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Intermolecular Hydrophosphination of Alkynes and Related Carbon-Carbon Multiple Bonds Catalyzed by Ytterbium-Imine Complexes

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Abstract—Catalytic intermolecular hydrophosphination of alkynes with Ph_2PH has been achieved by using a ytterbium-imine complex, $[Yb(\eta^2\text{-}Ph_2CNPh)(hmpa)_6]$. Thus, both terminal and internal alkynes were converted in high yields to the corresponding alkenylphosphines or phosphine oxides after oxidative workup. The present method was also applicable to various carbon-carbon multiple bonds such as conjugated diynes and dienes, allenes and styrene derivatives.

Keywords: hydrophosphination; lanthanide catalyst; alkynes; alkenylphosphines

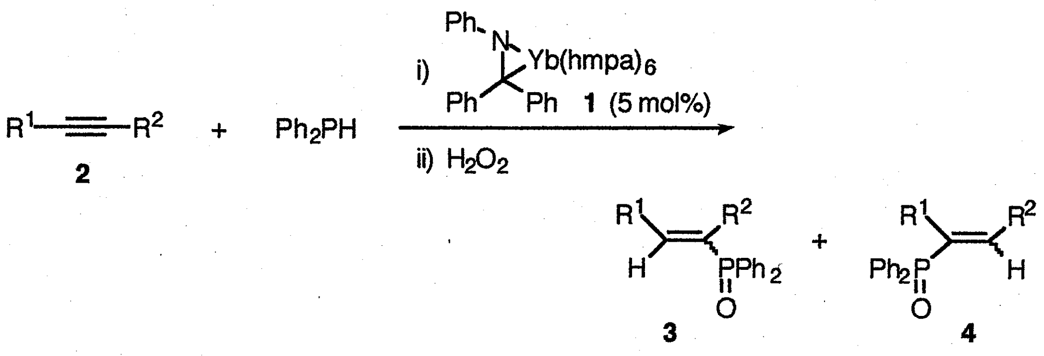
α,β-Unsaturated phosphorous compounds are useful building blocks in organic synthesis. Their catalytic synthesis has been explored based on the coupling reaction of alkenyl halides and triflates with dialkyl phosphites[1] and the addition reaction of phosphites and diphenylphosphine oxide to alkynes.[2] However, these reactions have been rarely applied to the synthesis of alkenylphosphines.[3] Studies on the P-H bond activation of phosphines by group 10 catalysts were limited to the reaction with activated olefins such as acrylate esters and acrylonitrile.[4] Recently, Marks and co-workers reported a lanthanocene-catalyzed intramolecular hydrophosphination of alkynyl- and alkenylphosphines.[5]

Previously, we have demonstrated that divalent ytterbium-imine complexes, [Yb(η^2-Ph_2CNAr)(hmpa)$_n$] (**1**), readily prepared in situ from Yb metal and aromatic imines in THF and HMPA,[6] exhibit good catalytic activity in the dehydrogenative silylation of terminal alkynes[7] and hydrosilylation of imines.[8] We report herein an intermolecular hydrophosphination of alkynes and related carbon-carbon multiple bonds like conjugated diynes and dienes by using the Yb-imine complexes **1**.

When diphenylphosphine and equimolar amounts of 1-phenyl-1-propyne (**2c**) were successively added to a THF solution of **1** (Ar=Ph, n=6, 5 mol%, 0.1 M) at room temperature, 1-phenyl-2-diphenylphosphino-1-propene (**3c'**) was quantitatively formed within 5 min (*E* / *Z* = 80 / 20). The alkenylphosphine **3c'** was isolated in decreased yield (80%) because of a partial oxidation to the corresponding alkenylphosphine oxide **3c** during the usual workup and column chromatography.[9] Thus, it was convenient to isolate the reaction product as the phosphine oxide **3c** after oxidation with H_2O_2. No reaction took place with Yb(O^{i}Pr)$_3$ and SmI_2 (10 mol%, rt, 12 h) as well as the reaction without a catalyst.[10] Moreover, many products, including polymeric materials, were formed with ^{n}BuLi (10 mol%, rt, 30 min).

Results on the reaction of various alkynes **2** are summarized in Table 1. The expected products **3** and **4** were obtained in high yields under mild conditions, except for aliphatic internal alkynes **2e-f** in which the reaction should be heated at 80 °C without the solvent (runs 5 and 6). With respect to regiochemistry, a Ph_2P group was introduced into the opposite side to the aryl substituents of the aromatic alkynes exclusively (runs 2-4), and into the less hindered side of the aliphatic alkynes (runs 6-8). Stereochemistry of the products **3** and **4**, determined by comparison of their $^3J_{P\text{-}H}$ of ^1H NMR and UV spectra with literature data,[11] was dependent on the substrates, i.e., (*E*)- and (*Z*)-isomers were preferentially formed from the aromatic and aliphatic alkynes, respectively. In contrast to these results, direct synthesis of **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.

