JOC Article

Hetero-Diels−Alder Reactions of 2*H*-Phospholes with Aldehydes

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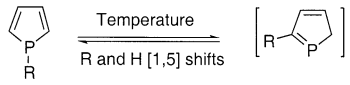
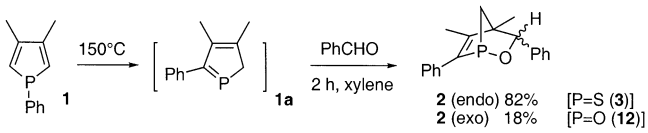
Transient 2-phenyl-3,4-dimethyl-5*H*-phosphole reacts at 150 °C with aldehydes RCH═O to give the corresponding [4 + 2] P−O cycloadducts with *endo*- (major) and *exo*-R-substituents. The cycloaddition with α,*β*-unsaturated aldehydes takes place both at the C═O (major) and C═C bonds. Upon heating under reduced pressure, the benzaldehyde cycloadduct dissociates to give back the 2*H*-phosphole, which either dimerizes, is trapped by diphenylacetylene, or is deprotonated by ^{t}BuOK.

It is well-known that aliphatic or aromatic aldehydes are relatively unreactive toward nonactivated dienes such as isoprene or 2,3-dimethylbutadiene.[1] Efficient [4 + 2] cycloadditions are only observed under promotion by Lewis acid catalysts, which are employed to activate the carbonyl group. Enantioselectivity can be achieved in such reactions in the presence of appropriate chiral catalysts.[2] The transition state of the model reaction between butadiene and formaldehyde is asymmetric, with the nascent C−O bond at 1.999 Å being substantially shorter than the C−C bond at 2.133 Å.[3] The experimentally observed mechanism of the more representative reaction between Danishefsky's diene and benzaldehyde in the presence of an aluminum catalyst is different and proceeds in two steps. The initial step involves the nucleophilic attack of the diene at the carbonyl carbon of the O-complexed aldehyde.[4] Against such a background, one might wonder what would be the outcome of the reaction of a 1-phosphadiene with aldehydes. Among the many questions are the regioselectivity of the cycloaddition (P−O versus P−C adducts), the potential need for an activating Lewis acid catalyst, and the possibility of side reactions at the phosphorus lone pair. The only data available in the literature concern the reaction of a 1-phosphadiene P-$W(CO)_5$ complex with benzaldehyde, where a clean [4 + 2] cycloaddition leading to the corresponding P−O cycloadduct was observed.[5] A deeper investigation of this hetero-Diels−Alder reaction would be welcome but is hampered by the limited availability of 1-phospha-1,3-dienes. Indeed, when not stabilized by bulky substituents, these species spontaneously and irreversibly electrocyclize to give 1,2-dihydro-1,2-diphosphetes.[6] One noteworthy exception concerns transient 2*H*-phospholes, which are easily obtained from

SCHEME 1



SCHEME 2



1*H*-phospholes by a series of [1,5] sigmatropic shifts of the P-substituents and hydrogen (Scheme 1).[7] In this paper, we investigate the reactivity of these 2*H*-phospholes toward various aldehydes.

Results and Discussion

The easily available 1-phenyl-3,4-dimethylphosphole **1**[8] is known to equilibrate with the 2-phenyl-3,4-dimethyl-5*H*-phosphole **1a** at around 150 °C.[7] We have attempted the hetero-Diels−Alder reaction with benzaldehyde under these conditions. The results are depicted in Scheme 2. According to the ^{31}P NMR spectrum of the crude reaction mixture, the cycloaddition is quantitative and yields two products with ^{31}P resonances at 111.4 (major) and 111.1 (minor). These chemical shifts are consistent with the two possible P−O [4 + 2] cycloadducts. After evaporation of xylene under reduced pressure, the major isomer slowly crystallized and was characterized by X-ray crystal structure analysis. The phenyl located on the P−O−C carbon is on the endo side of the bicyclic structure. This structure is highly strained as indicated by the sum of the O−P−C and C−P−C angles at phosphorus (Σ = 276.3°). The P−O and C(Ph)−C(Me)

