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Intermolecular Hydrophosphination of Alkynes and Related Carbon−Carbon Multiple Bonds Catalyzed by Organoytterbiums

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Intermolecular hydrophosphination of alkynes with diphenylphosphine is catalyzed by a Yb−imine complex, [Yb(η^2-Ph_2CNPh)$(hmpa)_3$], to give alkenylphosphines and phosphine oxides after oxidative workup in good yields under mild conditions. This reaction is also applicable to various carbon−carbon multiple bonds such as conjugated diynes and dienes, allenes, and styrene derivatives. Regio- and stereoselectivity and the scope and limitation of the present reaction clearly differ from those of the corresponding radical reaction. Instead, the reaction takes place through insertion of alkynes to a Yb−PPh_2 species, followed by protonation. In fact, the Yb−phosphido complex, [Yb$(PPh_2)_2$-$(hmpa)_3$], is obtained from the imine complex and phosphine, which exhibits similar catalyst activity for the hydrophosphination. The empirical rate law is $v = k$[catalyst]^2 [alkyne]^1[phosphine]^0 at least under the standard conditions.

Introduction

α,β-Unsaturated phosphorus compounds have been utilized as useful building blocks in organic synthesis. Conventionally, they are prepared by a substitution reaction of halophosphines with alkenylmetals, addition reaction of hydrophosphines to alkynes promoted by a base or radical initiator,[1] and elimination reaction of alkylphosphonates having leaving groups at the α or β-position.[2] The coupling reaction of alkenyl halides and triflates with dialkyl phosphites[3] and diphenylphosphine[4] has been also explored by using group 10 catalysts. In addition, hydrophosphinylation and hydrophosphorylation of alkynes via P−H bond activation by the metal catalysts, a more convenient approach for α,β-unsaturated phosphorus compounds, have been extensively investigated in the past decade. Pentavalent phosphorus compounds, i.e., dialkyl phosphites and diphenylphosphine oxide, were found to be applicable in the reaction of alkynes and alkenes with Pt and Pd catalysts, giving rise to the desired products with high regio- and stereoselectivity.[5] In the case of trivalent phosphines, this approach has been limited to the reaction with activated alkenes such as acrylate esters and acrylonitrile,[6] but successful examples for nonactivated alkynes and styrenes were reported very recently.[7] Besides the group 10 catalysts, trivalent lanthanocenes were found to exhibit high catalyst activities in the intramolecular hydrophosphination of phosphinoalkynes and -alkenes.[8]

Previously, we demonstrated that a divalent ytterbium-imine complex, [Yb(η^2-Ph_2CNPh)$(hmpa)_3$] (**1**), readily prepared in situ from Yb metal and $Ph_2C{=}NPh$,[9] served as a unique catalyst in the presence of hydrosilanes, for example, dehydrogenative silylation of terminal alkynes,[10] hydrosilylation of imines,[11] and dehydrogenative double silylation of conjugated dienes.[12] Moreover, preliminary

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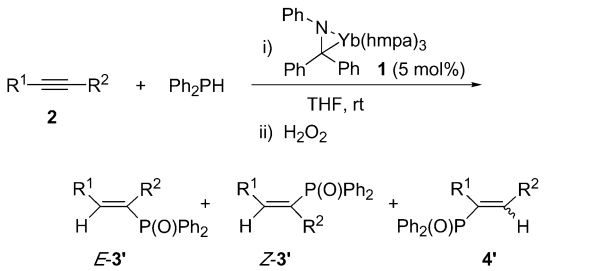
TABLE 1. Hydrophosphination of Alkynes with Diphenylphosphine



	alkyne				3′		4′
run		R^1	R^2	time	yield[a] (%)	*E*/*Z*	yield[a] (%)
1	**2a**	Ph	Ph	5 min	**3a′**, quant	100/0	
2	**2b**	Ph	$SiMe_3$	4 h	**3b′**, quant	100/0	**4b′**, 0
3	**2c**	Ph	Me	5 min	**3c′**, quant	80/20	**4c′**, 0
4	**2d**	Ph	H	5 min	**3d′**, quant	76/24	**4d′**, 0
5[b]	**2e**	^{n}Pr	^{n}Pr	6 h[c]	**3e′**, 95	0/100	
6[b]	**2f**	^{n}Pen	Me	6 h[c]	**3f′**, 61	0/100	**4f**,[d] 28
7[b]	**2g**	^{t}Bu	H	3 h	**3g′**, 62	0/100	**4g′**, 10
8	**2h**	^{n}Hex	H	5 min	**3h′**, 52	27/73	**4h′**, 48

[a] GC yield. [b] 10 mol % of **1** was used. [c] 80 °C in neat solution. [d] *E*/*Z* = 21/79.

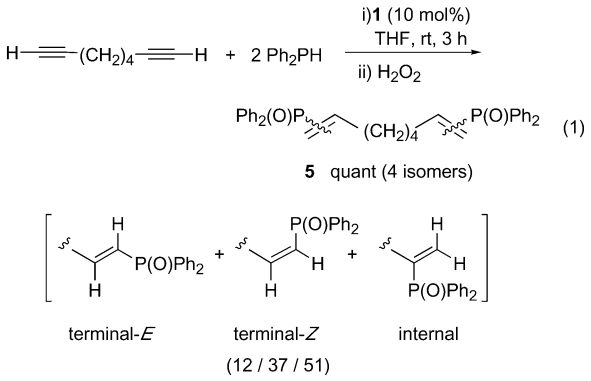
investigation indicated that the complex **1** could catalyze the intermolecular hydrophosphination of alkynes with diphenylphosphine.[13] We report herein a more detailed feature, particularly mechanistic aspect of the hydrophosphination.

Results and Discussion

When diphenylphosphine and equimolar amounts of 1-phenyl-1-propyne (**2c**) were successively added to a THF solution of **1** (5 mol %) at room temperature, 1-phenyl-2-diphenylphosphino-1-propene (**3c**) was quantitatively formed within 5 min, wherein the ratio of the *E*- to *Z*-isomer was 80/20. The other regioisomer, 1-phenyl-1-diphenylphosphino-1-propene (**4c**), was not detected. The alkenylphosphine **3c** was isolated in lower yield (~80%) because of partial oxidation to the corresponding phosphine oxide **3c′** during the usual workup and column chromatography. Thus, the reaction mixture was conveniently separated and analyzed as phosphine oxide **3c′** after oxidation with H_2O_2. No reaction took place with $Yb(O^iPr)_3$ and SmI_2 under similar conditions, whereas many products, including polymeric materials, were formed with ^{n}BuLi. Prolonged heating of a neat mixture of diphenylphosphine and **2c** in the absence of the catalysts (85 °C, 35 h) gave **3c** in 64% yield with a reversed *E*/*Z* ratio of 3/97.[14]

Results on the hydrophosphination of various alkynes **2** with diphenylphosphine are summarized in Table 1. Both terminal and internal alkynes gave the expected products **3′** and **4′** in good yields under mild conditions. In the case of less reactive aliphatic internal alkynes **2e** and **2f**, relatively drastic conditions are, however, necessary to complete the reaction (runs 5 and 6). It is worthy to note that the reaction of **2e** in refluxing THF gave **3e′** in lower yield (21%) than those obtained in neat or toluene solution, together with 4-diphenylphosphino-1-butanol, which should be formed by THF cleavage with the [Yb]−PPh_2 species (vide infra).[15]

The reaction of aromatic alkynes **2b**−**d** gave the products **3′** exclusively: a Ph_2P group was introduced into the opposite side of the aryl substituents (runs 2−4). A mixture of **3′** and **4′** was formed from aliphatic alkynes **2f**−**h** in preference of the former. Stereochemistry of the products **3′** and **4′** was determined on the basis of their coupling constants between the olefinic H and P(O): trans $^3J_{P-H}$ = ca. 40 Hz, cis $^3J_{P-H}$ = ca. 21, $^2J_{P-H}$ = ca. 24, in addition to comparison of ^{1}H NMR and UV spectra with literature data.[16] Thus, *E*-isomers were predominantly produced from aromatic alkynes (runs 1−4) and, in contrast, *Z*-adducts from aliphatic alkynes (runs 5−8). This stereoselectivity was not affected so much by the reaction conditions, except for **2c**, in which use of three times excess phosphine, for example, reversed the ratio to 25/75. Furthermore, the reaction of 1,7-octadiyne with two equimolar amounts of Ph_2PH gave double hydrophosphination product **5** quantitatively as a mixture of four isomers, but hydrophosphination/cyclization products were not formed (eq 1). Because the mixture **5** could not be separated by column chromatography, their structures were unclear. However, regio- and stereoselectivity of the total reaction could be determined by ^{1}H NMR spectra of the mixture: terminal-*E*/terminal-*Z*/internal = 12/37/51. In contrast to the above results, direct synthesis of the alkenylphosphine oxides **3′** and **4′** by the reaction with $Ph_2P(O)H$ was unsuccessful, wherein the catalyst **1** was immediately oxidized with the phosphine oxide to give some trivalent lanthanide species and Ph_2PH.



The present hydrophosphination was applied to other carbon−carbon multiple bonds to examine its scope and limitation (Table 2). The reaction of 7,9-hexadecadiyne with 2 equiv of the phosphine at −35 °C gave bis(diphenylphosphinyl)diene **6a** in 51% yield as the sole

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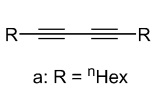
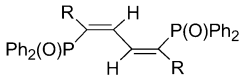
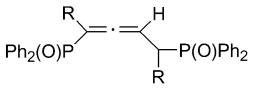
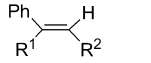
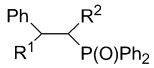
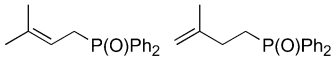
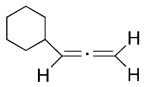
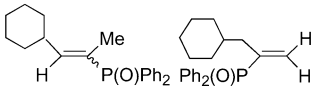
(13) Takaki, K.; Takeda, M.; Koshoji, G.; Shishido, T.; Takehira, K. *Tetrahedron Lett.* **2001**, *42*, 6357−6360.

(14) Of the substrates in Tables 1 and 2, similar thermal reaction was observed for phenylacetylene (**2d**) and α-methylstyrene in refluxing THF, giving rise to **3d** (80%, *E*/*Z* = 21/79) and **8a** (40%), respectively. However, these reactions did not occur at room temperature.

(15) Schumann, H.; Palamidis, E.; Loebel, J. *J. Organomet. Chem.* **1990**, *384*, C42−C52.

(16) (a) Taillefer, M.; Cristau, H. J. *Tetrahedron Lett.* **1998**, *39*, 7857−7860. (b) Taillefer, M.; Cristau, H. J.; Fruchier, A.; Vicent, V. *J. Organomet. Chem.* **2001**, *624*, 307−315 (c) Breslow, R.; Deuring, L. A. *Tetrahedron Lett.* **1984**, *25*, 1345−1348. Moreover, ^{31}P NMR signals of the *E*-alkenylphosphines **3** and **4** always appear in lower field than those of the *Z*; see ref 17.

TABLE 2. Hydrophosphination of Various C−C Multiple Bonds with Diphenylphosphine[a]

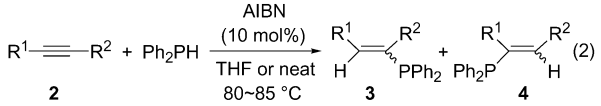
substrate	conditions	product and yield[b] (%)
 a: R = ^{n}Hex b: R = ^{t}Bu	-35 °C, 3 h[c]	 **6a** 51, **6b** 12
		 **7a** 0, **7b** 71
 a: R^1 = Me, R^2 = H b: R^1 = H, R^2 = Me	rt, 4 h	 **8a** 85, **8b** 95
	0 °C, 1.5 h[d]	 **9** 64 **10** 35
	rt, 30 min	 **11** 79 (*E*/*Z* = 71 / 29) **12** 13

[a] All reactions were carried out with 10 mol % of **1** in THF and the products were isolated after oxidation with H_2O_2. [b] GC yield except for **6** and **7** (isolated yield). [c] 2 equiv of Ph_2PH was used. [d] 2 equiv of isoprene was used.

