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Intramolecular Hydroboration of Unsaturated Phosphine Boranes

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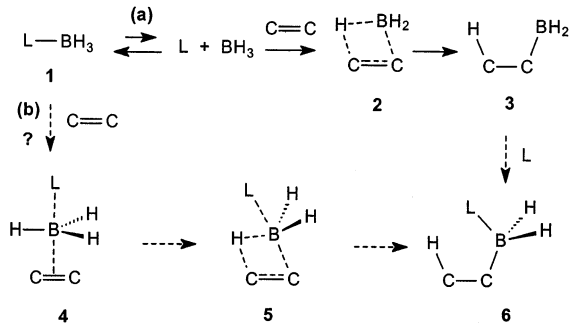
Homoallylic phosphine boranes undergo intramolecular hydroboration upon activation by triflic acid. The reaction occurs via an intermediate *B*-trifluorosulfonyloxyborane complex such as **15**, followed by S_N1-like or S_N2-like displacement of the triflate leaving group, apparently leading to the formation of a four-center transition state. In the case of trisubstituted double bonds, as in the substrates **29** and **32**, ionic hydrogenation of the alkene competes with internal hydroboration.

The use of Lewis base complexes of borane as hydroborating agents remains an active area of research after almost 50 years of study.[1] Midway through this effort, Brown and Chandrasekharan provided evidence that such hydroborations proceed in an S_N1-like manner[2] and that reversible dissociation of the Lewis base (L = ether, sulfide, or amine) in the borane complex **1** is followed by reaction of free BH_3 with the substrate (path a, Scheme 1) to give a four-center transition state **2** on the way to the initial hydroboration product **3**. Other groups have proposed S_N2-like mechanisms,[3] and Pasto et al. have invoked a modified bimolecular mechanism for hydroboration of 2,3-dimethyl-2-butene with BH_3·THF (path b).[3b] On the basis of entropy of activation data and other evidence, Pasto proposed that the alkene partially displaces THF from **1** (L = THF), resulting in a THF-bound four-center transition state **5** that leads directly to the solvated alkylborane product **6**. An olefin−borane π-complex **4** was viewed as a possible intermediate derived from the initial S_N2-like event, although conversion from **1** to **6** without intermediates was regarded as the simplest explanation that is consistent with the activation entropy data.[3b] The observation of low ee using chiral Lewis base−borane adducts has also been claimed as

SCHEME 1



evidence for a transition state similar to **5**, with the Lewis base still present.[3d] It is not clear how the mechanistic discrepancies can be reconciled in some of these cases. However, Brown's evidence for a dissociative mechanism (path a) is persuasive for several examples where rate inhibition by added Lewis base has been demonstrated.[2]

Unhindered amine boranes are not reactive hydroborating agents due to their relatively high dissociation temperatures, but reaction at room temperature is possible if the amine borane is destabilized by steric or electronic factors.[1] Similar thermal thresholds are observed with analogous unsaturated alkylamine boranes,[4] suggesting that there is no special advantage for an intramolecular pathway. This is consistent with the dissociative mechanism for hydroboration.

Phosphine boranes are also relatively stable. Although their use in hydroboration reactions has received limited attention,[5−7] evidence consistent with a dissociative process has been described.[5] In one unusual case, the

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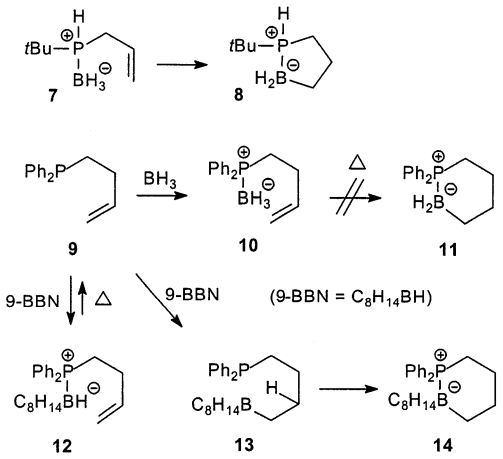
formation of a cyclic phosphine borane **8** from the secondary allylic phosphine borane complex **7** was observed at 30 °C.[6] However, Schmidbaur et al. were unable to convert the homoallylic phosphine **9** into **11** under a variety of conditions, suggesting that neither a dissociative pathway nor an internal hydroboration is accessible from **10**. Conversion to a cyclic borane **14** did occur when **9** was heated with 9-BBN in THF.[7] This evidence was interpreted to support reversible formation of **12**, followed by intermolecular hydroboration of **9** with 9-BBN to give **13** and cyclization to **14**.

We have been interested in the possibility of intramolecular hydroboration in Lewis base−borane complexes by mechanisms that do not require dissociation of the complex.[8] We began with the assumption that modified S_N1- or S_N2-like pathways may be possible if a sufficiently good leaving group X is attached to boron (as in the complex **15**) in addition to the bond between boron and Lewis basic phosphorus. Intramolecular nucleophilic attack by the alkene might then afford a borane π-complex **17** without having to break the bond from boron to phosphorus. Direct conversion from **15** to **17** is one possibility, but **15** might also undergo an S_N1-like ionization process to generate the cationic (borenium)[9] intermediate **16** on the way to the π-complex **17**. In either case, the formation of **17** should lead to the hydroboration products **18** and/or **19** and then to the tetravalent boron complexes **20** and/or **21**. Our preliminary report described several amine borane analogies for related cyclizations,[8] as well as the intramolecular hydroboration from an unsaturated phosphine borane **10**. We now describe additional studies in the phosphorus series that help to define scope and selectivity issues for internal hydroboration of homoallylic phosphine boranes.

Results and Discussion

To generate the π-complex **17**, the starting phosphine borane **10** must be converted into **15** with X being a potential leaving group. There is good precedent for the generation of such species from phosphine boranes.[10] Thus, Imamoto and Oshiki have isolated the water-labile $Me_3P{\cdot}BH_2OMs$ from $Me_3P{\cdot}BH_3$ by treatment with methanesulfonic acid.[10b,c] Furthermore, McKinstry and Livinghouse have described an acid-mediated decomplexation of phosphine boranes using anhydrous tetrafluoroboric acid.[10d] Conversion of $Ph_2MeP{\cdot}BH_3$ into the intermediate $Ph_2MeP{\cdot}BH_2F$ was shown by multinuclear NMR experiments, suggesting that the fluoroborane complex is responsible for facile hydrolytic cleavage. These reports indicate that displacement of a leaving group at tetravalent boron in complexes similar to **15** is facile, as also observed with the analogous amine borane complexes $R_3N{\cdot}BH_2X$.[9b,c] With these precedents in mind we set out to investigate the use of protic acids to activate phosphine boranes and to determine if intermediates such as **15** would be sufficiently reactive to undergo intramolecular hydroboration.

