Ytterbium-Catalyzed Dual Intermolecular Hydrophosphination: Synthesis of Bis(phosphinyl)dienes and Bis(alkenyl)phosphine Oxides

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Graphical Abstract

Ytterbium-Catalyzed Dual Intermolecular Hydrophosphination: Synthesis of Bis(phosphinyl)dienes and Bis(alkenyl)phosphina Oxide

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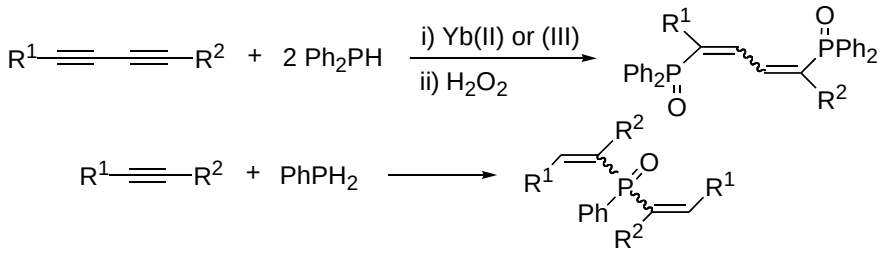


Abstract

Dual intermolecular hydrophosphination of conjugated diynes with two equivalents of diphenylphosphine was catalyzed by ytterbium complexes, Yb(η^2-Ph_2CNPh)$(hmpa)_3$ (**1**) and Yb$[N(SiMe_3)_2]_3(hmpa)_2$ (**2**), to give the corresponding 1,4-bis(diphenylphosphinyl)buta-1,3-dienes in high yields after oxidative work-up. Distribution of the four possible stereoisomers sharply depended on substituents of the substrates. (*Z*,*Z*)-Isomers were predominantly obtained from the disubstituted

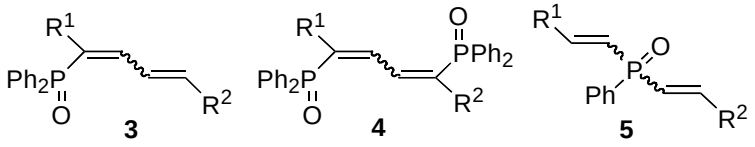
diynes, together with minor (*Z*,*E*)-isomers. On the other hand, the reaction of the terminal diynes provided major (*E*,*Z*) and minor (*E*,*E*)-butadienes. 1,4-Di-*tert*-butylbuta-1,3-diyne was exclusively converted to an allenic compound. Moreover, the dual hydrophosphination using phenyphosphine was also performed with **1** and **2**. Thus, the reaction of two equivalents of aromatic alkynes with $PhPH_2$ and subsequent oxidation gave bis(alkenyl)phosphine oxides in preference of the (*Z*,*Z*)-stereoisomers.

Introduction

α,β-Unsaturated phosphorus compounds are useful building blocks in organic synthesis.[1] Of their synthetic methods, addition reaction of $(RO)_2P(O)H$ and $R_2P(O)H$ to alkynes through oxidative addition of groups 9 and 10 catalysts to P-H bond has been recognized as the most promising and atom-economical process.[2] When this methodology was applied to the reaction of R_2PH, instead of pentavalent phosphorus, harsh conditions were necessary to promote the reaction, because of strong affinity of the late transition metals with the trivalent phosphines.[3] On the other hand, interaction between hard lanthanide metals and the soft phosphines could be so weak, and thus efficient intramolecular hydrophosphination of alkynyl and alkenylphosphines has been explored with lanthanocenes.[4]

Previously, we reported that a divalent ytterbium-imine complex, $Yb(\eta^2\text{-}Ph_2CNPh)(hmpa)_3$ (**1**), and a trivalent silylamide complex, $Yb[N(SiMe_3)_2]_3(hmpa)_2$ (**2**), served as highly effective precatalysts for intermolecular hydrophosphination of alkynes with diphenylphosphine and that the active species generated *in situ* were ytterbium phosphides, $Yb(PPh_2)_2$ and $Yb(PPh_2)_3$, which exhibited similar regio- and stereoselectivity irrespective of their valence state.[5] Based on this work, we intended to develop a simple method for the synthesis of potentially useful phosphorus compounds **3**-**5**. Diphenylphosphinyldienes **3** have been already prepared by the $Y[N(SiMe_3)_2]_3$-catalyzed dimerization of terminal alkynes, followed by hydrophosphination of the resulting enynes with Ph_2PH in one-pot.[6]

Compound **4** would be synthesized with dual hydrophosphination of conjugated diynes with 2 equivalents of Ph_2PH. However, two preliminary examples revealed that **4** was formed from primary alkyldiyne, but in contrast, tertiary alkyldiyne gave an allenic product.[5] Bis(alkeny)phosphines and their oxide **5** would be also prepared using $PhPH_2$, though it has been never used in the present system. To confirm these possibilities, we investigated the dual intermolecular hydrophosphination leading to **4** and **5**.

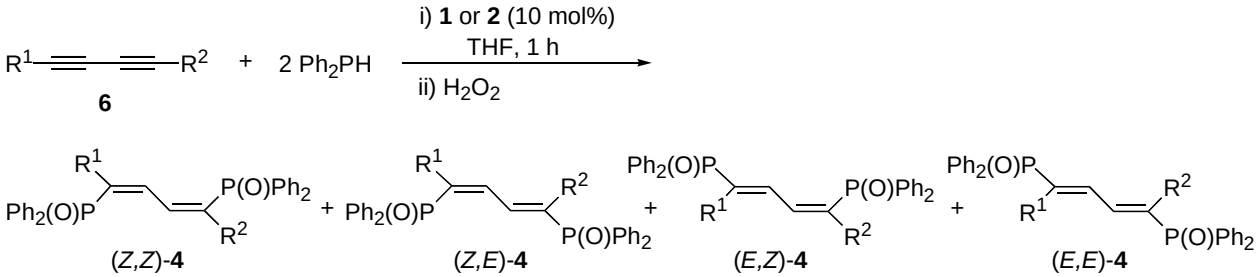


Results and Discussion

When hexadeca-7,9-diyne (**6a**) was treated with 2 equivalents of Ph_2PH in the presence of **1** (10 mol%) in THF at room temperature for 1 h, 7,10-bis(diphenylphosphinyl)hexadeca-7,9-diene (**4a**) was obtained in 80% total yield as a mixture of two stereoisomers (61 : 39) after oxidation with H_2O_2 (Table 1, run 1).[7] The major product showed one olefinic signal at 7.74 ppm with 34.8 Hz of *trans*-$^3J_{P\text{-}H}$ in ^{1}H NMR and one signal at 29.53 ppm in ^{31}P NMR. On the other hand, two olefinic signals at 6.83 (*cis*-$^3J_{P\text{-}H}$ = 20.6 Hz) and 7.13 ppm (*trans*-$^3J_{P\text{-}H}$ = 35.0 Hz) in ^{1}H NMR and two signals at 28.18 and 33.58 ppm in ^{31}P NMR were observed for the minor. Therefore, the major product was definitely assigned to the (*Z,Z*)-isomer, and the minor to the (*Z,E*)-isomer. The stereoselectivity was increased a little with decreasing temperature (run 2). The reaction was also conducted with the silylamide **2** effectively (run 3). Two cyclohexyl substituents in **6c** did not change the reaction mode, though its reactivity was somewhat decreased (run 5). Arylalkyldiynes **6d** and **6e** gave the (*Z,Z*) and (*Z,E*)-dienes **4d** and **4e**; in the latter substrate, a small amount of the (*E,Z*)-isomer was contaminated in the mixture (runs 6-9). 1,4-Diphenylbuta-1,3-diene (**6f**) was so reactive that no phosphinylated product **4f** was

obtained with **1**, other than polymers even at −78 °C (run 10). In the absence of Ph_2PH, **6f** was recovered unchanged by the treatment with **1** at room temperature. Use of milder precatalyst **2** afforded (*E*,*E*)-**4f** in low yield (run 11). The reaction of terminal diynes **6g** and **6h** gave the expected products **4g** and **4h**, but their stereochemistry was drastically altered, (*E*,*Z*) and (*E*,*E*)-isomers being major and minor, respectively (runs 12-15). Aromatic terminal diyne **6i** was exclusively polymerized with both **1** and **2**, because of its higher reactivity (run 16).

