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Hydrophosphination of alkynes and related reactions catalyzed by rare-earth amides

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Abstract

Intermolecular hydrophosphination of alkynes with Ph_2PH was effectively catalyzed by Yb-imine complex [Yb(η^2-Ph_2CNPh)$(hmpa)_3$], in which the empirical rate law was described as $v = k$ [catalyst]^2 [alkyne]^1 [phosphine]^0. The active catalysts were proved to be ytterbium(II) mono- and diphosphido species generated in situ. Although trivalent phosphido complex [Yb$(PPh_2)_3(hmpa)_n$], gave the same results as the divalent complexes, Yb metals of the both complexes seemed to keep their original oxidation state unchanged. When Ph_2PH was substituted by Ph_2P–$SiMe_3$, silylphosphination of aromatic internal alkynes took place to afford 1-trimethylsilyl-2-diphenylphosphinoalkenes in moderate yields. Moreover, one-pot synthesis of 1-diphenylphosphino-1,3-butadienes from terminal alkynes and Ph_2PH has been achieved using $Y[N(SiMe_3)_2]_3$ catalyst through the alkyne dimerization and subsequent hydrophosphination.

Keywords: Hydrophosphination; Silylphosphination; Rare-earth amides; Alkynes; Enynes

1. Introduction

Recently, P–H bond activation by group 10 catalysts, followed by alkyne insertion has attracted much attention as the useful synthetic method of α,β-unsaturated phosphorous compounds because of their high regio- and stereoselectivity [1]. However, application of this procedure was limited to pentavalent phosphorous compounds such as $(RO)_2P(O)H$ and $Ph_2P(O)H$, and the reaction of trivalent phosphine was generally unsuccessful [2]. Trivalent lanthanocenes were also found to exhibit high catalyst activity in the intramolecular hydrophosphination of phosphino-alkynes and alkenes [3]. In the course of our study on the synthetic application of Yb(II)–imine complex [Yb(η^2-Ph_2CNPh)$(hmpa)_3$] (**1**) [4], we found that intermolecular hydrophosphination of alkynes with Ph_2PH was effectively catalyzed by **1** [5]. We describe herein these results, particularly on the mechanistic aspect, and some related reactions.

2. 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 with a *E*/*Z* ratio of 80/20 within 5 min. The product **3c** was isolated as phosphine oxide **3c′** after oxidation with H_2O_2. Results on the hydrophosphination of various alkynes **2** are summarized in Table 1. Both terminal and internal alkynes gave the 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 were, however, necessary to complete the reaction (runs 5 and 6). The reaction of aromatic alkynes **2b**–**d** gave

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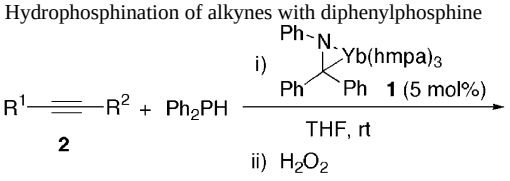
Table 1
Hydrophosphination of alkynes with diphenylphosphine



Run	Alkyne				3′			4′	
		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.

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. With respect to the stereochemistry, *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**, and its time-dependence was not observed on monitoring by ^{1}H and ^{13}C NMR.

A radical mechanism was completely excluded in the present system by some comparative study using AIBN initiator; for example, **3** was formed as a single regioisomer in lower yield with *Z*-selectivity irrespective of aromatic and aliphatic alkynes. In order to study the reaction process, a stoichiometric reaction of 1-phenyl-1-propyne (**2c**) with Ph_2PH was monitored by ^{13}C and ^{31}P NMR (Fig. 1). A dark red suspension of **1** was immediately changed to a bright red homogeneous solution on addition of the phosphine (2 equiv.). The signals of **1** [6] and Ph_2PH completely disappeared in ^{13}C NMR and those assignable to free or coordinated amine, $Ph_2CHNHPh$ (**5**), were clearly observed (Fig. 1, **G**, ◯). 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** (Fig. 1, **G**, △). In the ^{31}P NMR spectra, the signal of Ph_2PH at −40.1 ppm changed to 1.24 on the treatment (Fig. 1, **H**, △). When 2 equiv. of **2c** was added to the mixture, the ^{13}C NMR spectra became somewhat complicated, but the product **3c** was definitely identified (Fig. 1, **I**). Surprisingly, the phosphido species **A** disappeared and new signals assignable to [Yb]-N(Ph)$CHPh_2$ species **B** were found (Fig. 1, **I**, □). 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 (Fig. 1, **J**).