SCHEME 2



Phosphine borane **10** was synthesized from diphenylphosphine via alkylation of lithium diphenylphosphide and complex formation with borane−tetrahydrofuran. Competing hydroboration of the alkene was not observed, as expected from the earlier study by Schmidbaur et al.[7] A solution of **10** in CD_2Cl_2 was then treated with representative acids at room temperature, including anhydrous HCl, TsOH, MsOH, and trifluoromethanesulfonic acid (TfOH). The TfOH reaction was exceptional in that vigorous hydrogen evolution was observed immediately upon mixing. Treatment with basic hydrogen peroxide in aqueous methanol resulted in phosphorus oxidation as well as C−B cleavage and provided a separable mixture of the known alcohols **22**[11] and **23**[12] in a 3:1 ratio (87% isolated; Scheme 3). Activation took place at temperatures as low as −5 °C, but the ratio of products changed only slightly (4:1 **22**:**23**). The analogous MsOH reaction was much slower, but hydrogen evolution did occur over a time scale of hours at room temperature, and hydroboration products were obtained at partial conversion. However, neither the HCl nor the TsOH experiments gave significant conversion under similar conditions. Further studies were therefore conducted using the TfOH procedure.

The regioselectivity of this acid-mediated hydroboration is notable in that the major product is the secondary alcohol **22**. Intermolecular hydroboration of the terminal olefin would be expected to give ca. 90% or more of the

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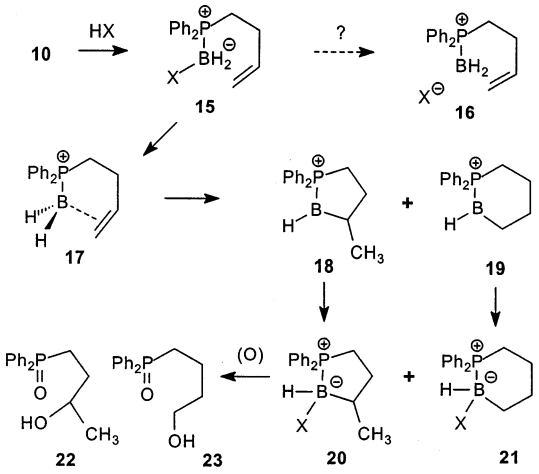
SCHEME 3



primary alcohol **23** after oxidation, by analogy to the reaction of simple 1-alkenes.[13] The unusual regioselectivity indicates that the TfOH-induced hydroboration proceeds via an intramolecular mechanism rather than by dissociation to a trivalent borane species no longer bound to phosphorus. Indeed, the control experiment using BH_3·THF (1.5 equiv in THF, °C) for the hydroboration of **10** provided the primary alcohol product **23** as the major regioisomer (12:88 **22**:**23**). Significantly, the ratio of alcohol products from TfOH activation of **10** was unchanged when the reaction was carried out over a range of concentrations from 5 mM to 1 M, providing further evidence for the intramolecular nature of the hydroboration. These observations suggest that nearly all of the hydroboration from the activated intermediate **15** takes place via the internal mechanism and affords cyclic boranes **20** and **21** as the initial hydroboration products. However, the NMR spectra of the crude reaction mixtures were too complex to establish the presence of structures **20** or **21** or to clarify the possible involvement of borenium species **18** and **19**. The assignments are tentative and are based on the formation of **22** and **23** after oxidative cleavage and also on the Imamoto analogies.[10b,c]

In contrast to the behavior of the presumed cyclization products **20** and **21**, the unactivated starting complex **10** was recovered unchanged from the alkaline peroxide workup conditions. The relatively facile cleavage of **20** and **21** suggests that nucleophilic displacement of the triflate leaving groups by hydroperoxide anion is an important first step in the oxidative cleavage process. However, the solvolytic reactivity of the activated boranes has also prevented isolation or characterization of **20** and **21** or the activated precursor **15** (X = OTf), a problem that was also encountered in the Imamoto studies.[10b,c]

To determine whether the intramolecular hydroboration from **15** is reversible, the reaction was performed with phosphine borane **10**-d_3, prepared from **9** and BD_3·THF.[15] Activation of **10**-d_3 with TfOD to effect hydroboration and oxidative workup provided the usual 3:1 ratio of secondary alcohol **22**-d_1 and primary alcohol **23**-d_1 in 78% combined yield. It was essential to use deuterated trifluoromethanesulfonic acid (TfOD) to obtain high levels of deuterium incorporation because TfOH afforded products containing only 68% deuterium. Similarly, treatment of the undeuterated phosphine borane **10** with TfOD resulted in measurable deuterium incorporation into the product alcohols after oxidation. Amine boranes are known to undergo rapid exchange of B−H for B−D in acidic D_2O, and the phosphine boranes apparently can undergo a similar exchange process.[16] In any event, both deuterated products **22**-d_1 and **23**-d_1 were those expected from irreversible, kinetic hydroboration of the olefin. If retrohydroboration had occurred at the stage of intermediates **18**-d_2 or **19**-d_2, then there would have been opportunities for incorporation of more than one deuterium label via **24** and **25**.

We next examined the effect of substitution at the alkene. The phosphine borane **26** was synthesized from diphenylmethylphosphine borane by lithiation and alkylation with cinnamyl bromide using the method of Imamoto[14] and treated with TfOH as before. Oxidative cleavage with alkaline hydrogen peroxide then afforded a 93:7 mixture of alcohols **27** and **28**. The regioselectivity of this reaction is notable because the hydroboration of simple (*E*)-disubstituted styrenes provides the benzylic alcohol as the major product.[17] The contrasting formation of **27** as the major product from **26** is further evidence for the intramolecular hydroboration pathway.

Two additional substrates **29** and **32** were prepared using the Imamoto method from methyldiphenylphosphine borane[18] and activated with TfOH as usual. The less highly substituted alcohol products (**30** and **33**, respectively) were obtained in each case, but in low yield (22 and 36%, respectively). Although none of the isomeric tertiary alcohols were detected, both reactions gave significant amounts of a less polar product that contained no hydroxyl group. The unexpected products proved to be the saturated phosphine oxides **31** (56%) and **34** (47%), corresponding to apparent hydrogenation of the double bond in the starting **29** and **32**. Tentatively, these products are attributed to the ionic hydrogenation of the double bond,[19] initiated by triflic acid protonation of the alkene followed by hydride transfer from the borane complex.