(1) Boyer, D. L.; Weinreb, S. H. *Hetero-Diels−Alder Methodology in Organic Synthesis*; Academic Press: San Diego, 1987; pp 94−119.
(2) Jørgensen, K. A. *Angew. Chem., Int. Ed.* **2000**, *39*, 3559.
(3) McCarrick, M. A.; Wu, Y.-D.; Houk, K. N. *J. Am. Chem. Soc.* **1992**, *114*, 1499; McCarrick, M. A.; Wu, Y.-D.; Houk, K. N. *J. Org. Chem.* **1993**, *58*, 3330.
(4) Roberson, M.; Jepsen, A. S.; Jørgensen, K. A. *Tetrahedron* **2001**, *57*, 907.
(5) Tran Huy, N. H.; Mathey, F. *Tetrahedron Lett.* **1988**, *29*, 3077.
(6) Dillon, K. B.; Mathey, F.; Nixon, J. F. *Phosphorus: The Carbon Copy*; Wiley: Chichester, 1998; pp 128−134.
(7) Mathey, F.; Mercier, F.; Charrier, C.; Fischer, J.; Mitschler, A. *J. Am. Chem. Soc.* **1981**, *103*, 4595. Theoretical study of the [1,5] shifts: Bachrach, S. H. *J. Org. Chem.* **1993**, *58*, 5414. Review on the reactivity of 2*H*-phospholes: Mathey, F. *Acc. Chem. Res.* **1992**, *25*, 90.
(8) Brèque, A.; Mathey, F.; Savignac, P. *Synthesis* **1981**, 983.

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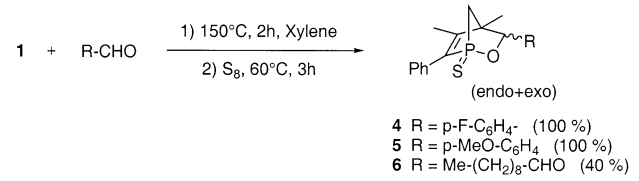
SCHEME 3



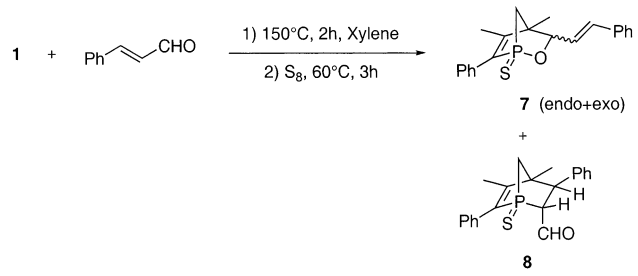
bonds are both long at 1.679(2) and 1.573(3) Å, respectively, suggesting the possibility of a [4 + 2] cycloreversion.

To characterize the minor isomer more fully, the crude mixture of **2** (endo + exo) was treated with sulfur at 50−60 °C in xylene for 3 h to give the P═S derivative **3**. Unlike the isomers of **2**, the two isomers of the sulfide **3** can be separated by chromatography on silica gel. The major isomer **3** (endo) was again characterized by X-ray crystal structure analysis. The overall geometry is similar to that of **2** (endo), but some significant differences appear in the sum of the angles at phosphorus (288.4° in **3** versus 276.3° in **2**) and the P−O bond length, which is shorter in **3** at 1.629(1) versus 1.679(2) Å in **2**. These data suggest less strain in the sulfide than in the tervalent derivative. The P═S bond of **3** (endo) is long at 1.924(1) Å. Any structural comparison between **3** (endo) and **3** (exo) must be made on the basis of the ^{13}C NMR data. In **3** (endo), the CH_2 bridge appears as a doublet at 53.13 ppm ($^1J_{C-P}$ = 70.5 Hz). In **3** (exo), the bridge appears at 45.65 ($^1J_{C-P}$ = 69.5 Hz) as a result of the shielding by the exo phenyl group. All other data are closely similar for **3** (endo) and **3** (exo). The structural characteristics of **2** and **3** can be compared to those of a series of less strained bicyclic phosphinites and their sulfides.[9]

We have attempted to generalize this first series of results. Usually, when the reaction works poorly or not at all, the 2*H*-phosphole [4 + 2] cyclodimer **9** (see Scheme 5) is formed as the major product. It is easily detected by its characteristic ^{31}P AB spectrum: $\delta(^{31}P) = -29.4$ and +37.3, $^1J_{P-P}$ = 198 Hz (xylene). The reaction goes to completion with *p*-fluoro- and *p*-methoxy-benzaldehydes and gives a 60:40 mixture of 2*H*-phosphole dimer and phosphinite with decanal. All of the products have been characterized as their P-sulfides (Scheme 3). We have been able to characterize **4** (exo) by X-ray crystal structure analysis. The structure closely resembles **3** (endo) except for the stereochemistry at the aldehyde-derived carbon.

The reaction appears to be very sensitive to the substitution patterns both on the phosphole and the aldehyde. ^{31}P monitoring of the reaction between 1,2,5-triphenylphosphole and benzaldehyde indicates a conversion into the corresponding [4 + 2] cycloadduct ($\delta(^{31}P)$ = +115.9 ppm) of only 17% after 24 h at 190 °C. Apparently, an equilibrium between cycloaddition and cycloreversion operates at this temperature. In the same vein, 1-phenyl-2,3,4,5-tetraethylphosphole reacts with benzaldehyde at 200 °C to give exclusively the monomeric phosphole oxide. In this case, the ethyl substituents in the 2 and 5 positions probably prevent the [1,5] shift. Steric hindrance on the carbonyl group has also a negative effect. With 2,4,6-trimethylbenzaldehyde, no reaction takes place and only 30% conversion is observed with 2,6-dimethoxybenzaldehyde.