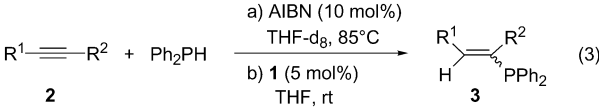
product after oxidative workup with H_2O_2. In contrast, 2,2,7,7-tetramethyl-3,5-octadiyne was converted to a mixture of diene **6b** and allene **7b** in 12% and 71% yields, respectively, under similar conditions. An attempt to obtain monophosphinylated products with equimolar amounts of the phosphine was unsuccessful, which afforded **6** and **7** in decreased yields together with a large amount of polymeric products. 1,4-Diphenyl-1,3-butadiyne polymerized rapidly even at −78 °C. Although the reaction of aliphatic alkenes did not occur, α- and *β*-methylstyrene afforded the products **8a** and **8b** in good yields. In the reaction of isoprene, the Ph_2P group was selectively delivered to the less hindered side of the two terminal carbons to give 1,4- and 1,2-addition products **9** and **10** in 64% and 35% yields, respectively. The phosphine added exclusively to the central carbon of cyclohexylallene to produce two olefinic phosphine oxides **11** and **12** in 79% and 13% yields, respectively. Other possible regioisomers formed by addition to the terminal carbon, which was reported in radical reaction, were not detected at all.[17]

As demonstrated above, the intermolecular hydrophosphination of various carbon−carbon unsaturation is effectively realized with the Yb−imine complex **1**. However, the reaction feature is very different from that with lanthanocenes. The high catalyst activity of the latter in many transformations of alkynes and alkenes such as hydrosilylation, hydroamination, hydrophosphination, dimerization, and so on is ascribed to the facile access of the substrates to the coordinatively unsaturated lanthanide metal, and thus, these reactions are normally conducted in hydrocarbon solvents.[18] In contrast, the present reaction preferred THF to toluene and hexane, and HMPA ligand is essential. Thus, our next effort was addressed to a mechanistic study for understanding the hydrophosphination with **1**.

At first, we considered the possibility of radical reaction, since it has been well-known that phosphine radicals, generated thermally, photochemically, or by a radical initiator, add to carbon−carbon multiple bonds readily. Thus, the reaction of alkynes **2** with diphenylphosphine was carried out in the presence of AIBN (eq 2). Comparing the reactions by AIBN and **1** (eq 2 vs Table 1), the former gave the products in lower yields than the latter, in particular for **2b** and **2g**. The regioisomer **4h** was not formed in the radical reaction. Stereoselectivity was the same for aliphatic alkyne **2h**, but opposite for aromatic alkynes **2a** and **2c**. However, the reaction of alkynes with Ph_2PH under radical conditions was reported to give normally *E*-alkenylphosphines as the primary products, which isomerized to the *Z*-isomers.[17] Thus, time-dependence of the stereochemistry in the reaction of aromatic and aliphatic alkyne **2c** and **2h** with AIBN was monitored by ^1H and ^{31}P NMR (eq 3). Although a slight increase of the *E*/*Z* ratio was observed, stereochemistry was not reversed during the reactions for both alkynes **2c** and **2h**. Similar results were obtained in the reaction with **1**, except for a slight decrease of the ratio.



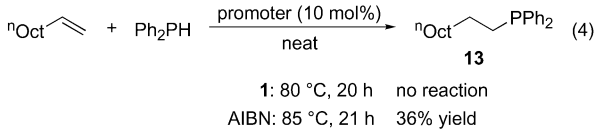
alkyne	time (h)	**3** (%)	*E*/*Z*	**4** (%)
2a	15	79	0 / 100	—
2b	15	15	not measured	0
2c	1.5	69	9 / 91	0
2g	18	tr	—	0
2h	4	71	22 / 78	0



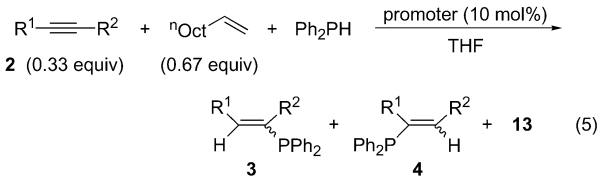
	a) with AIBN			b) with **1**		
alkyne	time	**3** (%)	*E*/*Z*	time	**3** (%)	*E*/*Z*
2c	10 min	10	1 / 99	5 min	quant	80 / 20
	30 min	30	5 / 95			
	1.5 h	69	9 / 91			
	30 h	68	17 / 83	38 h	quant	70 / 30
2h	30 min	26	13 / 87	5 min	52	27 / 73
	1 h	36	16 / 84			
	4 h	71	22 /78			
	52 h	68	28 / 72	24 h	57	9 / 91

The reaction of 1-decene initiated by AIBN gave addition product **13** in 36% yield, in contrast to that catalyzed by **1** (eq 4). In addition, if $Ph_2P^•$ could be generated from Ph_2PH and **1** plus alkyne, competitive reaction of the alkyne and 1-decene with **1** should yield

(17) Mitchell, T. N.; Heesche, K. *J. Organomet. Chem.* **1991**, *409*, 163−170.



both alkyne products **3** and **4** and decene product **13** together. The reaction of aliphatic alkyne **2h** and 1-decene with AIBN gave **3h** and **13** in 73% and 34% yields based on the substrates, respectively, whereas only **3h** and **4h** were produced in 43% and 32% yields, respectively, with **1** (eq 5). Similarly, competitive reaction of aromatic alkyne **2b** and 1-decene with **1** afforded only the alkyne product **3b** in 92% yield. Therefore, it can be concluded that the hydrophosphination with **1** does not involve a radical mechanism based on these results.



	3 (%)	**4** (%)	**13** (%)
2b: with **1**, rt, 31h	92	0	0
2h: with **1**, rt, 31h	43	32	0
2h: with AIBN, 85 °C, 36 h	73	0	34

Next, the imine complex **1** was treated separately with stoichiometric amounts of 1-phenyl-1-propyne (**2c**) and Ph_2PH in order to study the active species initially formed. The alkyne **2c** was reduced somewhat at room temperature for 1 h in THF to afford β-methylstyrene in 16% yield.[19] The reaction of **1** with Ph_2PH (2 equiv) was conducted in an NMR tube, and its ^{13}C and ^{31}P NMR spectra are shown in Figure 1. A dark red suspension of **1** was immediately changed to a bright red homogeneous solution by addition of the phosphine. The signals of **1**[9] and Ph_2PH completely disappeared in ^{13}C NMR, and those assignable to free or coordinated amine, $Ph_2CHNHPh$ (**14**), were clearly observed (Figure 1, **G**, ○).[20] Moreover, four additional new peaks, although small, could be found at 119.2, 127.5, 130.9, and 150.5 ppm, which might be assignable to [Yb]−PPh_2 species **A** (Figure 1, **G**, △). In the ^{31}P NMR spectra, the signal of Ph_2PH at −40.1 ppm changed to 1.24 upon treatment (Figure 1, **H**, △). When 2 equiv of the alkyne **2c** was added to the mixture, the ^{13}C NMR spectra became

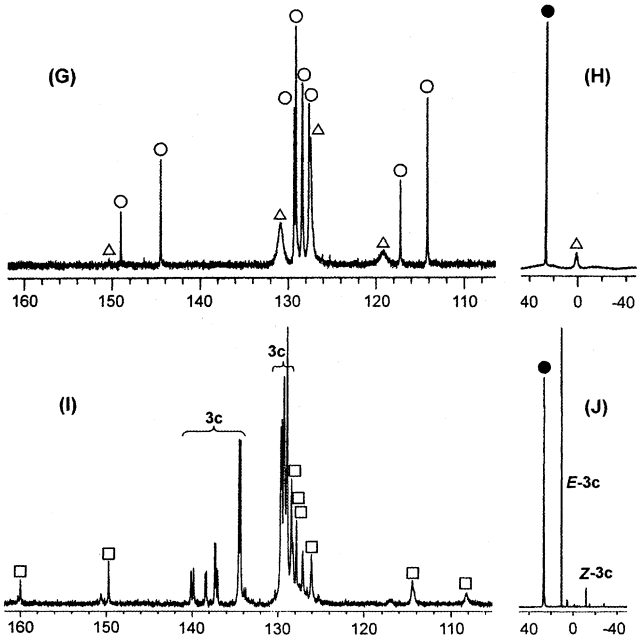
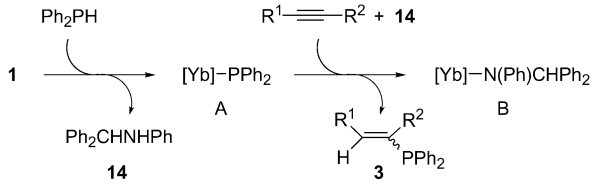


FIGURE 1. ^{13}C and ^{31}P NMR spectra of the reaction of **1** with Ph_2PH (2 equiv) in THF-d_8 (**G** and **H**), followed by addition of **2c** (2 equiv) (**I** and **J**). ●, ○, △, and □ denote the signals assignable to HMPA, the amine **14**, [Yb]-PPh_2 **A**, and [Yb]-N(Ph)$CHPh_2$ **B**, respectively.

SCHEME 1



somewhat complicated, but the product **3c** was definitely identified (Figure 1, **I**). Surprisingly, the phosphido species **A** disappeared and new signals assignable to [Yb]−N(Ph)$CHPh_2$ species **B** were found (Figure 1, **I**, □).[21] In the ^{31}P NMR spectra, signals other than those of the products **3c** were almost negligible, indicating that the phosphido species **A** was completely consumed in the final step of the reaction (Figure 1, **J**).

On the basis of the NMR study, the stoichiometric hydrophosphination can be envisioned as depicted in Scheme 1. That is, the phosphido **A**, an active species of this reaction, would be generated from the imine complex **1** and Ph_2PH, which is followed by addition to the alkyne and protonation with the liberated amine **14** to leave the product **3** and amido **B**. Thus, we tried to isolate the phosphido intermediate **A**. Treatment of hmpa-free imine complex **1′** with two equivalents of Ph_2PH gave orange crystals **15a** in 84% isolated yield (eq 6). The ^1H, ^{13}C and ^{31}P NMR spectra of **15a** were in good agreement with those reported for a divalent diphosphido complex, Yb-$(PPh_2)_2(thf)_4$.[22] Ligand substitution of **15a** by hmpa was readily performed to yield $Yb(PPh_2)_2(hmpa)_3$ (**15b**). The

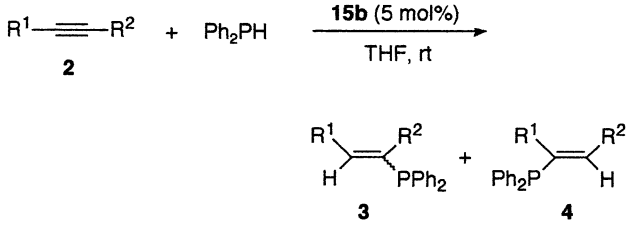
(18) For reviews, see: (a) Edelmann, F. T. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, 1995; Vol. 4, Chapter 2. (b) Herrmann, W. A., Ed. *Topics in Current Chemistry 179*; Springer: Berlin, 1996. (c) Molander, G. A.; Dowdy, E. D. In *Lanthanides: Chemistry and Use in Organic Synthesis*; Kobayashi, S., Ed.; Springer: Berlin, 1999; pp 119−154. (d) Molander, G. A.; Romero, J. A. *Chem. Rev.* **2002**, *102*, 2161−2185. (e) Dimerization: Heeres, H. J.; Heeres, A.; Teuben. J. H. *Organometallics* **1990**, *9*, 1508−1510. Heeres, H. J.; Teuben, J. H. *Organometallics* **1991**, *10*, 1980−1986. Kretschmer, W. P.; Troyanov, S. I.; Meetsma, A.; Hessen, B. H.; Teuben, J. H. *Organometallics* **1998**, *17*, 284−286.

(19) The imine complex **1** was reported to catalyze the selective isomerization of 1-alkynes to 2-alkynes, but this reaction did not occur in the presence of Ph_2PH; see: Makioka, Y.; Saiki, A.; Takaki, K.; Taniguchi, Y.; Kitamura, T.; Fujiwara, Y. *Chem. Lett.* **1997**, 27−28.

(20) ^{13}C NMR (THF-d_8): δ 63.3, 114.2, 117.3, 127.6, 128.4, 129.1, 129.4, 144.5, 149.0.