The hydroboration products **30** and **33** in the unusual reactions from **29** or **32** are plausible products of intramolecular hydroboration, but they are also the expected products from an intermolecular pathway where boron should be attached to the less substituted alkene carbon. Further evidence for the internal pathway was therefore sought. It occurred to us that the ionic hydro-

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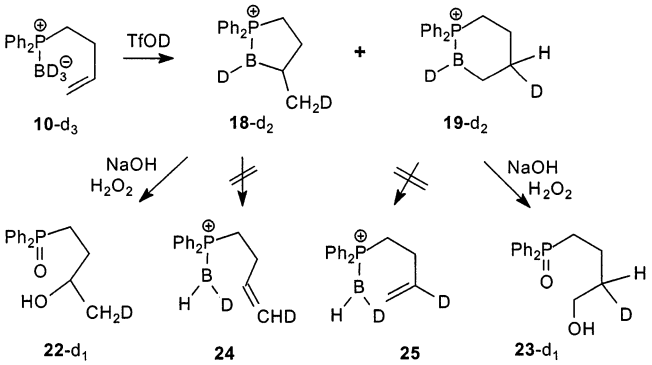
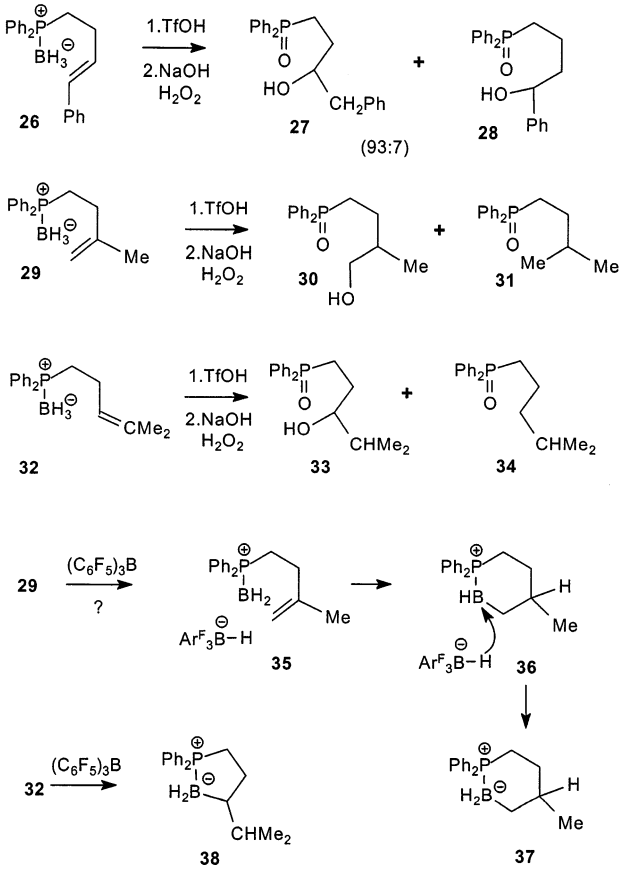
SCHEME 4



genation side reaction might be avoided if the starting phosphine boranes **29** and **32** could be activated in an S_N1-like manner, by simple hydride abstraction. In principle, this form of activation might be possible with $(C_6F_5)_3B$, a reagent that has been used for activation of silanes by reversible hydride abstraction[20] and has also been shown to induce the dehydrocoupling of primary phosphine boranes in a process that apparently involves hydride abstraction and eventual evolution of hydrogen.[21] Accordingly, the phosphine boranes **29** and **32** were treated with 5−10% $(C_6F_5)_3B$ in benzene. After 3 h at room temperature, the reactions were quenched with triethylamine and products were isolated by chromatography. In both cases, isomeric cyclic phosphine boranes were obtained. Structures **37** (69%) and **38** (91%) were established from characteristic ^{31}P and ^{11}B chemical shift data and $^{13}C-^{31}P$ coupling information and by oxidative cleavage to the alcohol phosphine oxides **30** and **33**. The isolation of stable, cyclic phosphine boranes supports the feasibility of intramolecular hydroboration from the unsaturated phosphine boranes **29** and **32** and also provides support for the possibility of an S_N1-like mechanism via borenium intermediates such as **35** and **36**. However, other mechanisms can be proposed for the observed isomerizations of unsaturated phosphine boranes **29** and **32** into the cyclic isomers. Further study will be required to establish whether borenium intermediates are involved in these unprecedented transformations.

In summary, we have demonstrated intramolecular hydroboration reactions of homoallylic phosphine boranes[22] by activation with TfOH or with $(C_6F_5)_3B$. The TfOH reaction is analogous to the intramolecular hydroborations of activated amine boranes,[8] but the isomerizations of **29** and **32** to cyclic phosphine boranes **37** and **38**, respectively, catalyzed by $(C_6F_5)_3B$ are unique if the mechanisms follow the pathway considered in Scheme 5. Furthermore, we have been unable to find close precedents for intramolecular ionic hydrogenations involving phosphine boranes, as implied by the conversions

SCHEME 5



to **31** and **34** from the unsaturated phosphine boranes. Further work to clarify the mechanisms of the new reactions is planned.

Experimental Section

(3-Butenyl)diphenylphosphine·BH_3[7,14b] (10). A solution of *n*-butyllithium (1.36 M in hexanes, 10.57 mL, 14.37.mmol) was added dropwise at −30 °C over 10 min to a solution of diphenylphosphine (2.5 mL, 14.37 mmol) in THF (30 mL). After the mixture was stirred at this temperature for 3 h, 4-bromo-1-butene (1.46 mL, 14.37 mmol) was added and the orange color disappeared. The reaction was warmed to 0 °C for 30 min before borane−tetrahydrofuran complex (1 M in THF, 14.37 mL, 14.37 mmol) was added dropwise. The reaction was warmed to room temperature overnight. The solution was diluted with EtOAc (20 mL) and then cautiously quenched with HCl (2 N, 30 mL). The aqueous layer was extracted with EtOAc, and the extracts were washed with brine, dried (Na_2SO_4), and concentrated (aspirator). Flash column chromatography of the crude material on silica gel (4 × 18 cm) eluted with 95:5 hexane/acetone (350 mL) followed by 9:1 hexane/acetone (300 mL) provided the title compound (2.477 g, 68%) as a gum that crystallized, mp = 42−44 °C. The NMR data were consistent with the literature.[7,14b]