Table 1. Hydrophosphination of Alkynes with Diphenylphosphine

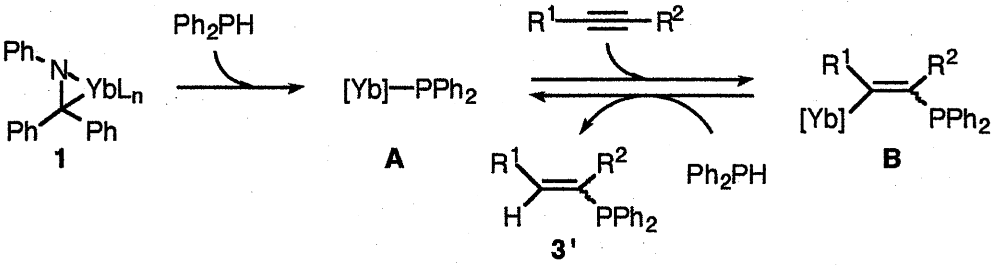


					3			4	
run	alkyne	R^1	R^2	conditions		yield[a] (%)	E / Z		yield[a] (%)
1	**2a**	Ph	Ph	THF, rt, 5 min	**3a**	quant	100 / 0	—	
2	**2b**	Ph	$SiMe_3$	THF, rt, 4 h	**3b**	quant	100 / 0	**4b**	0
3	**2c**	Ph	Me	THF, rt, 5 min	**3c**	quant	80 / 20	**4c**	0
4	**2d**	Ph	H	THF, rt, 5 min	**3d**	quant	76 / 24	**4d**	0
5	**2e**	^{n}Pr	^{n}Pr	neat, 80 °C, 6 h[b]	**3e**	95	0 / 100	—	
6	**2f**	^{n}Pen	Me	neat, 80 °C, 6 h[b]	**3f**	61	0 / 100	**4f**[c]	28
7	**2g**	^{t}Bu	H	THF, rt, 3 h[b]	**3g**	62	0 / 100	**4g**	10
8	**2h**	^{n}Hex	H	THF, rt, 5 min	**3h**	52	27 / 73	**4h**	34

[a] GC yield. [b] 10 mol% of **1** was used. [c] *E* / *Z* = 21 / 79.

It has been reported that Ph_2PH reacts with alkynes under radical conditions to yield normally (*E*)-diphenylphosphinoalkenes as the primary products, which isomerize to (*Z*)-isomers finally.[12] Thus, the reaction with AIBN (10 mol%, THF or neat, 80-85 °C, without oxidative workup) was performed for comparison with that with the imine complex **1**.[13] The radical reaction gave the alkenylphosphine **3'** as single regioisomers in lower yields than the latter, particularly in the reaction of **2b** and **2g**. On monitoring by ^1H and ^{31}P NMR, (*Z*)-isomers were preferentially formed irrespective of aromatic and aliphatic alkynes **2**, even at an early stage of the reaction, and this selectivity decreased gradually. These results clearly indicate that the hydrophosphination with **1** is different from the radical reaction in regard to regio- and stereochemistry.

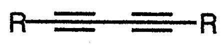
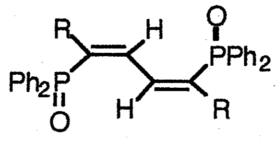
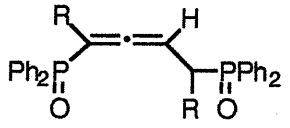
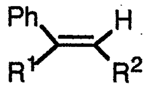
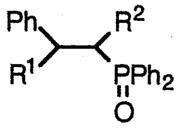
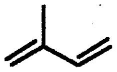
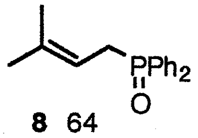
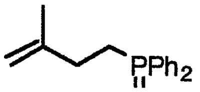
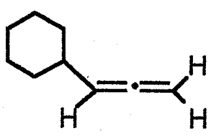
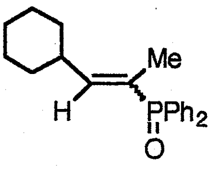
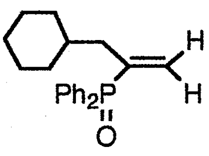
Although several mechanistic aspects remain unclear, the present reaction would include the following three steps (Scheme 1): (i) generation of phosphide intermediate **A** from **1** and diphenylphosphine, (ii) insertion of alkyne to **A** to give phosphinoalkenyl ytterbium **B**, (iii) formation of the product and regeneration of **A** by the protonation of **B** with Ph_2PH. These processes are similar to those of intramolecular hydrophosphination with trivalent lanthanocene catalysts.[5] With respect to step (i), the imine complex **1** reacted readily with equimolar amounts of Ph_2PD and, on quenching with H_2O, $Ph_2CDNHPh$ and Ph_2PH were detected in 65% and 35% yields, respectively, which implies that the phosphide species **A** is generated through a C-Yb bond cleavage of **1** with the phosphine.[14, 15] Lanthanide phosphide has been reported to react with THF at elevated temperature to yield a 4-phosphinobutoxylanthanide complex.[16] Thus, formation of 4-diphenyphosphino-1-butanol, a by-product obtained in 70% yield based on **1** by the reaction of aliphatic internal alkynes **2e-f** in refluxing THF, supports also the generation of **A**. Stereochemistry of the hydrophosphination would not be determined by isomerization of the products, because their *E / Z* ratio was nearly independent of the reaction time. Thus, (*Z*)-selectivity for the reaction of aliphatic alkynes seems to be somewhat curious in the light of syn addition step (ii). However, this point is not clear at present.