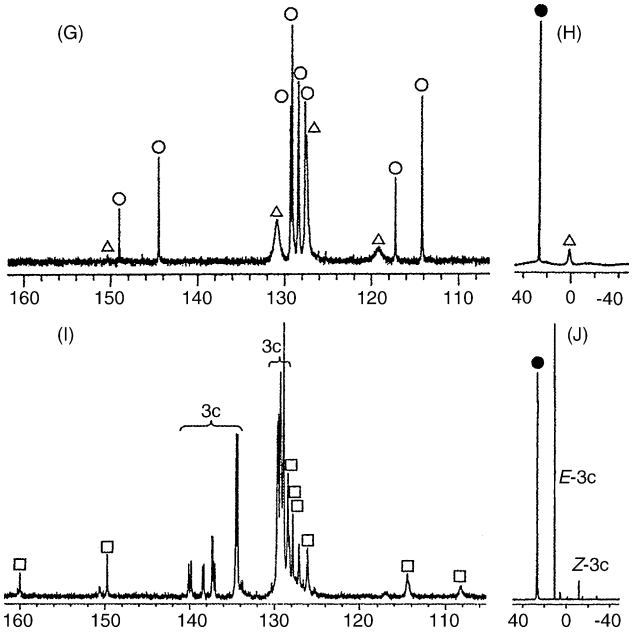
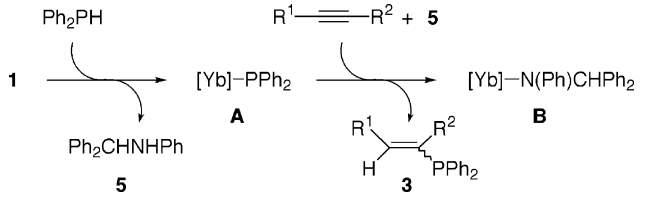
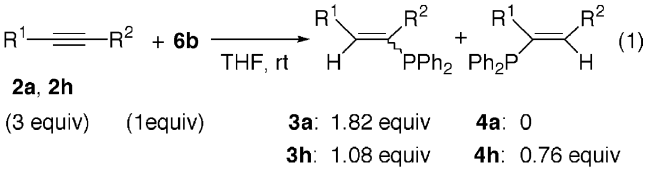


Fig. 1. ^{13}C and ^{31}P NMR spectra of the reaction of **1** with Ph_2PH (2 equiv.) in THF-d_8 (**G** and **H**), followed by addition of **2c** (2 equiv.) (**I** and **J**). ●, ◯, △, and □ denote the signals assignable to HMPA, the amine **5**, [Yb]-PPh_2 **A** and [Yb]-N(Ph)$CHPh_2$ **B**, respectively.

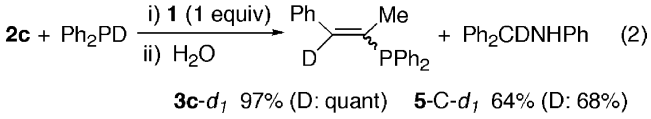


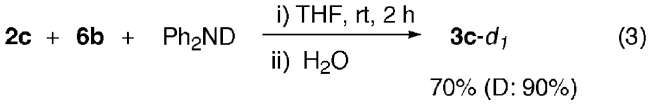
Scheme 1.

