.

Results and Discussion

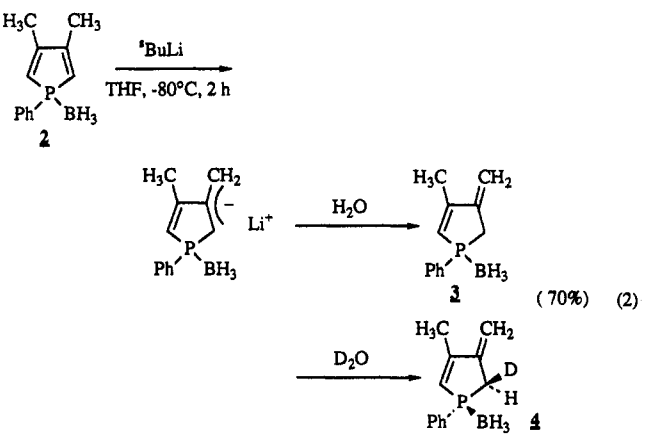
All our experiments were performed with 1-phenyl-3,4-dimethylphosphole–borane (**2**), which is readily prepared from the corresponding phosphole **1**[4] (eq 1).



(1)

The $^1J(^{31}P{-}^{11}B)$ coupling constant of 53.2 Hz is only slightly smaller in **2** than in $Me_3P{\cdot}BH_3$ and suggests P–B bonds of comparable strength.[5] Indeed, the crystalline **2** appears to be reasonably stable and proved to be a convenient starting material for our experiments.

Using the procedure of Imamoto,[2] we performed the metalation of **2** with *sec*-BuLi at −80 °C in THF. In order to get some insight into the structure and reactivity of the carbanion, we first studied its hydrolysis and deuterolysis (eq 2).



(2)

The hydrolysis almost exclusively produces **3**, an isomer of **2** with an exocyclic C=C double bond. The ^1H NMR spectrum of **3** is illustrative. It displays a CH_2—P unit as an ABX system (X = P): δ_A 2.90, δ_B 3.12, J_{AB} = 17.7 Hz, J_{AX} = 9 Hz, J_{BX} = 0 Hz. The exocyclic olefinic protons appear as two quasi-singlets at δ 5.32 and 5.45. The single intracyclic ethylenic proton gives a doublet at δ 6.10 (^2J(H–P) = 29.3 Hz). The formula is further confirmed by the ^{13}C spectrum. CH_2—P appears as a doublet at δ 31.63 (^1J(C–P) = 40.7 Hz), the exocyclic CH_2 as a doublet at δ 112.77 (^3J(C–P) = 8.8 Hz), and the endocyclic CH as a doublet at δ 124.19 (^1J(C–P) = 52 Hz). At 72.6 Hz, the $^1J(^{31}P{-}^{11}B)$ coupling is higher than in **2**, in line with the expected basicity of the isomeric phosphine being higher than that of the phosphole **1**. The deuterolysis produces only one of the two possible stereoisomers **4**, where deuterium replaces H_B. H_A appears as a broadened doublet at δ 2.86

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(1) Deschamps, E.; Mathey, F. *Bull. Soc. Chim. Fr.* **1992,** *129,* 486.
(2) Imamoto, T.; Oshiki, T.; Onozawa, T.; Kusumoto, T.; Sato, K. *J. Am. Chem. Soc.* **1990,** *112,* 5244.
(3) (a) Mathey, F. *Tetrahedron* **1976,** *32,* 2395. (b) Deschamps, B.; Mathey, F. *Organometallics* **1992,** *11,* 1411.
(4) Brèque, A.; Mathey, F.; Savignac, P. *Synthesis* **1981,** 983.
(5) Cowley, A. H.; Damasco, M. C. *J. Am. Chem. Soc.* **1971,** *93,* 6815.