SCHEME 4



It was interesting to study the competition between C═C and C═O as dienophiles toward 2*H*-phospholes. Thus we decided to investigate the reaction of **1** with *trans*-cinnamaldehyde. The results are depicted in Scheme 4. ^{31}P monitoring of the crude reaction mixture prior to sulfurization showed the formation of two phosphinites (δ = +110 (20%) and +109 ppm (50%)) and a phosphine (δ = −8.8 ppm (25%)). After sulfurization, the corresponding sulfides appear at 97.7 (minor), 97.1 (major) (**7** endo + exo) and 56.2 ppm (**8**). The major isomers of **7** and **8** were purified by chromatography and obtained in 20% and 14% yields, respectively. Phosphinite derivatives could be obtained either from a [4 + 2] cycloaddition between the 4π system of the cinnamaldehyde and the P═C double bond of the 2*H*-phosphole or from [4 + 2] cycloaddition between the C═O function and the 2*H*-phosphole acting as the diene. The second pathway was demonstrated by the inspection of the ^1H and ^{13}C spectra of **7**. The Ph−C−P(═S) sp^2 carbon appears at 138.71 ppm ($^1J_{C-P}$ = 83 Hz) and the C(H)−O−P(═S) sp^3 carbon at 86.60 ppm ($^2J_{C-P}$ = 3.5 Hz). The corresponding proton resonates in the normal range at 4.64 ppm. The phosphine sulfide **8** results from the cycloaddition between the 2*H*-phosphole acting as the diene and the C═C double bond of the cinnamaldehyde. It displays an aldehyde resonance at 9.99 (^1H) and 199.23 ppm (^{13}C). $^1H-^1H$ correlation indicates that the formyl group is located on the sp^3 CH−P(═S) carbon whose attached proton appears as a doublet of doublets at 3.78 ppm ($^2J_{H-P}$ = 16 Hz, $^3J_{H-H}$ = 5.5 Hz). The $^3J_{H-H}$ coupling shows that H_α and H_β are in exo and endo positions respectively,[11] thus demonstrating that the cycloaddition has taken place with retention of stereochemistry at the C═C double bond. The endo-CHO disposition is confirmed by the existence of a NOE effect between C_α-H and the CH_2 bridge. These results demonstrate that the carbonyl group of aldehydes can compete with activated alkenes in [4 + 2] cycloadditions with 1-phosphadienes. It is noteworthy that α,β-unsaturated aldehydes exclusively react via their C═C double bond with all-carbon dienes.[12] The precise origin of this difference between conjugated dienes is not established at the moment.

As a second part of this report, we decided to perform a preliminary study of the chemical properties of **2**. A first striking observation concerns the easy reversibility of the cycloaddition reaction. When heating **2** at 60 °C

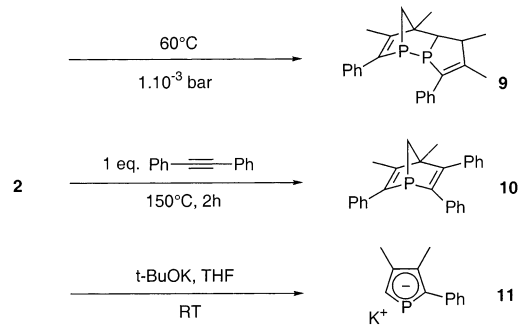
(9) Mattmann, E.; Mercier, F.; Ricard, L.; Mathey, F. *J. Org. Chem.* **2002**, *67*, 5422.

(10) Mercier, F.; Mathey, F. *J. Organomet. Chem.* **1984**, *263*, 55.

(11) Le Goff, P.; Mathey, F.; Ricard, L. *J. Org. Chem.* **1989**, *54*, 4754.

(12) See for example: Hollis, T. K.; Robinson, N. P.; Bosnich, B. *J. Am. Chem. Soc.* **1992**, *114*, 5464.

SCHEME 5



under 1×10^{-3} bar, a complete cycloreversion takes place with formation of the 2*H*-phosphole [4 + 2] dimer **9**.[13] Similarly, **2** reacts at 150 °C with 1 equiv of diphenylacetylene to give quantitatively the corresponding 1-phosphanorbornadiene **10**.[7] In contrast, the sulfide **3** does not react with diphenylacetylene even at 175 °C, thus demonstrating the high stability gained by the bicyclic system upon sulfurization. Compound **2** also reacts at room temperature with potassium *tert*-butoxide to give the phospholide ion **11** (Scheme 5).[14]

Finally, upon standing in air, **2** is oxidized to the corresponding P-oxide **12** (see Scheme 1). No hydrolysis of the P−O−C bond is observed. In a parallel experiment, the obtention of **12** has also been achieved after oxidation of **2** by hydrogen peroxide.