(21) ^{13}C NMR (THF-d_8) of the species **B**: δ 68.7($CHPh_2$), 108.3 (p-C_N), 114.4 (o-C_N), 126.1(p-C_C), 128.5 (o-C_C), 128.92 (m-C_N), 128, 95 (m-C_C), 149.7 (*ipso*-C_C), 159.9 (*ipso*-C_N), which was identical with that of $Yb[N(Ph)CHPh_2]_2(hmpa)_n$ prepared from **1** and **14**; unpublished results.

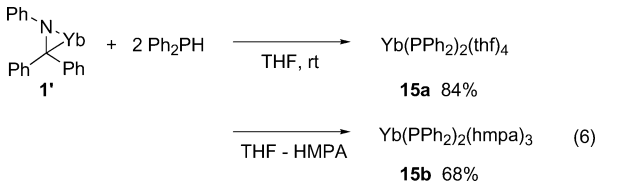
TABLE 3. Hydrophosphination of Alkynes Catalyzed by the Diphosphido Complex 15b



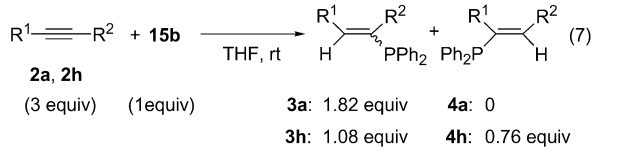
			3		4
run	alkyne	time (h)	yield[a] (%)	*E*/*Z*	yield[a] (%)
1	**2a**	1	**3a**, quant	95/5	
2	**2b**	27	**3b**, 74	89/11	**4b**, 0
3	**2c**	1	**3c**, quant	27/73	**4c**, 0
4	**2g**	8	**3g**, 68	0/100	**4g**, 14
5	**2h**	5	**3h**, 41	7/93	**4h**, 24

[a] GC yield.

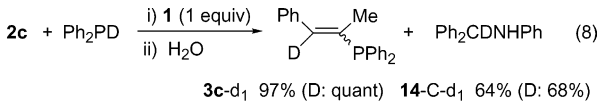
complex **15b** showed ^{13}C and ^{31}P NMR spectra analogous to those observed in the trace reaction described above, of course.

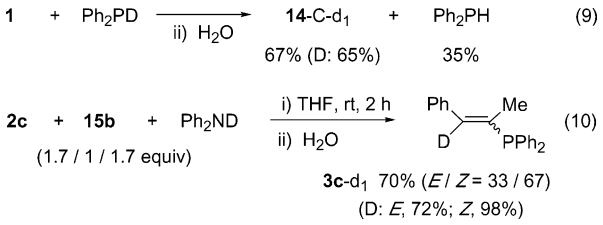


The phosphido complex **15b** was found to exhibit good catalyst activities in the hydrophosphination of the alkynes **2**, giving rise to similar results as with the imine catalyst **1** on the whole (Table 3). The ratio of *Z*-isomers **3** increased slightly (runs 1, 2, and 5), though preferential formation of *E* from aromatic alkynes and *Z* from aliphatic substrates was not altered, except for **2c**. Moreover, the reaction with **15b** needed longer reaction time than that with **1**. Interestingly, the diphosphido complex **15b** could deliver the two Ph_2P groups to alkynes. For example, reaction with 3 equiv of alkyne **2a** gave 1.82 equiv of the alkenylphosphine **3a** (eq 7). The products **3h** and **4h** were also formed from **2h** in 1.08 and 0.76 equiv, respectively.

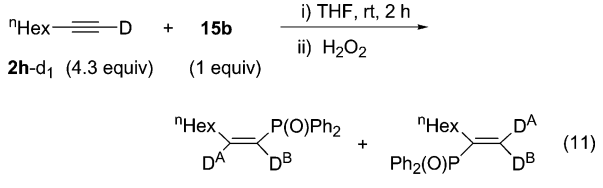


Next, we studied a labeling experiment by using various deuterated sources. The reaction of 1-phenyl-1-propyne (**2c**) with Ph_2PD in the presence of stoichiometric amounts of **1**, followed by H_2O quenching, afforded deuterated **3c**-d_1 in 97% yield (D: quant) together with the amine **14**-C-d_1 (64% yield, D: 68%) (eq 8). On the other hand, the reaction with Ph_2PH and quenching with D_2O resulted in the formation of nondeuterated **3c** and the amine **14**-N-d_1. The same results were obtained in the catalytic reaction with the imine complex **1** and the diphosphido **15b**. The deuterated amine **14**-C-d_1 was also produced directly on treatment of **1** with Ph_2PD (eq 9). When a semi-stoichiometric reaction of **2c** with **15b** was carried out in the presence of Ph_2ND, a model reaction in the second step in Scheme 1, the alkenylphosphine **3c**-d_1 was obtained in 70% yield based on **2c**, wherein D contents of the *E*- and *Z*-isomers were 72% and 98%, respectively (eq 10). These results implied that if the reaction proceeds through addition of [Yb]-PPh_2 **A** to the alkyne, the resulting β-(diphenylphosphino)alkenyl-Yb intermediate should not be a resting species in the catalytic reaction nor a long-lived species in the stoichiometric reaction. Instead, it was immediately protonated with Ph_2PH and/or $Ph_2CHNHPh$ (**14**).





It was difficult to identify the origin of the olefinic H of **3** and **4** in the stoichiometric reaction with **15b** in the absence of the proton sources, as indicated in eq 7. The reaction in THF-d_8 solvent and that by using **15b** having hmpa-d_{18} ligand gave no deuterated products **3**-d_1 and **4**-d_1 as was the case of D_2O quenching. Therefore, the proton should be derived from the substrates **2** and/or the products **3** and **4**. In fact, the reaction of excess 1-octyne-d_1(4.3 equiv) with the diphosphido **15b**, followed by oxidative workup produced alkenylphosphine oxides **3h′**-d_2 and **4h′**-d_2 in 1.04 and 0.9 equiv, respectively, with high deuterium contents (eq 11). Results suggesting the proton transfer from the products **3** and **4** were obtained in the NMR tube reaction of diphenyacetylene (**2a**) with **15b**, which will be discussed later.



Kinetics studies were carried out by using 1-phenyl-2-trimethylsilylacetylene (**2b**) and the Yb−imine catalyst **1** (Figure 2). As can be seen in the time-course plot, the reaction proceeded monotonically under the standard conditions (Figure 2, **A**). The initial reaction rate was second-order to the catalyst concentration below 0.4 M (2.18, $R^2 = 0.95$), but it was nearly constant at higher concentration (Figure 2, **B**). Thus, the complex **1** should be changed to some dimeric Yb species in the mixture that catalyzed the present hydrophosphination. The rate

(22) Rabe, G. W.; Yap, G. P. A.; Rheingold, A. L. *Inorg. Chem.* **1995**, *34*, 4521−4522.

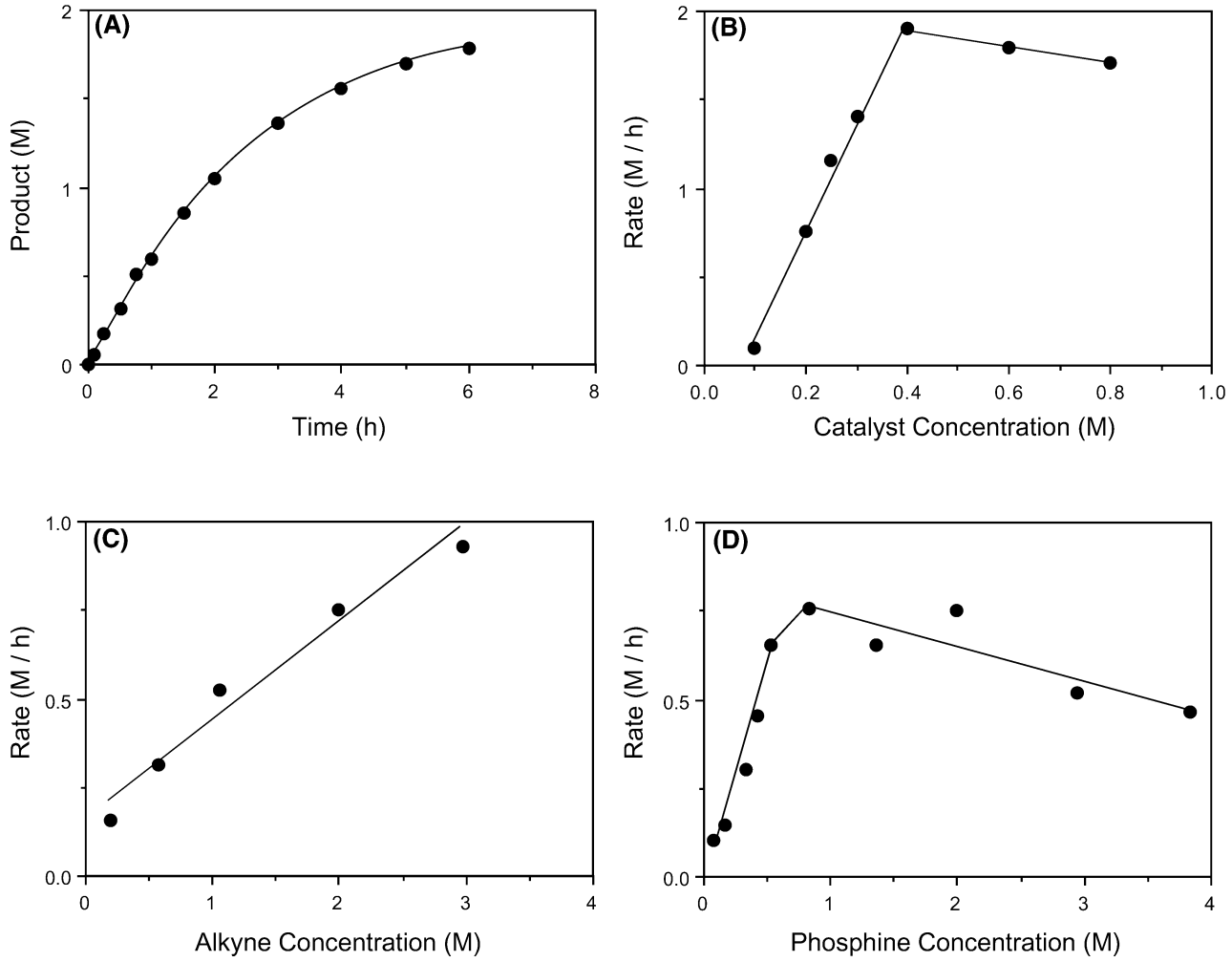
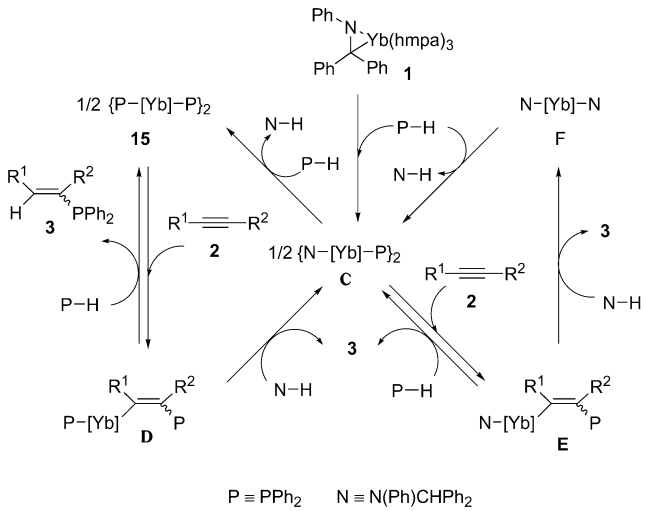


FIGURE 2. Time-course of the reaction of the alkyne **2b** with Ph_2PH catalyzed by **1**, and relations between initial reaction rate and concentration of the reagents. Standard conditions: **2b** (2.0 M), Ph_2PH (2.0M), **1** (0.20 M), THF, 22 °C.

was also proportional to the alkyne concentration over a 15-fold region (Figure 2, **C**). However, the reaction order was smaller than expected (0.67, $R^2 = 0.99$). To confirm this result, similar measurement was performed in the reaction of 3,3-dimethyl-1-butyne (**2g**), in which a reaction order of 0.93 ($R^2 = 0.95$) was obtained. Therefore, the rate is likely to be first-order to the alkyne concentration. With respect to the phosphine concentration, the rate increased with increasing of the concentration below 0.5 M (0.98, $R^2 = 0.97$), then became flat or decreased a little, though the plot was not exactly linear at the higher region (Figure 2, **D**). On the whole, the rate seems to be independent of the phosphine concentration around the standard conditions and, in contrast, is first-order at the lower region which may be correlated to the generation of the phosphido species. Accordingly, the empirical rate law can be described as $v = k[\text{catalyst}]^2[\text{alkyne}]^1[\text{phosphine}]^0$ at least under standard conditions.

