Ytterbium(II)-Aromatic Imine Dianion Complexes-Catalyzed Isomerization of Terminal Alkynes

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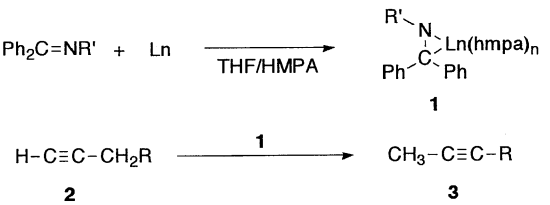
Ytterbium-aromatic imine dianion complexes, easily prepared from ytterbium metal and aromatic imines, can act as effective catalysts for the isomerization of terminal alkynes to afford internal alkynes in good to high yields.

Characteristic chemical properties of lanthanoid compounds have enabled the various transformations of organofunctional groups.[1] Our research has demonstrated that cationic carbonyl carbon of diaryl ketones becomes anionic by the treatment of diaryl ketones with ytterbium metal and that the ytterbium(II)-diaryl ketone dianion complexes, thus formed, react with electrophiles to afford corresponding adducts.[2] The dianion complex $[Yb(Ph_2CO)(hmpa)_2]_2$ has been successfully isolated and characterized by X-ray analysis.[3] We have also reported that the ytterbium-diaryl thioketone complex, which can be produced by the similar umpolung of thiocarbonyl carbon of diaryl thioketones with ytterbium, can be converted to diarylmethane by the desulfurization, tetraarylethenes by the desulfurizative homocoupling, and adducts by the treatment with electrophiles.[4] The same methology has been applied to aromatic imines, and α-amino acids can be obtained by the reaction of ytterbium-triarylimine complex with carbon dioxide.[5] In the continuous study on application of these dianionic complexes as catalysts toward organic reactions, we have found that terminal alkynes are irreversibly isomerized to internal ones, under the mild conditions in the presence of catalytic amounts of lanthanoid-triarylimine dianionic complexes (Scheme 1).



Scheme 1.

In the presence of a catalytic amount (10 mol%) of ytterbium-Ph_2CNPh complex (**1a**),[6,7] 1-hexyne (**2a**) was isomerized to 2-hexyne (**3a**) in 89% yield (rt, 17 h). It is interesting that only **3a** was obtained but neither 1,2- nor 2,4-hexadiene was produced.[8] In addition, **3a** can be isolated by trap-to-trap distillation of the reaction mixture and the similar treatment of the residue with an additional equimolar amount of **2a** causes the similar isomerization again, to give **3a** in 99%. Similar results were afforded by the repeated treatments of the residue with **2a**. Thus the catalytic system is reusable, when kept free from oxygen and moisture.

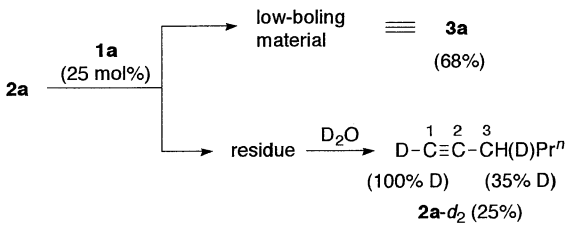
Table 1. Isomerization reactions of 1-hexyne (**2a**) catalyzed by Yb-imine complexes **1**[a]

Run	Lanthanoid-imine complex	R'	Ln	Yield of **3a** / %[b]
1	**1a**	Ph	Yb	89
2	**1b**	Ph	Sm	83
3	**1c**	C_6H_4Me-*p*	Yb	88
4	**1d**	C_6H_4Cl-*p*	Yb	85
5	**1e**	$C_6H_3Me_2$-*o,o'*	Yb	10
6	**1f**	$C_6H_3Pr^i_2$-*o,o'*	Yb	0
7	**1g**	CH_2Ph	Yb	0
8	**1h**	H	Yb	0

[a]Conditions: **1** (0.25 mmol); HMPA (1.0 mmol); **2a** (2.5 mmol); rt; 17 h. [b]GC yield.