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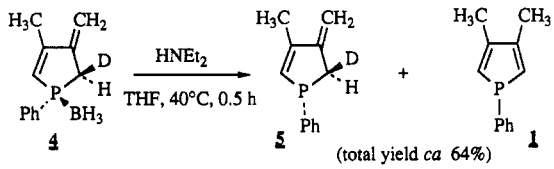
($^2J(H_A-P)$ = 9.1 Hz). In the ^{13}C spectrum, the CHD group gives a doublet of triplets at δ 31.16 ($^1J(C-D)$ = 20.3 Hz, $^1J(C-P)$ = 40.5 Hz).

In order to establish the stereochemistry of **4**, we performed its decomplexation by diethylamine. This is known to proceed with retention of configuration at phosphorus[2] (eq 3).

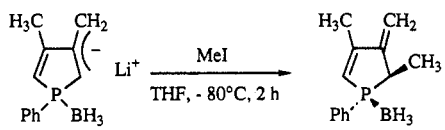


(3)

4 **5** **1**

The reaction gives a mixture containing the expected phosphine **5** along with some phosphole **1**, whose presence was established by ^1H and ^{31}P NMR. According to the ^1H spectrum of the mixture, the ratio **5**:**1** is ca. 4:1. In the same spectrum, the CHD group of **5** appears as a multiplet at δ 2.65 with $^2J(H-P)$ = 5.4 Hz and $^2J(H-D)$ = 2.3 Hz. Taking into account the magnetogyric ratios of ^1H and ^2H, we calculate a $^2J(H-H)$ coupling of 15.0 Hz. These data closely resemble those obtained for the CH_2P group of 1-phenyl-3,4-dimethylphosphol-3-ene[6] ($J(H_A-P)$ = 25 Hz, $J(H_B-P)$ = 6 Hz, $J(H_A-H_B)$ = 15.5 Hz) and indicate that the deuterium replaces H_A, which is *trans* to P-Ph. Thus, the protonation of the anion of **2** selectively takes place on the side of BH_3.

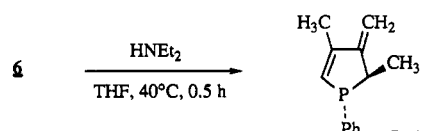
The anion of **2** proved to be a good starting point for the preparation of phosphole derivatives. The methylation readily takes place as shown in eq 4.



(4)

6 (85%)

Only one regio- and stereoisomer is obtained, in high yield. The α-methyl group of **6** appears as a characteristic doublet of doublets in the ^1H NMR spectrum: $\delta(Me-C_2)$ 1.37, $^3J(H-H)$ = 7.4 Hz, $^3J(H-P)$ = 16.9 Hz. Otherwise, the ^1H spectrum is very similar to that of **4**. The decomplexation of **6** by diethylamine takes place without isomerization (eq 5).

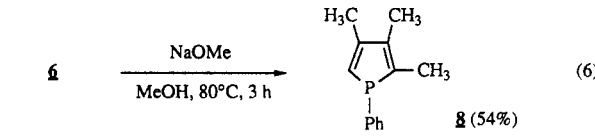


(5)

7 (65%)

The ^{13}C NMR spectrum of **7** gives a clue to the stereochemistry at C_2. The α-methyl group appears as a doublet at δ 19.26 ($^2J(C-P)$ = 30 Hz). This large $^2J(C-P)$ coupling is characteristic of a methyl *cis* to the lone pair.[7] Thus, the methylation of the anion takes place on the side of BH_3, as expected from the deuteration experiments.

The decomplexation by a stronger base such as sodium methoxide gives the previously unknown isomeric phosphole **8** (eq 6).

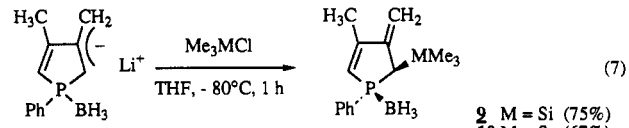


(6)

6 **8** (54%)

Phospole **8** is characterized by its olefinic proton at δ 6.24, which shows a strong $^2J(H-P)$ coupling of 38.7 Hz, and its α-methyl group at δ 1.93 ($^3J(H-P)$ = 8.6 Hz).