3-(Butenyl)diphenylphosphine·BD_3 (10-*d*$_3$). Iodine (61.3 mg, 0.24 mmol) was added in portions to a slurry of sodium borodeuteride (22.4 mg, 0.53 mmol) in THF (3 mL) at 0 °C using the method of Periasamy.[16] Hydrogen gas was evolved. After 2 h at 0 °C, a solution of (3-butenyl)diphenylphosphine (∼117 mg, 0.49 mmol) in THF (2 mL) was added via a cannula. The reaction was warmed to room temperature. After 14 h, the reaction was diluted with EtOAc (10 mL) and water (6 mL) and then quenched with aqueous HCl (2 N, 2 mL). The aqueous layer was extracted with EtOAc, and the extracts

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(22) Analogous activation of allylic or bis-homoallylic phosphine boranes gave hydrogen evolution, but no evidence for intramolecular hydroboration was detected.

were washed with brine and dried (Na_2SO_4). After removal of solvent (aspirator), the residue was purified by flash chromatography on Whatman silica 60A (12 × 2 cm, 5 mL fractions, fractions 12−17) with 95:5 hexane/acetone as the eluent to give phosphine−BD_3 complex (64 mg, 51%) as a colorless liquid: analytical TLC on K6F silica gel 60A, 3:1 hexane/acetone, R_f = 0.76; 400 MHz NMR ($CDCl_3$, ppm) δ 7.72−7.64 (4H, m), 7.52−7.41 (6H, m), 5.88−5.76 (1H, m), 5.04 (1H, d, J = 17.2 Hz), 4.98 (1H, d, J = 10.3 Hz), 2.34−2.21 (4H, m). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 137.4 (d, J_{C-P} = 16.0 Hz), 132.1 (d, J_{C-P} = 9.2 Hz), 131.2 (d, J_{C-P} = 3.1 Hz), 128.8 (d, J_{C-P} = 9.9 Hz), 115.3, 27.0, 24.8 (d, J_{C-P} = 36.6 Hz), ipso-C not detected; ^{31}P NMR (162 MHz, $CDCl_3$, ppm) δ 15.9 (m); ^{11}B NMR (115.5 MHz, $CDCl_3$, ppm) δ −40.2 (br, $W_{1/2}$ = 140 Hz). Also isolated was 51 mg (44%) of starting phosphine as a colorless liquid.

Laboratory-Scale Procedure for Internal Hydroboration; (4-Diphenylphosphinoyl)-2-butanol[11] (22) and (4-Diphenylphosphinoyl)-1-butanol[12] (23). A solution of (3-butenyl)diphenylphosphine borane **10** (124.4 mg, 0.490 mmol) in DCM (0.49 mL) was cooled to 0 °C and treated dropwise with trifluoromethanesulfonic acid (50 μL, 0.563 mmol). Vigorous gas evolution was observed along with an exotherm. After 15 min, TLC analysis indicated consumption of the starting borane complex, so the DCM was removed by a stream of N_2. The residue, a colorless gum, was dissolved in MeOH (10 mL, gas evolution) and then made basic by the addition of NaOH (15% aq, 1 mL). The solution was cooled to 0 °C and treated dropwise with H_2O_2 (30% aq, 1 mL) to control the exotherm. A colorless, granular precipitate formed immediately. After 15 min, the MeOH was removed (aspirator), and the residue was diluted with water and extracted with DCM. The extracts were washed with brine, dried (Na_2SO_4), and concentrated to give a 76:24 ratio of alcohols **22**:**23** (129 mg, 96%) as a colorless gum. Analytical samples were purified by PLC on silica 60A (20 × 20 × 0.1 cm) with 9:1 DCM/MeOH as the eluent to give (4-diphenylphosphinoyl)-2-butanol and (4-diphenylphos-phinoyl)-1-butanol. The NMR data for these compounds were consistent with those in the literature.[11,12]

General Procedure for Acid-Mediated Hydroboration with Monitoring by NMR. Trifluoromethanesulfonic acid (1.1 equiv) was added to a solution of phosphine−borane complex in $CDCl_3$ (~0.15 M solution), and vigorous gas evolution was observed. After 15 min, ^1H NMR indicated consumption of the alkene. The reaction was transferred to a 25 mL round-bottom flask with three DCM washes (2 mL each), and the DCM was removed by a stream of N_2. The residue, a colorless gum, was dissolved in MeOH (5 mL, gas evolution), made basic by the addition of NaOH (15% aq, 0.25 mL), and treated with H_2O_2 (30% aq, 0.25 mL). A colorless precipitate formed immediately. After 30 min, the MeOH was evaporated (aspirator). The residue was diluted with water and extracted with DCM, and the extracts were dried (Na_2SO_4) and concentrated (aspirator) to give a colorless gum that was purified by preparative TLC.

(4-Diphenylphosphinoyl)-2-butanol[11] (22) and (4-Diphenylphosphinoyl)-1-butanol[12] (23). (3-Butenyl)diphenylphosphine−borane (8.7 mg, 34.2 mmol) was activated as described in the general procedure above, and gave a 75:25 mixture of 2°/1° alcohols (7.9 mg, 85%) as a colorless gum. NMR data were consistent with those reported in the literature.[11,12]