Table 1 summarizes the results of the isomerization reaction of **2a** by various lanthanoid-aromatic imine complexes. *N*-Aryl ketimine dianionic complexes **1a-d** caused the isomerization of **2a**, and **1a** showed the best result (entries 1-4). Samarium can be used instead of ytterbium (entry 2). Electronic factor of substituents on aromatic ring does not seem to influence the reactivity, but isomerization is ceased in case of **1e** or **1f** having methyl or isopropyl groups on *o,o'*-ArN carbons (entries 3-6). *N*-benzyl ketimine or benzophenoneimine dianion complexes **1g** and **1h** result in a recovery of **2a** (entries 7 and 8). Ytterbium-benzophenone complex $[Yb(Ph_2CO)(hmpa)_2]_2$ does not work. In the reaction of **2a** catalyzed by **1a** (10 mol%), only HMPA is effective and isomerization did not occur in the presence of additives such as 1,3-dimethyl-2-imidazolidinone (DMI) and pyridine. From these results, one can conclude that the existence of an aryl group on the imine nitrogen atom and HMPA as an additive is essential to bring about the reaction.

It seems that the active species of the isomerization is a ytterbium monoacetylide formed by the reaction of **1** with an equimolar amount of **2** from the following experiments. After the isomerization of **2a** catalyzed by **1** (25 mol%), the low-boiling material was separated by trap-to-trap distillation, and



Scheme 2.

Table 2. Isomerization reactions of 1-hexyne (**2a**) catalyzed by Yb-imine complex **1a**[a]

Run	2	R	3	Yield / %[b]
1	**2a**	Pr^n	**3a**	89
2	**2b**	Pen^n	**3b**	89
3	**2c**	$(CH_2)_3CCH$	**3c**	89[c]
4	**2d**	$(CH_2)_2OSiPr^i_3$	**3d**	63[d]
5	**2e**	$(CH_2)_2OSiMe_2Bu^t$	**3e**	67[d]
6	**2f**	$(CH_2)_2OSiMe_3$	**3f**	39[d]
7	**2g**	$(CH_2)_3CCSiMe_2Bu^t$	**3g**	78[d]
8	**2h**	$(CH_2)_3CCSiMe_3$	**3h**	25[d,e]

[a]Conditions: **1a** (0.25 mmol); HMPA (1.0 mmol); **2** (2.5 mmol); rt; 17 h. [b]GC yield. [c]The product is 2,6-octadiyne. [d]Used **1a** (0.50 mmol) and HMPA (2.0 mmol). [e]1,8-Bis(trimethylsilyl)-1,7-octadiyne was also formed in 24% yield.

the residue was treated with D_2O. In the case of the reaction catalyzed by **1a**, using HMPA as an additive, the low-boiling material was only **3a** (68%), and completely C1- and partly (35%) C3-deuteriated $DC{\equiv}CCH(D)Pr^n$ was obtained in 25% (1 equivalent to **1a**) yield as shown in Scheme 2. These results indicate that the ytterbium monoacetylide A should be formed by the reaction of **1a** with 1 equiv of **2a**. The nitrogen anion of A would be stabilized with the phenyl group and still exist without reacting with another molecule of **2a**. Thus A would cause the abstraction of the propargyl proton of the acetylide moiety in another molecule of A to afford $Ph_2CHNHPh$ and the bimetallic intermediate B, which would lead to production of **3a** through allenyl- and propargyl anion-ytterbium.[8]

$(Ph_2CH)PhNPhYb(C{\equiv}CCH_2Pr^n)L_n$ (A)

$L_nYb-C{\equiv}C-\underset{|}{C}HPr^n$
$^nPrHC-C{\equiv}C-YbL_n$ (B)

The isomerization of various terminal alkynes **2** was also performed by using the catalyst **1a** (Table 2). Non-functionalized alkynes **2a** and **2b**, and 1,7-octadiyne (**2c**) were smoothly converted to corresponding **3a-c** in good yields (entries 1-3). Trialkylsilyl-protected 4-pentyn-1-ol **2d-f** readily isomerized to 3-pentyn-1-ol derivatives **3d-f** and the yields seem to be higher as those trialkylsilyl groups become sterically larger (entries 4-6). The similar tendency was observed in the reactions of 1-trialkylsilyl-1,7-octadiyne **2g** and **2h**; the former reaction is selective to give **3g** in 78% yield (entry 7) whereas **3h** was afforded in a low yield (25%) because of the formation of 1,8-bis(trimethylsilyl)-1,7-octadiyne (24%) as a byproduct (entry 8). The starting alkyne was quantitatively recovered in the reaction of internal alkyne **3a** and no other hydrocarbons derived from **3a** was obtained. Thus the isomerization of terminal alkynes is irreversible.