Silylation and stannylation of the anion are also possible (eq 7).

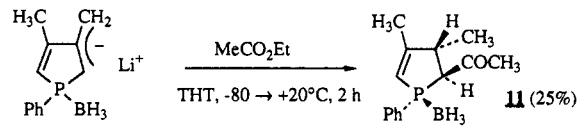


(7)

9 M = Si (75%)
10 M = Sn (67%)

Both **9** and **10** have the same stereochemistry as **4** or **6**, as shown by the magnitude of the $^2J(H-C_2-P)$ coupling constants of 9.4 and 5.7 Hz, respectively.

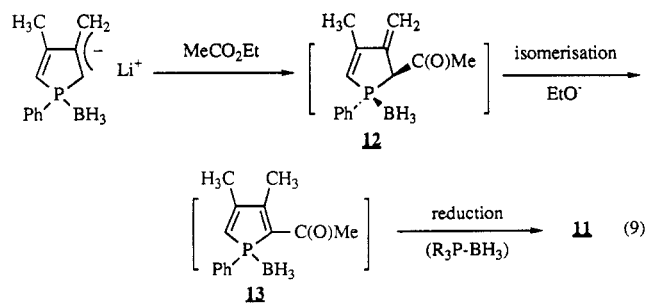
The reaction of the anion of **2** with esters proved to be far more complex. Two examples will illustrate the alternative paths that can be followed. The condensation of ethyl acetate leads to the dihydrophosphole derivative **11** (eq 8).



(8)

11 (25%)

Besides the three methyl groups, the ^1H NMR spectrum shows α-CH as a doublet of doublets at δ 3.51 ($^3J(H_\alpha-H_\beta)$ = 6.8 Hz, $^2J(H_\alpha-P)$ = 13.5 Hz), demonstrating its *trans* relationship to BH_3 by comparison with the data of **4** and suggesting a *trans* relationship to H_β. β-CH appears as a doublet of quadruplets at δ 3.68 with two almost equal $^3J(H-H)$ couplings. CH_3-CH gives a doublet at δ 1.22. The ^{13}C spectrum is also illustrative. The two sp^3 CH groups appear at δ 44.71 (s) and 62.06 ($^1J(C-P)$ = 26.2 Hz). CO appears as a singlet at δ 201.44. A similar absence of coupling has been noted for the α-methyl of **6**, thus confirming the stereochemistry of **11** at the α-carbon. We interpret this result as shown in eq 9.

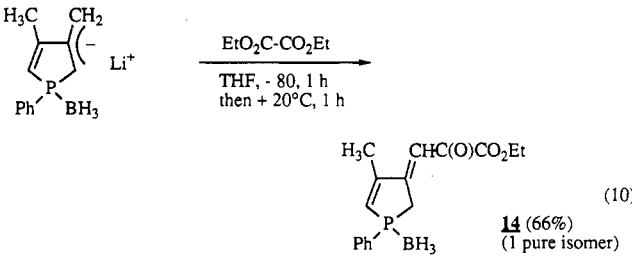


12 **13** **11** (9)

The conjugative ability of CO favors the isomerization of **12** into **13** in the basic medium. The electron-poor C=C double bond of **13** is then easily reduced by $R_3P{\cdot}BH_3$, via a 1,4-hydroboration of the α,β-unsaturated ketone. The use of phosphine–boranes as hydroboration reagents has already been described in the literature.[8]

(6) Gagnaire, D.; Robert, J. B.; Verrier, J. *Chem. Commun.* **1967**, 819.
(7) Breen, J. J.; Featherman, S. I.; Quin, L. D.; Stocks, R. C. *J. Chem. Soc., Chem. Commun.* **1972**, 658.
(8) Pelter, A.; Rosser, R.; Mills, S. *J. Chem. Soc., Chem. Commun.* **1981**, 1014.

The case of diethyl oxalate is again different. The functionalization takes place at the γ-position, as shown in eq 10.