A plausible reaction mechanism is proposed in Scheme 2. At first, the imine complex **1** is protonated stepwisely with the phosphine to yield the diphosphido **15** via Yb(amido)(phosphido) species **C**; here, the two intermediates would exist as dimers. Addition of **15** to alkyne, a rate-determining step, affords the β-diphenylphosphinoalkenyl−Yb species **D**, which is immediately protonated with Ph_2PH to give the product **3** and the diphosphido

SCHEME 2



15. As proved by the labeling study with Ph_2ND, this major reaction should be accompanied with a bypath in which product formation and regeneration of **15** is achieved by protonation with the liberated amine **14** instead of Ph_2PH, followed by amido−phosphido exchange of **C**.

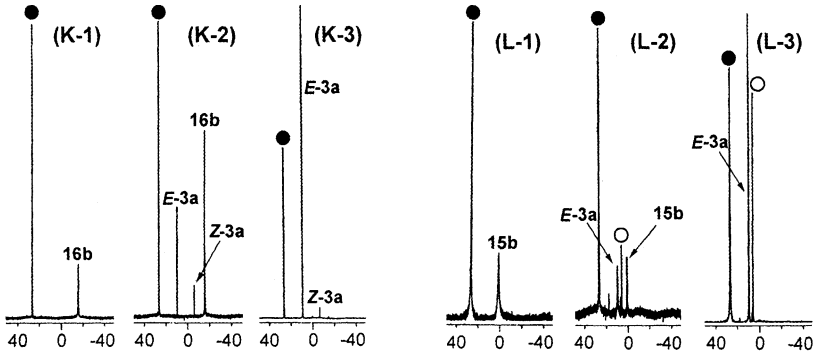


FIGURE 3. ^{31}P NMR trace reaction of **2a** with Ph_2PH by using **16b** (**K**) and **15b** (**L**): **K-1**, generation of **16b** from $Yb[N(SiMe_3)_2]_3(thf)_2$ and Ph_2PH (3 equiv) in THF-d_8 and HMPA (2 equiv); **K-2**, addition of **2a** (0.44 equiv); **K-3**, addition of **2a** (total 2.9 equiv); **L-1**, generation of **15b** from $Yb(PPh_2)_2(thf)_1$ in THF-d_8 and HMPA (2 equiv); **L-2**, addition of **2a** (1.4 equiv); **L-3**, addition of **2a** (total 2.6 equiv). ● and ○ denote the signals of HMPA and unidentified product, respectively.

If the reaction process is only composed of the left wing of Scheme 2, quantitative yields of the products **3** could not be attained; i.e., the phosphine should be recovered at least in equimolar amounts to **1**.[23] Combined with the fact that the reaction with the diphosphido **15** is slower than that with **1**, it should be reasonable to consider the addition reaction of the monophosphido **C** to alkyne. Thus, the reaction of **C** and protonation of the resulting intermediate **E** with Ph_2PH or, alternatively, with the amine **14** would produce the products **3** as depicted in the right wing of Scheme 2. Since the two cycles should be switchable in the reaction and probably exhibit similar kinetics, it is difficult to distinguish between the two. However, a minor change in the reaction with **1** and **15** would be caused by the contribution of the two processes. Moreover, complete consumption of the phosphine could be performed by the generation of the diamido species **F** as the final form of the catalyst, that was proved by the NMR tube reaction (Figure 1). Of course, the intermediates **D** and **E** would be protonated with the substrates **2** and/or products **3** and **4** in the absence of the phosphine and amine **14**.

Stereochemistry of the alkyne hydrophosphination still remains unclear. In particular, anti-addition leading to the *Z*-isomer for the aliphatic alkynes **2e**−**h** seems to be unusual, though a couple of examples of anti-addition have been reported for organotransition metals.[24] Isomerization of the products **3** and **4** or of the intermediates **D** and **E** is found to be implausible as mentioned above. One explanation may be possible in terms of the mode of alkyne approach to the dimeric phosphido species **15** and **C**; i.e., anti-addition for the aliphatic alkynes **2e**−**h** takes place inside the dimeric intermediates, whereas aromatic alkynes **2a**−**d** approach the outside to yield the *E*-isomer.[25]

Last, we investigated the valence state of the Yb catalyst in the reaction, because it is possible that the divalent lanthanide shows catalyst activity actually as a trivalent species.[26] The divalent and trivalent phosphido complexes **16a** and **16b** were generated in situ by the treatment of $Yb[N(SiMe_3)_2]_2(Et_2O)_1$ and $Yb[N(SiMe_3)_2]_3(thf)_2$ with 2 or 3 equiv of Ph_2PH, respectively (eqs 12 and 13).[22] The reaction of **2c** with divalent **16a** gave the product **3c** quantitatively with an *E*/*Z* ratio of 24/76, which was, of course, in good agreement with the results with the diphosphido **15b** (eq 14 and Table 3, run 3). The same results were obtained with the trivalent catalyst **16b**. Complete similarity between the two reactions of **2a** with divalent and trivalent catalysts **15b** and **16b** was also ascertained. Accordingly, active catalysts to promote the reaction are likely to be trivalent based on these results. However, an objection to this assumption was raised in the NMR trace reaction of diphenylacetylene (**2a**) with divalent **15b** and trivalent **16b** (Figure 3).

$$Yb[N(SiMe_3)_2]_2(Et_2O)_1 \xrightarrow[\text{THF - HMPA (6 equiv)}]{2\ Ph_2PH} \underset{\textbf{16a}}{Yb(PPh_2)_2(hmpa)_n} \quad (12)$$

$$Yb[N(SiMe_3)_2]_3(thf)_2 \xrightarrow[\text{THF - HMPA (6 equiv)}]{3\ Ph_2PH} \underset{\textbf{16b}}{Yb(PPh_2)_3(hmpa)_n} \quad (13)$$

$$Ph{-}{\equiv}{-}R^2 + Ph_2PH \xrightarrow[\text{THF, rt}]{\textbf{16a} \text{ or } \textbf{16b}\ (10\ mol\%)} \underset{H}{\overset{Ph}{}}\!\!=\!\!\underset{PPh_2}{\overset{R^2}{}} \quad (14)$$

2a, 2c

3a: with **16b** quant (*E*/*Z* = 97 / 3)
3c: with **16a** quant (*E*/*Z* = 24 / 76)
with **16b** 98% (*E*/*Z* = 24 / 76)

When the trivalent phosphido **16b** was generated from $Yb[N(SiMe_3)_2]_3(thf)_2$ and Ph_2PH (3 equiv) in THF-d_8 and HMPA (2 equiv), one signal appeared at −15.51 ppm in ^{31}P NMR (Figure 3, **K-1**). On addition of **2a** (0.44 equiv) to the mixture, two signals of *E*- and *Z*-**3a** appeared at

(23) Insertion of another alkyne to [Yb]−PPh_2 moiety of **D** is less likely, because **D** should be a short-lived intermediate as evidenced by kinetics and the labeling studies.

(24) For examples, see: (a) Zeijden, A. A. H.; Bosch, H. W.; Berke, H. *Organometallics* **1992**, *11*, 563−573 and references therein. (b) Ojima, I.; Li, Z.; Zhu, J. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: New York, 1998; Vol. 2, pp 1687−1792. (c) Jia, C.; Lu, W.; Oyamada, J.; Kitamura, T.; Matsuda, K., Irie, M.; Fujiwara, Y. *J. Am. Chem. Soc.* **2000**, *122*, 7252−7263.

(25) Complete *Z*-selectivity in head-to-head dimerization of terminal alkynes with dimeric lanthanide alkynide catalysts was recently reported, see: Nishiura, M.; Hou, Z.; Wakatsuki, Y.; Yamaki, T.; Miyamoto, T. *J. Am. Chem. Soc.* **2003**, *125*, 1184−1185.

(26) Gagne, M. R.; Nolan, S. P.; Marks, T. J. *Organometallics* **1990**, *9*, 1716−1718.

9.75 and −5.85 ppm, respectively, together with that of **16b** whose chemical shift was unchanged (Figure 3, **K-2**). Then, **16b** disappeared on addition of excess **2a** (2.9 equiv) (Figure 3, **K-3**). Interestingly, ^{1}H NMR signals of the liberated amine, HN(Si*Me*$_3$)$_2$, at 0.01 ppm in the stage of **K-1** changed to −0.20 ppm in **K-3**, which could be assignable to Yb[N(Si*Me*$_3$)$_2$]$_3$. This phenomenon would provide additional evidence for the final form of the catalysts as shown in Scheme 2. In contrast, the divalent phosphido **15b**, generated from Yb(PPh$_2$)$_2$(thf)$_1$ and HMPA (2 equiv), exhibits one signal at 1.37 ppm in ^{31}P NMR (Figure 3, **L-1**). When 1.4 equiv of **2a** was added to the mixture, signals of **15b** and *E*-**3a** were observed together with an unidentified peak (○) at 5.95 ppm, but the signal assignable to the trivalent phosphido around at −15 ppm was not found (Figure 3, **L-2**). Two signals of *E*-**3a** and an unidentified product survived on addition of excess **2a** (2.6 equiv) (Figure 3, **L-3**). Comparing these two reactions, the divalent and trivalent phosphido species kept their original chemical shifts in ^{31}P NMR during the reaction, i.e., the valence state of the Yb metal did not seem to be changed. Thus, a possibility of a divalent species to catalyze the reaction cannot be ruled out at present.

It is worthwhile to comment on the unidentified signal observed in Figure 3, **L-2** and **L-3**. This compound should be a precursor of *E*-**3a**, because quenching of this mixture with H$_2$O gave only *E*-**3a** in quantitative yield. Moreover, when the reaction of **2a** was conducted with **16a**, generated from Yb[N(SiMe$_3$)$_2$]$_2$(Et$_2$O)$_1$ and Ph$_2$PH (2 equiv) in THF-d_8 and HMPA (2 equiv), the reaction proceeded in a manner similar to that with **15b** with monitoring by ^{31}P NMR, except for the unidentified signal that was not seen with **16a**. The reaction mixture with **16a** included a liberated HN(SiMe$_3$)$_2$, whereas there were no proton sources with **15b**. Therefore, the unidentified signal would be assignable to the alkenylphosphine **3a** metalated probably at the Ph$_2$P moiety.[27]

Summary

We have developed a new catalytic intermolecular hydrophosphination of alkynes with the Yb−imine complex **1** to give alkenylphosphines or phosphine oxides after oxidative workup in high yields. Stereoselectivity depends on the substituents of the alkynes: (*E*)- and (*Z*)-products are selectively formed from aromatic and aliphatic alkynes, respectively. This method is also applicable to a wide range of carbon−carbon multiple bonds such as conjugated diynes and dienes, allenes, and styrene derivatives. It has been also found that the Yb−imine complex **1** reacts immediately with the phosphine to generate the Yb−phosphido species. Insertion of alkynes to the phosphido, a rate-determining step, followed by protonation with Ph$_2$PH and/or the liberated amine affords the alkenylphosphines. After complete consumption of the phosphine, the Yb-diamido species is formed in the final stage of the catalytic cycle, as proved by NMR. Thus, the imine complex **1** could be categorized as a base catalyst similar to Yb[N(SiMe$_3$)$_2$]$_n$, and it exhibits far higher activity than conventional bases such as ^{t}BuOK and RLi. Although further work to improve regio- and stereoselectivity is necessary for synthetic purposes, the present results provide a potentially useful method for the preparation of α,*β*-unsaturated phosphines under mild conditions by using readily available organoytterbium catalysts.

(27) If it is the case, deuteration would take place at the aromatic rings of the Ph$_2$P moiety on D$_2$O quenching, but definite conclusion could not be obtained by their NMR and MS spectra.