In summary, ytterbium-aromatic imine dianionic complexes **1** cause the isomerization of terminal alkynes **2** to internal ones **3**. As the most of the isomerization reactions catalyzed by base catalysts, for example sodium alkoxides and potassium *tert*-butoxide/dimethylsulfoxide, have been documented to be reversible and afford 1,2- and/or 2,4-dienes as byproducts,[8] the ytterbium-imine complex could be a useful catalytic system for the isomerization of terminal alkynes for their higher selectivity and mild reaction conditions. Further synthetic application of **1** is now underway.

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References and Notes

1 a) Imamoto, T. "Lanthanides in Organic Synthesis," Academic Press, London (1994), p. 21. b) Y. Fujiwara, K. Takaki, and Y. Taniguchi, *J. Alloys Compd.*, **192**, 200 (1993).

2 a) Z. Hou, K. Takamine, K. Aoki, O. Shiraishi, Y. Fujiwara, and H. Taniguchi, *J. Org. Chem.*, **53**, 6077 (1988). b) K. Takaki, S. Tanaka, F. Beppu, Y. Tsubaki, and Y. Fujiwara, *Chem. Lett.*, **1991**, 203. c) Y. Makioka, M. Tsuno, K. Takaki, Y. Taniguchi, and Y. Fujiwara, *Chem. Lett.*, **1995**, 821.

3 a) Z. Hou, H. Yamazaki, Y. Fujiwara, and H. Taniguchi, *Organometallics*, **11**, 2711 (1992). b) Z. Hou, H. Yamazaki, K. Kobayashi, Y. Fujiwara, and H. Taniguchi, *J. Chem. Soc., Chem. Commun.*, **1992**, 722.

4 a) Y. Makioka, S. Uebori, M. Tsuno, Y. Taniguchi, K. Takaki, and Y. Fujiwara, *Chem. Lett.*, **1994**, 611. b) Y. Makioka, M. Tsuno, S. Uebori, Y. Taniguchi, K. Takaki, and Y. Fujiwara, *J. Org. Chem.*, **61**, 372 (1996).

5 a) K. Takaki, Y. Tsubaki, S. Tanaka, F. Beppu, and Y. Fujiwara, *Chem. Lett.*, **1990**, 203. b) K. Takaki, S. Tanaka, and Y. Fujiwara, *Chem. Lett.*, **1991**, 493.

6 Typical procedure for the isomerization of **2a** to **3a** is as follows. Ytterbium (43 mg, 0.25 mmol) and *N*-diphenylmethylideneaniline (64 mg, 0.25 mmol) were placed under argon. Then THF (0.5 mL), HMPA (179 mg, 1.0 mmol), and MeI (to activate the surface of ytterbium, 0.5 μL) were added successively. The mixture was stirred for 4 h to give red crystals of **1a**. After the removal of THF *in vacuo*, **2a** (205 mg, 2.5 mmol) was slowly added, and the mixture was stirred for 17 h. The isomerized alkyne **3a** (182 mg, 2.23 mmol, 89%) was obtained in by trap-to trap distillation of the mixture *in vacuo*.

7 The ^1H and ^{13}C NMR spectra of the ytterbium-aromatic imine dianioni complex **1a** showed: ^1H NMR (THF-d_8/HMPA) δ 5.52 (1 H, t, J = 6.8 Hz), 5.58 (2 H, t, J = 7.7 Hz), 5.82 (1 H, d, J = 6.8 Hz), 6.30 (1 H, t, J = 6.8 Hz), 6.35 (1 H, d, J = 6.8 Hz), 6.42 (4 H, t, J = 7.7 Hz), 6.56 (1 H, t, J = 6.8 Hz), 6.95 (4 H, d, J = 7.7 Hz); ^{13}C NMR (THF-d_8/HMPA) δ 94.2, 105.1, 107.3, 112.8, 116.3, 117.9, 127.4, 128.6, 128.9, 143.4, 162.0.

8 L. Brandsma, "Preparative Acetylenic Chemistry," Elsevier, Amsterdam (1971), p. 143.