Based on 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 **5** to leave the product **3c** and amido **B**. Thus, we tried to isolate the phosphido intermediate **A**. Treatment of hmpa-free imine complex **1′** with 2 equiv. of Ph_2PH gave diphosphido complex $[Yb(PPh_2)_2(thf)_4]$ (**6a**), in 84% isolated yield [7]. Ligand substitution of **6a** by hmpa afforded $[Yb(PPh_2)_2(hmpa)_3]$ (**6b**), which showed ^{13}C and ^{31}P NMR spectra analogous to those observed in the trace reaction described above, of course. The complex **6b** exhibited a good catalyst activity in the hydrophosphination, giving rise to similar results as with the imine complex **1** on the whole, though the ratio of *Z*-isomers **3** slightly increased and the reaction became somewhat slower. Interestingly, the diphosphido complex **6b** could deliver the two Ph_2P groups to alkynes as shown in Eq. (1), which explained the complete consumption of **A** in the NMR reaction:



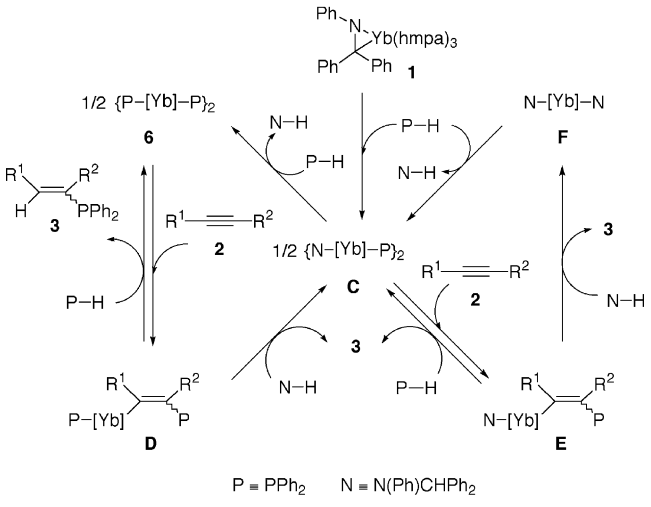
The reaction of 1-phenyl-1-propyne (**2c**) with Ph_2PD in the presence of stoichiometric amounts of **1**, followed by H_2O quenching, afforded deuterated **3c**-d_1 in 97% yield together with the amine **5**-C-d_1 (Eq. (2)). On the other hand, the reaction with Ph_2PH and quenching with D_2O resulted in the formation of non-deuterated **3c** and the amine **5**-N-d_1. The same results were obtained in the catalytic reaction with the imine complex **1** and the diphosphido **6b**. Similarly, the reaction of **2c** with **6b** in the presence of Ph_2ND, a model reaction in the second step in Scheme 1, gave alkenylphosphine **3c**-d_1 (Eq. (3)). In the reaction without proton source as shown in Eq. (1), olefinic proton of the product **3** was proved to be derived from another molecule of terminal alkyne and/or PPh_2 moiety of the product. 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 $Ph_2CHNHPh$ (**5**).





Kinetic studies were carried out using 1-phenyl-2-trimethylsilylacetylene (**2b**) and the Yb-imine catalyst **1**. As a result, the empirical rate law can be described as $v = k$ [catalyst]^2 [alkyne]^1 [phosphine]^0 at least under standard conditions, indicating that the complex **1** should be changed to some dimeric Yb species in the mixture.