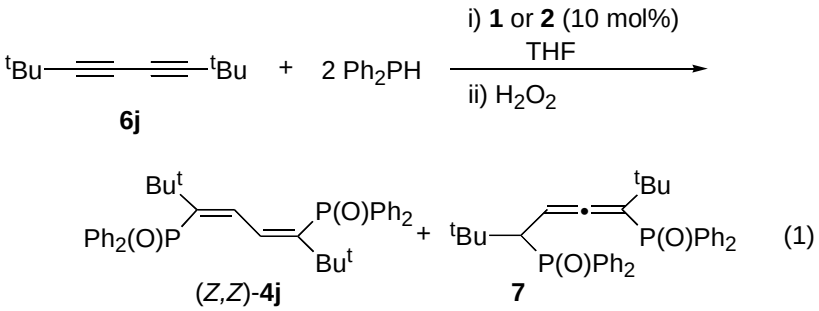
TABLE 1. Dual Hydrophosphination of Conjugated Diynes with Diphenylphosphine



run	**6**	R^1	R^2	precatalyst	temp (°C)	**4**	total yield (%)[a]	ratio of isomers (*Z*,*Z*):(*Z*,*E*):(*E*,*Z*):(*E*,*E*)
1	**6a**	^{n}Hex	^{n}Hex	**1**	rt	**4a**	80	61 : 39 : - : 0
2				**1**	-15		82	74 : 26 : - : 0
3				**2**	-15		82	61 : 39 : - : 0
4	**6b**	^{n}Bu	^{n}Bu	**1**	-15	**4b**	92	67 : 33 : - : 0
5	**6c**	c-C_6H_{11}	c-C_6H_{11}	**1**	-15	**4c**	74	86 : 14 : - : 0
6	**6d**	Ph	^{n}Hex	**1**	-15	**4d**	98	73 : 27 : 0 : 0
7				**2**	-15		95	72 : 28 : 0 : 0
8	**6e**	4-MeOPh	^{n}Hex	**1**	-15	**4e**	85	73 : 19 : 8 : 0
9				**2**	-15		65	74 : 18 : 8 : 0
10	**6f**	Ph	Ph	**1**	-78	**4f**	0	polymerization
11				**2**	-78		28	0 : 0 : - : 100
12	**6g**	H	^{n}Hex	**1**	-78[b]	**4g**	80	0 : 0 : 61 : 39
13				**2**	-78[b]		89	6 : 0 : 75 : 19
14	**6h**	H	^{n}Bu	**1**	-78[b]	**4h**	89	16 : 0 : 64 : 20
15				**2**	-78[b]		72	7 : 0 : 61 : 32
16	**6i**	H	Ph	**1** or **2**	-78	**4i**	0	polymerization

[a] NMR yield. [b] -78 °C for 1 h then room temperature for 2 h.

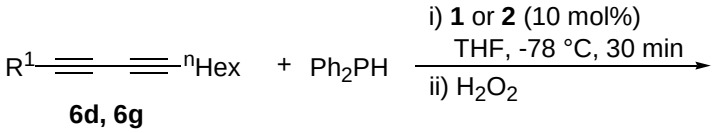
The behavior of di-*tert*-butyldiyne **6j** seems to be very different from that of others. Thus, the reaction with **1** at –35 °C gave bis(diphenylphosphinyl)allene **7** and (*Z*,*Z*)-diene **4j** in 71% and 12% yields, respectively (Eq. 1). When the reaction was performed at room temperature with **1** and **2**, the allene **7** was exclusively obtained in high yields.

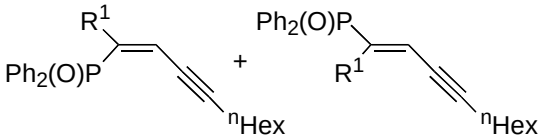


(1)

with **1**	-35 °C	12%	71%
	rt	0%	89%
with **2**	rt	0%	80%

Then, single hydrophosphination of unsymmetrical diynes **6d** and **6g** was carried out using equimolar amounts of Ph_2PH to learn the reaction process (Eq. 2). Apparently, the first reaction in **6d** took place at the α-alkyne carbon attached to the Ph group, with high selectivity for *anti*-addition, to yield (*Z*)-**8d**. This result contrasts well with the regio- and stereoselectivity observed for simple aromatic alkynes, in which *syn*-addition of Ph_2P occurred at the β-alkyne carbon to the aryl substituents, giving rise to (*E*)-products.[5] In the reaction of the terminal diyne **6g**, enyne compound (*Z*)-**8g** was formed as a single isomer through *anti*-addition to the terminal position.



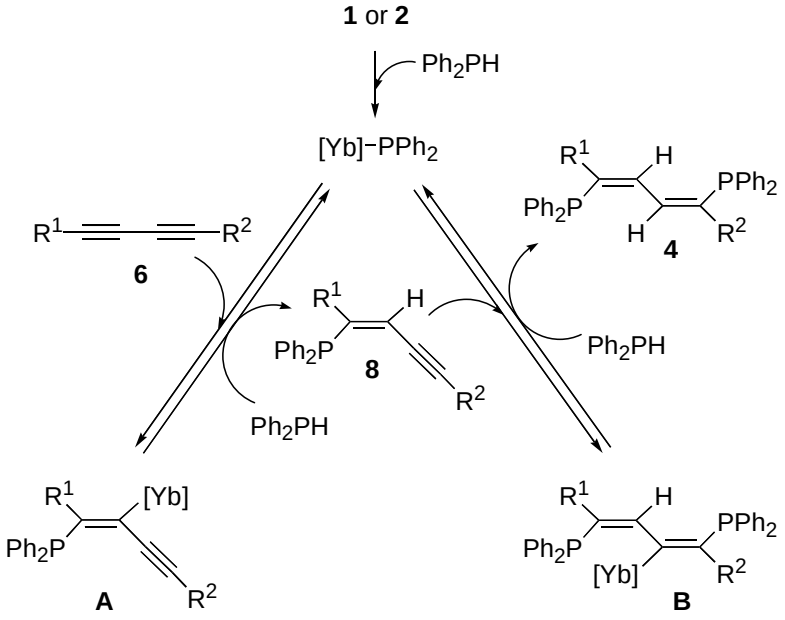


(2)

8d: R^1 = Ph with **1** (*Z*) 85% (*E*) 8%
8g: R^1 = H with **1** (*Z*) 89% (*E*) 0%
with **2** (*Z*) 94% (*E*) 0%

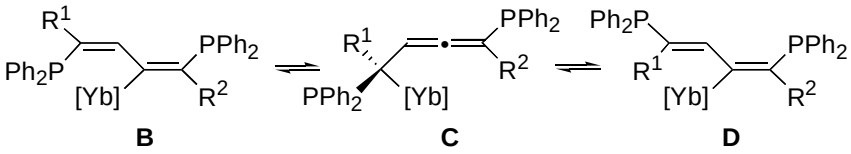
Combining these results with the reaction mechanism for the hydrophosphination of simple alkynes,[5] the process of the present system would be accounted for as follows (Scheme 1). At first, bis or tris(diphenylphosphino)ytterbium species, [Yb]-PPh_2, was generated *in situ* from the precatalysts **1** or **2** as previously proved. *anti*-Addition of the phosphide complex to the diyne **6** gave the intermediate **A**, which was readily protonated with Ph_2PH to yield the enyne compound **8** and regenerate the active phosphide species. The enyne **8** reacted further with the phosphide in a manner similar to the first cycle to yield the diene **4** *via* dienylytterbium **B**.

SCHEME 1



Regiochemistry was independent of the substituents of the diyne **6**, i.e., two Ph_2P were introduced to the 1- and 4-position of the butadiyne moiety, whereas stereochemistry was significantly variable. As proposed in Scheme 1, repeated *anti*-addition of the Yb-phosphide complex could produce (*Z*,*Z*)-**4**, which is the case of the internal diynes **6a**-**6e**. In general, the overall stereoselectivity would be rationalized by the isomerization of the intermediate **B** formed by the second addition, which proceeds through allenic species **C** (Scheme 2). In the case of the terminal diynes **6g** and **6h**, **B** (R^1 = H) changes readily to other dienylytterbium **D** to avoid the steric repulsion between Ph_2P and Yb in the structure of **B**, giving rise to (*E*,*Z*)-**4g** and **4h** as major products. Moreover, it is likely that all four stereoisomeric dienylytterbiums such as **B** and **D** are interconvertible *via* **C**, but the equilibrium would not be attained completely, because of the rapid protonation of the intermediates with Ph_2PH. Therefore, stereoselectivity of the present reaction would be a reflection of both kinetic and thermodynamic factors.

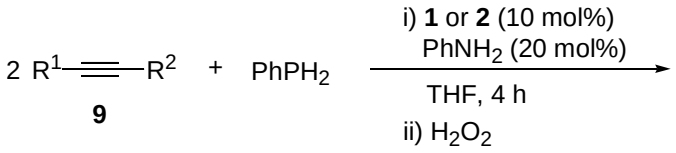
SCHEME 2

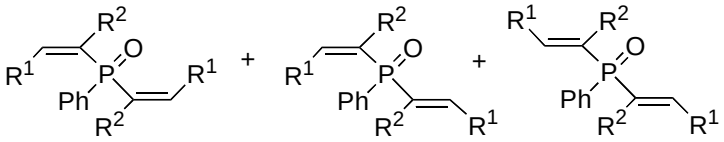


Formation of the allene **7** from di-*tert*-butyldiyne **6j** substantiates the scenario described above. In this case, two tertiary substituents caused severe steric crowding in the form of a dienylytterbium species, and thus the allenic **C** should be the most stable intermediate, giving rise to **7** exclusively at room temperature. However, when the reaction was carried out at lower temperature, the (*Z*,*Z*)-diene **4j** derived from **B** was included as a minor product. Thus, **4j** and **7** could be kinetic and thermodynamic products, respectively.