Experimental Section

General Methods. ^{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. 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. Ytterbium metal (40 mesh) was washed with anhydrous hexane under argon and dried in vacuo. 7,9-Hexadecadiyne and 2,2,7,7-tetramethyl-3,5-octadiyne were synthesized by oxidative coupling of the corresponding terminal alkynes with CuI−TMEDA.[28] Cyclohexylallene was prepared from cyclohexylmagnesium chloride and propargyl chloride in the presence of CuBr.[28] Yb[N(SiMe$_3$)$_2$]$_2$(Et$_2$O)$_1$[29] and Yb[N(SiMe$_3$)$_2$]$_3$(thf)$_2$[30] were obtained by the reaction of YbI$_2$ or YbCl$_3$ with sodium or lithium bis(trimethylsilyl)amido, respectively, according to the literature method. All other materials were commercially available and were used after drying and distillation. CAS Registry numbers were provided by the author.

Hydrophosphination of Alkynes with the Yb−Imine Complex 1. Ytterbium metal (17 mg, 0.1 mmol) and diphenylmethylideneaniline (26 mg, 0.1 mmol) were placed in a Schlenk tube. HMPA (108 mg, 0.6 mmol) and THF (1 mL) were added to the mixture. After addition of MeI (0.2 μL) to activate the metal, the mixture was stirred for 4 h at room temperature to give a homogeneous reddish-black solution of the Yb−imine complex **1**.[9] Diphenylphosphine (372 mg, 2.0 mmol) and the alkyne **2** (2.0 mmol) were successively added to the solution, and the mixture was stirred at room temperature for the appropriate time as indicated in Table 1 with monitoring by GC. After the reaction was complete, dodecane was added to the mixture as an internal standard. Then, hydrogen peroxide (30%, 2 mL) was added to the mixture at 0 °C and stirring was continued for 30 min. The reaction mixture was extracted with benzene, washed with brine, dried over MgSO$_4$, and concentrated in vacuo. The products **3′** and **4′** were isolated by MPLC (silica gel) with hexanes−ethyl acetate or chloroform−acetone eluent. Product yields and ratios of regio- and stereoisomers were determined by GC analyses and NMR spectra of the crude mixtures.

For isolation of the alkenylphosphines **3** and **4**, the reaction was quenched with water and HCl (2 M), and the mixture was extracted with ether, washed with brine, and dried over MgSO$_4$. Alternatively, the reaction mixture was directly passed through a short silica gel column with benzene eluent to remove metallic residue and HMPA without the aqueous workup. Purification by MPLC gave the phosphine products **3** and **4**, which were, of course, oxidized with H$_2$O$_2$ to the corresponding phosphine oxides **3′** and **4′** with no change in regio- and stereochemistry. When the reaction was carried out at elevated temperature (Table 1, runs 5 and 6), THF was removed under vacuum after preparation of **1**.

(*E*)-1-Diphenylphosphinyl-1,2-diphenylethylene (3a′) [14447-40-6]. Isolated as (*E*)-1-diphenylphosphino-1,2-diphen-

(28) Sonogashira, K. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, 1991; Vol. 3, pp 521−561.

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ylethylene (**3a**) (85% yield) and oxidized with H_2O_2: white solid; mp 156−157 °C; IR (Nujol) 1177 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.92−7.53 (16H, m), 7.58 (1H, d, J = 21.0 Hz, olefinic), 7.64−7.70 (4H, m); ^{13}C NMR ($CDCl_3$) δ 127.7 (d, J = 1.5 Hz), 128.16, 128.22 (d, J = 12.3 Hz), 128.7 (d, J = 1.6 Hz), 128.9, 129.9 (d, J = 4.1 Hz), 130.2 (d, J = 1.6 Hz), 131.0 (d, J = 103.4 Hz), 131.8 (d, J = 2.5 Hz), 132.3 (d, J = 9.0 Hz), 134.9 (d, J = 2.4 Hz), 135.2 (d, J = 73.0 Hz), 135.7 (d, J = 26.3 Hz), 143.0 (d, J = 9.0 Hz); UV (EtOH) λ_{max} 268 (ϵ 1.24 × 10^4) nm [lit.[16c] λ_{max} (*E*)-isomer 268, (*Z*)-isomer 284]. Anal. Calcd for $C_{26}H_{21}OP$: C, 82.09; H, 5.56. Found: C, 82.07; H, 5.50.

(*E*)-2-Diphenylphosphinyl-2-trimethylsilylstyrene (3b′). Isolated as (*E*)-2-diphenylphosphino-2-trimethylsilylstyrene (**3b**) (69% yield) and oxidized with H_2O_2: white solid; mp 122−123 °C; IR (Nujol) 1177 cm^{-1}; ^1H NMR ($CDCl_3$) δ −0.03 (3H, d, J = 1.0 Hz), 0.0 (6H, s), 7.21−7.82 (16H, m); ^{13}C NMR ($CDCl_3$) δ 1.1 (d, J = 7.4 Hz), 1.5 (d, J = 2.5 Hz), 127.2, 127.8, 127.9 (d, J = 1.4 Hz), 128.0 (d, J = 1.6 Hz), 128.4 (d, J = 3.3 Hz), 128.5, 128.8, 131.4 (d, J = 3.6 Hz), 131.9 (d, J = 9.9 Hz), 133.4 (d, J = 99.3 Hz), 134.6 (d, J = 20.5 Hz), 139.0 (d, J = 41.1 Hz), 139.4 (d, J = 77.9 Hz), 141.0 (d, J = 6.6 Hz). Anal. Calcd for $C_{23}H_{25}OPSi$: C, 73.37; H, 6.69. Found: C, 73.04; H, 6.57. Stereochemistry of **3b′** was confirmed by the selective conversion to (*E*)-**3d′** with Bu_4NF.

1-Phenyl-2-diphenylphosphinyl-1-propene (3c′) [62556-17-6]. (*E*)-Isomer (major): isolated as (*E*)-1-phenyl-2-diphenylphosphino-1-propene (**3c**) (67% yield) and oxidized with H_2O_2: white solid; mp 129−130 °C; IR (Nujol) 1177 cm^{-1}; MS *m*/*z* 318 (M^+), 303 (M^+ − Me), 241 (M^+ − Ph), 201 (Ph_2PO^+); ^1H NMR ($CDCl_3$) δ 2.03 (3H, d, J = 14.0 Hz), 7.13 (1H, d, J = 22.2 Hz), 7.19−7.50 (11H, m), 7.66−7.71 (4H, m); ^{13}C NMR-($CDCl_3$) δ 15.0 (d, J = 10.7 Hz), 128.3 (d, J = 4.0 Hz), 128.5, 128.6, 129.4, 129.6 (d, J = 40.6 Hz), 131.2 (d, J = 102.5 Hz), 131.9 (d, J = 2.5 Hz), 132.1 (d, J = 9.8 Hz), 135.8 (d, J = 18.9 Hz), 142.7 (d, J = 11.5 Hz); HRMS calcd for $C_{21}H_{19}OP$ (M^+) 318.1175, found 318.1182. (*Z*)-Isomer (minor): isolated as (*Z*)-1-phenyl-2-diphenylphosphino-1-propene (**3c**) (13% yield) and oxidized with H_2O_2: white solid; mp 120−123 °C; IR (Nujol) 1173 cm^{-1}; MS *m*/*z* 318 (M^+), 303 (M^+ − Me), 241 (M^+ − Ph), 201 (Ph_2PO^+); ^1H NMR ($CDCl_3$) δ 1.90 (3H, dd, J = 12.3, 1.5 Hz), 6.89−6.96 (3H, m), 7.18−7.31 (8H, m), 7.36 (1H, dm, J = 37.1, 1.5 Hz), 7.53−7.62 (4H, m); ^{13}C NMR ($CDCl_3$) δ 24.7 (d, J = 13.1 Hz), 127.5, 127.7, 128.2 (d, J = 12.3 Hz), 129.3 (d, J = 1.6 Hz), 129.4 (d, J = 92.7 Hz), 131.2 (d, J = 3.3 Hz), 131.3 (d, J = 9.0 Hz), 132.9 (d, J = 102.5 Hz), 135.7 (d, J = 6.6 Hz), 145.7 (d, J = 7.4 Hz). Anal. Calcd for $C_{21}H_{19}OP$: C, 79.23; H, 6.02. Found: C, 79.33; H, 6.03.

2-Diphenylphosphinylstyrene (3d′) [3582-82-9 and 78045-10-0]. Isolated as a mixture of (*E*)- and (*Z*)-isomer (76:24) in 87% yield: white solid; mp 87−89 °C; IR (Nujol) 1176 cm^{-1}; MS *m*/*z* 304 (M^+), 227 (M^+ − Ph), 201 (Ph_2PO^+), 124 ($PhPO^+$); ^1H NMR[16a] δ 6.23 (0.24H, dd, J = 19.6, 14.0 Hz, C=C(H)P, *Z*-isomer), 6.76 (0.76H, dd, J = 22.2, 17.4 Hz, C=C(H)P, *E*-isomer), 7.07−7.70 (16H, m). Anal. Calcd for $C_{20}H_{17}OP$: C, 78.93; H, 5.63. Found: C, 78.55; H, 5.34.

Regiochemistry of **3d′** was confirmed by hydrogenation [EtOH, H_2 (1 atm), rt, 10 h], giving rise to 1-diphenylphosphinyl-2-phenylethane (81% yield): white solid; mp 68−70 °C; IR (Nujol) 1169 cm^{-1}; MS *m*/*z* 306 (M^+), 201 (Ph_2PO^+), 105 ($PhC_2H_4^+$); ^1H NMR ($CDCl_3$) δ 2.50 (2H, m), 2.85 (2H, m), 7.04−7.20 (5H, m), 7.37−7.47 (6H, m), 7.63−7.72 (4H, m); ^{13}C NMR ($CDCl_3$) δ 27.5 (d, J = 3.3 Hz), 31.8 (d, J = 70.6 Hz), 126.2, 128.0, 128.59, 128.62 (d, J = 17.2 Hz), 130.7 (d, J = 9.0 Hz), 131.7 (d, J = 2.5 Hz), 132.7 (d, J = 98.4 Hz), 141.4 (d, J = 15.6 Hz); HRMS calcd for $C_{20}H_{19}OP$ (M^+) 306.1175, found 306.1196.

(*Z*)-4-Diphenylphosphinyl-4-octene (3e′) [195148-52-8]. Isolated in 61% yield: colorless oil; IR (neat) 1188 cm^{-1}; MS *m*/*z* 312 (M^+), 283 (M^+-Et), 201 (Ph_2PO^+), 185 (Ph_2P^+); ^1H NMR ($CDCl_3$) δ 0.65 (3H, t, J = 7.3 Hz), 0.66 (3H, t, J = 7.3 Hz), 1.16−1.24 (4H, m), 1.96 (2H, dt, J = 13.8, 6.9 Hz), 2.16 (2H, dq, J = 3.0, 7.3 Hz), 6.29 (1H, dt, J = 37.9, 7.3 Hz), 7.34−7.46 (6H, m), 7.60−7.72 (4H, m); ^{13}C NMR ($CDCl_3$) δ 13.5, 13.6, 22.4 (d, J = 1.6 Hz), 22.9 (d, J = 3.3 Hz), 32.6 (d, J = 7.4 Hz), 37.7 (d, J = 13.1 Hz), 128.3 (d, J = 12.3 Hz), 131.5, 131.6 (d, J = 11.8 Hz), 131.9 (d, J = 96.8 Hz), 133.8 (d, J = 100.0 Hz), 148.6(d, J = 8.2 Hz); HRMS calcd for $C_{20}H_{25}OP$ (M^+) 312.1641, found 312.1626.

(*Z*)-2-Diphenylphosphinyl-2-octene (3f′) [187471-88-1]. Isolated in 51% yield: colorless oil; IR (neat) 1188 cm^{-1}; MS *m*/*z* 312 (M^+), 269 (M^+ − Pr), 201 (Ph_2PO^+), 185 (Ph_2P^+); ^1H NMR ($CDCl_3$) δ 0.79 (3H, t, J = 6.9 Hz), 1.11−1.31 (6H, m), 1.74 (3H, d, J = 12.3 Hz), 2.29−2.38 (2H, m), 6.41 (1H, dt, J = 37.5, 6.3 Hz), 7.46−7.54 (6H, m), 7.66−7.72 (4H, m); ^{13}C NMR ($CDCl_3$) δ 13.9, 22.3, 23.8 (d, J = 14.0 Hz), 28.8, 30.4 (d, J = 6.6 Hz), 31.3, 126.9 (d, J = 95.2 Hz), 128.4 (d, J = 12.3 Hz), 131.48 (d, J = 4.9 Hz), 131.54 (d, J = 2.5 Hz), 133.4 (d, J = 101.7 Hz), 149.8(d, J = 8.2 Hz); HRMS calcd for $C_{20}H_{25}OP$ (M^+) 312.1641, found 312.1624.

