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Radical Addition Reaction of Bis(naphth-1,8-diyl-8-oxy)hydrophosphorane to Olefins

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ABSTRACT: *In the presence of 1,1′-azobis(cyclohexanecarbonitrile) (ACHCN), the reaction of bis(naphth-1,8-diyl-8-oxy)hydrophosphorane with an equimolar amount of terminal and internal olefins gave the corresponding alkylphosphoranes. In the reactions with styrene and methyl acrylate, 2:1 olefin–hydrophosphorane adducts were obtained as a minor product. The reactions with terminal olefins were entirely regioselective and more efficient than those with internal olefins. In the absence of ACHCN, the radical addition reaction of the hydrophosphorane to terminal and internal olefins could also proceed slowly.* © 2011 Wiley Periodicals, Inc. Heteroatom Chem 22:538–544, 2011; View this article online at wileyonlinelibrary.com. DOI 10.1002/hc.20719

INTRODUCTION

Organophosphorus compounds have played a significant role as chemical reagents, transition metal ligands, and biologically active substances for medical and agricultural use. Among various synthetic approaches to organophosphorus compounds, the formal addition reaction of a P—H bond to an unsaturated C—C bond, catalyzed by transition metal compounds [1,2] or induced by radical initiators [3,4], has attracted much attention because most of the reactions are convenient and regioselective. Although numerous radical addition reactions of tri- or tetracoordinate phosphorus compounds bearing P—H bond to various olefins have been reported, only a few examples of the radical addition reactions of pentacoordinate hydrophosphoranes to terminal olefins are known [5].

The preparation, structural characterization, and reactions of phosphoranyl radicals have been well documented [6]. The substantial issues involving the reaction of phosphoranyl radical have been the steric demand and α-scission reaction (Scheme 1) of the phosphoranyl radical. In the case of phosphoranyl radicals containing alkoxy and sulfenyl groups on the phosphorus atom, β-scission reaction (Scheme 2) can also occur. The scission reactions of spiro- or bicyclic phosphoranyl radicals are slower than those of acyclic ones [5a,6c,6e]. Thus, the reactions of tetraoxyspirophosphoranyl radicals with ethyl vinyl ether [5b], 1-hexene [5a], or 3,3-dimethyl-1-butene [5a] have been reported, whereas the resulting alkylphosphoranes should be unstable to moisture [7]. However, radical addition reactions of hydrophosphoranes to haloolefins, aryl or alkyl acrylates, styrene, and internal olefins have never

Dedicated to Professor Kin-ya Akiba on the occasion of his 75th birthday.

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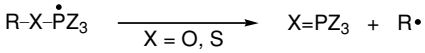
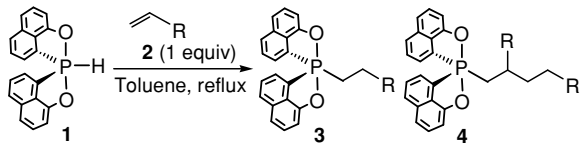
SCHEME 1



SCHEME 2



SCHEME 3

been reported. In the presence of a radical initiator, tri- and tetracoordinate phosphorus compounds bearing P—H bond are known to mediate radical reduction of haloolefins [3,8] such as the reaction of tributyltin hydride [9], whereas acrylates and styrene are either unreactive with phosphorus hydrides or susceptible to polymerization [4b,c,g]. Additionally, to the best of our knowledge, the thermal formal addition of the P—H bond to the unsaturated C—C bond is rare [10,11].

We have reported the synthesis of bis(naphth-1,8-diyl-8-oxy)hydrophosphorane (**1**) and the reactivity of lithium phosphoranide generated from hydrophosphorane **1** [12]. Subsequently, our attention was focused on the radical addition reaction of **1** to unsaturated compounds. The spirophosphoranyl radical generated from **1** is compact compared with reported spirophosphoranyl radicals [5a,b,6f] and the rigidity of naphthalene moiety should also suppress the scission reactions of the phosphoranyl radical. Additionally, hydrophosphorane **1** and alkylphosphorane derived from **1** are stable to moisture [12a,b]. The spirophosphorane is potentially useful as a reagent for Horner–Wadsworth–Emmons-type reaction [12f] and a chiral building block. Here, we report on the radical addition reaction of hydrophosphorane **1** to both terminal and internal olefins induced by a radical initiator or in the absence of an initiator.