Next, we studied the dual hydrophosphination with phenylphosphine for the synthesis of bis(alkenyl)phosphines and their oxides **5**. The reaction of 1-phenylprop-1-yne (**9a**) (2 equiv.) with $PhPH_2$ using the imine complex **1** (10 mol%) was slower than that with Ph_2PH, and required heating (Table 2, runs 1 and 2). After oxidative work-up with H_2O_2, three isomers of bis(β-methylstyryl)phenylphosphine oxide (**5a**) were formed in 43% total yield (run 2).[7] The silylamide precatalyst **2** gave better yield, which was further increased to 64% yield, though still non-selective, by addition of 20 mol% of aniline (runs 3 and 4). The reaction using equimolar amounts of the alkyne **9a** and $PhPH_2$ gave an intractable mixture, in which bis(1-methyl-2-phenylethyl)phenylphosphine oxide, a reduced product of **5a**, was mainly detected. In the reaction of phenylacetylene (**9b**), the aniline additive showed a significant effect for improvement of the selectivity as well as total yield of **5b** (run 5 *vs.* 6). Thus, the (*Z*,*Z*)- and (*Z*,*E*)-isomers were obtained in 80% and 20% yields, respectively. Similarly, various aromatic alkynes **9c**-**9f** were converted to the expected products **5c**-**5f** in high yields (runs 7-10).

TABLE 2. Dual Hydrophosphination of Alkynes with Phenylphosphine

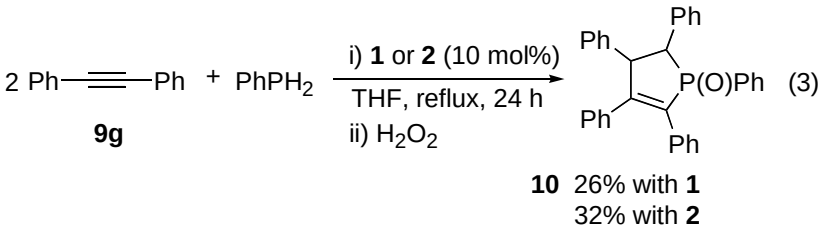




run	**9**	R^1	R^2	precat	temp (°C)	**5**	total yield (%)[a]	ratio of isomers (*Z*,*Z*):(*Z*,*E*):(*E*,*E*)
1	**9a**	Ph	Me	**1**[b]	rt [c]	**5a**	7	100 : 0 : 0
2				**1**[b]	reflux		43	37 : 37 : 26
3				**2**[b]	reflux		59	46 : 34 : 20
4				**2**	reflux		64	36 : 34 : 30
5	**9b**	Ph	H	**2**[b]	rt	**5b**	75	48 : 52 : 0
6				**2**	rt		quant	80 : 20 : 0
7	**9c**	4-MeOPh	H	**2**	rt	**5c**	quant	82 : 18 : 0
8	**9d**	4-MePh	H	**2**	rt	**5d**	97	89 : 11 : 0
9	**9e**	4-ClPh	H	**2**	rt	**5e**	89	78 : 22 : 0
10	**9f**	4-BrPh	H	**2**	rt	**5f**	89	81 : 19 : 0

[a] NMR yield. [b] In the absence of $PhNH_2$. [c] Reaction period is 15 h.

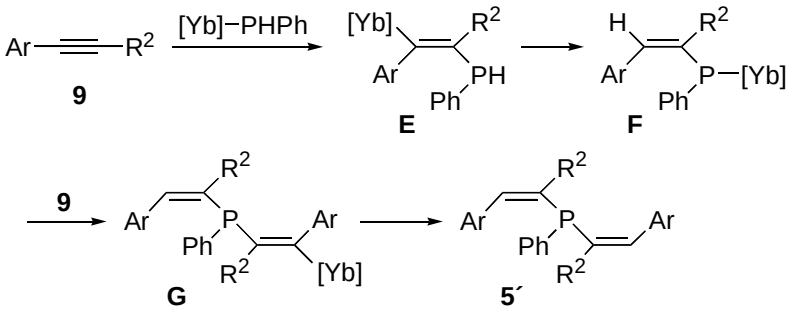
Unfortunately, this method was not applicable to the reaction of aliphatic alkynes, which resulted in recovery of the starting materials or exclusive consumption of $PhPH_2$ under various conditions. Moreover, the reaction of diphenylacetylene (**9g**) gave cyclic phosphine oxide **10** unexpectedly in low yields, together with small amounts of *trans*-stilbene (Eq. 3).[8]



(3)

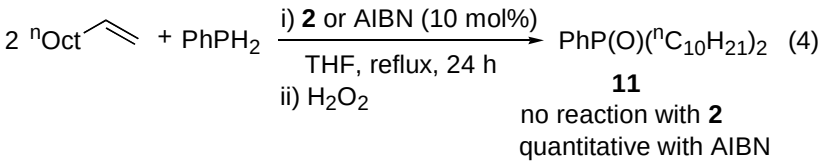
The present reaction would proceed in a mechanism analogous to that with diphenylphosphine as shown in Scheme 3. Addition of phenylphosphinoytterbium, [Yb]-PHPh, to aromatic alkyne **9**, followed by intramolecular proton transfer would yield alkenylphosphide species **F**, which reacts further with the second molecule of **9** to give bis(alkenyl)phosphine **5´** through the intermediate **G**.

SCHEME 3



The regiochemistry was in agreement with that observed for the reaction with Ph_2PH, whereas the stereochemistry was reversed. Since isomerization of the intermediates and products is less likely in the present system, *anti*-addition of the phosphide species would take place preferentially to afford the (*Z*,*Z*)-isomers. The high (*Z*)-selectivity may be caused by a radical mechanism instead of the process proposed in Scheme 3.[9] However, this possibility was completely ruled out. Thus, the reaction of two equivalents of 1-decene with $PhPH_2$ did not occur with **2**, but in contrast, addition product **11** was quantitatively formed under radical conditions (Eq. 4). Alternatively, the (*Z*)-selectivity would be attributed to the amine additive, which has been known to change the activity of the lanthanide

catalysts and product selectivity in various reactions as a proton source and ligand.[6,10] In fact, aliphatic amines like amylamine decreased the yield and selectivity in contrast to aniline. However, the reason for the difference between the reaction with $PhPH_2$ and Ph_2PH is still unclear at present.



(4)

In summary, dual intermolecular hydrophosphination of conjugated diynes with two equivalents of Ph_2PH has been achieved using ytterbium (II) and (III) precatalysts **1** and **2** to give bis(diphenylphosphinyl)dienes **4** in high yields. Addition reaction of the active species, Yb-phosphide, was found to proceed in an *anti*-fashion, but the resulting intermediates could isomerize *via* an allenic species. Thus, the stereochemistry of the products **4** was determined both kinetically and thermodynamically, depending on their substituents. Moreover, bis(alkenyl)phosphine oxides **5** were effectively obtained from two equivalents of aromatic alkynes and $PhPH_2$ by the dual reaction in the presence of an aniline additive.

Experimental Section

General. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded at 396, 99, and 160 MHz, respectively. IR spectra were taken on an FT-IR spectrophotometer. Mass spectra (EI) were obtained at 70 eV on a GC-MS apparatus. MALDI-TOF mass spectra were acquired using 1,8,9-trihydroxyanthracene as the matrix. Microanalyses were performed at our analytical laboratory. Melting points are uncorrected. All reactions were carried out under argon. THF was distilled from sodium/benzophenone ketyl

immediately prior to use. HMPA was distilled from CaH_2 and stored over molecular sieves. The Yb-imine precatalyst **1** was generated *in situ* from Yb metal, Ph_2C=NPh, and HMPA (6 equiv) in THF as previously reported.[5] The silylamide precatalyst **2** was also generated by treatment of $Yb[N(SiMe_3)_2]_3(thf)_2$[11] with HMPA (2 equiv) in THF. Symmetrical diynes **6a**-**6c** and **6f**,[12] unsymmetrical diynes **6d** and **6e**,[13] and terminal diynes **6g**-**6i**[14] were prepared according to the literature methods. All other materials were commercially available and were used after drying and distillation.

Dual Hydrophosphination of the Conjugated Diynes 6 with Diphenylphosphine. Ph_2PH (2.0 mmol) was added to a solution of **1** or **2** (0.1 mmol) in THF (1 mL) and the mixture was stirred for 30 min at room temperature. After cooling the mixture to the appropriate temperature indicated in Table 1, diyne **6** (1.0 mmol) was added to the solution and stirring was continued for 1 h at this temperature. In the case of terminal diynes, the mixture was stirred for 1 h at –78 °C, and then for 2 h at room temperature to ensure the completion of the reaction. The reaction was quenched with H_2O (1 mL) and HCl solution (1M, 1 mL), and the mixture was oxidized with H_2O_2 (30%, 1 mL) at 0 °C. Dimethyl terephthalate was added to the mixture as an internal standard. The reaction mixture was extracted with $CHCl_3$, washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The product yield and ratio were determined by ^1H and ^{31}P NMR spectra of the crude mixture. Analytically pure compounds **4** were isolated by column chromatography on silica gel with chloroform-acetone eluent.

For determination of the stereochemistry of the products, the coupling constants between the olefinic protons and $Ph_2P(O)$ in ^1H NMR are informative; *trans*-$^3J_{P\text{-}H}$ (ca. 35Hz), *cis*-$^3J_{P\text{-}H}$ (ca. 19Hz), and $^2J_{P\text{-}H}$ (ca. 22 Hz). In addition, ^{31}P NMR signals of the olefinic (*Z*)-$Ph_2P(O)$ always appear in higher field than those of the (*E*).[9] For examples, (alkyl)[P(O)]C=CHR appears at ca. 29 (*Z*) and 33 ppm (*E*), (aryl)[P(O)]C=CHR at ca. 26 (*Z*) and 31 ppm (*E*), (H)[P(O)]C=CHR at ca. 22 (*Z*) and 25 ppm (*E*).