(*Z*)-1-Diphenylphosphinyl-3,3-dimethyl-1-butene (3g′). Isolated in 52% yield: white solid; mp 116−117 °C; IR (Nujol) 1180 cm^{-1}; MS *m*/*z* 284 (M^+), 269 (M^+-Me), 201 (Ph_2PO^+), 124 ($PhPO^+$); ^1H NMR ($CDCl_3$) δ 1.21 (9H, s), 5.97 (1H, dd, J = 22.4, 14.6 Hz), 6.68 (1H, dd, J = 43.5, 14.6 Hz), 7.41−7.50 (6H, m), 7.71−7.77 (4H, m); ^{13}C NMR ($CDCl_3$) δ 30.3 (d J = 9.8 Hz), 35.4 (d, J = 5.7 Hz), 119.2 (d, J = 97.5 Hz), 128.4 (d, J = 12.3 Hz), 130.8 (d, J = 9.8 Hz), 131.3, 135.7 (d, J = 105.0), 164.5. Anal. Calcd for $C_{18}H_{21}OP$: C, 76.04; H, 7.44. Found: C, 76.14; H, 7.32.

1-Diphenylphosphinyl-1-octene (3h′) [195148-53-9 and 178943-30-1]. (*Z*)-Isomer (major): isolated in 34% yield; white solid; MS *m*/*z* 312 (M^+), 255 (M^+ − Bu), 241 (M^+ − Pen); ^1H NMR ($CDCl_3$) δ 0.83 (3H, t, J = 7.1 Hz), 1.10−1.28 (6H, m), 1.34 (2H, quin, J = 7.1 Hz), 2.54 (2H, qm, J = 7.1 Hz), 6.11 (1H, ddt, J = 25.6, 12.8, 3.0 Hz), 6.69 (1H, ddt, J = 40.5, 12.8, 7.1 Hz), 7.42−7.51 (6H, m), 7.71−7.77 (4H, m); ^{13}C NMR ($CDCl_3$) δ 14.0, 22.5, 28.76 (d, J = 3.3 Hz), 28.78, 30.9 (d, J = 8.2 Hz), 31.5, 121.2 (d, J = 100.9 Hz), 128.5 (d, J = 12.2 Hz), 130.9 (d, J = 9.8 Hz), 131.4 (d, J = 2.5 Hz), 134.6 (d, J = 103.4 Hz), 155.2. (*E*)-Isomer (minor): isolated in 4% yield; white solid; ^1H NMR ($CDCl_3$) δ 0.87 (3H, t, J = 7.0 Hz), 1.17−1.34 (6H, m), 1.48 (2H, quin, J = 7.0 Hz), 2.29 (2H, qm, J = 7.0 Hz), 6.22 (1H, ddm, J = 24.5, 17.0 Hz), 6.73 (1H, ddt, J = 19.6, 17.0, 7.0 Hz), 7.27−7.53 (6H, m), 7.67−7.77 (4H, m); ^{13}C NMR ($CDCl_3$) δ 14.0, 22.5, 27.8, 28.8, 31.5, 34.5 (d, J = 16.4 Hz), 121.6 (d, J = 103.4 Hz), 128.5 (d, J = 12.3 Hz), 131.3 (d, J = 9.9 Hz), 131.6, 133.2 (d, J = 104.2 Hz), 152.9.

3-Diphenylphosphinyl-2-octene (4f′). Isolated as a mixture of (*E*)- and (*Z*)-isomer (21:79) in 18% yield: yellow oil; MS *m*/*z* 312 (M^+), 201 (Ph_2PO^+); ^1H NMR ($CDCl_3$) (*Z*)-isomer (major) δ 0.75 (3H, t, J = 7.5 Hz), 1.03−1.31 (6H, m), 1.85 (3H, d, J = 7.0 Hz), 1.96−2.06 (2H, m), 6.51 (1H, dq, J = 37.9, 7.0 Hz), 7.43−7.53 (6H, m), 7.67−7.81 (4H, m); (*E*)-isomer (minor) (clearly assignable peaks) 0.77 (t, J = 7.0 Hz), 1.74 (d, J = 6.8 Hz), 6.25 (dq, J = 21.3, 6.8 Hz).

2-Diphenylphosphinyl-3,3-dimethyl-1-butene (4g′). Isolated in 8% yield: white solid; mp 133−135 °C; IR (Nujol) 1180 cm^{-1}; MS *m*/*z* 284 (M^+), 227 (M^+ − ^{t}Bu), 201 (Ph_2PO^+), 124 ($PhPO^+$); ^1H NMR ($CDCl_3$) δ 1.27 (9H, s), 5.20 (1H, d, J = 22.2 Hz), 5.99 (1H, d, J = 45.6 Hz), 7.36−7.53 (6H, m), 7.64−7.76 (4H, m); ^{13}C NMR ($CDCl_3$) δ 30.5 (d, J = 8.2 Hz), 38.0 (d, J = 9.0 Hz), 127.6 (d, J = 9.0 Hz), 128.3 (d, J = 11.5 Hz), 131.4, 131.6 (d, J = 9.8 Hz), 133.6 (d, J = 105.0), 152.7 (d, J = 87.8 Hz). Anal. Calcd for $C_{18}H_{21}OP$: C, 76.04; H, 7.44. Found: C, 76.09; H, 7.50.

2-Diphenylphosphinyl-1-octene (4h′). Isolated in 22% yield: white solid; mp 140−142 °C; IR (Nujol) 1188 cm^{-1}; MS *m*/*z* 312 (M^+), 297 (M^+ − Me), 269 (M^+ − Pr), 241 (M^+ − Pen), 201 (Ph_2PO^+); ^1H NMR ($CDCl_3$) δ 0.83 (3H, t, J = 6.8 Hz), 1.13−1.30 (6H, m), 1.42−1.52 (2H, m), 2.30 (2H, q, J = 8.5 Hz), 5.62 (1H, d, J = 21.0 Hz), 5.94 (1H, d, J = 43.0 Hz), 7.45−7.56 (6H, m), 7.68−7.73 (4H, m); ^{13}C NMR ($CDCl_3$) δ 14.0, 22.5, 28.0 (d, J = 5.8 Hz), 28.9, 31.5, 31.6 (d, J = 9.0 Hz), 128.5 (d, J = 12.3 Hz), 128.6 (d, J = 10.7 Hz), 131.5 (d, J = 101.7 Hz),

131.8, 131.9 (d, J = 9.8 Hz), 144.1 (d, J = 91.9 Hz). Anal. Calcd for $C_{20}H_{25}OP$: C, 76.90; H, 8.07. Found: C, 76.67; H, 8.13.

1-Diphenylphosphino-1,2-diphenylethylene (3a). (*E*)-Isomer [14447-37-1]: white solid; MS *m*/*z* 364 (M^+), 287 (M^+ − Ph), 185 (PPh_2^+), 179 (M^+ − PPh_2), 108 (PPh^+); ^{1}H NMR ($CDCl_3$) δ 6.53 (1H, d, J = 8.9 Hz), 6.95 (2H, d, J = 5.8 Hz), 7.09−7.58 (18H, m); ^{13}C NMR ($CDCl_3$) δ 126.9, 127.2, 127.9, 128.35 (d, J = 1.6 Hz), 128.42, 128.9, 129.1 (d, J = 16.5 Hz), 129.3, 134.2 (d, J = 20.6 Hz), 135.3 (d, J = 12.3 Hz), 136.8 (d, J = 6.6 Hz), 138.0 (d, J = 18.9 Hz), 139.9 (d, J = 13.2 Hz), 141.4 (d, J = 18.0 Hz); ^{31}P NMR ($CDCl_3$) δ 8.45, (THF-d_8) δ 9.75. Anal. Calcd for $C_{26}H_{21}P$: C, 85.69; H, 5.81. Found: C, 85.54; H, 5.79. (*Z*)-Isomer [14447-38-2]: obtained by the reaction with AIBN; yellow solid; MS *m*/*z* 364 (M^+), 179 (M^+ − PPh_2), 108 (PPh^+); ^{1}H NMR ($CDCl_3$) δ 6.95−7.07 (4H, m), 7.22−7.44 (14H, m), 7.51 (1H, d, J = 24.2 Hz), 7.59 (2H, d, J = 7.2 Hz); ^{13}C NMR ($CDCl_3$) δ 126.2, 127.3, 127.8, 127.99, 128.03 (d, J = 14.8 Hz), 128.05, 128.3, 129.8 (d, J = 7.4 Hz), 133.3 (d, J = 18.9 Hz), 136.2 (d, J = 11.5 Hz), 136.7 (d, J = 4.9 Hz), 139.2 (d, J = 27.9 Hz), 142.9 (d, J = 4.1 Hz), 144.9 (d, J = 27.9 Hz); ^{31}P NMR ($CDCl_3$) δ −7.32, (THF-d_8) δ −5.85. Anal. Calcd for $C_{26}H_{21}P$: C, 85.69; H, 5.81. Found: C, 85.30; H, 5.78.

2-Diphenylphosphino-2-trimethylsilylstyrene (3b). (*E*)-Isomer [372167-08-3]: yellow liquid; MS *m*/*z* 360 (M^+), 287 (M^+ − TMS), 185 (PPh_2^+), 108 (PPh^+); ^{1}H NMR ($CDCl_3$) δ −0.06 (9H, s), 6.96 (1H, d, J = 15.2 Hz), 7.09−7.52 (14H, m), 7.77 (1H, t, J = 8.8 Hz); ^{13}C NMR ($CDCl_3$) δ 1.1 (d, J = 6.6 Hz), 127.3, 127.9 (d, J = 23.8 Hz), 128.4 (d, J = 6.6 Hz), 128.9, 131.9 (d, J = 9.8 Hz), 134.6 (d, J = 19.7 Hz), 136.3 (d, J = 12.3 Hz), 141.0 (d, J = 6.6 Hz), 141.9 (d, J = 45.9 Hz), 152.1; ^{31}P NMR ($CDCl_3$) δ −0.06. Anal. Calcd for $C_{23}H_{25}PSi$: C, 76.63; H, 6.99. Found: C, 76.68; H, 6.70. (*Z*)-Isomer: ^{31}P NMR ($CDCl_3$) δ −10.40; analytically pure sample could not be obtained, but the structure was confirmed by converting it to (*Z*)-**3d′** with H_2O_2 and then Bu_4NF.

1-Phenyl-2-diphenylphosphino-1-propene (3c). (*E*)-Isomer [107394-76-3]: colorless liquid; MS *m*/*z* 302 (M^+), 225 (M^+ − Ph), 185 (PPh_2^+), 117 (M^+ − PPh_2); ^{1}H NMR ($CDCl_3$) δ 2.00 (3H, dd, J = 9.2, 1.5 Hz), 6.69 (1H, dm, J = 13.5 Hz), 7.20−7.47 (15H, m); ^{13}C NMR($CDCl_3$) δ 17.9 (d, J = 16.4 Hz), 127.0, 128.2, 128.5, 128.6, 128.8 (d, J = 21.3 Hz), 133.8 (d, J = 19.7 Hz), 136.0 (d, J = 14.0 Hz), 136.1 (d, J = 11.5 Hz), 137.6 (d, J = 12.3 Hz), 139.0 (d, J = 27.9 Hz); ^{31}P NMR (THF-d_8) δ 9.21. Anal. Calcd for $C_{21}H_{19}P$: C, 83.42; H, 6.33. Found: C, 83.52; H, 6.34. (*Z*)-Isomer [135219-14-6]: colorless liquid; MS *m*/*z* 302 (M^+), 225 (M^+ − Ph), 185 (PPh_2^+); ^{1}H NMR ($CDCl_3$) δ 1.79 (3H, dd, J = 2.9, 1.5 Hz), 7.21−7.42 (16H, m); ^{13}C NMR($CDCl_3$) δ 24.3 (d, J = 4.1 Hz), 127.3, 127.8, 128.3, 128.4 (d, J = 5.8 Hz), 129.4 (d, J = 7.4 Hz), 133.2 (d, J = 18.9 Hz), 133.9 (d, J = 21.3 Hz), 136.9 (d, J = 12.3 Hz), 137.4 (d, J = 6.6 Hz), 143.1 (d, J = 9.5 Hz); ^{31}P NMR (THF-d_8) δ −12.69. Anal. Calcd for $C_{21}H_{19}P$: C, 83.42; H, 6.33. Found: C, 83.49; H, 6.31.