(10)

14 (66%) (1 pure isomer)

The ^1H NMR spectrum of **14** is quite characteristic. At 400 MHz in $CDCl_3$, the CH_2P group appears as an ABMX system (M = γ-CH=, X = P: δ_A 3.39, δ_B 3.44, J_{AB} = 20.1 Hz, J_{AM} = 1.8 Hz, J_{AX} = 6.8 Hz, J_{BM} = 2 Hz, J_{BX} = 0 Hz), the intracyclic olefinic proton as a doublet at δ 6.70 (^2J(H–P) = 27.6 Hz), and the exocyclic olefinic proton as a pseudotriplet at δ 7.25. In the ^{13}C spectrum ($CDCl_3$), the ketonic carbonyl appears as a singlet at δ 182.36 and the carboxylic carbonyl as a singlet at δ 161.54, showing the shift to high field which is characteristic of α-keto acids.

From the two experiments described in eqs 8 and 10, it can be deduced that the allylic anion of **2** is not a convenient source of α-carbonyl phosphole derivatives, although the compounds resulting from the condensation of esters with this anion may have some other types of applications.

Experimental Section

All reactions were carried out under argon, and silca gel (70–230 mesh) was used for chromatographic separations. NMR spectra were recorded in Bruker AC 200 SY and AM 400 spectrometers at 200.13 and 400.13 MHz for ^1H, 50.32 MHz for ^{13}C, and 81.01 MHz for ^{31}P. Chemical shifts are expressed in parts per million downfield from internal $(CH_3)_4Si$ (^1H and ^{13}C) or external 85% H_3PO_4 (^{31}P). Mass spectra were obtained by the direct inlet method, at 70 eV with a Shimadzu GC–MS QP 1000 spectrometer. Elemental analyses were performed by the "Service de Microanlyse du CNRS" at Gif-sur-Yvette, France.

(1-Phenyl-3,4-dimethylphosphole)–Borane (2). To phosphole **1**[4] (10 g, 53 × 10^{-3} mol) in pentane (30 mL) was added a diethyl ether solution of BH_3·SMe_2 (2 M, 60 mL) at 0 °C. The mixture was stirred at 0 °C for 15 min. After evaporation, the residue was chromatographed with pentane/CH_2Cl_2 (6:4). Compound **2** was recovered as white crystals in 93% yield (10 g). ^{31}P NMR (CH_2Cl_2): δ 30.6 ($^1J(^{31}P–^{11}B)$ = 53.2 Hz). ^1H NMR (CD_2Cl_2): δ 2.18 (s, 6H, Me), 6.29 (d, ^2J(H–P) = 33 Hz, 2H, =CHP), 7.39–7.67 (m, 5H, Ph). ^{13}C NMR ($CDCl_3$): δ 17.81 (d, ^3J(C–P) = 12.5 Hz, Me), 124.12 (d, ^1J(C–P) = 55.14 Hz, =CHP), 155.25 (d, ^2J(C–P) = 9.5 Hz, Me–*C*). MS (^{11}B): *m/z* 202 (M^+, 6%), 188 ($M^+ - BH_3$, 100%). Anal. Calcd for $C_{12}H_{16}BP$: C, 71.34; H, 7.98. Found: C, 70.9; H, 7.8.

(1-Phenyl-3-methylene-4-methyl-2,3-dihydrophosphole)–Borane (3) and Its 2-Deuterio Derivative 4. To phosphole–borane **2** (1 g, 5 × 10^{-3} mol) in THF (15 mL) was added at −80 °C a cyclohexane/hexane (92:8) solution of *sec*-butyllithium (4 mL, 1.4 M, 5.6 × 10^{-3} mol). The mixture was stirred at −80 °C for 2 h. Water or D_2O (0.3 mL) was added at −80 °C and the medium further stirred for 0.5 h. After evaporation, the organic residue was chromatographed with pentane/CH_2Cl_2 (1:1). Yield of **3** or **4**: 0.7 g (70%), colorless oil.