1-Deuterio-4-diphenylphosphinoyl-2-butanol (22-d_1) and 2-Deuterio-4-diphenylphosphinoyl-1-butanol (23-d_1). Use of the general procedure above with (3-butenyl)diphenylphosphine−BD_3 complex (16.9 mg, 65.7 μmol) gave 17 mg (95%) of crude product as a colorless gum. ^{31}P NMR analysis indicated a 68:32 mixture of **22**-d_1:**23**-d_1. After removal of solvent (aspirator), the residue was purified by PLC on silica 60A (20 × 20 × 0.1 cm) with 12:1 DCM/MeOH as the eluent to provide 9.7 mg (54%) of secondary alcohol **22**-d_1 with 92% D incorporation as a colorless oil: 400 MHz NMR ($CDCl_3$, ppm) δ 7.79−7.71 (4H, m), 7.56−7.44 (6H, m), 3.94−3.85 (1H, br), 3.57−3.49 (1H, br), 2.52−2.35 (2H, m), 1.93−1.79 (1H, m), 1.76−1.61 (1H, m), 1.17 (2H, d, J = 6.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 132.7 (d, J_{C-P} = 99.9), 131.8 (m), 130.8 (d, J_{C-P} = 9.2 Hz), 130.8 (d, J_{C-P} = 9.2), 128.8 (d, J_{C-P} = 11.4 Hz), 67.5 (d, J_{C-P} = 9.9 Hz), 31.3 (d, J_{C-P} = 4.6), 26.5 (d, J_{C-P} = 71.7 Hz), 23.0 (t, J_{C-D} = 19.5 Hz); ^{31}P NMR (162 MHz, $CDCl_3$, ppm) δ 34.5. A more polar zone gave 5.1 mg (28%) of primary alcohol **23**-d_1 as a colorless oil: 400 MHz NMR ($CDCl_3$, ppm) δ 7.75−7.70 (4H, m), 7.55−7.44 (6H, m), 3.64 (2H, d, J = 5.1 Hz), 2.37−2.27 (3H, m), 1.82−1.62 (3H, m). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 133.8 (d, J_{C-P} = 98.4 Hz), 131.7 (d, J_{C-P} = 3.1 Hz), 130.8 (d, J_{C-P} = 9.9 Hz), 128.7 (d, J_{C-P} = 11.4 Hz), 61.7, 33.0 (td, J_{C-D} = 19.0 Hz, J_{C-P} = 12.1 Hz), 28.9 (d, J_{C-P} = 71.7 Hz), 17.8 (d, J_{C-P} = 3.8 Hz); ^{31}P NMR (162 MHz, $CDCl_3$, ppm) δ 33.1. The identity of the deuterated compounds and the extent of deuterium incorporation were determined by comparison with data for the undeuterated compounds.[11,12] The key data are the appearance of the deuterated carbons in the ^{13}C NMR spectra as a triplet or a triplet of doublets and the simplification of splitting patterns in the ^1H NMR spectra.

Diphenyl(4-phenyl-3-butenyl)phosphine·BH_3 (26). A solution of *s*-butyllithium (1.13 M in pentane, 2.32 mL, 2.62 mmol) was added dropwise at −78 °C to a solution of diphenylmethylphosphine−borane complex[18] (374.3 mg, 1.75 mmol) in THF (10 mL), and a pale yellow color developed. After stirring at −78 °C for 2 h, a solution of cinnamyl bromide (517 mg, 2.62 mmol) in THF (5 mL) was added via a cannula. The reaction was stirred at −78 °C for 2 h and then warmed to room temperature. After 15 h, the reaction was quenched with water and extracted with EtOAc, and the extracts were washed with brine, dried (Na_2SO_4), and concentrated (aspirator) to give 825 mg of crude yellow gum. A sample (39.1 mg) of the residue was purified by PLC on silica 60A (20 × 20 × 0.1 cm) with 3:2 hexane/DCM as the eluent to provide 29 mg (76% calcd yield) of 94:6 desired product:starting phosphine borane; analytical TLC on K6F silica gel 60A, 3:1 hexane/acetone, R_f = 0.35. Pure material was obtained by crystallization from chloroform, mp 98−100 °C, fine powder: HRMS for $C_{22}H_{24}{}^{11}BP$; M − 13, m/z 317.1447, error = 4 ppm, base peak = 317 amu; IR (neat, cm^{-1}) 2382, B−H; 400 MHz NMR ($CDCl_3$, ppm) δ 7.74−7.66 (4H, m), 7.53−7.41 (6H, m), 7.31−7.16 (5H, m), 6.38 (1H, d, J = 15.8 Hz), 6.16 (1H, dt, J = 15.8, 6.4 Hz), 2.50−2.33 (4H, m), 1.50−0.50 (3H, m); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 137.1, 132.1 (d, J_{C-P} = 8.4 Hz), 131.2 (d, J_{C-P} = 2.3 Hz), 130.8, 129.3 (d, J_{C-P} = 54.9 Hz), 129.0 (d, J_{C-P} = 15.3 Hz), 128.9 (d, J_{C-P} = 9.9 Hz), 128.5, 26.5, 25.5 (d, J_{C-P} = 35.9 Hz); ^{31}P NMR (162 MHz, $CDCl_3$, ppm) δ 15.7 (m); ^{11}B NMR (115.5 MHz, $CDCl_3$, ppm) δ −39.8 (m, $W_{1/2}$ = 260 Hz).

(4-Diphenylphosphinoyl)-1-phenyl-2-butanol (27) and 4-(Diphenylphosphinoyl)-1-phenyl-1-butanol (28). Use of the general procedure above with diphenyl(4-phenyl-3-butenyl)phosphine−borane complex **26** (13.0 mg, 39.4 mmol) gave 12.1 mg (88%) of a colorless liquid. ^1H and ^{31}P NMR analysis of the crude mixture indicated a 91:9 ratio of homobenzylic:benzylic alcohols. The residue was purified by PLC on silica 60A (20 × 20 × 0.1 cm) with 95:5 DCM/MeOH as the eluent to provide (4-diphenylphosphinoyl)-1-phenyl-2-butanol (**27**), 10.6 mg (77%); analytical TLC on K6F silica gel 60A, 9:1 DCM/MeOH, R_f = 0.48. Pure material was obtained by crystallization from chloroform, mp 160−161 °C, colorless blocks: HRMS for $C_{22}H_{23}O_2P$; M + 1, m/z 351.1518, error = 1 ppm, base peak = 351 amu; IR (neat, cm^{-1}) 3320, O−H; 1170, P═O; 400 MHz NMR ($CDCl_3$, ppm) δ 7.78−7.70 (4H, m), 7.56−7.43 (6H, m), 7.30−7.13 (5H, m), 3.96−3.87 (1H, m), 3.42 (1H, d, J = 4.0 Hz), 2.77 (1H, dd, J = 13.6, 7.3 Hz), 2.71 (1H, dd, J = 13.6, 5.9 Hz), 2.53−2.34 (2H, m), 2.02−1.88 (1H, m), 1.77−1.62 (1H, m); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 138.4, 132.4 (d, J_{C-P} = 84.7 Hz), 131.8 (d, J_{C-P} = 2.3 Hz), 130.8 (d, J_{C-P} = 2.3 Hz), 130.7 (d, J_{C-P} = 2.3 Hz), 129.3, 128.8, 128.6, 126.4, 72.5 (d, J_{C-P} = 9.1 Hz), 43.8, 28.7 (d, J_{C-P} = 4.6 Hz), 26.8, 26.1; ^{31}P NMR (162 MHz, $CDCl_3$, ppm) δ 34.4. Also isolated was **28**, (4-diphenylphosphinoyl)-1-phenyl-1-butanol (0.4 mg, 3%); ana-