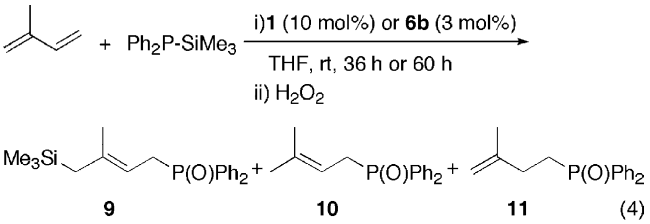
A possible reaction mechanism is proposed in Scheme 2. At first, the imine complex **1** is protonated stepwisely with the phosphine to yield the diphosphido **6** via Yb(amido)(phosphido) species **C**; here, the two intermediates would exist as dimers. Addition of **6** to alkyne, a rate-determining step, affords the β-(diphenylphosphino)alkenyl-Yb species **D**, which is immediately protonated with Ph_2PH to give the product **3** and the diphosphido **6**. 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 **6** is achieved by protonation with the liberated amine **5** instead of Ph_2PH, followed by amido-phosphido exchange of **C** (left wing). Combined with the fact that the phosphine was completely consumed after the reaction and that the reaction with the diphosphido **6** is slower than that with **1**, it should be reasonable to consider the addition reaction of the monophosphido **C** to alkyne as depicted in the right wing. Thus, the reaction of **C** and protonation of the resulting intermediate **E** with Ph_2PH or, alternatively, with the amine **5** would produce the products **3** together with diamido species **F** as the final form of the catalyst.



Scheme 2.

Valence state of the Yb species was investigated using the divalent and trivalent phosphido complexes [Yb(PPh_2)$_{2\ or\ 3}$(hmpa)$_n$] (**7a** and **b**), which were generated in situ from [Yb(btsa)$_{2\ or\ 3}$(hmpa)$_n$], [btsa = N($SiMe_3$)$_2$], and 2 or 3 equiv. of Ph_2PH. The two catalysts **7a** and **b** gave nearly the same results with respect to the yield and stereochemistry of the products **3**. ^{31}P NMR spectra of **7a** and **b** showed a different signal at 1.37 and −15.51 ppm in THF-d_8, respectively. When less than 2 equiv. of alkyne **2a** was added separately to the complexes, signals assignable to *E*- and *Z*-**3a** were observed at 9.75 and −5.85 ppm, respectively, together with those of **7a** and **b** whose chemical shifts were not changed. Then, **7a** and **b** disappeared on addition of excess **2a**. Accordingly, the divalent and trivalent Yb metals are likely to keep their valence state unchanged during the reaction.

Next, we studied a reaction of alkynes with Ph_2P–$SiMe_3$ with a hope that if β-(diphenylphosphino)alkenyl-Yb species **D** and **E** in Scheme 2 would be quickly silylated with the silylphosphine instead of the protonation with Ph_2PH, catalytic silylphosphination of alkynes would be possible. When 1-phenyl-1-propyne (**2c**) was treated with Ph_2P–$SiMe_3$ (1.5 equiv.) in the presence of the imine complex **1** (10 mol%) in THF, expected silylphosphination product **8c** and hydrophosphination product **3c** were formed in 55 and 36% yields, respectively, with a 60% selectivity of the former (Table 2, run 5). Similar reaction with the diphosphido complex **6b** gave **8c** with 83% selectivity (run 6). As can be seen in Table 2, the silylphosphination took place over 50% selectivity in the aromatic internal alkynes (runs 1–6) and, in contrast, the selectivity and efficiency decreased seriously for terminal alkynes and aliphatic alkynes (runs 7–9). The products **8** were never obtained by the reaction with AIBN or HMPA and by thermal reaction without **1** and **6b** that afforded small amounts of **3** (∼30% yield). The stereochemistry of **3** was similar to the results of hydrophosphination with Ph_2PH in Table 1, whereas that of **8** was variable. The present silylphosphination was also applicable to isoprene, giving rise to the expected product **9** in high yield, particularly with **6b** (Eq. (4)):

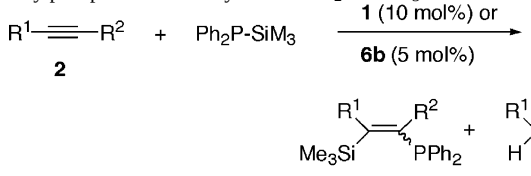


	9	**10**	**11**
with **1**	66%	21%	4%
with **6b**	82%	1%	3%

(4)