To conclude, this new 2*H*-phosphole cycloaddition reaction provides an easy access to a series of bicyclic phosphinites. As checked in the case of **2**, these species have good coordinating properties. Complexes such as $LW(CO)_5$, L_2PdCl_2, L_2PtCl_2, L_2NiBr_2, $L(PEt_3)PtCl_2$, (*p*-cymene)$RuLCl_2$ (L = **2**) are all easily accessible via conventional methods. We plan to investigate the possible uses of these complexes in homogeneous catalysis. Resolution of the chiral phosphorus center can also lend to interesting results in enantioselective catalysis. Further studies along these lines are currently being carried out.

Experimental Section

All reactions were performed under nitrogen. NMR spectra were recorded on a multinuclear spectrometer operating at 300.13 MHz for ^{1}H, 75.47 MHz for ^{13}C, and 121.50 MHz for ^{31}P. Chemical shifts are expressed in parts per million (ppm) downfield from internal solvents residual peaks (^{1}H and ^{13}C) and external 85% aqueous H_3PO_4 (^{31}P).

3,6-Diphenyl-4,5-dimethyl-1-phospha-2-oxanorborn-5-ene 2. 1-Phenyl-3,4-dimethylphosphole (940 mg, 5 mmol) and freshly distilled benzaldehyde (510 μL, 5 mmol) were placed via a septum in a 20-mL Schlenk tube containing distilled xylene (4 mL). The tube was closed and heated at 150 °C for 2 h. The complete consumption of the starting materials and the quantitative formation of the two diastereoisomers of the adduct was monitored by ^{31}P NMR spectroscopy: δ (*p*-xylene) = +111.1 (minor) and δ = +111.4 (major). Xylene was removed under vacuum without heating the reaction mixture. Slow crystallization of the major isomer occurred on standing. Data for **2 (**endo**)**: ^{1}H NMR ($CDCl_3$) δ 1.13 (s, 3H), 1.41 (s, 3H), 1.94 (m, 2H), 4.67 (s, 1H), 6.90−7.30 (m, 10H); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 15.40 (s), 18.84 (s), 56.32 (d, $^2J_{C-P}$ = 17 Hz), 62.48 (s), 83.52 (d, $^2J_{C-P}$ = 8 Hz), 126.9−130.4 (s), 138.48 (d, $^2J_{C-P}$ = 8 Hz), 139.44 (s), 149.58 (d, $^2J_{C-P}$ = 8 Hz), 152.04 (s); ^{31}P{^{1}H} NMR (*p*-xylene) δ +111.4; MS *m*/*z* 188 ($M^+ - C_7H_6O$, 100).

3,6-Diphenyl-4,5-dimethyl-1-phospha-2-oxanorborn-5-ene Sulfide 3. 1-Phenyl-3,4-dimethylphosphole (940 mg, 5 mmol) and freshly distilled benzaldehyde (510 μL, 5 mmol) were placed via a septum in a 20-mL Schlenk tube containing distilled xylene (4 mL). The tube was closed and heated to 150 °C for 2 h. Sulfur (160 mg 5 mmol) was added, and the solution was heated to 60 °C for 3 h. The solvents were removed under reduced pressure to give a yellow solid. Chromatography on silica gel with a hexane/ether (85/15) eluent gave first **3a** (300 mg) then **3b** (1230 mg). Total yield: 94%. Data for **3a**: ^{1}H NMR ($CDCl_3$) δ 1.17 (s, 3H), 1.90 (dd, AB system, $^2J_{H-H}$ = 13 Hz, $^4J_{H-H}$ = 2 Hz, 1H), 2.13 (d, $^4J_{H-H}$ = 2 Hz, 3H), 2.16 (d, AB system, $^2J_{H-H}$ = 13 Hz, 1H), 4.68 (d, $^3J_{H-P}$ = 7 Hz, 1H), 7.30−7.55 (m, 10H); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 14.21 (d, $^3J_{C-P}$ = 13 Hz), 18.32 (d, $^3J_{C-P}$ = 19 Hz) 45.65 (d, $^1J_{C-P}$ = 70 Hz), 51.88 (d, $^2J_{C-P}$ = 17.5 Hz), 85.07 (s), 126.9−129.6 (s), 132.47 (s), 136.83 (s), 138.7 (d, $^1J_{C-P}$ = 81 Hz), 157.94 (d, $^2J_{C-P}$ = 16 Hz); ^{31}P{^{1}H} NMR ($CDCl_3$) δ +98.8; MS *m*/*z* 326 (M^+, 49), 220 ($M^+ - C_7H_6O$, 100), 205 ($M^+ - C_7H_6O$ − 15, 34), 187 ($M^+ - C_7H_6O$ − S − 1, 14); HRMS for **3a** +1 calcd 327.0973, found 327.0967. Data for **3b**: ^{1}H NMR ($CDCl_3$) δ 1.32 (d, *J* = 2 Hz, 3H), 1.56 (s, 3H), 2.25 (s, 1H), 2.26 (d, J_{H-P} = 3.5 Hz), 5.18 (d, $^3J_{H-P}$ = 2 Hz, 1H), 7.10−7.50 (m, 10H); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 15.79 (d, $^3J_{C-P}$ = 13 Hz), 18.39 (s, $^3J_{C-P}$ = 19 H), 53.08 (d, $^2J_{C-P}$ = 18 Hz), 53.13 (d, $^1J_{C-P}$ = 70.5 Hz), 86.56 (d, $^2J_{C-P}$ = 3.5 Hz), 126.5−129.9 (s), 132.37 (d, J_{C-P} = 10.5 Hz), 136.83 (d, J_{C-P} = 3.5 Hz), 138.80 (d, $^1J_{C-P}$ = 85.5 Hz), 154.91 (d, $^2J_{C-P}$ = 15 Hz); ^{31}P{^{1}H} NMR ($CDCl_3$) δ +97.9; MS *m*/*z* 326 (M^+, 60), 220 ($M^+ - C_7H_6O$, 100), 205 ($M^+ - C_7H_6O$ − 15, 35), 187 ($M^+ - C_7H_6O$ − S − 1, 12); HRMS for **3b** + 1 calcd 327.0973, found 327.0976. Anal. Calcd for **3b**: C, 69.94; H, 5.83. Found: C, 69.29; H, 5.81.