7,10-Bis(diphenylphosphinyl)hexadeca-7,9-diene (4a). (*Z*,*Z*)-isomer: white solid; mp 137-140 °C; IR (KBr) 1180 cm^{-1}; MS (MALDI) *m/z* 619.99 (M^+-2); MS *m/z* 622 (M^+), 551 (M^+-C_5H_{11}), 421 (M^+-Ph_2PO), 201 (Ph_2PO^+); ^1H NMR ($CDCl_3$) δ 0.75 (6H, t, *J* = 7.2 Hz), 0.83-0.97 (12H, m), 1,00-1.09 (4H, m), 1.86-1.97 (4H, m), 7.45-7.55 (12H m), 7.64-7.69 (8H, m), 7.76 (2H, d, *J* = 35.0 Hz); ^{13}C NMR ($CDCl_3$) δ 13.9, 22.3, 28.6, 29.3 (d, *J* = 3.7 Hz), 31.2, 35.7 (d, *J* = 12.3 Hz), 128.5 (d, *J* = 8.3 Hz), 131.7 (d, *J* = 2.5 Hz), 131.8 (d, *J* = 10.7 Hz), 133.2 (d, *J* = 101.7 Hz), 137.6 (d, *J* = 86.2 Hz), 140.9 (dd, *J* = 10.3 and 3.7 Hz); ^{31}P NMR ($CDCl_3$) δ 29.53. Anal. Calcd for $C_{40}H_{48}O_2P_2$: C, 77.15; H, 7.77. Found: C, 77.03; H, 7.74. (*Z*,*E*)-Isomer: yellow oil; IR (Neat) 1178 cm^{-1}; MS (MALDI) *m/z* 621.17 (M^+-1); ^1H NMR ($CDCl_3$) δ 0.81 (3H, t, *J* = 7.0 Hz), 0.84 (3H, t, *J* = 7.0 Hz), 1.09-1.37 (16H, m), 2.21 (2H, dt, *J* = 13.8, 6.9 Hz), 2.50 (2H, dt, *J* = 16.1, 7.7 Hz), 6.83 (1H, dd, *J* = 20.6, 11.8 Hz), 7.13 (1H, ddd, *J* = 35.0, 11.8, 1.2 Hz), 7.27-7.53 (20H, m); ^{13}C NMR ($CDCl_3$) δ 13.9, 14.0, 22.4, 22.5, 28.7, 29.3, 29.5 (d, *J* = 4.1 Hz), 30.5 (d, *J* = 1.7 Hz), 31.3, 31.4, 36.4 (d, *J* = 1.7 Hz), 36.5 (d, *J* = 1.6 Hz), 128.3 (d, *J* = 11.4 Hz), 128.5 (d, *J* = 12.3 Hz), 131.1 (d, *J* = 101.7 Hz), 131.5 (d, *J* = 9.8 Hz), 131.62 (d, *J* = 10.7 Hz), 131.63 (d, *J* = 10.1 Hz), 131.8 (d, *J* = 9.0 Hz), 132.7 (d, *J* = 101.7 Hz), 136.7 (dd, *J* = 19.7, 5.7 Hz), 136.9 (dd, *J* = 14.0, 9.8 Hz), 140.1 (dd, *J* = 96.0, 2.1 Hz), 140.9 (d, *J* = 86.1 Hz); ^{31}P NMR ($CDCl_3$) δ 28.18, 33.58.

5,8-Bis(diphenyphophinyl)dodeca-5,7-diene (4b). (*Z*,*Z*)-Isomer: white solid; mp 162-163 °C; IR (KBr) 1180 cm^{-1}; MS (MALDI) *m/z* 564.81 (M^+-2); ^1H NMR ($CDCl_3$) δ 0.56 (6H, t, *J* = 6.9 Hz), 0.85-0.92 (8H, m), 1.92 (4H, dt, *J* = 13.5, 6.7 Hz), 7.44-7.55 (12H, m), 7.64-7.69 (8H, m), 7.76 (2H, d, *J* = 34.8 Hz); ^{13}C NMR ($CDCl_3$) δ 13.4, 21.9, 31.2, 35.3 (d, *J* = 12.3 Hz), 128.4 (d, *J* = 12.3 Hz), 131.72, (d, *J* = 9.8 Hz), 131.73, 133.1 (d, *J* = 100.9 Hz), 137.5 (dd, *J* = 88.2, 2.1 Hz), 140.8 (dd, *J* = 9.8, 4.1 Hz); ^{31}P NMR ($CDCl_3$) δ 29.57. Anal. Calcd for $C_{36}H_{40}O_2P_2$: C, 76.31; H, 7.12. Found: C, 76.51; H, 7.08. (*Z*,*E*)-Isomer: yellow oil; IR (Neat) 1182 cm^{-1}; MS (MALDI) *m/z* 564.86 (M^+-2); ^1H NMR ($CDCl_3$) δ

0.74 (3H, t, *J* = 7.2 Hz), 0.83 (3H, t, *J* = 7.1 Hz), 1.14-1.37 (8H, m), 2.21 (2H, dt, *J* = 13.7, 6.6 Hz), 2.53 (2H, dt, *J* = 15.4, 7.6 Hz), 6.81 (1H, dd, *J* = 20.6, 11.4 Hz), 7.13 (1H, dd, *J* = 35.0, 11.4 Hz), 7.34-7.50 (20H, m); ^{13}C NMR ($CDCl_3$) δ 13.5, 13.6, 22.1, 22.7, 27.2 (d, *J* = 9.0 Hz), 31.6 (d, *J* = 4.1 Hz), 32.6, 36.1 (d, *J* = 10.6 Hz), 128.3 (d, *J* = 12.3 Hz), 128.4 (d, *J* = 12.3 Hz), 131.1 (d, *J* = 102.5 Hz), 131.4 (d, *J* = 9.8 Hz), 131.61(d, *J* = 9.8 Hz), 131.62 (d, *J* = 9.8 Hz), 131.7 (d, *J* = 9.8 Hz), 132.6 (d, *J* = 101.7 Hz), 136.5 (dd, *J* = 19.7, 6.5 Hz), 136.8 (dd, *J* = 14.7, 9.8 Hz), 140.0 (dd, *J* = 96.8, 2.1 Hz), 140.9 (d, *J* = 87.6 Hz); ^{31}P NMR ($CDCl_3$) δ 28.25, 33.71.

1,4-Bis(diphenylphosphinyl)-1,4-dicyclohexylbuta-1,3-diene (4c). (*Z*,*Z*)-Isomer: white solid; mp 238-239 °C; IR (KBr) 1174 cm^{-1}; MS (MALDI) *m/z* 616.76 (M^+-2); ^{1}H NMR ($CDCl_3$) δ 0.68-0.74 (10H, m), 1.25-1.43 (10H, m), 2.00 (2H, quin, *J* = 11.5 Hz), 7.43-7.55 (14H, m), 7.63-7.67 (8H, m); ^{13}C NMR ($CDCl_3$) δ 25.4, 26.3, 33.0 (d, *J* = 10.6 Hz), 44.2 (d, *J* = 10.6 Hz), 128.3 (d, *J* = 12.3 Hz), 131.56, (d, *J* = 9.8 Hz), 131.57, 133.4 (d, *J* = 100.9 Hz), 138.2 (dd, *J* = 10.7, 4.1 Hz), 143.0 (dd, *J* = 87.0, 2.4 Hz); ^{31}P NMR ($CDCl_3$) δ 29.61. Anal. Calcd for $C_{40}H_{44}O_2P_2$: C, 77.65; H, 7.17. Found: C, 77.77; H, 7.21. (*Z*,*E*)-Isomer: isolated as a mixture with (*Z*,*Z*)-isomer; MS (MALDI) *m/z* 617.46 (M^+-1); ^{1}H NMR ($CDCl_3$) (clearly assignable peaks) δ 6.69 (1H, dd, *J* = 22.1, 11.7 Hz); ^{13}C NMR ($CDCl_3$) δ 25.80, 25.83, 26.6, 26.9, 32.3 (d, *J* = 3.3 Hz), 33.9 (d, *J* = 4.1 Hz), 40.1 (d, *J* = 9.0 Hz), 42.0 (d, *J* = 11.5 Hz), 128.2 (d, *J* = 11.5 Hz), 128.5 (d, *J* = 12.3 Hz), 131.4 (d, *J* = 2.4 Hz), 131.5 (d, *J* = 42.7 Hz), 131.64 (d, *J* = 9.8 Hz), 131.65 (d, *J* = 2.4 Hz), 131.9 (d, *J* = 9.8 Hz), 132.9 (d, *J* = 101.7 Hz), 135.1 (dd, *J* = 20.9, 5.3 Hz), 136.9 (dd, *J* = 15.6, 9.8 Hz), 144.0 (dd, *J* = 93.5, 1.6 Hz), 145.1 (d, *J* = 86.1, 1.6 Hz); ^{31}P NMR ($CDCl_3$) δ 29.92, 35.16.