lytical TLC on K6F silica gel 60A, 9:1 DCM/MeOH, $R_f = 0.45$: HRMS for $C_{22}H_{23}O_2P$; M + 1, *m*/*z* 351.1522, error = 2 ppm, base peak = 351 amu; IR (neat, cm^{-1}) 3304, O−H; 1173, P═O; 400 MHz NMR ($CDCl_3$, ppm) δ 7.77−7.68 (4H, m), 7.56−7.42 (6H, m), 7.37−7.20 (5H, m), 4.73−4.66 (1H, m), 2.45 (1H, d, $J = 3.7$ Hz), 2.41−2.27 (2H, m), 1.97−1.68 (4H, m); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 131.7, 130.8, 130.8 (d, $J_{C-P} = 19.1$ Hz), 128.6 (d, $J_{C-P} = 13.0$ Hz), 128.5, 127.5, 125.7, 73.8, 39.8 (d, $J_{C-P} = 13.0$ Hz), 29.2 (d, $J_{C-P} = 71.7$ Hz), 18.2 (d, $J_{C-P} = 3.8$ Hz); ^{31}P NMR (162 MHz, $CDCl_3$, ppm) δ 32.8.

(3-Methyl-3-butenyl)diphenylphosphine·BH_3 (29). A solution of *s*-butyllithium (1.3 M in pentane, 0.88 mL, 1.140 mmol) was added dropwise at −78 °C to a solution of diphenylmethylphosphine−borane complex[18] (195.4 mg, 0.913 mmol) in THF (5 mL) and a pale yellow color developed. After stirring at −78 °C for 2 h, methallyl bromide (115 μL, 1.140 mmol) was added. After warming to room temperature for 2 h, the reaction was quenched with water and extracted with EtOAc. The extracts were washed with brine and dried (Na_2SO_4). After removal of solvent (aspirator), the residue was purified by flash chromatography on EM silica gel 60 (3 × 14 cm) with 95:5 hexane/acetone as the eluent to provide 196 mg (80%) of the desired compound as a colorless liquid; analytical TLC on K6F silica gel 60A, 19:1 hexane/acetone, $R_f = 0.25$. Pure material was obtained by crystallization from acetone, mp 49−51 °C: HRMS for $C_{17}H_{22}{}^{11}BP$; M − 1, *m*/*z* 267.1475, error = 0 ppm, base peak = 253 amu; IR (neat, cm^{-1}) 2382, B−H; 2343, B−H; 1652, C═C; 400 MHz NMR ($CDCl_3$, ppm) δ 7.72−7.65 (4H, m), 7.53−7.42 (6H, m), 4.74 (1H, s), 4.71 (1H, s), 2.39−2.30 (2H, m), 2.22−2.14 (2H, m), 1.71 (3H, s), 1.50−0.50 (3H, m); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 144.8 (d, $J_{C-P} = 13.7$ Hz), 132.1 (d, $J_{C-P} = 9.2$ Hz), 131.2 (d, $J_{C-P} = 3.1$ Hz), 129.3 (d, $J_{C-P} = 54.9$ Hz), 128.8 (d, $J_{C-P} = 10.7$ Hz), 110.2, 30.6, 24.0 (d, $J_{C-P} = 37.4$ Hz), 22.4; ^{31}P NMR (162 MHz, $CDCl_3$, ppm) δ 16.1 (m); ^{11}B NMR (115.5 MHz, $CDCl_3$, ppm) δ −39.9 (m, $W_{1/2} = 250$ Hz).

(4-Diphenylphosphinoyl)-2-methyl-1-butanol (30) and Diphenyl(3-methylbutyl)phosphine Oxide (31). Use of the general procedure above with (3-methyl-3-butenyl)diphenylphosphine−borane **29** (16.7 mg, 62.3 μmol) gave 14.6 mg (81%) of crude product as a colorless liquid. ^1H and ^{31}P NMR analysis indicated a 69:31 mixture of **31**:**30**. After removal of solvent (aspirator), the residue was purified by PLC on silica 60A (20 × 20 × 0.1 cm) with 95:5 DCM/MeOH as the eluent. The less polar zone was collected to give diphenyl(3-methylbutanyl)phosphine oxide (**31**, 10.0 mg, 56%) as a colorless solid; analytical TLC on K6F silica gel 60A, 9:1 DCM/MeOH, $R_f = 0.53$. Pure material was obtained by crystallization from chloroform, mp 97.5−99 °C plates: HRMS for $C_{17}H_{21}OP$; M + 1, *m*/*z* 273.1411, error = 1 ppm, base peak = 216 amu; IR (neat, cm^{-1}) 1177, P═O; 400 MHz NMR ($CDCl_3$, ppm) δ 7.78−7.70 (4H, m), 7.55−7.44 (6H, m), 2.30−2.20 (2H, m), 1.68−1.46 (3H, m), 0.89 (6H, d, $J = 6.6$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 133.1 (d, $J_{C-P} = 97.7$ Hz), 131.6 (d, J_{C-P}= 3.1 Hz), 130.8 (d, $J_{C-P} = 9.2$ Hz), 128.6 (d, $J_{C-P} = 10.7$ Hz), 29.9 (d, $J_{C-P} = 3.8$ Hz), 29.1 (d, $J_{C-P} = 14.5$ Hz), 27.6 (d, $J_{C-P} = 72.5$ Hz), 22.0; ^{31}P NMR (162 MHz, $CDCl_3$, ppm) δ 34.0. The more polar zone gave (4-diphenylphosphinoyl)-2-methyl-1-butanol (**30**) 3.9 mg (22%) as a colorless oil; analytical TLC on K6F silica gel 60A, 9:1 DCM/MeOH, $R_f = 0.42$: HRMS for $C_{17}H_{21}O_2P$; M + 1, *m*/*z* 289.1356, error = 1 ppm, base peak = 269 amu; IR (neat, cm^{-1}) 3374, O−H; 1170, P═O; 400 MHz NMR ($CDCl_3$, ppm) δ 7.78−7.71 (4H, m), 7.56−7.44 (6H, m), 3.57−3.43 (2H, m), 2.44 (1H, t, $J = 6.2$ Hz), 2.42−2.21 (2H, m), 1.82−1.50 (3H, m), 0.91 (3H, d, $J = 6.6$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 133.3 (d, $J_{C-P} = 97.7$ Hz), 131.8 (d, $J_{C-P} = 3.1$ Hz), 130.8 (d, $J_{C-P} = 8.4$ Hz), 128.7 (d, $J_{C-P} = 12.2$ Hz), 66.8, 26.3 (d, $J_{C-P} = 11.4$ Hz), 26.4 (d, $J_{C-P} = 71.7$ Hz), 24.5 (d, $J_{C-P} = 3.8$ Hz), 16.4; ^{31}P NMR (162 MHz, $CDCl_3$, ppm) δ 34.0.