3-(4′-Fluorophenyl)-6-phenyl-4,5-dimethyl-1-phospha-2-oxanorborn-5-ene Sulfide 4. 1-Phenyl-3,4-dimethylphosphole (940 mg, 5 mmol) and freshly distilled 4-fluorobenzaldehyde (540 μL, 5 mmol) were placed via a septum in a 20-mL Schlenk tube containing distilled xylene (4 mL). The tube was closed and heated to 150 °C for 2 h. The complete consumption of the starting materials and the quantitative formation of the two diastereoisomers of the adduct was monitored by ^{31}P NMR spectroscopy: δ (*p*-xylene) = +113.3 (minor) and δ = +113.7 (major). Sulfur (160 mg, 5 mmol) was added, and the solution was heated to 60 °C for 3 h. The solvents were removed under reduced pressure to give a yellow solid. Chromatography over silica gel with a hexane/ether (90/10) eluent gave first **4a** (250 mg) then **4b** (900 mg). Total yield: 67%. Data for **4a**: ^{1}H NMR ($CDCl_3$) δ 1.11 (s, 3H), 1.87 (d, $^2J_{H-P}$ = 2,6 Hz, 1H), 2.07 (m, 1H), 2.08 (d, *J* = 1,5 Hz, 3H), 4.62 (d, $^3J_{H-P}$ = 7 Hz, 1H), 7.00−7.40 (m, 9H); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 13.63 (d, $^3J_{C-P}$ = 13 Hz), 17.71 (s, $^3J_{C-P}$ = 19 Hz), 45.08 (d, $^1J_{C-P}$ = 69.5 Hz), 51.30 (d, $^2J_{C-P}$ = 17.5 Hz), 83.93 (d, $^2J_{C-P}$ = 4.5 Hz), 115.43 (d, $^2J_{C-F}$ = 21.5 Hz), 127.86 (d, *J* = 1 Hz), 128.41 (s), 128.67 (d, *J* = 8 Hz), 128.95 (d, $^3J_{C-F}$ = 6 Hz), 131.93 (d, *J* = 11 Hz), 132.14 (pst, *J* = 2.5 Hz), 138.18 (d, $^1J_{C-P}$ = 83.5 Hz), 157.35 (d, $^2J_{C-P}$ = 16 Hz), 162.79 (d, $^1J_{C-F}$ = 247.5 Hz); ^{31}P{^{1}H} NMR ($CDCl_3$) δ +97.3; MS *m*/*z* 344 (M^+, 33), 220 ($M^+ - C_7H_5OF$, 100), 205 ($M^+ - C_7H_5OF$ − 15, 41); HRMS for **4a** + 1 calcd 345.0878, found 345.0887. Data for **4b**: ^{1}H NMR ($CDCl_3$) δ 1.27 (t, *J* = 1 Hz, 3H), 1.46 (s, 3H), 2.17 (s, 1H), 2.19 (d, $^2J_{H-P}$ = 3.5 Hz, 1H), 5.07 (s, 1H), 6.90−7.35 (m, 9H); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 15.30 (d, $^3J_{C-P}$ = 13 Hz), 17.81 (s, $^3J_{C-P}$ = 19 Hz), 52.55 (d, $^2J_{C-P}$ = 17.5 Hz), 52.63 (d, $^1J_{C-P}$ = 70.5 Hz), 85.51 (d, $^2J_{C-P}$ = 4.5 Hz), 115.28 (d, $^2J_{C-F}$ = 21.5 Hz′), 127.76 (d, *J* = 8 Hz), 128.00 (d, *J* = 1 Hz), 128.58 (s), 129.21 (d, $^3J_{C-F}$ = 6 Hz′), 131.60 (pst, *J* = 7.5 Hz), 131.78 (d, *J* = 10.5 Hz), 138.58 (d, $^1J_{C-P}$ = 82.5 Hz), 154.16 (d, $^2J_{C-P}$ = 15 Hz), 162.82 (d, $^1J_{C-F}$ = 247.5 Hz′); ^{31}P{^{1}H} NMR ($CDCl_3$) δ +97.1; MS *m*/*z* 344 (M^+, 17), 220 ($M^+ - C_7H_5OF$, 100), 205 ($M^+ - C_7H_5OF$ − 15, 29); HRMS for **4b** + 1 calcd 345.0878, found 345.0881.