RESULTS AND DISCUSSION

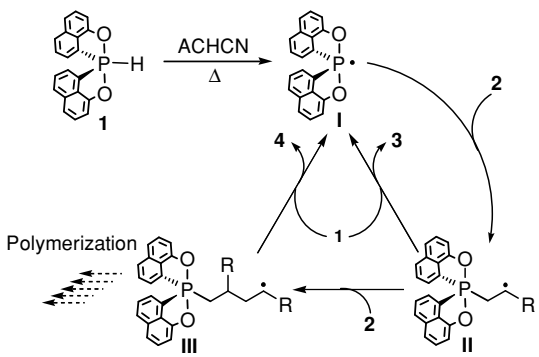
Radical addition reaction of hydrophosphorane **1** to terminal olefins **2a–d** (1 equiv) could be achieved by refluxing toluene solutions for 3 h in the presence of a catalytic amount of 1,1′-azobis(cyclohexanecarbonitrile) (ACHCN) as the radical initiator to give alkylphosphoranes **3a–d**, which were 1:1 adducts (Scheme 3, Table 1: run 1–4). The phosphoranes 3 were formal anti-Markovnikov products, whose ^{1}H NMR spectra exhibited the diastereotopic resonances for the α-methylene protons, and no regioisomer was detected. The ^{31}P NMR analyses of the crude products showed that most, if not all, of hydrophosphorane **1** has been consumed. It is worth noting that only stoichiometric amounts were required in contrast to excesses of tri- or tetracoordinate phosphorus compounds bearing P—H bond usually required in many radical addition reactions to olefins [4c–f]. The chain mechanism for the radical addition reaction is depicted in Scheme 4. The reactions are entirely regioselective, showing formal anti-Markovnikov selectivity due to the bulkiness of the phosphoranyl radical **I** and the generation of the more stable carbon-centered radical intermediate.

TABLE 1 Results of the Radical Addition Reaction of **1** to Terminal Olefins **2**[a]

Run	*ACHCN*	*R*	*Time (h)*	***3*** *(%)*[b]	***4*** *(%)*[b] *(dr*[c]*)*
1	0.2 equiv	C_8H_{17}	3	92	–
2	0.2 equiv	Ph	3	82	5 (52:48)
3	0.2 equiv	CO_2Me	3	82	11 (53:47)
4	0.2 equiv	$(CH_2)_4Br$	3	97	–
5	None	C_8H_{17}	7	82	–
6	None	Ph	7	81	5 (52:48)
7	None	CO_2Me	7	78	8 (53:47)
8	None	$CH_2)_4Br$	7	82	–

[a]The reaction of **1** (0.632 mmol) with olefin (0.632 mmol) was conducted in the absence or presence of ACHCN (0.127 mmol) in toluene (5.0 mL).
[b]Isolated yield.
[c]Determined by ^{1}H NMR spectroscopic analysis.

In the reaction with styrene (**2b**) or methyl acrylate (**2c**), the formation of a 2:1 olefin–hydrophosphorane adduct **4b** or **4c** as a minor product was also observed. This implies that the

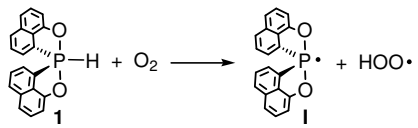


SCHEME 4

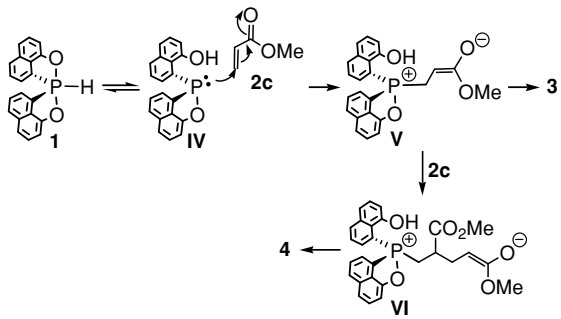
abstraction of the hydrogen atom from the P—H bond in **1** by a carbon-centered radical in **II** and **III** (Scheme 4) to give **3** and **4**, respectively, is faster than polymerization probably due to the low bond dissociation energy of the P—H bond in **1** [4h]. The radical reduction of 6-bromo-1-hexene (**2d**) to give methylcyclopentane via radical cyclization of the 5-hexenyl radical [13] was averted. This may have been due to the instability of the bromophosphorane that would have arisen by the abstraction of the bromine atom from **2d** by radical **I**.