Scheme 1.

The present hydrophosphination was applied to other carbon-carbon multiple bonds to examine its scope and limitations (Table 2). The reaction of 7,9-hexadecadiyne with Ph_2PH (2 equiv) gave bis(diphenylphosphinyl)diene **5a** in 51% yield as a single regio- and stereoisomer after the oxidative workup. In contrast, 2,2,7,7-tetramethyl-3,5-octadiyne was converted to a mixture of diene **5b** and allene **6b** in 12% and 71% yields, respectively, under similar conditions. An attempt to get monophosphinylated products with equimolar amounts of the phosphine was unsuccessful because of rapid oligomerization of the diynes even at -78 °C.

Table 2. Hydrophosphination of Various C-C Multiple Bonds with Diphenyphosphine[a]

substrate	conditions	product and yield[b] (%)
 a: R = ^{n}Hex b: R = ^{t}Bu	-35 °C, 3 h[c]	 **5a** 51, **5b** 12  **6a** 0, **6b** 71
 a: R^1 = Me, R^2 = H b: R^1 = H, R^2 = Me	rt, 4 h	 **7a** 85, **7b** 95
	0 °C, 1.5 h[d]	 **8** 64  **9** 35
	rt, 30 min	 **10** 79 (E / Z = 71 / 29)  **11** 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 **5** and **6** (isolated yield). [c] 2 equiv of Ph_2PH were used. [d] 2 equiv of isoprene were used.

Although the reaction of aliphatic alkenes did not occur, α- and β-methylstyrene afforded **7a** and **7b** 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 **8** and **9** in 64% and 35% yields, respectively. Two olefinic phosphine oxides **10** and **11** were formed in 79% and 13% yields, respectively, by the reaction of cyclohexylallene, but 1-cyclohexyl-3-diphenylphosphinyl-1-propene was not detected in contrast to the radical reaction.[12]

In 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. This method is also applicable to a wide range of carbon-carbon multiple bonds such as conjugated diynes and dienes, allenes, and styrene derivatives. Further work on the mechanistic aspects and synthetic applications is in progress.

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3. Alkenylphosphines are prepared conventionally from alkenylmetals (Mg and Li) and R_2PCl. Radical and base (^{t}BuOK and PhLi)-catalyzed addition of R_2PH to alkynes are also available for their synthesis, for example, see: (a) Heesche-Wagner, K.; Mitchell, T. N. *J. Organomet. Chem.* **1994**, *468*, 99-106. (b) Schmidbaur, H.; Frazao, C. M.; Reber, G.; Muller, G. *Chem. Ber.* **1989**, *122*, 259-263.
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9. Similarly, alkenylphosphines **3a'** and **3b'** were obtained in 85% and 69% isolated yields, respectively, by the reaction of **2a** and **2b** without the oxidative workup (cf., Table 1).
10. Of the substrates in Tables 1 and 2, phenylacetylene and α-methylstyrene reacted with Ph_2PH in the absence of the catalyst **1** under reflux for 13 h: the former gave **3d** in quantitative yield with reversed stereoselectivity ($E / Z = 32 / 68$) and the latter gave **7a** in lower yield (40%). However, no reaction took place at room temperature.
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13. Following results were obtained: **3a'**, 15 h reaction, 79% yield, *E* / *Z* = 0 / 100; **3b'**, 15 h, 10%; **3c'**, (10 min, 10%, 1 / 99), (1.5 h, 69%, 9 / 91), (30 h, 69%, 17 / 83); **3g'**, 18 h, trace; **3h'**, (30 min, 26%, 13 / 87), (4 h, 71%, 22 / 78), (52 h, 62%, 28 / 72).

14. $Ph_2CDN(Ph)$-Yb-PPh_2, a primary product from **1** and Ph_2PD, can be presumed as the intermediate **A**, but it may be changed to other phosphide species like $Yb(PPh_2)_2$ by further reaction with the phosphine or disproportionation.

15. It has been known that trivalent lanthanide amides catalyze inter- and intramolecular hydroamination of alkynes and alkenes, see: (a) Li, Y.; Marks, T. J. *Organometallics* **1996**, *15*, 3770-3772. (b) Li, Y.; Marks, T. J. *J. Am. Chem. Soc.* **1996**, *118*, 9295-9306, and references therein. However, products anticipated by this type of reaction were not detected in the present system.

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