1,4-Bis(diphenylphosphinyl)-1-phenyldeca-1,3-diene (4d). (*Z*,*Z*)-Isomer: white solid; mp 124-126 °C; IR (KBr) 1180 cm^{-1}; MS (MALDI) *m/z* 613.77 (M^+-1); ^{1}H NMR ($CDCl_3$) δ 0.77 (3H, t, *J* = 7.4

Hz), 0.87-1.00 (6H, m), 1.07 (2H, quint, *J* = 7.1 Hz), 1.95-2.00 (2H, m), 6.69 (2H, d, *J* = 7.0 Hz), 6.94 (2H, t, J = 7.4 Hz), 7.01 (1H, t, J = 7.3 Hz), 7.32-7.68 (20H, m), 7.82 (1H, dd, *J* = 35.5, 11.0 Hz), 7.89 (1H, dd, *J* = 33.9, 11.0 Hz); ^{13}C NMR ($CDCl_3$) (clearly assignable peaks) δ 13.9, 22.2, 28.6, 29.1 (d, *J* = 4.1 Hz), 31.1, 35.6 (d, *J* = 11.5 Hz), 132.8 (d, *J* = 101.7 Hz), 133.5 (d, *J* = 102.5 Hz), 138.5 (dd, *J* = 90.2, 2.1 Hz), 139.5 (d, *J* = 9.8 Hz), 140.3 (dd, *J* = 87.4, 2.0 Hz); ^{31}P NMR ($CDCl_3$) δ 26.13, 29.43. Anal. Calcd for $C_{40}H_{40}O_2P_2$: C, 78.16; H, 6.56. Found: C, 78.03; H, 6.68. (*Z,E*)-Isomer: colorless oil; IR (Neat) 1182 cm^{-1}; MS (MALDI) *m/z* 613.04 (M^+-1); ^{1}H NMR ($CDCl_3$) δ 0.80 (3H, t, *J* = 7.3 Hz), 1.09-1.45 (8H, m), 2.54 (2H, dd, *J* = 16.0, 8.0 Hz), 6.99-7.01 (2H, m), 7.07-7.18 (4H, m), 7.27-7.53 (21H, m); ^{13}C NMR ($CDCl_3$) (clearly assignable peaks) δ 13.9, 22.4, 27.5 (d, *J* = 9.0 Hz), 29.2, 30.4, 31.2, 136.5 (dd, *J* = 14.8, 9.1 Hz), 139.9 (dd, *J* = 9.9, 1.7 Hz), 141.8 (dd, *J* = 88.6, 1.6 Hz), 143.0 (dd, *J* = 95.2, 1.7 Hz); ^{31}P NMR ($CDCl_3$) δ 25.52, 33.38.

1,4-Bis(diphenylphosphinyl)-1-(4-methoxyphenyl)deca-1,3-diene (4e). (*Z,Z*)-Isomer: white solid; mp 113-115 °C; IR (KBr) 1178 cm^{-1}; MS (MALDI) *m/z* 643.88 (M^+-1); ^{1}H NMR ($CDCl_3$) δ 0.77 (3H, t, *J* = 7.2 Hz), 0.79-1.12 (8H, m), 1.91-2.00 (2H, m), 3.67 (3H, s), 6.48 (2H, d, *J* = 8.2 Hz), 6.59 (2H, d, *J* = 8.2 Hz), 7.35-7.68 (20H, m), 7.78 (1H, dd, *J* = 35.3, 12.1 Hz), 7.83 (1H, dd, *J* = 34.5, 12.1 Hz); ^{13}C NMR ($CDCl_3$) δ 14.0, 22.3, 28.7, 29.2 (d, *J* = 3.3 Hz), 31.2, 35.7 (d, *J* = 10.7 Hz), 55.1, 113.1, 128.3 (d, *J* = 12.3), 128.5 (d, *J* = 11.5 Hz), 129.9 (d, *J* = 4.9 Hz), 131.5 (d, *J* = 2.4 Hz), 131.6 (d, *J* = 9.8 Hz), 131.7 (d, *J* = 9.8 Hz), 131.8 (d, *J* = 2.4 Hz), 132.1 (d, *J* = 10.7 Hz), 133.0 (d, *J* = 101.7 Hz), 133.7 (d, *J* = 102.5 Hz), 138.0 (dd, *J* = 90.7, 2.1 Hz), 140.0 (dd, *J* = 87.4, 2.1 Hz), 140.4 (dd, *J* = 8.6, 4.5 Hz), 140.9 (dd, *J* = 9.4, 5.3 Hz), 158.8; ^{31}P NMR ($CDCl_3$) δ 26.18, 29.41. Anal. Calcd for $C_{41}H_{42}O_3P_2$: C, 76.38; H, 6.57. Found: C, 75.96; H, 6.52. (*Z,E*)-Isomer: isolated as a mixture of (*Z,E*) and (*E,Z*)-isomer (65 : 35): yellow oil; MS (MALDI) *m/z* 643.88 (M^+-1); ^{1}H NMR ($CDCl_3$) δ 0.81 (3H, t, *J* = 7.1 Hz), 0.99-1.39 (8H, m), 2.49-2.57 (2H,m), 3.72 (3H, s), 6.65 (2H, d, *J* = 8.7 Hz), 6.93 (2H, d, *J* = 8.7

Hz), 7.07 (1H, dd, *J* = 20.4, 11.7 Hz), 7.28-7.57 (21H, m); ^{31}P NMR ($CDCl_3$) δ 25.69, 33.58. (*E,Z*)-Isomer: ^{1}H NMR ($CDCl_3$) (clearly assignable peaks) δ 0.77 (3H, t, *J* = 7.4 Hz), 2.06-2.11 (2H, m), 3.75 (3H, s), 6.81 (2H, d, *J* = 8.7 Hz), 7.22 (2H, d, *J* = 8.9 Hz); ^{31}P NMR ($CDCl_3$) δ 28.33, 31.37.

(*E,E*)-1,4-Bis(diphenylphosphinyl)-1,4-diphenylbuta-1,3-diene (4f). White solid; mp 267-270 °C; IR (KBr) 1182 cm^{-1}; MS (MALDI) *m/z* 605.67 (M^+-1); ^{1}H NMR ($CDCl_3$) δ 6.76 (2H, d, *J* = 16.9 Hz), 7.04-7.16 (10H, m), 7.27-7.43 (12H, m), 7.53-7.58 (8H, m); ^{13}C NMR ($CDCl_3$) δ 128.1 (d, *J* = 30.4 Hz), 128.2 (d, *J* = 2.4 Hz), 128.3 (d, *J* = 2.4 Hz), 129.5 (d, *J* = 2.4 Hz), 130.7 (d, *J* = 104.2 Hz), 131.78 (d, *J* = 9.0 Hz), 131.82 (d, *J* = 7.4 Hz), 134.1 (d, *J* = 4.5 Hz), 137.9 (d, *J* = 14.4 Hz), 142.8 (dd, *J* = 94.3, 1.4 Hz); ^{31}P NMR ($CDCl_3$) δ 29.97. Anal. Calcd for $C_{40}H_{32}O_2P_2$: C, 79.20; H, 5.32. Found: C, 79.13; H, 5.02

1,4-Bis(diphenylphosphinyl)deca-1,3-diene (4g). (*Z,Z*)-Isomer: white solid; mp 174-176 °C; IR (KBr) 1195, 1176 cm^{-1}; MS (MALDI) *m/z* 536.73 (M^+-2); ^{1}H NMR ($CDCl_3$) δ 0.76 (3H, t, *J* = 7.1 Hz), 0.91-1.14 (8H, m), 1.98-2.05 (2H, m), 6.12 (1H, dd, *J* = 24.6, 12.3 Hz), 7.45-7.53 (12H, m), 7.64-7.74 (8H, m), 8.15 (1H, dd, *J* = 34.8, 12.3 Hz), 8.27 (1H, dt, *J* = 37.4, 12.3 Hz); ^{13}C NMR ($CDCl_3$) δ 13.8, 22.2, 28.6, 29.2 (d, *J* = 4.1 Hz), 31.0, 35.7 (d, *J* = 11.5 Hz), 124.0 (dd, *J* = 96.8, 1.6 Hz), 124.4 (d, *J* = 6.6 Hz), 128.5 (d, *J* = 7.6 Hz) 130.9 (d, *J* = 9.8 Hz), 131.6 (d, *J* = 2.4 Hz), 131.7 (d, *J* = 9.8 Hz), 131.8 (d, *J* = 3.3 Hz), 132.5 (d, *J* = 102.6 Hz), 133.8 (d, *J* = 105.0 Hz), 140.9 (dd, *J* = 10.2, 4.5 Hz), 141.0 (dd, *J* = 84.5, 2.1 Hz), 144.7 (dd, *J* = 9.4, 2.9 Hz); ^{31}P NMR ($CDCl_3$) δ 22.32, 30.73. Anal. Calcd for $C_{34}H_{36}O_2P_2$: C, 75.82; H, 6.74. Found: C, 75.46; H, 6.71. (*E,Z*)-Isomer: colorless oil; IR (Neat) 1182 cm^{-1}; MS (MALDI) *m/z* 538.13 (M^+); ^{1}H NMR ($CDCl_3$) δ 0.81 (3H, t, *J* = 7.1 Hz), 1.05-1.24 (6H, m), 1.32 (2H, quin, *J* = 7.5 Hz), 2.20 (2H, dt, *J* = 12.7, 7.5 Hz), 6.33 (1H, t, *J* = 16.7 Hz), 6.91 (1H, dd, *J* = 34.9, 11.4 Hz), 7.16 (1H, td, *J* = 16.7, 11.4 Hz), 7.37-7.43 (8H, m), 7.48-7.55 (12H, m); ^{13}C NMR