In the absence of ACHCN, completely regioselective radical addition reaction of **1** to terminal olefins **2a–d** could also proceed slower than the ACHCN-induced reaction under similar conditions (Table 1: run 5–8). Although the reactions described in Table 1 were conducted under a nitrogen atmosphere, the radical reaction in the absence of ACHCN may be initiated by molecular oxygen (Scheme 5) because oxygen could not be excluded completely. However, the addition reaction of **1** to **2a–c** in the absence of ACHCN under a nitrogen atmosphere was not retarded by addition of a radical inhibitor, hydroquinone, 4-tert-butylcatechol, or 2,6-di-tert-butyl-4-methylphenol, probably due to high reaction temperature. A mechanism involving the concerted addition of the P—H bond to the C—C double bond, which could also give **3**, may be excluded because the formation of the 2:1 adducts **4** requires reaction via a stepwise mechanism depicted in Scheme 4 without ACHCN. In the reaction with methyl acrylate (**2c**), however, a mechanism involving phosphonium zwitterions (Scheme 6) cannot be fully excluded [11b].

We also examined the reactions with symmetrical internal olefins (Scheme 7). Alkylphosphoranes **6A–C** were obtained in good yields (Table 2: run 1–5) by the radical addition of hydrophosphorane **1** to internal olefins **5A–C** (*cis*-stilbene, *trans*-stilbene, dimethyl maleate, dimethyl fumarate, and cyclohexene) under conditions similar to those of reactions to terminal olefins using ACHCN, although the reactions were relatively slow (5 h). However, in the reaction of **1** with 1 equiv of **5** in the absence of ACHCN, consumption of **1** was not complete



SCHEME 5

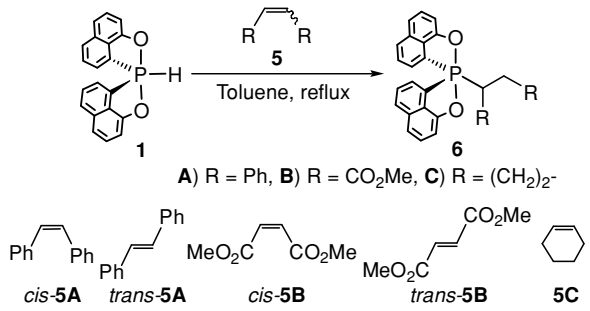


SCHEME 6

TABLE 2 Results of Radical Addition Reaction of **1** to Internal Olefins **5**[a]

Run	*ACHCN*	*Olefin*	***5** (equiv)*	*Time (h)*	***6** (%)*[b] *(dr*[c]*)*
1	0.2 equiv	*cis*-**5A**	1	5	80 (59:41)
2	0.2 equiv	*trans*-**5A**	1	5	73 (60:40)
3	0.2 equiv	*cis*-**5B**	1	5	91 (60:40)
4	0.2 equiv	*trans*-**5B**	1	5	84 (55:45)
5	0.2 equiv	**5C**	1	5	67
6	None	*cis*-**5A**	1	5	16 (60:40)
7	None	*trans*-**5A**	1	5	6 (60:40)
8	None	*cis*-**5B**	1	5	88 (61:39)
9	None	*trans*-**5B**	1	5	63 (53:47)
10	None	**5C**	1	5	12
11	None	*cis*-**5A**	50	7	63 (57:43)
12	None	*trans*-**5A**	80	7	69 (57:43)
13	None	*trans*-**5B**	4	7	85 (53:47)
14	None	**5C**	40	7	62

[a]The reaction of **1** (0.632 mmol) with 1 equiv or an excess of olefin was conducted in the absence or presence of ACHCN (0.127 mmol) in toluene (5.0 mL).
[b]Isolated yield.
[c]Determined by ^{1}H NMR spectroscopic analysis.