2-Diphenylphosphinostyrene (3d). (*E*)-Isomer [14090-06-3]: isolated as a mixture of (*E*)- and (*Z*)-isomers; ^{1}H NMR ($CDCl_3$) δ 6.94 (1H, d, J = 10.9 Hz), 7.26−7.53 (16H, m); ^{31}P NMR ($CDCl_3$) δ −11.35. Anal. Calcd for $C_{20}H_{17}P$: C, 83.32; H, 5.94. Found: C, 83.78; H, 5.93. (*Z*)-Isomer [14090-07-4]: obtained by the thermal reaction of **2d** without the catalyst; white solid; MS *m*/*z* 288 (M^+), 211 (M^+ − Ph), 134 (M^+ − 2Ph), 108 (PhP^+); ^{1}H NMR ($CDCl_3$) δ 6.45 (1H, dd, J = 12.7 and 2.8 Hz), 7.24−7.54 (16H, m); ^{13}C NMR($CDCl_3$) δ 128.1, 128.47, 128.48, 128.6, 129.45 (d, J = 16.4 Hz), 129.51 (d, J = 8.2 Hz), 132.7 (d, J = 18.9 Hz), 136.9 (d, J = 2.5 Hz), 139.3 (d, J = 9.8 Hz), 144.1 (d, J = 18.9 Hz); ^{31}P NMR ($CDCl_3$) δ −24.59.

1-Diphenylphosphino-1-octene (3h). (*Z*)-Isomer [14090-08-5]: white solid; MS *m*/*z* 296 (M^+), 185 (Ph_2P^+), 108 (PhP^+); ^{1}H NMR ($CDCl_3$) δ 0.87 (3H, t, J = 6.8 Hz), 1.20−1.39 (6H, m), 1.43 (2H, quin, J = 6.8 Hz), 2.21 (2H, q, J = 6.3 Hz), 6.18 (1H, dd, J = 16.5, 4.8 Hz), 6.25 (1H, ddt, J = 31.7, 16.5, 6.3 Hz), 7.26−7.44 (10H, m); ^{31}P NMR (THF-d_8) δ −29.32. (*E*)-Isomer: analytically pure sample could not be obtained; ^{31}P NMR (THF-d_8) δ −11.28.

Reaction of 1,7-Octadiyne with Diphenylphosphine. The reaction was carried out in a manner similar to that above by using 2 equiv of Ph_2PH at room temperature for 3 h and quenched with H_2O_2. Column chromatography of the reaction mixture gave **5** in quantitative yield, which contained four regio- and stereoisomers by GC analyses: IR (neat) 1180 cm^{-1}; MS *m*/*z* 510 (M^+), 309 (M^+-Ph_2PO), 201 (Ph_2PO^+); ^{1}H NMR ($CDCl_3$) δ 1.20−1.38 (4H, m), 2.06−2.52 (4H, m), 5.48 (0.51H, dd, J = 20.9, 3.8 Hz, internal PC=C*H*H), 5.78 (0.51H, dd, J = 43.1, 3.8 Hz, internal PC=CH*H*), 6.01 (0.37H, dd, J = 25.6, 12.8 Hz, terminal-*Z* HC=C*H*P), 6.11 (0.12H, dd, J = 25.1 and 16.8 Hz, terminal-*E* HC=C*H*P), 6.43−6.68 (0.49H, m, terminal-*E* and *Z* *H*C=CHP), 7.22−7.60 (20H, m).

Hydrophosphination of Carbon−Carbon Multiple Bonds Other than Alkynes with the Yb−Imine Complex 1. The reaction was carried out similarly to that of alkynes by using 10 mol % of **1** under appropriate conditions as indicated in Table 2. The reaction mixture was oxidized with H_2O_2 and then purified by column chromatography. Yields and regio- and stereoselectivity were determined by GC and NMR of the crude mixture. In the reaction of isoprene, 2 equiv of this substrate was used to make up for evaporation loss.

(*Z*,*Z*)-7,10-Bis(diphenylphosphinyl)-7,9-hexadecadiene (6a). Isolated in 51% yield: white solid; mp 137−140 °C; IR (Nujol) 1180 cm^{-1}; MS *m*/*z* 622 (M^+), 551 (M^+ − C_5H_{11}), 421 (M^+-Ph_2PO), 201 (Ph_2PO^+); ^{1}H 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, 3.7 Hz). Anal. Calcd for $C_{40}H_{48}O_2P_2$: C, 77.15; H, 7.77. Found: C, 77.03; H, 7.74.

(*Z*,*Z*)-3,6-Bis(diphenylphosphinyl)-2,2,7,7-tetramethyl-3,5-octadiene (6b). Isolated in 12% yield: white solid; IR (Nujol) 1188 cm^{-1}; MS *m*/*z* 566 (M^+), 509 (M^+ − ^{t}Bu), 365 (M^+ − Ph_2PO), 201 (Ph_2PO^+); ^{1}H 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.

3,6-Bis(diphenylphosphinyl)-2,2,7,7-tetramethyl-3,4-octadiene (7b). Isolated in 71% yield: white solid; mp 202−204 °C; IR (Nujol) 1184 cm^{-1}; 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^+); ^{1}H NMR ($CDCl_3$) δ 1.16 (9H, s), 1.33 (9H, s), 2.81 (1H, ddd, J = 7.7, 5.9, 4.3 Hz), 5.30 (1H, ddd, J = 16.7, 11.6, 7.7 Hz), 6.94−7.76 (20H, m); ^{13}C NMR ($CDCl_3$) (clearly assignable peaks) 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, 4.9 Hz), 90.6 (d, J = 13.9 Hz), 107.8 (d, J = 96.8 Hz), 207.1 (d, J = 26.3 Hz). Anal. Calcd for $C_{36}H_{40}O_2P_2$: C, 76.31; H, 7.11. Found: C, 76.02; H, 7.00.

1-Diphenylphosphinyl-2-phenylpropane (8a) [147701-16-4]. Isolated in 67% yield: white solid; mp 115−118 °C; IR (Nujol) 1180 cm^{-1}; MS *m*/*z* 320 (M^+), 215 (M^+ − PhC_2H_4), 201 (Ph_2PO^+); ^{1}H NMR ($CDCl_3$) δ 1.38 (3H, d, J = 7.0 Hz), 2.57 (1H, ddd, J = 15.4, 12.3, 9.0 Hz), 2.67 (1H, ddd, J = 20.4, 9.0, 4.7 Hz), 3.27−3.38 (1H, m), 7.12−7.22 (5H, m), 7.36−7.50 (6H, m), 7.63−7.77 (4H, m); ^{13}C NMR ($CDCl_3$) δ 23.4 (d, J = 4.9 Hz), 34.2 (d, J = 3.3 Hz), 38.4 (d, J = 68.9 Hz), 126.3, 126.6, 128.4 (d, J = 11.7 Hz), 128.6 (d, J = 7.2 Hz), 130.5 (d, J = 9.0 Hz), 130.8 (d, J = 9.0 Hz), 131.4 (d, J = 2.5 Hz), 131.5 (d, J = 2.5 Hz), 132.8 (d, J = 98.4 Hz), 134.4 (d, J = 97.6 Hz), 147.0 (d, J = 10.7 Hz). Anal. Calcd for $C_{21}H_{21}OP$: C, 78.73; H, 6.61. Found: C, 78.65; H, 6.44.

1-Phenyl-2-diphenylphosphinylpropane (8b) [7302-07-0]. Isolated in 82% yield: white solid; mp 185−186 °C; IR (Nujol) 1177 cm^{-1}; MS *m*/*z* 320 (M^+), 201 (Ph_2PO^+), 185

(Ph_2P^+), 104 ($PhC_2H_3^+$); ^{1}H NMR ($CDCl_3$) δ 1.07 (3H, dd, J = 16.4, 6.5 Hz), 2.56−2.67 (2H, m), 2.92−3.09 (1H, m), 7.10−7.28 (5H, m), 7.45−7.52 (6H, m), 7.81−7.92 (4H, m); ^{13}C NMR ($CDCl_3$) δ 11.7 (d, J = 2.5 Hz), 34.5 (d, J = 71.4 Hz), 35.0, 126.3, 128.4, 128.6 (d, J = 11.5 Hz), 128.7 (d, J = 12.3 Hz), 128.9 131.0 (d, J = 9.0 Hz), 131.55 (d, J = 2.5 Hz), 131.63 (d, J = 2.5 Hz), 132.16 (d, J = 95.2 Hz), 132.22 (d, J = 94.3 Hz), 139.5 (d, J = 14.7 Hz). Anal. Calcd for $C_{21}H_{21}OP$: C, 78.73; H, 6.61. Found: C, 78.68; H, 6.50.

1-Diphenylphosphinyl-3-methyl-2-butene (9) [13303-61-2]. Isolated in 55% yield: white solid; mp 115−118 °C; IR (Nujol) 1180 cm^{-1}; MS m/z 270 (M^+), 201 (Ph_2PO^+); ^{1}H NMR ($CDCl_3$) δ 1.45 (3H, d, J = 2.4 Hz), 1.67 (3H, d, J = 3.4 Hz), 3.08 (2H, dd, J = 14.7, 7.5 Hz), 5.18−5.25 (1H, m), 7.43−7.54 (6H, m), 7.71−7.76 (4H, m); ^{13}C NMR ($CDCl_3$) δ 18.0 (d, J = 2.5 Hz), 25.8 (d, J = 2.5 Hz), 30.8 (d, J = 70.6 Hz), 112.2 (d, J = 9.0 Hz), 128.4 (d, J = 11.5 Hz), 131.1 (d, J = 9.0 Hz), 131.6 (d, J = 2.6 Hz), 132.9 (d, J = 97.6 Hz), 137.6 (d, J = 12.3 Hz). Anal. Calcd for $C_{17}H_{19}OP$: C, 75.54; H, 7.08. Found: C, 75.53; H, 6.97.

2-Methyl-4-diphenylphosphinyl-1-butene (10) [126338-58-7]. Isolated in 25% yield: white solid; mp 121−123 °C; IR (Nujol) 1177 cm^{-1}; MS m/z 270 (M^+), 201 (Ph_2PO^+); ^{1}H NMR ($CDCl_3$) δ 1.72 (3H, s), 2.26−2.34 (2H,m), 2.36−2.44 (2H, m), 4.71 (1H, br s), 4.74 (1H, br s), 7.45−7.55 (6H, m), 7.68−7.77 (4H, m); ^{13}C NMR ($CDCl_3$) δ 22.4, 28.1 (d, J = 72.2 Hz), 29.1 (d, J = 2.5 Hz), 110.1, 128.7 (d, J = 11.5 Hz), 130.8, 131.7 (d, J = 3.3 Hz), 132.9 (d, J = 98.5 Hz), 144.7 (d, J = 15.6 Hz). Anal. Calcd for $C_{17}H_{19}OP$: C, 75.54; H, 7.08. Found: C, 75.13; H, 6.86.

1-Cyclohexyl-2-diphenylphophinyl-1-propene (11). (*E*)-Isomer (major): isolated in 53% yield; colorless oil; IR (neat) 1188 cm^{-1}; MS m/z 324 (M^+), 241 ($M^+ - C_6H_{11}$), 201 (Ph_2PO^+); ^{1}H NMR ($CDCl_3$) δ 1.06−1.35 (5H, m), 1.61−1.75 (5H, m), 1.84 (3H, dd, J = 13.1, 1.5 Hz), 2.39−2.50 (1H, m), 6.09 (1H, ddm, J = 21.5, 9.4 Hz), 7.43−7.54 (6H, m), 7.64−7.69 (4H, m); ^{13}C NMR ($CDCl_3$) δ 13.1 (d, J = 12.3 Hz), 25.6, 25.8, 31.9 (d, J = 1.6 Hz), 37.9 (d, J = 14.8 Hz), 126.5 (d, J = 99.3 Hz), 128.4 (d, J = 12.3 Hz), 131.6 (d, J = 2.5 Hz), 131.7 (d, J = 101.7 Hz), 132.0 (d, J = 9.9 Hz), 151.7 (d, J = 7.4 Hz); HRMS calcd for $C_{21}H_{25}OP$ (M^+) 324.1641, found 324.1612. (*Z*)-Isomer (minor): obtained as a mixture of (*Z*)-**11** and **12** (2:1); colorless oil; MS m/z 324 (M^+), 241 ($M^+ - C_6H_{11}$), 201 (Ph_2PO^+), 185 (Ph_2P^+); ^{1}H NMR ($CDCl_3$) δ 0.91−1.17 (5H, m), 1.48−1.71 (5H, m), 1.74 (3H, dd, J = 12.6, 1.5 Hz), 2.64−2.75 (1H, m), 6.16 (1H, ddm, J = 37.7, 10.6 Hz), 7.43−7.55 (6H, m), 7.68−7.73 (4H, m); ^{13}C NMR ($CDCl_3$) (clearly assignable peaks) δ 23.2 (d, J = 13.9 Hz), 25.2, 25.7, 32.4 (d, J = 1.7 Hz), 38.3 (d, J = 6.5 Hz).