(4-Methyl-3-pentenyl)diphenylphosphine·BH_3 (32). A solution of *s*-butyllithium (1.3 M in pentane, 0.65 mL, 0.840 mmol) was added dropwise at −78 °C to a solution of diphenylmethylphosphine−borane complex[18] (143.9 mg, 0.672 mmol) in THF (5 mL), and a pale yellow color developed. After the mixture was stirred at −78 °C for 2 h, prenyl bromide (97 μL, 0.840 mmol) was added. After 14 h at room temperature, the reaction was quenched with water and extracted with EtOAc. The extracts were washed with brine and dried (Na_2SO_4). After removal of solvent (aspirator), the residue was purified by flash chromatography on EM silica gel 60 (14 × 2 cm) with 24:1 hexane/acetone as the eluent to give 138 mg (73%) of the desired compound as a colorless liquid; analytical TLC on K6F silica gel 60A, 19:1 hexane/acetone, $R_f = 0.34$: HRMS for $C_{18}H_{24}{}^{11}BP$; M − 1, *m*/*z* 281.1621, error = 3 ppm, base peak = 269 amu; IR (neat, cm^{-1}) 2382, B−H; 1436, C═C; 400 MHz NMR ($CDCl_3$, ppm) δ 7.71−7.64 (4H, m), 7.51−7.40 (6H, m), 5.12−5.06 (1H, m), 2.27−2.13 (4H, m), 1.62 (3H, s), 1.51 (3H, s), 1.50−0.50 (3H, m); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 133.1, 132.1 (d, $J_{C-P} = 9.2$ Hz), 131.1 (d, $J_{C-P} = 3.0$ Hz), 129.5 (d, $J_{C-P} = 54.9$ Hz), 128.7 (d, $J_{C-P} = 10.0$ Hz), 123.2 (d, $J_{C-P} = 15.3$ Hz), 25.9 (d, $J_{C-P} = 35.8$ Hz), 25.6, 21.7, 17.6; ^{31}P NMR (162 MHz, $CDCl_3$, ppm) δ 15.4 (m); ^{11}B NMR (115.5 MHz, $CDCl_3$, ppm) δ −39.9 (m, $W_{1/2} = 250$ Hz).

(5-Diphenylphosphinoyl)-2-methyl-3-pentanol (33) and Diphenyl(4-methylpentanyl)-phosphine Oxide (34). Use of the general procedure above with (4-methyl-3-pentenyl)-diphenylphosphine−borane complex **32** (14.7 mg, 52.1 μmol) gave 13.0 mg (83%) of crude product as a colorless liquid. ^1H and ^{31}P NMR analysis indicated a 53:47 mixture of **34**:**33**. After removal of solvent (aspirator), the residue was purified by PLC on silica 60A (20 × 20 × 0.1 cm) with 95:5 DCM/MeOH as the eluent. The less polar zone provided diphenyl(4-methylpentanyl)phosphine oxide **34** (7.4 mg, 47%) as a colorless solid; analytical TLC on K6F silica gel 60A, 9:1 DCM/MeOH, $R_f = 0.53$: HRMS for $C_{18}H_{23}OP$; M + 1, *m*/*z* 287.1576, error = 4 ppm, base peak = 287 amu; IR (neat, cm^{-1}) 1181, P═O; 400 MHz NMR ($CDCl_3$, ppm) δ 7.78−7.70 (4H, m), 7.55−7.44 (6H, m), 2.28−2.19 (2H, m), 1.68−1.46 (3H, m), 1.32−1.24 (2H, m), 0.82 (6H, d, $J = 6.6$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 133.2 (d, $J_{C-P} = 97.7$ Hz), 131.6 (d, $J_{C-P} = 3.1$ Hz), 130.7 (d, $J_{C-P} = 9.2$ Hz), 128.6 (d, $J_{C-P} = 11.4$ Hz), 40.3 (d, $J_{C-P} = 14.5$ Hz), 29.9 (d, $J_{C-P} = 71.7$ Hz), 27.6, 22.4, 19.3 (d, $J_{C-P} = 3.8$ Hz); ^{31}P NMR (162 MHz, $CDCl_3$, ppm) δ 32.5. The more polar zone provided (5-diphenylphosphinoyl)-2-methyl-3-pentanol **33** (5.6 mg, 36%) as a colorless gum. Pure material was obtained by crystallization from chloroform, mp 117.5−118.5 °C fine powder: HRMS for $C_{18}H_{23}O_2P$; M + 1, *m*/*z* 303.1519, error = 2 ppm, base peak = 303 amu; IR (neat, cm^{-1}) 3350, O−H; 1173, P═O; 400 MHz NMR ($CDCl_3$, ppm) δ 7.79−7.72 (4H, m), 7.56−7.44 (6H, m), 3.44−3.36 (1H, m), 3.06 (1H, d, $J = 5.1$ Hz), 2.55−2.32 (2H, m), 1.95−1.82 (1H, m), 1.73−1.58 (2H, m), 0.90 (3H, d, $J = 6.6$ Hz), 0.86 (3H, d, $J = 7.0$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 132.6 (d, $J_{C-P} = 79.3$ Hz), 131.8 (m), 130.8 (d, $J_{C-P} = 9.2$ Hz), 128.7 (d, $J_{C-P} = 1.5$ Hz), 128.6 (d, $J_{C-P} = 1.5$ Hz), 76.5 (d, $J_{C-P} = 9.2$ Hz), 33.7, 26.7 (d, $J_{C-P} = 71.7$ Hz), 26.5 (d, $J_{C-P} = 3.8$ Hz), 18.7, 17.8; ^{31}P NMR (162 MHz, $CDCl_3$, ppm) δ 34.5.