Lastly, we investigated a one-pot synthesis of 1-diphenylphosphino-1,3-butadiene derivatives from 2 equiv. of terminal alkynes and Ph_2PH (Eq. (5)). For the first step, it has been reported that terminal alkynes are dimerized regio- and stereoselectively to give *Z*-enyne compounds **12** with trivalent Y-amide catalyst [Y(btsa)$_3$] and amine additives [8]. Thus, subsequent treatment of the reaction mixture with Ph_2PH in the presence of HMPA would produce the butadiene derivatives **13** by the aid of some Y-amide species survived. In fact, the coupling products **13** were obtained in high yields, wherein olefinic stereochemistry of **12** was changed during

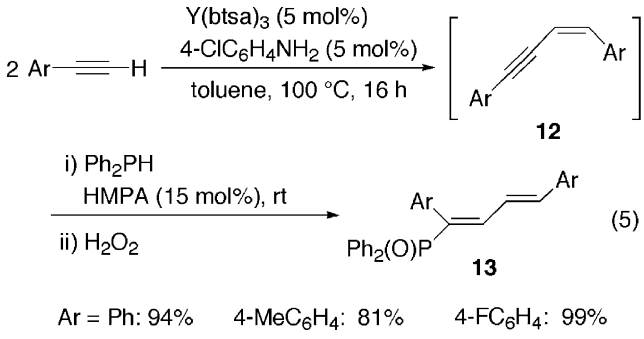
Table 2
Silylphosphination of alkynes with Ph_2P–$SiMe_3$



Run	Alkyne (**2**)	Conditions[a]	**8**			**3**		Selectivity of **8** (%)
			Yield[b]	(%)	*E*/*Z*[c]	Yield[b]	(%)	
1	**2a**	**1**, neat, 0 °C, 28 h	**8a**	68	100/0	**3a**	12	85
2		**6b**,THF, rt, 17 h		65			27	71
3	**2b**	**1**, neat, 90 °C, 27 h	**8b**	59	25/75	**3b**	31	66
4		**6b**, neat, 90 °C, 36 h		55			7	89
5	**2c**	**1**, THF, rt, 45 min	**8c**	55	100/0	**3c**	36	60
6		**6b**, THF, rt, 1 h		81			17	83
7	**2d**	**1**, THF, rt, 22 h	**8d**	10	-[d]	**3d**	37	21
8	**2e**	**1**, neat, 90 °C, 62 h	**8e**	10	-[d]	**3e**	18	36
9	**2h**	**1**, THF, rt, 30 min	**8h**	0		**3h**	14	0

[a] Silylphosphine/**2** = 1.5.
[b] GC yield.
[c] Relation between PPh_2 and $SiMe_3$.
[d] Stereochemistry was not determined.

the hydrophosphination.



3. Conclusion

We have developed a new catalytic intermolecular hydrophosphination of alkynes with the Yb-imine complex **1** to give alkenylphosphines in high yields. The mechanistic study indicated that insertion of alkynes to the dimeric Yb-phosphido species generated from **1** and Ph_2PH was a rate-determining step. After complete consumption of the phosphine, the Yb-diamido species was formed in the final stage of the catalytic cycle. Thus, the imine complex **1** could be categorized as a base catalyst similar to $Yb(btsa)_n$, and it exhibited far higher activity than conventional bases such as *t*BuOK and RLi. When $Ph_2P–SiMe_3$ was used instead of Ph_2PH, silylphosphination of aromatic internal alkynes and isoprene took place in moderate yields. Moreover, 1-diphenylphosphino-1,3-butadienes were synthesized from terminal alkynes and the phosphine in one-pot reaction through dimerization of the alkynes and subsequent hydrophosphination using $Y(btsa)_3$ catalyst.

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