SCHEME 7

(Table 2: run 6,7,9,10) in 5 h except for the case of *cis*-**5B** (Table 2: run 8), whereas it could be achieved by using a large excess of **5** and elongating the reaction time (Table 2: run 11–14). The relatively slow reaction with internal olefins must reflect the bulkiness of phosphoranyl radical **I**. Thus, the reaction with tetraphenylethylene did not proceed. The higher reactivities of *cis* and *trans*-**5B** indicate that the phosphoranyl radical **I** is nucleophilic [14]. The reactions of *cis*-**5** were more effective than those of *trans*-**5**, because *cis*-olefins are thermodynamically less stable than *trans*-olefins.

CONCLUSION

In conclusion, the radical addition reaction of hydrophosphorane **1** to both terminal and internal olefins could be achieved by activation with ACHCN. The reactions were entirely regioselective, and polymerization and reduction of the olefins were suppressed. This reactivity may be intrinsic to hydrophosphoranes, i.e., hypervalent [15] phosphorus hydrides. It was also revealed that the thermal addition to both terminal and internal olefins of **1** could also be achieved. The formal addition of the P—H bond to the C—C double bond without the use of extraneous reagents is rare [4a,10,11]. Kinetic examinations, theoretical studies, and the reactions of **1** with other olefins or alkynes are currently under investigation.

EXPERIMENTAL

All reactions were carried out under a nitrogen atmosphere. Hexane, THF, and toluene used in the reactions were freshly distilled from Na, Na-benzophenone, and CaH_2, respectively, and transferred under the positive pressure of nitrogen via a syringe. Column chromatography was performed using Silica Gel 60N (Kanto Chemical Co., Inc., 0.063–0.210 mm). Preparative GPC was performed on a LC-9201 recycling preparative HPLC (Japan Analytical Industry Co., Ltd) with tandem GPC columns (JAIGEL-1H and 2H, chloroform, 3.5 mL/min).

Melting points were measured with a Yanaco micro melting point apparatus and are uncorrected. ^{1}H (600 MHz), ^{13}C (151 MHz), and ^{31}P (243 MHz) NMR spectra were recorded on a Brucker AVANCE-II (600 MHz) spectrometer. HRMS was measured on a Hitachi M-2500 mass spectrometer. Elemental analyses were performed on a Perkin-Elmer 2400 CHN elemental analyzer.

*2-λ^5–2,2′-Spirobi[2H-naphth[1,8-cd]-1,2-oxaphosphole] (**1**)*

To a suspension of 1-naphthol (20 g, 139 mmol) in 300 mL of hexane was added *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (41.9 mL, 278 mmol). *n*-BuLi (1.60 M *n*-hexane solution, 175 mL, 280 mmol) was added dropwise to the resulting solution and the mixture was refluxed for 20 h followed by the slow addition of a solution of PCl_3 (6.05 mL, 69.3 mmol) in 100 mL of hexane at −78°C. After removal of the cooling bath, the reaction mixture was allowed to warm to ambient temperature and THF (300 mL) was added. The mixture was quenched with 6 M HCl (400 mL) and extracted with 2:1 THF/Et_2O (300 mL × 5). The collected organic layer was dried over $MgSO_4$ and the volatile was removed under reduced pressure. Purification of the residue was carried out on silica gel column chromatography (benzene) to give **1** as pale yellow powder. Yield: 4.70 g, 21%. mp: 273°C. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 9.16 (d, 1H, J = 737 Hz), 8.22 (dd, 2H, J = 12.6, 7.2 Hz), 7.98 (dd, 2H, J = 8.4, 3.0 Hz), 7.61 (dt, 2H, J = 7.8, 6.6 Hz), 7.51 (t, 2H, J = 8.4 Hz), 7.35 (dd, 2H, J = 8.4, 1.8 Hz), 6.99 (d, 2H, J = 7.8 Hz). ^{13}C NMR ($CDCl_3$, 151 MHz): δ 156.9, 133.8 (d, J = 9.4 Hz), 132.0 (d, J = 14.5 Hz), 131.2 (d, J = 4.4 Hz), 129.7 (d, J = 26.1 Hz), 129.3, 128.2 (d, J = 16.6 Hz), 122.4 (d, J = 154.1 Hz), 116.1, 104.2. ^{31}P NMR ($CDCl_3$, 243 MHz): δ −49.9. Anal. Calcd for $C_{20}H_{13}O_2P$: C, 75.95; H, 4.14. Found: C, 75.78; H, 4.26.