(13) Mercier, F.; Mathey, F. *J. Organomet. Chem.* **1984**, *263*, 55.
(14) Holand, S.; Jeanjean, M.; Mathey, F. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 98.

3-(4′-Methoxyphenyl)-6-phenyl-4,5-dimethyl-1-phospha-2-oxanorborn-5-ene Sulfide 5. 1-Phenyl-3,4-dimethylphosphole (940 mg, 5 mmol) and freshly distilled 4-methoxybenzaldehyde (610 μL, 5 mmol) were placed via a septum in a 20-mL Schlenk tube containing distilled xylene (4 mL). The tube was closed and heated to 150 °C for 2 h. The complete consumption of the starting materials and the quantitative formation of the 2 diastereoisomers of the adduct was monitored by ^{31}P NMR spectroscopy: δ (*p*-xylene) = +111.7 (minor) and δ = +112.0 (major). Sulfur (160 mg, 5 mmol) was added, and the solution was heated to 60 °C for 3 h. The solvents were removed under reduced pressure to give a yellow solid. Chromatography over silica gel with a hexane/ether (90/10) eluent yielded an impure fraction of the major isomer. A recrystallization using a hexane/ether solution gave 900 mg of white crystals. Yield: 51%. ^{1}H NMR ($CDCl_3$) δ 1.38 (d, J = 2 Hz, 3H), 1.54 (s, 3H), 2.25 (s, 1H), 2.27 (d, $^2J_{H-P}$ = 2.5 Hz, 1H), 3.80 (s, 3H), 5.13 (d, $^3J_{H-P}$ = 2 Hz, 1H), 6.85 (d, AB system, $^3J_{H-H}$ = 8.5 Hz, 2H), 7.12 (d, AB system, $^3J_{H-H}$ = 8.5 Hz, 2H), 7.30−7.55 (m, 5H); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 15.35 (d, $^3J_{C-P}$ = 13 Hz), 17.83 (s, $^3J_{C-P}$ = 19 Hz), 52.53 (d, $^2J_{C-P}$ = 17.5 Hz), 52.58 (d, $^1J_{C-P}$ = 70.5 Hz), 55.36 (s), 85.99 (d, $^2J_{C-P}$ = 4 Hz), 113.59 (s), 127.26 (s), 127.66 (d, J_{C-P} = 4 Hz), 127.82 (d, J_{C-P} = 1 Hz), 128.50 (s), 129.24 (d, J_{C-P} = 4 Hz), 132.00 (d, J_{C-P} = 11 Hz), 138.32 (d, $^1J_{C-P}$ = 83 Hz), 154.56 (d, $^2J_{C-P}$ = 15 Hz), 159.71 (s); ^{31}P{^{1}H} NMR ($CDCl_3$) δ +98.1; MS *m*/*z* 355 (M^+ − 1, 9), 219 ($M^+ - C_7H_6O$ − 1, 100), 205 ($M^+ - C_7H_6O$ − 15, 28), 187 ($M^+ - C_7H_6O - S$ − 1, 13); HRMS for **5** + 1 calcd 357.1078, found 357.1075. Anal. Calcd for **5**: C, 67.42; H, 5.90. Found: C, 66.91; H, 5.91.