3: ^{31}P NMR ($CDCl_3$) δ 26.9 ($^1J(^{31}P–^{11}B)$ = 72.6 Hz); ^1H NMR ($CDCl_3$) δ 2.16 (s, 3H, Me), 2.90 (*ABX*, ^2J(A–B) = 17.7 Hz, ^2J(A–X) = 9 Hz, 1H, CH_2P), 3.12 (*ABX*, ^2J(B–X) = 0 Hz, 1H, CH_2P), 5.32 (pseudo s, 1H, =CH_2), 5.45 (pseudo s, 1H, =CH_2), 6.10 (d, ^2J(H–P) = 29.3 Hz, 1H, =CHP); ^{13}C NMR ($CDCl_3$) δ 16.87 (d, ^3J(C–P) = 12.1 Hz, Me), 31.63 (d, ^1J(C–P) = 40.7 Hz, CH_2P), 112.77 (d, ^3J(C–P) = 8.8 Hz, =CH_2), 124.19 (d, ^1J(C–P) = 52 Hz, =CHP), 147.54 (s, *C*=CH_2), 157.36 (pseudo s, *C*Me).

4: ^{31}P NMR ($CDCl_3$) δ 26.6 ($^1J(^{31}P–^{11}B)$ = 69.1 Hz); ^1H NMR ($CDCl_3$) δ 2.12 (s, 3H, Me), 2.86 (broad d, ^2J(H–P) = 9.1 Hz, 1H, CHD), 5.29 (pseudo s, 1H, =CH_2), 5.42 (pseudo s, 1H, =CH_2), 6.06 (d, ^2J(H–P) = 28.9 Hz, 1H, =CHP); ^{13}C NMR ($CDCl_3$) δ 16.63 (d, ^3J(C–P) = 12.4 Hz, Me), 31.16 (m, ^1J(C–D) = 20.3 Hz, ^1J(C–P) = 40.5 Hz, CHD), 112.59 (d, ^3J(C–P) = 8.9 Hz, =CH_2), 123.98 (d, ^1J(C–P) = 51.7 Hz, =CHP), 147.24 (s, *C*=CH_2), 157.09 (d, ^2J(C–P) = 4.8 Hz, *C*Me).

1-Phenyl-2-deuterio-3-methylene-4-methyl-2,3-dihydrophosphole (5). Borane adduct **4** (0.25 g, 1.2 × 10^{-3} mol) in THF (5 mL) was stirred at 40 °C for 0.5 h with diethylamine (0.3 mL, 2.9 × 10^{-3} mol). After evaporation, the residue was quickly chromatographed with degassed pentane/CH_2Cl_2 (10:1). Phosphine **5** was obtained as a colorless oil in 64% yield (0.15 g). ^1H NMR showed that **5** was contaminated by 20% of phosphole **1**.

^{31}P NMR ($CDCl_3$): δ −16.7. ^1H NMR ($CDCl_3$): δ 2.04 (pseudo s, 3H, Me), 2.65 (m, ^2J(H–P) = 5.4 Hz, ^2J(H–D) = 2.3 Hz, 1H, CHD), 5.07 (s, 1H, =CH_2), 5.14 (d, *J* = 2 Hz, 1H, =CH_2), 6.25 (d, ^2J(H–P) = 38 Hz, =CHP).