($CDCl_3$) δ 13.9, 22.3, 28.7, 29.4 (d, *J* = 3.3 Hz), 31.2, 35.9 (d, *J* = 9.8 Hz), 128.4 (d, *J* = 12.3 Hz), 128.5, (d, *J* = 11.5 Hz), 128.6 (br d, *J* = 103.3 Hz) 131.3 (d, *J* = 97.6 Hz), 131.4 (d, *J* = 9.8 Hz), 131.5 (d, *J* = 9.9 Hz), 131.8 (d, *J* = 6.5 Hz), 132.4 (d, *J* = 102.6 Hz), 141.5 (dd, *J* = 22.5, 5.6 Hz), 142.7 (br d, *J* = 86.1 Hz), 143.0 (dd, *J* = 9.5, 6.2 Hz); ^{31}P NMR ($CDCl_3$) δ 26.31, 28.25. Anal. Calcd for $C_{34}H_{36}O_2P_2$: C, 75.82; H, 6.74. Found: C, 75.64; H, 6.53. (*E*,*E*)-Isomer: white solid; mp 212-214 °C; IR (KBr) 1186 cm^{-1}; MS (MALDI) *m/z* 537.94 (M^+-1); ^{1}H NMR ($CDCl_3$) δ 0.78 (3H, t, *J* = 7.2 Hz), 0.96-1.17 (8H, m), 2.32-2.40 (2H, m), 6.53 (1H, dd, *J* = 22.6, 17.0 Hz), 6.84 (1H, dd, *J* = 19.3, 11.2 Hz), 7.37 (1H, td, *J* = 17.0, 11.2 Hz), 7.46-7.57 (13H, m), 7.65-7.72 (7H, m); ^{13}C NMR ($CDCl_3$) δ 13.9, 22.4, 28.9 (d, *J* = 9.8 Hz), 29.3, 30.6, 31.2, 128.5 (d, *J* = 11.5 Hz), 128.6 (d, *J* = 12.3 Hz), 129.5 (d, *J* = 100.9 Hz) 131.2 (d, *J* = 102.5 Hz), 131.3 (d, *J* = 9.9 Hz), 131.9 (d, *J* = 9.9 Hz), 132.0 (d, *J* = 2.4 Hz), 132.4 (d, *J* = 67.3 Hz), 139.5 (dd, *J* = 20.5, 10.7 Hz), 140.5 (dd, *J* = 18.4, 3.7 Hz), 142.6 (br d, *J* = 91.9 Hz); ^{31}P NMR ($CDCl_3$) δ 23.77, 31.68.

1,4-Bis(diphenylphosphinyl)octa-1,3-diene (4h). (*Z*,*Z*)-Isomer: isolated as a mixture of (*Z*,*Z*) and (*E*,*E*)-isomer (52 : 48); white solid; IR (KBr) 1178 cm^{-1}; MS (MALDI) *m/z* 509.78 (M^+-1); ^{1}H NMR ($CDCl_3$) δ 0.60 (3H, t, *J* = 7.2 Hz), 0.94-1.10 (4H, m), 1.97-2.04 (2H, m), 6.12 (1H, dd, *J* = 25.3, 12.4 Hz), 7.44-7.73 (20H, m), 8.14 (1H, dd, *J* = 34.6, 12.4 Hz), 8.26 (1H, dt, *J* = 37.8, 12.4 Hz); ^{31}P NMR ($CDCl_3$) δ 22.41, 30.82. (*E*,*Z*)-Isomer: isolated as a mixture of (*E*,*Z*) and (*E*,*E*)-isomer (57 : 43); white solid; MS (MALDI) *m/z* 510.25 (M^+); ^{1}H NMR ($CDCl_3$) δ 0.71 (3H, t, *J* = 7.2 Hz), 1.05-1.32 (4H, m), 2.16-2.23 (2H, m), 6.31 (1H, t, *J* = 17.3 Hz), 6.89 (1H, dd, *J* = 34.8, 11.1 Hz), 7.11 (1H, td, *J* = 17.3, 11.1 Hz), 7.34-7.54 (16H, m), 7.63-7.70 (4H, m); ^{31}P NMR ($CDCl_3$) δ 26.71, 28.41. Anal. Calcd for $C_{32}H_{32}O_2P_2$: C, 75.28; H, 6.32. Found: C, 75.43; H, 6.30. (*E*,*E*)-Isomer: ^{1}H NMR ($CDCl_3$) (clearly assignable peaks) δ 0.66 (3H, t, *J* = 7.2 Hz), 2.32-2.39 (2H, m), 6.53 (1H, dd, *J* = 22.4, 16.8 Hz), 6.83 (1H, dd, *J* = 19.5, 11.2 Hz), 7.36 (1H, td, *J* = 16.8, 11.2 Hz); ^{31}P NMR ($CDCl_3$) δ 23.71, 31.70.

(*Z*,*Z*)-3,6-Bis(diphenylphosphinyl)-2,2,7,7-tetramethylocta-3,5-diene (4j). White solid; IR (Nujol) 1188 cm^{-1}; MS (EI) *m/z* 566 (M^+); ^1H NMR ($CDCl_3$) δ 0.85 (18H, s), 7.35-7.53 (14H, m), 7.68 (4H, tm, *J* = 8.8 Hz), 7.90 (4H, tm, *J* = 8.8 Hz); ^{13}C NMR ($CDCl_3$) (clearly assignable peaks) δ 29.7, 36.7. Anal. Calcd for $C_{36}H_{40}O_2P_2$: C, 76.31; H, 7.11. Found: C, 76.80; H, 7.47.

Dual Hydrophosphination of Aromatic Alkynes 9 with Phenylphosphine. The reaction was carried out in a manner similar to that of the diynes **6** described above, using the aromatic alkynes **9** (2.0 mmol), $PhPH_2$ (1.0 mmol), and **1** or **2** (0.1 mmol) in THF (1 mL). In the reaction with aniline, this additive and $PhPH_2$ were successively added to a solution of **1** or **2**, and the mixture was stirred for 30 min at room temperature.

Bis(β-methylstyryl)phenylphosphine Oxide (5a). (*Z*,*Z*)-Isomer: IR (Nujol) 1178 cm^{-1}; MS (EI) *m/z* 358 (M^+); ^1H NMR ($CDCl_3$) δ 1.96 (6H, dd, *J* = 12.2, 1.5 Hz), 7.03 (2H, dd, *J* = 37.0, 1.5 Hz), 7.17-7.19 (6H, m), 7.28-7.40 (7H, m), 7.66-7.71 (2H, m); ^{13}C NMR ($CDCl_3$) δ 23.9 (d, *J* = 13.1 Hz), 127.3, 127.9, 128.1, 128.4 (d, *J* = 50.9 Hz), 129.5 (d, *J* = 1.6 Hz), 131.1 (d, *J* = 3.2 Hz), 131.5 (d, *J* = 9.0 Hz), 132.5 (d, *J* = 99.9 Hz), 136.0 (d, *J* = 6.5 Hz), 144.6 (d, *J* = 6.5 Hz); ^{31}P NMR ($CDCl_3$) δ 27.52 Anal. Calcd for $C_{24}H_{23}OP$: C, 80.43; H, 6.47. Found: C, 80.29; H, 6.51. (*Z*,*E*)-Isomer: MS (EI) *m/z* 358 (M^+); ^1H NMR ($CDCl_3$) δ 1.75 (3H, dd, *J* = 14.0, 1.0 Hz), 2.09 (3H dd, *J* = 12.0, 1.2 Hz), 7.05-7.49 (15H, m), 7.66-7.71 (2H, m); ^{13}C NMR ($CDCl_3$) δ 14.4 (d, *J* = 11.4 Hz), 23.8 (d, *J* = 12.3 Hz), 127.3, 127.5, 127.9 (d, *J* = 12.6 Hz), 128.1, 128.2 (d, *J* = 11.5 Hz), 128.8 (d, *J* = 90.9 Hz), 129.2, 129.5 (d, *J* = 1.6 Hz), 131.0 (d, *J* = 81.1 Hz), 131.1 (d, *J* = 3.3 Hz), 131.3 (d, *J* = 21.5 Hz), 132.0 (d, *J* = 84.4 Hz), 135.8 (d, *J* = 5.7 Hz), 136.0 (d, *J* = 18.9 Hz), 141.3 (d, *J* = 9.8 Hz), 145.4 (d, *J* = 7.3 Hz); ^{31}P NMR ($CDCl_3$) δ 29.81. (*E*,*E*)-Isomer: MS (EI) *m/z* 358 (M^+); ^1H NMR ($CDCl_3$) δ 2.17 (6H, dd, *J* = 13.2, 1.2 Hz), 7.25-7.57 (15H, m), 7.80-7.85 (2H, m); ^{13}C NMR ($CDCl_3$) δ 15.0 (d, *J* = 9.8 Hz), 128.3, 128.4,

128.68, 128.71 (d, *J* = 29.5 Hz), 129.4, 129.6 (d, *J* = 41.7 Hz), 131.4 (d, *J* = 92.6 Hz), 132.0 (d, *J* = 9.8 Hz), 135.9 (d, *J* = 18.0 Hz), 142.4 (d, *J* = 10.6 Hz); ^{31}P NMR ($CDCl_3$) δ 38.40.