3-*n*-Nonyl-6-phenyl-4,5-dimethyl-1-phospha-2-oxanorborn-5-ene Sulfide 6. 1-Phenyl-3,4-dimethylphosphole (940 mg, 5 mmol) and freshly distilled decanal (940 μL, 5 mmol) were placed via a septum in a 20-mL Schlenk tube containing distilled xylene (2 mL). The tube was closed and heated to 150 °C for 2 h. The complete consumption of the starting materials and the formation of the two diastereoisomers of the adduct in 50% yield, along with the formation of 2*H*-phosphole dimers in 50% yield, was monitored by ^{31}P NMR spectroscopy: δ (*p*-xylene) = +106.8 (major) and δ = +109.5 (minor) (ratio 10:1). Sulfur (160 mg, 5 mmol) was added, and the solution was heated to 60 °C for 3 h. The solvents were removed under reduced pressure to give a yellow solid. Chromatography over silica gel with a hexane/ether (90/10) eluent yielded 730 mg of **6** as white crystals. Yield: 39%. ^{1}H NMR ($CDCl_3$) δ 0.79 (t, $^3J_{H-H}$ = 7 Hz, 3H), 1.17 (m, 16H), 1.34 (s, 3H), 1.88 (d, $^4J_{H-H}$ = 2 Hz, 3H), 2.17 (d, $^2J_{H-P}$ = 10 Hz, 1H), 2.19 (dd, $^2J_{H-P}$ = 11 Hz, $^4J_{H-H}$ = 2 Hz, 1H), 3.99 (d, 1H, $^3J_{H-P}$ = 11 Hz), 7.15−7.30 (m, 5H); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 14.05 (s), 15.87 (d, $^3J_{C-P}$ = 13 Hz), 17.17 (s, $^3J_{C-P}$ = 19 Hz), 22.55 (s), 26.43 (s), 29.16 (s), 29.32 (s), 29.34 (s), 29.35 (s), 30.32 (d, J_{C-P} = 2 Hz), 31.74 (s), 50.15 (d, $^2J_{C-P}$ = 18.5 Hz), 52.70 (d, $^1J_{C-P}$ = 71 Hz), 87.30 (d, $^2J_{C-P}$ = 4 Hz), 127.43 (d, J = 1 Hz), 128.08 (s), 128.97 (d, J = 6 Hz), 131.92 (d, J = 10.5 Hz), 138.14 (d, $^1J_{C-P}$ = 83.5 Hz), 154.63 (d, $^2J_{C-P}$ = 15 Hz); ^{31}P{^{1}H} NMR ($CDCl_3$) δ +95.2; MS *m*/*z* 376 (M^+, 94), 220 ($M^+ - C_{10}H_{20}O$, 100), 205 ($M^+ - C_{10}H_{20}O$ −15, 26), 187 ($M^+ - C_{10}H_{20}O - S$ −1, 10); HRMS for **6** + 1 calcd 377.2068, found 377.2070.

Study of the Reaction between 2-*H* Phosphole and *trans*-Cinnamaldehyde. 1-Phenyl-3,4-dimethylphosphole (940 mg, 5 mmol) and freshly distilled *trans*-cinnamaldehyde (630 μL, 5 mmol) were placed via a septum in a 20-mL Schlenk tube containing distilled xylene (2 mL). The tube was closed and heated to 150 °C for 2 h. The complete consumption of the starting materials and the obtention of three different products was monitored by ^{31}P NMR spectroscopy: δ (*p*-xylene) = +110.2 (20%), δ = +109.3 (55%) and δ = −8.8 (25%). Sulfur (160 mg, 5 mmol) was added, and the solution was heated at 60 °C for 3 h. The solvents were removed under reduced pressure to give a yellow solid. Chromatography on silica gel with a hexane/ether (90/10 then 75/25) eluent yielded successively **8** (220 mg) as a beige oil and **7** (340 mg) as white crystals. Total yield: 32%.

2-Formyl-3,6-diphenyl-4,5-dimethylphosphanorborn-5-ene sulfide 7: ^{1}H NMR ($CDCl_3$) δ 1.46 (s, 3H), 1.84 (s, 3H), 2.07 (m, 2H), 4.64 (d, $^3J_{H-H}$ = 6.5 Hz, 1H), 5.52 (dd, $^3J_{H-H}$ = 16 Hz, $^3J_{H-H}$ = 6.5 Hz, 1H), 6.60 (d, $^3J_{H-H}$ = 16 Hz, 1H), 7.15−7.35 (m, 10H); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 15.66 (d, $^3J_{C-P}$ = 13 Hz), 17,46 (s, $^3J_{C-P}$ = 19 Hz), 51.59 (d, $^2J_{C-P}$ = 17.5 Hz), 52.15 (d, $^1J_{C-P}$ = 70 Hz), 86.26 (d, $^2J_{C-P}$ = 3.5 Hz), 123.00 (s), 127.67 (s), 127.84 (d, J_{C-P} = 1 Hz), 128.38 (s), 128.42 (s), 128.83 (s), 129.30 (d, J_{C-P} = 6 Hz), 131.85 (d, $^2J_{C-P}$ = 10.5 Hz), 133.87 (s′), 135.85 (s), 138.25 (d, $^1J_{C-P}$ = 83 Hz), 154.64 (d, $^2J_{C-P}$ = 15 Hz); ^{31}P{^{1}H} NMR ($CDCl_3$) δ +98.8; MS *m*/*z* 352 (M^+, 100), 220 ($M^+ - C_9H_8O$, 93), 205 ($M^+ - C_7H_6O$ − 15, 37); HRMS for **7** + 1 calcd 353.1129, found 353.1127.