(1-Phenyl-2,4-dimethyl-3-methylene-2,3-dihydrophosphole)–Borane (6). The anion of phosphole–borane **2** (2 g, 1 × 10^{-2} mol) was prepared in THF (30 mL) as indicated for the synthesis of **4**. After 2 h at −80 °C, methyl iodide (0.8 mL, 13 × 10^{-3} mol) was added to the reaction mixture, which was further stirred at −80 °C for 2 h. After the mixture was warmed to room temperature and stirred for an additional 1 h, the solvent was evaporated and the organic residue chromatographed with pentane/CH_2Cl_2 (1:1). Compound **6** was obtained in 85% yield (1.8 g) as a colorless oil. ^{31}P NMR ($CDCl_3$): δ 38.6 ($^1J(^{31}P–^{11}B)$ = 60.1 Hz). ^1H NMR ($CDCl_3$): δ 1.37 (dd, ^3J(H–H) = 7.4 Hz, ^3J(H–P) = 16.9 Hz, 3H, C—*Me*), 2.06 (s, 3H, Me), 2.91 (m, 1H, C*H*—Me), 5.16 (s, 1H, =CH_2), 5.40 (s, 1H, =CH_2), 5.93 (d, ^2J(H–P) = 27.1 Hz, 1H, =CHP), 7.39 (m, 3H, Ph *m*, *p*), 7.60 (m, 2H, Ph *o*). ^{13}C NMR ($CDCl_3$): δ 15.19 (d, ^2J(C–P) = 2.9 Hz, CH–*Me*), 16.60 (d, ^3J(C–P) = 11.5 Hz, Me), 37.09 (d, ^1J(C–P) = 39.1 Hz, CHP), 111.22 (d, ^3J(C–P) = 6.6 Hz, =CH_2), 121.53 (d, ^1J(C–P) = 52.0 Hz, =CHP), 153.18 (d, ^2J(C–P) = 6.2 Hz, *C*=CH_2), 156.10 (d, ^2J(C–P) = 5.7 Hz, Me—*C*=). MS (^{11}B): *m/z* 216 (M^+, 4%), 202 ($M^+ - BH_3$, 100%). Anal. Calcd for $C_{13}H_{18}BP$: C, 72.28; H, 8.34. Found: C, 72.1; H, 8.2.

1-Phenyl-2,4-dimethyl-3-methylene-2,3-dihydrophosphole (7). The same procedure as for **5** was used. From 1 g of borane adduct **6**, 0.6 g (65%) of phosphine **7** was obtained as a colorless oil. ^{31}P NMR ($CDCl_3$): δ 6.0. ^1H NMR (400 MHz, $CDCl_3$): δ 1.47 (dd, ^3J(H–H) = 7.4 Hz, ^3J(H–P) = 19.2 Hz, 3H, CH—C*H*$_3$), 2.06 (dd, *J* = 1.3 and 2.3 Hz, 3H, Me), 2.87 (m, ^2J(H–P) = 2 Hz, 1H, CHP), 4.99 (pseudo t, *J* = 1.8 Hz, 1H, =CH_2), 5.19 (d, *J* = 2.4 Hz, 1H, =CH_2), 6.20 (d, ^2J(H–P) = 35.5 Hz, 1H, =CHP). ^{13}C NMR ($CDCl_3$): δ 17.01 (s, Me—C=), 19.26 (d, ^2J(C–P) = 30 Hz, Me—CH), 43.14 (d, ^1J(C–P) = 4.2 Hz, CHP), 106.42 (s, =CH_2), 130.90 (d, ^1J(C–P) = 12.8 Hz, =CHP), 149.60 (s, *C*=CH_2), 157.66 (s, Me—*C*=). MS: *m/z* 202 (M^+, 100%).

1-Phenyl-2,3,4-trimethylphosphole (8). To the borane adduct **6** (0.65 g, 2.3 × 10^{-3} mol) in methanol (5 mL) was added a piece of sodium metal (*ca.* 0.1 g, 4.3 × 10^{-2} mol). After reaction, the mixture was refluxed at 80 °C for 3 h. After cooling and evaporation the residue was quickly chromatographed with degassed pentane/CH_2Cl_2 (10:1). Phosphole **8** was obtained in 54% yield (0.25 g) as a colorless oil.