*General Procedure for the Radical Addition Reaction of Hydrophosphorane **1** Activated with ACHCN*

To a solution of **1** (200 mg, 0.632 mmol) and ACHCN (31.0 mg, 0.127 mmol) in 5.0 mL of toluene was added an equimolar amount of an olefin at room temperature and the solution was refluxed for 3 h (for terminal olefins) or 5 h (for internal olefins). The reaction mixture was cooled to room temperature and the solvents were removed under reduced

pressure. Purification of the residue was carried out by silica gel column chromatography or by silica gel column chromatography and preparative GPC.

*2-Decyl-2,2′λ^5-spirobi[2H-naphth[1,8-cd]-1,2-oxaphosphole] (**3a**)*

Silica gel column chromatography (benzene/hexane 1:1) afforded **3a** as a yellowish white powder. Yield: 265 mg, 92%. mp: 68–69°C. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.27 (dd, J = 11.8, 7.2 Hz, 2H), 7.94 (dd, J = 8.0, 2.7 Hz, 2H), 7.58 (ddd, J = 8.0, 7.1, 6.3 Hz, 2H), 7.46 (dd, J = 8.2, 7.6 Hz, 2H), 7.28 (dd, J = 8.3, 1.9 Hz, 2H), 6.89 (d, J = 7.4 Hz, 2H), 2.67 (dddd, J = 14.4, 12.6, 11.4, 5.3 Hz, 1H), 2.52 (ddt, J = 12.7, 11.4, 5.2 Hz, 1H), 1.75–1.65 (m, 1H), 1.61–1.51 (m, 1H), 1.29–1.12 (m, 14H), 0.85 (t, J = 7.3 Hz, 3H). ^{13}C NMR ($CDCl_3$, 151 MHz): δ 156.7, 133.8 (d, J = 8.6 Hz), 132.0 (d, J = 14.0 Hz), 130.8 (d, J = 4.2 Hz), 129.6 (d, J = 23.8 Hz), 129.2, 128.1 (d, J = 15.7 Hz), 125.4 (d, J = 154.3 Hz), 115.5, 103.8, 37.5 (d, J = 117.5 Hz), 31.9, 30.7 (d, J = 21.0 Hz), 29.43, 29.37, 29.2, 29.0, 23.9 (d, J = 5.9 Hz), 22.7, 14.1. ^{31}P NMR ($CDCl_3$, 243 MHz): δ −24.0. Anal. Calcd for $C_{30}H_{33}O_2P$: C, 78.92; H, 7.29. Found: C, 79.08; H, 7.30.

*2-(2-Phenylethyl)-2,2′λ^5-spirobi[2H-naphth[1,8-cd]-1,2-oxaphosphole] (**3b**) and 2-(2,4-Diphenylbutyl)-2,2′λ^5-spirobi[2H-naphth[1,8-cd]-1,2-oxaphosphole] (**4b**)*

A mixture of **3b** and **4b** was obtained by silica gel column chromatography (benzene/hexane 1:1). Preparative GPC afforded **3b** as a yellowish white powder. Yield: 217 mg, 82%. mp: 137–139°C. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.29 (dd, J = 11.7, 7.1 Hz, 2H), 7.95 (dd, J = 7.7, 2.7 Hz, 2H), 7.59 (ddd, J = 8.0, 7.1, 6.3 Hz, 2H), 7.47 (dd, J = 8.3, 7.5 Hz, 2H), 7.29 (dd, J = 8.3, 2.0 Hz, 2H), 7.14–7.11 (m, 2H), 7.08–7.04 (m, 3H), 6.91 (d, J = 7.4 Hz, 2H), 3.05–2.96 (m, 2H), 2.93–2.84 (m, 2H). ^{13}C NMR ($CDCl_3$, 151 MHz): δ 156.5, 141.1 (d, J = 21.0 Hz), 134.0 (d, J = 8.4 Hz), 132.0 (d, J = 14.3 Hz), 130.9 (d, J = 4.3 Hz), 129.6 (d, J = 24.2 Hz), 129.2, 128.2 (d, J = 18.9 Hz), 128.1 (d, J = 15.9 Hz), 126.0, 125.1 (d, J = 155.2 Hz), 115.6, 103.9, 38.9 (d, J = 116.6 Hz), 30.1 (d, J = 5.1 Hz). ^{31}P NMR ($CDCl_3$, 243 MHz): δ −26.0. Anal. Calcd for $C_{28}H_{21}O_2P$: C, 79.99; H, 5.03. Found: C, 80.28; H, 5.11.