3-(2′-Phenylethenyl)-6-phenyl-4,5-dimethyl-1-phospha-2-oxanorborn-5-ene 8: ^{1}H NMR ($CDCl_3$) δ 1.32 (s, 3H), 1.39 (d, J = 2.5 Hz, 3H), 2.14 (m, 2H), 3.75 (dd, $^2J_{H-P}$ = 16.5 Hz, $^3J_{H-H}$ = 5.5 Hz, 1H), 3.86 (d, $^3J_{H-H}$ = 5.5 Hz, 1H), 6.95−7.50 (m, 10H), 9.99 (d, $^3J_{H-P}$ = 1.5 Hz, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 16.43 (d, $^3J_{C-P}$ = 12,5 Hz), 19.70 (s, $^3J_{C-P}$ = 17.5 Hz), 50.40 (d, $^2J_{C-P}$ = 20.5 Hz), 51.68 (s), 52.48 (d, $^1J_{C-P}$ = 56.5 Hz), 58.44 (d, $^1J_{C-P}$ = 30 Hz), 127.88 (s), 128.22 (d, $^4J_{C-P}$ = 1.5 Hz), 128.36 (s), 128.61 (s), 128.74 (s), 129.41 (d, $^3J_{C-P}$ = 5 Hz), 131.81 (d, J_{C-P} = 10.5 Hz), 134.00 (d, $^1J_{C-P}$ = 68 Hz), 137.73 (d, J_{C-P} = 6 Hz), 157.85 (d, $^2J_{C-P}$ = 15 Hz), 198.98 (d, $^2J_{C-P}$ = 1 Hz); ^{31}P{^{1}H} NMR ($CDCl_3$) δ +56.0; MS *m*/*z* 351 (M^+ − 1, 9), 220 ($M^+ - C_9H_8O$, 100), 205 ($M^+ - C_7H_6O$ − 15, 30); HRMS for **8** + 1 calcd 353.1129, found 353.1134.

3,6-Diphenyl-4,5-dimethyl-1-phospha-2-oxanorborn-5-ene Oxide 12. 1-Phenyl-3,4-dimethylphosphole (940 mg, 5 mmol) and freshly distilled benzaldehyde (510 μL, 5 mmol) were placed via a septum in a 20-mL Schlenk tube containing distilled xylene (4 mL). The tube was closed and heated to 150 °C for 2 h. Hydrogen peroxide (100 vol,10 mL) were added, and the solution was stirred to room temperature for 30 min. The solvents were removed under reduced pressure to give a white solid. Chromatography on silica gel with ether as the eluent yielded 1260 mg of the compound **12** as white crystals. Yield: 82%. ^{1}H NMR ($CDCl_3$) δ 1.27 (d, J = 2 Hz, 3H), 1.46 (s, 3H), 1.96 (s, 1H), 1.99 (d, J_{H-P} = 8.5 Hz, 1H), 5.06 (d, $^3J_{H-P}$ = 2 Hz, 1H), 7.10−7.35 (m, 10H); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 14.57 (d, $^3J_{C-P}$ = 15 Hz), 18.41 (s, $^3J_{C-P}$ = 20 Hz), 46.00 (d, $^1J_{C-P}$ = 88 Hz), 49.29 (d, $^2J_{C-P}$ = 23 Hz), 85.70 (s), 126.31 (s), 128.13 (s), 128.52 (s), 128.79 (s), 129.15 (d, $^3J_{C-P}$ = 2 Hz), 129.24 (s), 132.38 (d, J_{C-P} = 9 Hz), 136.91 (d, J_{C-P} = 4 Hz), 134.09 (d, $^1J_{C-P}$ = 110 Hz), 155.48 (d, $^2J_{C-P}$ = 18 Hz); ^{31}P{^{1}H} NMR (*p*-xylene) δ + 58.6; MS *m*/*z* 188 ($M^+ - C_7H_6O$, 100). HRMS for **12** + 1 calcd 311.1201, found 311.1200.

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Supporting Information Available: Crystallographic data for **2** (endo) and **3** (endo). This material is available free of charge via the Internet at http://pubs.acs.org.

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