^{31}P NMR ($CDCl_3$): δ 6.6. ^1H NMR ($CDCl_3$): δ 1.93 (d, ^3J(H–P) = 8.6 Hz, 3H, α-Me), 2.00 (s, 3H, β-Me), 2.07 (dd, 3H, β′-Me), 6.24 (d, ^2J(H–P) = 38.7 Hz, 1H, =CHP). ^{13}C NMR ($CDCl_3$): δ 13.35 (d, ^2J(C–P) = 21.4 Hz, α-Me), 13.48 (s, Me), 18.84 (s, Me), 124.56 (s, =CHP), 141.06 (s, P—*C*—Me), 141.62 (d, ^2J(C–P) = 11.2 Hz, β-C), 151.03 (d, ^2J(C–P) = 8 Hz, β-C). MS: *m/z* 202 (M^+, 100%). Anal. Calcd for $C_{13}H_{15}P$: C, 77.22; H, 7.42. Found: C, 77.3; H, 7.7.

(1-Phenyl-2-(trimethylsilyl)-3-methylene-4-methyl-2,3-dihydrophosphole)–Borane (9). The anion of phosphole–borane **2** (1 g, 5 × 10^{-3} mol) was prepared in THF (15 mL) as indicated

for the synthesis of **4**. After 2 h at −80 °C, trimethylchlorosilane (0.8 mL, 6.3×10^{-3} mol) in THF (10 mL) was added to the reaction mixture, which was further stirred at −80 °C for 1 h and then at +25 °C for 1 h. After evaporation, the residue was chromatographed with pentane/CH_2Cl_2 (4:1). Compound **9** was obtained in 75% yield (1 g) as a colorless oil. ^{31}P NMR (CH_2Cl_2): δ 30.9 ($^1J(^{31}P-^{11}B)$ = 61.7 Hz). ^1H NMR ($CDCl_3$): δ 0.22 (s, 9H, Me_3Si), 2.12 (s, 3H, Me), 2.42 (d, ^2J(H-P) = 9.4 Hz, P—CH—Si), 5.09 (s, 1H, =CH_2), 5.35 (s, 1H, =CH_2), 6.00 (d, ^2J(H-P) = 30.1 Hz, 1H, =CHP). ^{13}C NMR ($CDCl_3$): δ −1.57 (s, Me_3Si), 16.37 (d, ^3J(C-P) = 12.2 Hz, Me—C), 34.00 (d, ^1J(C-P) = 21.8 Hz, P—CH—Si), 110.20 (d, ^3J(C-P) = 7.9 Hz, =CH_2), 124.22 (d, ^1J(C-P) = 52.5 Hz, =CHP), 151.07 (s, C=CH_2), 157.02 (d, ^2J(C-P) = 4.9 Hz, =*C*—Me). Anal. Calcd for $C_{15}H_{24}BPSi$: C, 65.74; H, 8.76. Found: C, 65.9; H, 9.0.

(1-Phenyl-2-(trimethylstannyl)-3-methylene-4-methyl-2,3-dihydrophosphole)-Borane (10). The same procedure as for **9** was used. From 1 g of **2** and 1.2 g of Me_3SnCl (6×10^{-3} mol), 1.2 g (67%) of **10** was obtained as a colorless oil after chromatography with pentane/CH_2Cl_2 (6:4). ^{31}P NMR (CH_2Cl_2): δ 31.8 ($^1J(^{31}P-^{11}B)$ = 71.8 Hz). ^1H NMR ($CDCl_3$): δ 0.29 (s, 9H, Me_3-Sn), 2.14 (pseudo t, 3H, Me), 2.69 (d, ^2J(H-P) = 5.7 Hz, 1H, P—CH—Sn), 5.02 (d, 1H, =CH_2), 5.17 (s, 1H, =CH_2), 6.11 (d, ^2J(H-P) = 30 Hz, 1H, =CH—P). ^{13}C NMR ($CDCl_3$): δ −7.37 (s, Me_3Sn), 16.38 (d, ^3J(C-P) = 12.2 Hz, Me—C), 28.28 (d, ^1J(C-P) = 26.8 Hz, P—CH—Sn), 106.81 (d, ^3J(C-P) = 10.2 Hz, =CH_2), 124.46 (d, ^1J(C-P) = 51 Hz, =CHP), 153.12 (s, *C*=CH_2), 156.34 (d, ^2J(C-P) = 6.2 Hz, Me—C=). MS (^{120}Sn): *m/z* 366 (M^+, 13%), 352 ($M^+ - BH_3$, 17%), 165 (Me_3Sn^+, 100%). Anal. Calcd for $C_{15}H_{24}BPSn$: C, 49.39; H, 6.58. Found: C, 49.4; H, 6.7.