The 2:1 adduct **4b** was also isolated as a yellow oil with preparative GPC. Yield: 15.5 mg, 5% (diastereomeric mixture). ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.17; 8.05 (dd, 2H, J = 11.9, 7.2 Hz, minor isomer; J = 11.9, 7.1 Hz, major isomer), 7.90–7.86 (m, 2H), 7.53; 7.47 (dd, 2H, J = 7.8, 6.5 Hz, major isomer; J = 7.9, 6.5 Hz, minor isomer), 7.46–7.40 (m, 2H), 7.25–6.80 (m, 14H), 3.17–2.91 (m, 3H), 2.28 (t, J = 8.0 Hz, 2H), 2.25–1.76 (m, 2H). ^{31}P NMR ($CDCl_3$, 243 MHz) δ −27.1; −27.7 (major isomer; minor isomer). HRMS Calcd for $C_{36}H_{29}O_2P$: 524.1905. Found: m/z 524.1713.

*2-(2-Methoxycarbonylethyl)-2,2′λ^5-spirobi[2H-naphth[1,8-cd]-1,2-oxaphosphole] (**3c**) and 2-[2,4-Bis(methoxycarbonyl)butyl]-2,2′λ^5-spirobi[2H-naphth[1,8-cd]-1,2-oxaphosphole] (**4c**)*

A mixture of **3c** and traces of impurities was obtained by silica gel column chromatography (benzene). Preparative GPC afforded **3c** as a yellowish white powder. Yield: 208 mg, 82%. mp: 133–135°C. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.27 (dd, J = 11.9, 7.1 Hz, 2H), 7.96 (dd, J = 8.0, 2.7 Hz, 2H), 7.60 (dt, J = 6.9, 6.8 Hz, 2H), 7.47 (t, J = 8.0 Hz, 2H), 7.31 (dd, J = 8.3, 2.0 Hz, 2H), 6.89 (d, J = 7.4 Hz, 2H), 3.41 (s, 3H), 3.08–2.95 (m, 2H), 2.74 (ddt, J = 18.1, 17.0, 7.6 Hz, 1H), 2.59 (dddd, J = 20.0, 16.9, 8.1, 6.7 Hz, 1H). ^{13}C NMR ($CDCl_3$, 151 MHz): δ 172.5 (d, J = 15.9 Hz), 156.2, 134.1 (d, J = 8.4 Hz), 132.0 (d, J = 14.3 Hz), 131.0 (d, J = 4.0 Hz), 129.4 (d, J = 25.0 Hz), 129.2, 128.1 (d, J = 16.3 Hz), 125.0 (d, J = 157.3 Hz), 115.8, 104.0, 51.6, 32.5 (d, J = 122.2 Hz), 29.5 (d, J = 4.1 Hz). ^{31}P NMR ($CDCl_3$, 243 MHz): δ −28.5. Anal. Calcd for $C_{24}H_{19}O_4P$: C, 71.64; H, 4.76. Found: C, 71.42; H, 4.79.

Silica gel column chromatography (benzene-ethyl acetate 10:1) afforded **4c** as a yellow oil. Yield: 34.1 mg, 11% (diastereomeric mixture). ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.26–8.21 (m, 2H), 7.94–7.91 (m, 2H), 7.59–7.54 (m, 2H), 7.47–7.44 (m, 2H), 7.30–7.27 (m, 2H), 6.88 (d, J = 7.4 Hz, 2H), 3.57; 3.54 (s, 3H, major isomer; minor isomer), 3.37–2.72 (m, 3H), 3.32; 3.04 (s, 3H, minor isomer; major isomer), 2.32–2.17 (m, 2H), 1.94–1.80 (m, 2H). ^{31}P NMR ($CDCl_3$, 243 MHz): δ −30.1; −30.8 (minor isomer; major isomer). HRMS Calcd for $C_{28}H_{25}O_6P$: 488.1389. Found: m/z 488.1391.