1-Cyclohexyl-2-diphenylphophinyl-2-propene (12). Obtained as a mixture of (*Z*)-**11** and **12**: colorless oil; MS m/z 324 (M^+), 241 ($M^+ - C_6H_{11}$), 228 (241 − CH^+), 201 (Ph_2PO^+); ^{1}H NMR ($CDCl_3$) δ 0.91−1.17 (5H, m), 1.48−1.71 (5H, m), 2.20 (2H, dd, J = 12.1, 7.0 Hz), 2.29−2.35 (1H, m), 5.64 (1H, br d, J = 20.8 Hz), 5.75 (1H, dd, J = 43.0, 1.2 Hz), 7.43−7.55 (6H, m), 7.68−7.73 (4H, m); ^{13}C NMR ($CDCl_3$) (clearly assignable peaks) δ 26.0, 26.4, 33.0, 35.7 (d, J = 4.1 Hz), 39.8 (d, J = 10.7 Hz); HRMS calcd for $C_{21}H_{25}OP$ (M^+) 324.1641, found 324.1667.

The Reaction of Alkynes with Ph_2PH under Radical Conditions. A mixture of alkynes **2** (1 mmol), Ph_2PH (186 mg, 1 mmol), and AIBN (16 mg, 0.1 mmol) in THF (1 mL) (for **2a** and **2h**) or without a solvent (for **2b**, **2c**, and **2g**) was heated to 80−85 °C with stirring for appropriate time as shown in eq 2. After cooling, docosane was added as an internal standard to the mixture, and the products were extracted with ether, dried over $MgSO_4$, and concentrated in vacuo. Yields and regio- and stereochemistry were determined by GC and NMR of the crude mixture. If necessary, the analyses were repeated after oxidation with H_2O_2. In the reaction of **2b**, 50 mol % of AIBN was used to promote the reaction.

Competitive Reaction of Alkynes and 1-Decene with Ph_2PH. Diphenylphosphine (372 mg, 2 mmol) was added to a solution of the imine complex **1** (0.2 mmol) in THF (1 mL), and the mixture was stirred at room temperature for 30 min. Then, alkyne **2b** (115 mg, 0.66 mmol) or **2h** (73 mg, 0.66 mmol) and 1-decene (188 mg, 1.34 mmol) were added to the mixture, and stirring was continued for 31 h at room temperature. The reaction was quenched with water and aqueous HCl (2 M). After addition of docosane as an internal standard, the mixture was extracted with ether, dried over $MgSO_4$, and concentrated in vacuo. Identification of the products **3**, **4**, and **13** and their yields were determined by GC and NMR. Similarly, the reaction with AIBN (10 mol %) was conducted in THF at 85 °C for 36 h. 1-Diphenylphosphinodecane (**13**): MS m/z 326 (M^+), 185 (Ph_2P^+), 108 (PhP^+); ^{1}H NMR ($CDCl_3$) δ 0.87 (3H, t, J = 6.1 Hz), 1.09−1.52 (16H, m), 2.03 (2H, m), 7.16−7.82 (10H, m).

Preparation of the Diphosphido Complexes 15a and 15b. A mixture of Yb metal (2.076 g, 12 mmol), Ph2C═NPh (2.573 g, 10 mmol), and MeI (10 μL) in THF (25 mL) was stirred for 18 h at room temperature to yield HMPA-free imine complex **1′** as reddish-brown precipitates. Diphenylphosphine (3.724 g, 20 mmol) was added to the mixture, and stirring was continued for 10 h at room temperature. The resulting homogeneous red solution was concentrated under vacuum, and the residue was solidified by addition of ether (20 mL). After washing with ether (20 mL × 5), the solid was dissolved in THF and transferred to another Schlenk flask to remove metallic residue. Addition of a small amount of ether and cooling gave $Yb(PPh_2)_2(thf)_4$ (**15a**) as red crystals (7.021 g, 84%). The diphosphido complex **15a** (3.346 g, 4 mmol) was treated with HMPA (3.0 g, 17 mmol) in THF (10 mL) at room temperature for 1 h. An attempt to crystallize the product was unsuccessful. Thus, the mixture was concentrated under vacuum, and the residue was solidified by addition of ether (15 mL). The precipitate was washed with ether (15 mL × 5) and dried under vacuum to give reddish-black powdered $Yb(PPh_2)_2(hmpa)_3$ (**15b**) (2.973 g, 68%). Direct synthesis of **15b** from **1** having HMPA ligand and Ph_2PH was not suitable, because the product was obtained as an untractable gum. **15a**:[22] ^{1}H NMR (THF-d_8) δ 6.54 (4H, brs), 6.79 (8H, brs), 7.34 (8H, brs); ^{13}C NMR(THF-d_8) δ 26.4, 68.3, 121.3, 127.8, 131.5, 153.1 (d, J = 30.0 Hz); ^{31}P NMR (THF-d_8) δ −1.50. This complex was desolvated on drying over longer time periods under high vacuum to yield $Yb(PPh_2)_2(thf)_1$. **15b**: ^{1}H NMR (THF-d_8) δ 2.59 (54H, s), 6.51 (4H, brs), 6.76 (8H, brs), 7.44 (8H, brs); ^{13}C NMR-(THF-d_8) δ 37.2, 119.6, 127.3, 131.1, 156.1 (d, J = 42.7 Hz); ^{31}P NMR (THF-d_8) δ 2.36.

Hydrophosphination of Alkynes with the Diphosphido Complex 15b. The diphosphido complex **15b** (65 mg, 0.06 mmol) was dissolved in THF (1 mL). Alternatively, **15b** was generated from $Yb(PPh_2)_2(thf)_1$ (37 mg, 0.06 mmol) and HMPA (32 mg, 0.18 mmol) in THF (1 mL). To this solution was added Ph_2PH (223 mg mg, 1.2 mmol), and the mixture was stirred for 30 min. Then, alkyne (1.2 mmol) was added to the mixture, and stirring was continued at room temperature for appropriate time as shown in Table 3. The reaction was quenched with water (2 mL) and aqueous HCl (2 M, 1 mL). After addition of docosane as an internal standard, the mixture was extracted with ether, washed with brine, dried over $MgSO_4$, and concentrated in vacuo. Yields and regio- and stereochemistry of the products **3** and **4** were determined by GC and NMR.

Stoichiometric Reaction of Alkynes 2a and 2h with the Diphosphido Complex 15b. Diphenyacetylene (**2a**) (54 mg, 0.3 mmol) was added to a solution of $Yb(PPh_2)_2(hmpa)_3$ (**15b**) (108 mg, 0.1 mmol) in THF (1 mL), and the mixture was stirred for 15 h at room temperature. The reaction mixture was worked up as usual. GC and NMR analyses of the crude mixture indicated that 0.182 mmol (1.82 equiv of **15b**) of alkenylphosphine **3a** was formed. Similar reaction of **2h** gave **3h** (1.08 equiv) and **4h** (0.76 equiv).

Labeling Reaction. Labeling reaction was conducted in manner similar to the corresponding reactions described above

by using Ph_2PD, Ph_2ND, HexC≡CD, HMPA-d_{18}, THF-d_8, and D_2O, respectively. Deuterium content of the products was measured by GC−MS and ^1H NMR.

Hydrophosphination of Alkynes 2a and 2c with Divalent and Trivalent Phosphido Complexes 16a and 16b. $Yb[N(SiMe_3)_2]_2(Et_2O)_1$[29] (137 mg, 0.24 mmol) was dissolved in THF (1 mL), and HMPA (258 mg, 1.44 mmol), Ph_2PH (450 mg, 2.4 mmol) were successively added to the solution, and stirring was continued for 30 min at room temperature to generate divalent species **16a**. During addition of the phosphine, color of the solution turned to red from orange. Then, 1-phenyl-1-propyne (**2c**) (280 mg, 2.4 mmol) was added to the solution, and the mixture was stirred for 30 min at room temperature. After addition of an internal standard (docosane) and usual aqueous workup, the crude mixture was analyzed by GC and NMR, showing that the alkenylphosphine **3c** was formed quantitatively with an *E*/*Z* ratio of 24/76. Similarly, the alkyne **2c** (280 mg, 2.4 mmol) was added to the red solution of trivalent phosphido **16b**, generated from $Yb[N(SiMe_3)_2]_3(thf)_2$[30] (192 mg, 0.24 mmol) and Ph_2PH (450 mg, 2.4 mmol) in THF (1 mL) containing HMPA (258 mg, 1.44 mmol), and stirring was continued for 30 min at room temperature. The reaction mixture was found to contain **3c** (98% yield, *E*/*Z* = 24/76) by GC and NMR. The reaction of diphenylacetylene (**2a**) with **16b** was carried out in a similar manner to afford alkenylphosphine **3a** quantitatively with an *E*/*Z* ratio of 97/3.

Hydrophosphination of Alkynes in an NMR Tube. Yb metal (69 mg, 0.4 mmol) and Ph_2C═NPh (52 mg, 0.2 mml) were placed in an NMR tube, and HMPA (108 mg, 0.6 mmol), MeI (0.5 μL), and THF-d_8 (0.5 mL) were added to the tube. The mixture was sonicated for 10 h at 35 °C to give a deep red solution of the imine complex **1**. After confirmation of the quantitative formation of **1**, Ph_2PH (75 mg, 0.4 mmol) was added to the solution, and the resulting pale red mixture was sonicated for 12 h with monitoring by ^{13}C and ^{31}P NMR. The reaction was found to complete within 30 min to generate the diphosphido complex **15b** and the amine **14** (Figure 1, **G** and **H**). Then, 1-phenyl-1-propyne (**2c**) (47 mg, 0.4 mmol) was added to the mixture, whereby the color of the mixture turned to purple-red. Monitored by NMR, the alkenylphosphine **3c** and an amido species such as $Yb(NPhCPh_2)_2(hmpa)_n$ were formed, and the diphosphido **15b** almost disappeared within 4 h (Figure 1, **I** and **J**).

$Yb[N(SiMe_3)_2]_3(thf)_2$ (18 mg, 0.02 mmol) was placed in an NMR tube and dissolved in THF-d_8 (0.45 mL) and HMPA (8 mg, 0.04 mmol). To the solution was added Ph_2PH (13 mg, 0.07 mmol), and the mixture was sonicated for 30 min at 35 °C. ^{13}C and ^{31}P NMR indicated the formation of trivalent phosphido complex **16b** (Figure 3, **K**). Then, diphenylacetylene (**2a**) (12 mg, 0.07 mmol) was added in limited amounts to the mixture, whereby the color of the solution changed from orange to yellow. NMR was measured at every addition of **2a**. The reaction with **15b** and **16a**, generated from $Yb(PPh_2)_2(thf)_1$ and $Yb[N(SiMe_3)_2]_2(Et_2O)_1$, respectively, was carried out similarly (Figure 3, **L**).

Kinetics. Under standard conditions, the imine complex **1** was prepared from Yb (34.6 mg, 0.20 mmol), Ph_2C═NPh (51.5 mg, 0.20 mmol), and HMPA (107.5 mg, 0.60 mmol) in THF (1.0 mL) containing docosane (20.0 mg) as an internal standard. Ph_2PH (372.4 mg, 2.0 mmol) was added to the solution, and the mixture was stirred for 30 min at 22 °C. Then, the alkyne **2b** (348.6, 2.0 mmol) was added to the mixture and stirring was continued over 3 h. Meanwhile, the product yields were determined by GC at 5, 15, 30, 45, 60, 90, and 120 min and then, every 1 h. The initial reaction rate was determined by the least-squares method. Similarly, kinetic data were obtained by changing the concentration of the catalyst **1**, alkyne **2b**, and phosphine.

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