(1-Phenyl-2-acetyl-3,4-dimethyl-2,3-dihydrophosphole)-Borane (11). The same procedure as for **9** was used, with 1 g of **2** and 1 mL of ethyl acetate. Chromatography of the organic residue with pentane/CH_2Cl_2 (3:1) yielded 200 mg of **3** (20%); then, with pentane/CH_2Cl_2 (1:12), 300 mg of **11** (25%) was recovered. ^{31}P NMR ($CDCl_3$): δ 42.1. ^1H NMR (400 MHz, $CDCl_3$): δ 1.22 (d, ^3J(H-H) = 7 Hz, 3H, *Me*—CH), 1.98 (s, 3H, Me), 2.08 (d, 3H, Me), 3.51 (dd, ^3J(H-H) = 6.8 Hz, ^2J(H-P) = 13.5 Hz, 1H, CHP), 3.68 (dq, $^3J(H_\alpha-H_\beta) \approx {}^3J(H_\beta-CH_3) \approx$ 6.8–7 Hz, 1H, Me—C*H*), 5.56 (d, ^2J(H-P) = 34.3 Hz, 1H, =CHP). ^{13}C NMR ($CDCl_3$): δ 19.14–19.41 (d + s, 2Me), 31.33 (s, *Me*CO), 44.71 (s, β-CH), 62.06 (d, ^1J(C-P) = 26.2 Hz, CH—P), 113.27 (d, ^1J(C-P) = 56.5 Hz, =CHP), 166.02 (quasi s, Me—*C*=), 201.44 (s, CO). MS: *m/z* 246 (M^+, 10%), 245 ($M^+ - H$, 48%), 232 ($M^+ - BH_3$, 32%), 189 (100%).

Compound 14. The same procedure as for **9** and **11** was used, with 1 g of **2** and 0.7 mL (5.2×10^{-3} mol) of diethyl oxalate. Chromatography of the organic residue with pentane/CH_2Cl_2 (2:5) yielded 1 g (66%) of **14**. ^{31}P NMR ($CDCl_3$): δ 29.8. ^1H NMR (400 MHz, $CDCl_3$): δ 1.39 (t, ^3J(H-H) = 7 Hz, 3H, CH_3—CH_2), 2.28 (d, 3H, CH_3—C=), 3.39 (m, ^2J(H-H) = 20.1 Hz, ^2J(H-P) = 6.8 Hz, 1H, P—CH_2), 3.44 (m, 1H, P—CH_2), 4.36 (q, 2H, OCH_2), 6.70 (d, ^2J(H-P) = 27.6 Hz, 1H, =CH—P), 7.25 (pseudo t, 1H, =C*H*—CO). ^{13}C NMR ($CDCl_3$): δ 13.88 (s, CH_3—CH_2), 16.67 (d, ^3J(C-P) = 11.3 Hz, CH_3—C=), 32.40 (d, ^1J(C-P) = 39.4 Hz, CH_2P), 62.50 (s, OCH_2), 117.27 (d, ^3J(C-P) = 4.4 Hz, =CH-), 135.53 (d, ^1J(C-P) = 47.7 Hz, =CHP), 156.27 (d, ^2J(C-P) = 6.2 Hz, Me—*C*=), 160.88 (s, *C*=CH-), 161.54 (s, CO_2Et), 182.36 (s, CO). MS: *m/z* 302 (M^+, 4%), 288 ($M^+ - BH_3$, 100%). IR (CCl_4): 1729.4 (str, ν_{CO} conjugated ester), 1686.9 cm^{-1} (str, ν_{CO} conjugated ketone). Anal. Calcd for $C_{16}H_{20}BO_3P$: C, 63.57; H, 6.68. Found: C, 62.8; H, 6.7.

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