*2-(6-Bromohexyl)-2,2′λ^5-spirobi[2H-naphth[1,8-cd]-1,2-oxaphosphole] (**3d**)*

Silica gel column chromatography (benzene–hexane 1:1) afforded **3d** as a yellowish white powder. Yield: 293 mg, 97%. mp: 106–107°C. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.26 (dd, J = 11.8, 7.1 Hz, 2H), 7.93 (dd, J = 8.0, 2.7 Hz, 2H), 7.58 (ddd, J = 8.0, 7.1, 6.4 Hz, 2H), 7.46 (dd, J = 8.2, 7.6 Hz, 2H), 7.28 (dd, J = 8.3, 2.0 Hz, 2H), 6.90 (d, J = 7.4 Hz, 2H),

3.25 (t, $J = 7.8$ Hz, 2H), 2.67 (dddd, $J = 14.6$, 12.7, 11.1, 5.4 Hz, 1H), 2.52 (ddt, $J = 12.9$, 11.0, 5.3 Hz, 1H), 1.75–1.65 (m, 3H), 1.62–1.55 (m, 1H), 1.30–1.27 (m, 4H). ^{13}C NMR ($CDCl_3$, 151 MHz): δ 156.6, 133.8 (d, $J = 8.1$ Hz), 132.0 (d, $J = 14.2$ Hz), 130.9 (d, $J = 3.8$ Hz), 129.6 (d, $J = 24.1$ Hz), 129.2, 128.1 (d, $J = 15.7$ Hz), 125.3 (d, $J = 154.6$ Hz), 115.5, 103.8, 37.4 (d, $J = 117.9$ Hz), 33.7, 32.5, 29.7 (d, $J = 20.9$ Hz), 27.6, 23.7 (d, $J = 6.3$ Hz). ^{31}P NMR ($CDCl_3$, 243 MHz): δ −24.5. Anal. Calcd for $C_{26}H_{24}BrO_2P$: C, 65.15; H, 5.05. Found: C, 65.35; H, 5.10.

*2-(1,2-Diphenylethyl)-2,2′λ^5-spirobi[2H-naphth[1,8-cd]-1,2-oxaphosphole] (**6A**)*

Silica gel column chromatography (benzene–hexane 1:1) afforded **6A** as a yellowish white powder. Yield: 252 mg, 80% (diastereomeric mixture) from *cis*-stilbene (*cis*-**5A**); Yield: 228 mg, 73% (diastereomeric mixture) from *trans*-stilbene (*trans*-**5A**). mp: 142–145°C. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.19; 8.12 (dd, $J = 11.5$, 7.1 Hz, 2H, minor isomer; major isomer), 7.84; 7.82 (dd, $J = 8.0$, 2.7 Hz, 2H, minor isomer; major isomer), 7.51–7.44 (m, 2H), 7.43; 7.39 (dd, $J = 8.2$, 7.5 Hz, 2H, major isomer; minor isomer), 7.30–7.28; 7.15–7.13 (m, 2H, major isomer; minor isomer), 7.21; 7.19 (dd, $J = 8.3$, 2.0 Hz, 2H, major isomer; minor isomer), 6.94–6.80 (m, 2H), 4.48; 4.42 (ddd, $J = 16.6$, 10.2, 5.2 Hz, 1H, major isomer; $J = 16.9$, 10.0, 5.4 Hz, minor isomer), 3.62; 3.37 (1H, ddd, $J = 15.3$, 14.9, 10.0 Hz, minor isomer; dt, $J = 14.2$, 10.1 Hz, major isomer), 3.53; 3.17 (ddd, 1H, $J = 14.4$, 13.9, 5.4 Hz, minor isomer; $J = 14.1$, 13.5, 5.0 Hz, major isomer). ^{31}P NMR ($CDCl_3$, 243 MHz): δ −24.1; −24.4 (major isomer; minor isomer). Anal. Calcd for $C_{34}H_{25}O_2P$: C, 82.24; H, 5.07. Found: C, 82.10; H, 5.09.