1,1-Dihydrido-2,2-diphenyl-5-methyl-1,2-boraphosphinane (37). A solution of $B(C_6F_5)_3$ (9.0 mg, 0.018 mmol) in benzene (0.25 mL) was added to a solution of (3-methyl-3-butenyl)diphenylphosphine·BH_3 (**35**) (60.9 mg, 0.227 mmol) in benzene (2 mL). After 3 h, the reaction was quenched with triethylamine (1 mL). After removal of solvent (aspirator), the residue was purified by PLC on Whatman silica 60A (20 × 20 × 0.1 cm) with 4:1 hexane/DCM as the eluent to give 42 mg (69%) of cyclic phosphine borane (**37**) as a colorless oil; analytical TLC on K6F silica gel 60A, 4:1 hexane/DCM, $R_f = 0.59$: HRMS for $C_{17}H_{22}BP$; M − 1, *m*/*z* 267.1476, error = 1 ppm; base peak = 267 amu; IR (neat, cm^{-1}) 2243, B−H; 2262, B−H; 400 MHz NMR ($CDCl_3$, ppm) δ 7.85−7.78 (2H, m), 7.59−7.46 (5H, m), 7.46−7.35 (3H, m), 2.62−2.50 (1H, m), 2.30−0.80 (2H, br), 2.19−2.08 (1H, m), 1.97−1.82 (1H, m), 1.70−1.55 (1H, br), 1.21−1.00 (2H, m), 0.91 (3H, d, $J = 6.6$ Hz), 0.35−0.20 (1H, m); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 132.9

(d, J_{C-P} = 9.2 Hz), 131.5 (d, J_{C-P} = 9.2 Hz), 131.2 (d, J_{C-P} = 2.3 Hz), 130.8 (d, J_{C-P} = 2.3 Hz), 130.7 (d, J_{C-P} = 51.9 Hz), 129.0 (d, J_{C-P} = 9.2 Hz), 128.7 (d, J_{C-P} = 9.2 Hz), 127.0 (d, J_{C-P} = 48.8 Hz), 34.7 (d, J_{C-P} = 4.6 Hz), 32.3 (d, J_{C-P} = 1.5 Hz), 26.3, 22.7 (d, J_{C-P} = 34.3 Hz), 22.2 (br); ^{31}P NMR (162 MHz, $CDCl_3$, ppm) δ 1.6 (m); ^{11}B NMR (115.5 MHz, $CDCl_3$, ppm) δ −29.5 (m, $W_{1/2}$ = 260 Hz). Also isolated was 9 mg (15%) of starting linear phosphine borane.

Oxidative Cleavage of 37 to (4-Diphenylphosphinoyl)-2-methyl-1-butanol (30). A solution of cyclic six-membered phosphine−borane (**37**) (6.2 mg, 0.023 mmol) in MeOH (4 mL) was made basic with NaOH (15% aq, 0.2 mL) and treated with H_2O_2 (30% aq, 0.2 mL). After 14 h at reflux, the reaction was concentrated with a stream of N_2, diluted with water (8 mL), and extracted with DCM (3 × 8 mL). The extracts were dried through a column of Na_2SO_4 (2 × 2 cm). Removal of the solvent (aspirator) provided 6 mg (89%) of product alcohol **30** as a colorless liquid, identical by NMR assay to the material described above.

1,1-Dihydrido-2,2-diphenyl-5-isopropyl-1,2-borapospholane (38). A solution of $B(C_6F_5)_3$ (12.6 mg, 0.025 mmol) in benzene (0.25 mL) was added to a solution of (4-methyl-3-pentenyl)diphenylphosphine·BH_3 (**32**) (72.8 mg, 0.258 mmol) in benzene (2.0 mL). The reaction was quenched with triethylamine (1 mL) after 3 h. After removal of solvent (aspirator), the residue was purified by PLC on Whatman silica 60A (20 × 20 × 0.1 cm) with 4:1 hexane/DCM as the eluent to give 66 mg (91%) of cyclic phosphine−borane (**38**) as a colorless liquid; analytical TLC on K6F silica gel 60A, 4:1 hexane/DCM, R_f = 0.62: HRMS for $C_{18}H_{24}BP$; M − 1, *m*/*z* 281.1621, error = 3 ppm; base peak = 281 amu; IR (neat, cm^{-1}) 2378, B−H; 2262, B−H; 400 MHz NMR ($CDCl_3$, ppm) δ 7.68−7.60 (4H, m), 7.50−7.39 (6H, m), 2.59−2.49 (1H, m), 2.40−1.00 (2H, br), 2.27−2.06 (2H, m), 1.63−1.51 (1H, m), 1.46−1.34 (1H, m), 1.03−0.87 (1H, br), 1.01 (3H, d, J = 7.0 Hz), 0.96 (3H, d, J = 6.6 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 132.6 (d, J_{C-P}= 3.1 Hz), 132.5 (d, J_{C-P} = 2.3 Hz), 130.9 (d, J_{C-P} = 2.3 Hz), 130.8 (d, J_{C-P} = 2.3 Hz), 128.8 (d, J_{C-P} = 9.2 Hz), 128.7 (d, J_{C-P} = 9.2 Hz), 42.4 (br), 34.4 (d, J_{C-P} = 17.5 Hz), 31.9 (d, J_{C-P} = 16.8 Hz), 29.4, 29.0, 23.2 (d, J_{C-P} = 18.3 Hz), ipso-Cs obscured; ^{31}P NMR (162 MHz, $CDCl_3$, ppm) δ 28.4 (m); ^{11}B NMR (115.5 MHz, $CDCl_3$, ppm) δ −24.8 (br, $W_{1/2}$ = 115 Hz).

Oxidative Cleavage of 38 to (5-Diphenylphosphinoyl)-2-methyl-3-pentanol (33). A solution of cyclic five-membered phosphine−borane (**38**) (13.7 mg, 0.049 mmol) in MeOH (4 mL) was made basic with NaOH (15% aq, 0.2 mL) and treated with H_2O_2 (30% aq, 0.2 mL). After 2 h at reflux, the reaction was concentrated with a stream of N_2, diluted with water (8 mL), and extracted with DCM (3 × 8 mL). The extracts were dried through a column of Na_2SO_4 (2 × 2 cm). Removal of the solvent (aspirator) provided 10 mg (70%) of product alcohol **33** as a colorless oil, identical to the material described above by NMR assay.

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Supporting Information Available: NMR spectra of new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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