Bis(styryl)phenylphosphine Oxide (5b). (*Z,Z*)-Isomer: white solid; mp 78-80 °C; IR (KBr) 1178 cm^{-1}; MS (EI) *m/z* 330 (M^+); ^{1}H NMR ($CDCl_3$) δ 6.07 (2H, dd, *J* = 19.5, 14.0 Hz), 7.18-7.32 (11H, m), 7.65-7.72 (6H, m); ^{13}C NMR ($CDCl_3$) δ 123.9 (d, *J* = 100.0 Hz), 127.8, 128.0, 129.1, 130.0, 130.7 (d, *J* = 9.8 Hz), 131.0 (d, *J* = 2.5 Hz), 133.7 (d, *J* = 107.5 Hz), 135.2 (d, *J* = 7.4 Hz), 148.0; ^{31}P NMR ($CDCl_3$) δ 15.03. Anal. Calcd for $C_{22}H_{19}OP$: C, 79.98; H, 5.80. Found: C, 79.87; H, 5.81. (*Z,E*)-Isomer: white solid; MS (EI) *m/z* 330 (M^+); ^{1}H NMR ($CDCl_3$) δ 6.22 (1H, dd, *J* = 19.0, 13.9 Hz), 6.41 (1H, dd, *J* = 22.9, 17.4 Hz), 7.11-7.54 (13H, m), 7.68-7.79 (4H, m); ^{13}C NMR ($CDCl_3$) δ 120.3 (d, *J* = 105.0 Hz), 122.5 (d, *J* = 100.1 Hz), 127.3, 127.8, 128.3, 128.5 (d, *J* = 9.0 Hz), 129.2, 129.6, 129.8 (d, *J* = 1.6 Hz), 130.4 (d, *J* = 9.8 Hz), 131.3 (d, *J* = 3.3 Hz), 133.5 (d, *J* = 107.5 Hz), 134.9 (d, *J* = 7.4 Hz), 135.1 (d, *J* = 18.0 Hz), 146.0 (d, *J* = 3.3 Hz), 148.9; ^{31}P NMR ($CDCl_3$) δ 17.56.

Bis(4-methoxystyryl)phenylphosphine Oxide (5c). (*Z,Z*)-Isomer: IR (Neat) 1180 cm^{-1}; MS (EI) *m/z* 390 (M^+); ^{1}H NMR ($CDCl_3$) δ 3.76 (6H, s), 5.92 (2H, dd, *J* = 19.5, 14.0 Hz), 6.75-6.79 (4H, m), 7.17 (2H, dd, *J* = 40.5, 14.0 Hz), 7.26-7.34 (3H, m), 7.70-7.76 (6H, m); ^{13}C NMR ($CDCl_3$) δ 55.2, 113.4, 121.1 (d, *J* = 100.9 Hz), 128.07 (d, *J* = 18.9 Hz), 128.09, 130.8 (d, *J* = 9.8 Hz), 131.0 (d, *J* = 3.3 Hz), 132.1 (d, *J* = 1.6 Hz), 134.3 (d, *J* = 106.6 Hz), 147.5 (d, *J* = 1.6 Hz), 160.4; ^{31}P NMR ($CDCl_3$) δ 15.91. Anal. Calcd for $C_{24}H_{23}O_3P$: C, 73.83; H, 5.94. Found: C, 73.43; H, 5.98. (*Z,E*)-Isomer: MS (EI) *m/z* 390 (M^+); ^{1}H NMR ($CDCl_3$) δ 3.72 (3H, s), 3.80 (3H, s), 6.04 (1H, dd, *J* = 19.4, 13.8 Hz), 6.30 (1H, dd, *J* = 22.6, 17.2 Hz), 6.74-6.85 (4H, m), 7.29-7.48 (7H, m), 7.64-7.80 (4H, m); ^{13}C NMR ($CDCl_3$) δ 55.2, 55.3, 113.4, 114.1, 117.8 (d, *J* = 107.5 Hz), 119.7 (d, *J* = 100.9), 127.9 (d, *J* = 7.4 Hz),

128.2, 128.4 (d, *J* = 12.3 Hz), 129.1, 130.6 (d, *J* = 9.8 Hz), 131.3 (d, *J* = 2.4 Hz), 132.0, 134.2 (d, *J* = 107.5 Hz), 145.5 (d, *J* = 4.2 Hz), 148.4, 160.5, 160.9; ^{31}P NMR ($CDCl_3$) δ 18.57.

Bis(4-methylstyryl)phenylphosphine Oxide (5d). (*Z,Z*)-Isomer: white solid; mp 98-99 °C; IR (KBr) 1178 cm^{-1}; MS (EI) *m/z* 358 (M^+); ^{1}H NMR ($CDCl_3$) δ 2.29 (6H, s), 6.00 (2H, dd, *J* = 19.8, 14.0 Hz), 7.04-7.32 (10H, m), 7.61-7.72 (5H, m); ^{13}C NMR ($CDCl_3$) δ 21.3, 122.8 (d, *J* = 100.9 Hz), 127.9 (d, *J* = 11.5 Hz), 128.7, 130.2 (d, *J* = 1.6 Hz), 130.8 (d, *J* = 9.8 Hz), 130.9 (d, *J* = 3.3 Hz), 132.5 (d, *J* = 7.4 Hz), 134.2 (d, *J* = 107.5 Hz), 139.4, 147.9 (d, *J* = 1.6 Hz); ^{31}P NMR ($CDCl_3$) δ 15.29. Anal. Calcd for $C_{24}H_{23}OP$: C, 80.43; H, 6.47. Found: C, 80.21; H, 6.43. (*Z,E*)-Isomer: MS (EI) *m/z* 358 (M^+); ^{1}H NMR ($CDCl_3$) δ 2.24 (3H, s), 2.33 (3H, s), 6.14 (1H, dd, *J* = 19.0, 14.0 Hz), 6.35 (1H, dd, *J* = 22.8, 17.2 Hz), 6.92-7.79 (15H, m): ^{13}C NMR ($CDCl_3$) δ 21.2, 21.3, 119.3 (d, *J* = 105.8 Hz), 121.5 (d, *J* = 100.1 Hz), 127.4, 128.4 (d, *J* = 12.3 Hz), 128.7, 129.3. 130.1, 130.6 (d, *J* = 9.8 Hz), 131.3 (d, *J* = 3.3 Hz), 132.4 (d, *J* = 7.4 Hz), 132.7 (d, *J* = 18.9 Hz), 134.0 (d, *J* = 107.5 Hz), 139.5. 139.9, 145.9 (d, *J* = 3.3 Hz), 148.9; ^{31}P NMR ($CDCl_3$) δ 18.09.

Bis(4-chlorostyryl)phenylphosphine Oxide (5e). (*Z,Z*)-Isomer: white solid; mp 111-112 °C; IR ($CHCl_3$) 1175 cm^{-1}; MS (EI) *m/z* 398 (M^+); ^{1}H NMR ($CDCl_3$) δ 6.09 (2H, dd, *J* = 19.6, 14.0 Hz), 7.15-7.39 (9H, m), 7.64-7.68 (6H, m); ^{13}C NMR ($CDCl_3$) δ 124.4 (d, *J* = 100.0 Hz), 128.1, 128.3, 130.7 (d, *J* = 9.8 Hz), 131.39, 131.44 (d, *J* = 3.2 Hz), 133.2 (d, *J* = 106.5 Hz), 133.5 (d, *J* = 8.2 Hz), 135.3, 147.0; ^{31}P NMR ($CDCl_3$) δ 14.78. Anal. Calcd for $C_{22}H_{17}Cl_2OP$: C, 66.18; H, 4.29. Found: C, 66.12; H, 4.01. (*Z,E*)-Isomer: white solid; mp 150-151 °C; IR ($CHCl_3$) 1180 cm^{-1}; MS (EI) *m/z* 398 (M^+); ^{1}H NMR ($CDCl_3$) δ 6.25 (1H, dd, *J* = 19.1, 13.8 Hz), 6.40 (1H, dd, *J* = 22.7, 17.1 Hz), 7.20-7.50 (11H, m), 7.64-7.77 (4H, m); ^{31}P NMR ($CDCl_3$) δ 17.21. Anal. Calcd for $C_{22}H_{17}Cl_2OP$: C, 66.18; H, 4.29. Found: C, 66.19; H, 4.16.

Bis(4-bromostyryl)phenylphosphine Oxide (5f). (*Z*,*Z*)-Isomer: white solid; mp 117-118 °C; IR ($CHCl_3$) 1180 cm^{-1}; MS (EI) *m/z* 486 (M^+); ^1H NMR ($CDCl_3$) δ 6.10 (2H, dd, *J* = 19.7, 14.0 Hz), 7.20 (2H, dd, *J* = 40.1, 14.0 Hz), 7.27-7.39 (7H, m), 7.58-7.68 (6H, m); ^{13}C NMR ($CDCl_3$) δ 123.8, 124.6 (d, *J* = 99.2 Hz), 128.2 (d, *J* = 12.3 Hz), 130.7 (d, *J* = 9.8 Hz), 131.2, 131.5 (d, *J* = 2.5 Hz), 131.6 (d, *J* = 1.2 Hz), 133.2 (d, *J* = 107.3 Hz), 134.0 (d, *J* = 7.4 Hz), 147.1; ^{31}P NMR ($CDCl_3$) δ 12.14. Anal. Calcd for $C_{22}H_{17}Br_2OP$: C, 54.13; H, 3.51. Found: C, 54.18; H, 3.51. (*Z*,*E*)-Isomer: white solid; MS (EI) *m/z* 486 (M^+); ^1H NMR ($CDCl_3$) δ 6.25 (1H, dd, *J* = 19.1, 14.0 Hz), 6.40 (1H, dd, *J* = 23.0, 17.4 Hz), 7.19-7.76 (15H, m); ^{13}C NMR ($CDCl_3$) δ 121.0 (d, *J* = 104.9 Hz), 123.4 (d, *J* = 99.2 Hz), 124.1, 128.7 (d, *J* = 12.2 Hz), 128.9, 129.1, 130.5 (d, *J* = 10.7 Hz), 131.2, 131.6, 131.8, 132.0, 133.1 (d, *J* = 112.0 Hz), 133.98, 134.03 (d, *J* = 25.4 Hz), 145.1 (d, *J* = 3.3 Hz), 147.8; ^{31}P NMR ($CDCl_3$) δ 14.61.