*2-[1,2-Bis(methoxycarbonyl)ethyl]-2,2′λ^5-spirobi[2H-naphth[1,8-cd]-1,2-oxaphosphole] (**6B**)*

A mixture of **6B** and traces of impurities was obtained by silica gel column chromatography (benzene–ethyl acetate 10:1). Preparative GPC afforded **6B** as a yellowish white powder. Yield: 264 mg, 91% (diastereomeric mixture) from dimethyl maleate (*cis*-**5B**); Yield: 243 mg, 84% (diastereomeric mixture) from dimethyl fumarate (*trans*-**5B**). mp: 146–150°C. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.30; 8.27 (dd, 2H, $J = 12.1$, 7.1 Hz, major isomer; $J = 12.0$, 7.1 Hz, minor isomer), 8.01–7.98 (m, 2H), 7.65–7.61 (m, 2H), 7.48; 7.46 (dd, $J = 8.3$, 7.5 Hz, 2H, minor isomer; major isomer), 7.35–7.32 (m, 2H), 6.91; 6.89 (d, $J = 7.4$ Hz, 2H, major isomer; minor isomer), 4.34; 4.14 (ddd, 1H, $J = 22.3$, 11.6, 3.4 Hz, major isomer; $J = 21.4$, 11.0, 3.9 Hz, minor isomer), 3.56; 3.55 (s, 3H, minor isomer; major isomer), 3.51; 3.08 (d, $J = 0.8$ Hz, 3H, minor isomer; major isomer), 3.13; 2.91–2.79 (1H, ddd, $J = 17.2$, 11.7, 9.6 Hz, major isomer; m, minor isomer), 2.91–2.79; 2.44 (1H, m, minor isomer; ddd, $J = 17.1$, 12.3, 3.4 Hz, major isomer). ^{31}P NMR ($CDCl_3$, 243 MHz): δ −29.8; −30.8 (major isomer; minor isomer). Anal. Calcd for $C_{26}H_{21}O_6P$: C, 67.83; H, 4.60. Found: C, 67.83; H, 4.53.

*2-Cyclohexyl-2,2′λ^5-spirobi[2H-naphth[1,8-cd]-1,2-oxaphosphole] (**6C**)*

Silica gel column chromatography (benzene–hexane 1:1) afforded **6C** as a yellowish white powder. Yield: 170 mg, 67%. mp: 163–169°C. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.28 (dd, $J = 11.4$, 7.1 Hz, 2H), 7.93 (dd, $J = 8.0$, 2.7 Hz, 2H), 7.58 (dt, $J = 6.9$, 7.3 Hz, 2H), 7.46 (t, $J = 7.9$ Hz, 2H), 7.27 (dd, $J = 8.3$, 1.9 Hz, 2H), 6.89 (d, $J = 7.4$ Hz, 2H), 2.75–2.68 (m, 1H), 1.79–1.62 (m, 6H), 1.50–1.42 (m, 1H), 1.25–1.20 (m, 3H). ^{13}C NMR ($CDCl_3$, 151 MHz) δ 157.0, 134.2 (d, $J = 7.8$ Hz), 132.0 (d, $J = 14.1$ Hz), 130.7 (d, $J = 3.8$ Hz), 129.8 (d, $J = 23.2$ Hz), 129.1, 128.1 (d, $J = 16.1$ Hz), 124.9 (d, $J = 154.1$ Hz), 115.3, 103.5, 48.1 (d, $J = 113.4$ Hz), 27.9 (d, $J = 4.2$ Hz), 27.7 (d, $J = 3.2$ Hz) 26.7 (d, $J = 19.0$ Hz), 26.3 (d, $J = 19.6$ Hz), 26.0 (d, $J = 2.0$ Hz). ^{31}P NMR ($CDCl_3$, 243 MHz): δ −21.7. Anal. Calcd for $C_{26}H_{23}O_2P$: C, 78.38; H, 5.82. Found: C, 78.69; H, 5.88.

*General Procedure for the Radical Addition Reaction of Hydrophosphorane **1** in the Absence of ACHCN*

To a solution of **1** (200 mg, 0.632 mmol), in 5.0 mL of toluene was added an equimolar (for terminal and internal olefins) or an excess (for internal olefins) amount of an olefin at room temperature and the solution was refluxed for 5 h (for terminal and internal olefins) or 7 h (for internal olefins). Otherwise, the procedure is identical to what is described in the general procedure for the reaction activated with ACHCN.

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