3,6-Bis(diphenylphosphinyl)-2,2,7,7-tetramethylocta-3,4-diene (7). White solid; mp 202-204 °C; IR (KBr) 1203, 1186 cm^{-1}; MS (MALDI) *m/z* 564.01 (M^+-2); MS m/z 566 (M^+), 509 (M^+-^{t}Bu), 452(M^+-2^{t}Bu), 365 (M^+-Ph_2PO), 308 (365-^{t}Bu$^+$), 201 (Ph_2PO^+); ^1H NMR ($CDCl_3$) δ 1.16 (9H, s), 1.33 (9H, s), 2.81 (1H, ddd, *J* = 7.7, 5.9, and 4.3 Hz), 5.30 (1H, ddd, *J* = 16.7, 11.6, and 7.7 Hz), 6.94-7.76 (20H, m); ^{13}C NMR ($CDCl_3$) δ 29.8 (d, *J* = 5.7 Hz), 29.9 (d, *J* = 4.1 Hz), 37.5 (d, *J* = 6.6 Hz), 37.8 (d, *J* = 5.7 Hz), 45.3 (dd, *J* = 70.6 and 4.9 Hz), 90.6 (d, *J* = 13.9 Hz), 107.8 (d, *J* = 96.8 Hz), 127.9 (d, *J* = 11.5 Hz), 128.1 (d, *J* = 100.9 Hz), 128.7, 130.2 (d, *J* = 1.6 Hz), 130.8 (d, *J* = 9.8 Hz), 130.9 (d, *J* = 12.3 Hz), 128.3 (d, *J* = 11.5 Hz), 128.4 (d, *J* = 11.5 Hz), 130.0 (d, *J* = 9.1 Hz), 130.5 (d, *J* = 8.2 Hz), 130.7 (d, *J* = 2.5 Hz), 131.1 (d, *J* = 3.3 Hz), 131.4 (d, *J* = 2.5 Hz), 131.5 (d, *J* = 3.3 Hz), 131.6 (d, *J* = 9.0 Hz), 132.0 (d, *J* = 10.7 Hz), 132.9 (d, *J* = 100.9 Hz), 134.0 (d, *J* = 96.0 Hz), 135.6 (d, *J* = 95.2 Hz), 137.8 (d, *J* = 108.3 Hz), 207.1 (d, *J* = 26.3 Hz); ^{31}P NMR ($CDCl_3$) δ 28.78 (d, *J* = 5.9 Hz), 31,68 (d, *J* = 5.9 Hz). Anal. Calcd for $C_{36}H_{40}O_2P_2$: C, 76.31; H, 7.11. Found: C, 76.53; H, 7.11.

1-Diphenylphosphinyl-1-phenyldec-1-en-3-yne (8d). Isolated as a mixture of (*Z*) and (*E*)-isomer (91 : 9); yellow oil; IR (Neat) 1190 cm^{-1}; MS (EI) *m/z* 412 (M^+); ^1H NMR ($CDCl_3$) δ (*Z*)-isomer : 0.84 (3H, t, *J* = 6.9 Hz), 1.14-1.56 (8H, m), 2.53-2.61 (2H, m), 6.52 (1H, d, *J* = 36.2 Hz), 6.87 (2H, d, *J* = 7.0 Hz), 7.15-7.57 (9H, m), 7.70-7.86 (4H, m); (*E*)-isomer: 6.22 (d, *J* = 18.1 Hz); ^{13}C NMR ($CDCl_3$) δ (*Z*)-isomer: 14.0, 22.4, 28.7, 29.4 (d, *J* = 3.2 Hz), 31.5, 34.9 (d, *J* = 8.2 Hz), 86.7 (d, *J* = 10.6 Hz), 99.8 (d, *J* = 1.6 Hz), 120.8 (d, *J* = 6.5 Hz), 127.9, 128.3 (d, *J* = 12.3 Hz), 128.5, 131.3, 131.73, 131.76 (d, *J* = 10.7 Hz), 131.8, 132.5 (d, *J* = 103.4 Hz), 146.8 (d, *J* = 90.5 Hz); ^{31}P NMR ($CDCl_3$) δ (*Z*)-isomer: 27.76, (*E*)-isomer: 31.77. Anal. Calcd for $C_{28}H_{29}OP$: C, 81.53; H, 7.09. Found: C, 81.56; H, 7.22.

(*Z*)-1-Diphenylphosphinyldec-1-en-3-yne (8g). Yellow oil; IR (Neat) 1188 cm^{-1}; MS (EI) *m/z* 336 (M^+); ^1H NMR ($CDCl_3$) δ 0.86 (3H, t, *J* = 7.1 Hz), 1.15-1.27 (8H, m), 1.97-2.00 (2H, m), 6.47 (1H, dd, *J* = 18.7, 13.2 Hz), 6.53 (1H, ddt, *J* = 35.8, 13.2, 2.4 Hz), 7.43-7.53 (6H, m), 7.76-7.81 (4H, m); ^{13}C NMR ($CDCl_3$) δ 14.0, 19.6, 22.4, 27.7, 28.4, 31.2, 77.3 (d, *J* = 12.3 Hz), 104.8, 128.3 (d, *J* = 12.3 Hz), 128.4 (d, *J* = 1.6 Hz), 131.26 (d, *J* = 9.8 Hz), 131.30 (d, *J* = 99.3 Hz), 131.6 (d, *J* = 3.5 Hz), 133.0 (d, *J* = 105.8 Hz); ^{31}P NMR ($CDCl_3$) δ 21.46. Anal. Calcd for $C_{22}H_{25}OP$: C, 78.55; H, 7.49. Found: C, 78.60; H, 7.58.

1,2,3,4,5-Pentaphenyl-1-phosphacyclopent-2-ene 1-Oxide (10). Isolated as a single isomer with unknown stereochemistry; white solid; mp 295-297 °C; IR (KBr) 1215 cm^{-1}; MS (MALDI) *m/z* 482.60 (M^+); ^1H NMR ($CDCl_3$) δ 3.98 (1H, dd, *J* = 10.1, 8.2 Hz), 4.96 (1H, dd, *J* = 27.3, 8.2 Hz), 7.01-7.39 (23H, m), 7.67-7.72 (2H, m); ^{13}C NMR ($CDCl_3$) δ 51.0 (d, *J* = 69.7 Hz), 59.7 (d, *J* = 7.3 Hz), 126.7, 127.0, 127.4, 127.7, 128.1, 128.27, 128.34, 128.40 (d, *J* = 10.6 Hz), 128.85, 128.90, 129.7, 130.8 (d, *J* = 7.5 Hz), 131.5 (d, *J* = 9.8 Hz), 131.6 (d, *J* = 2.4 Hz), 133.1 (d, *J* = 119.6 Hz), 133.7 (d, *J* = 1.0 Hz),

133.9, 134.0, 136.1 (d, J = 92.6 Hz), 136.6 (d, J = 15.5 Hz), 137.2, 157.9 (d, J = 25.4 Hz); ^{31}P NMR ($CDCl_3$) δ 52.06. Anal. Calcd for $C_{34}H_{27}OP$: C, 84.63; H, 5.64. Found: C, 84.44; H, 5.68.

Di(decyl)phenylphosphine Oxide (11). White solid; mp 56-57 °C; IR (KBr) 1165 cm^{-1}; MS (EI) *m/z* 406 (M^+); ^{1}H NMR ($CDCl_3$) δ 0.86 (6H, t, J = 6.7 Hz), 1.21-2.17 (36H, m), 7.47-7.52 (3H, m), 7.66-7.71 (2H, m); ^{13}C NMR ($CDCl_3$) δ 14.1, 21.4 (d, J = 4.1 Hz), 22.7, 29.1, 29.3, 29.4, 29.5 30.0 (d, J = 68.1 Hz), 31.0 (d, J = 13.8), 31.9, 128.6 (d, J = 11.4 Hz), 130.4 (d, J = 8.2 Hz), 131.4 (d, J = 3.2 Hz), 132.3 (d, J = 91.8 Hz); ^{31}P NMR ($CDCl_3$) δ 40.72. Anal. Calcd for $C_{26}H_{47}OP$: C, 76.80; H, 11.65. Found: C, 76.84; H, 11.65.

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(8) Although the mechanism leading to **10** is unknown at present, it may be formed by cyclization of (*Z*)-phosphinoalkenylytterbium species, (*Z*)-isomer corresponding to G depicted in Scheme 3.

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