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Isomerization of terminal alkynes catalyzed by ytterbium(II)-aromatic imine complexes

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Summary — Ytterbium-aromatic imine dianion complexes **2**, wich can easily be prepared from metallic ytterbium and aromatic imines **1**, can act as effective catalysts for the isomerization of terminal alkynes **3** under mild conditions to afford internal alk-2-ynes **4** in good yields. In the reaction of 1-hexyne **3a**, 2-hexyne **4a** can be simply obtained by trap-to-trap distillation and the catalytic system can be reused for the isomerization of **3a** without other treatments.

lanthanoid-imine complex / terminal alkyne / isomerization / alk-2-yne

Résumé — Isomérisation d'alcynes vrais par des complexes d'ytterbium II d'imines aromatiques. Les complexes d'ytterbium II de dianions d'imines aromatiques **2**, préparés facilement à partir d'ytterbium métallique et des imines aromatiques **1**, peuvent agir comme des catalyseurs efficaces pour l'isomérisation d'alcynes vrais **3**, dans des conditions douces, conduisant aux 2-alcynes **4** avec de bons rendements. Dans la réaction de l'hex-1-yne **3a**, l'hex-2-yne **4a** peut être simplement obtenu par simple distillation directe et le système catalytique peut être réutilisé pour l'isomérisation de **3a** sans autres traitements.

complexe lanthanide-imine / alcyne vrai / isomérisation / 2-alcyne

Introduction

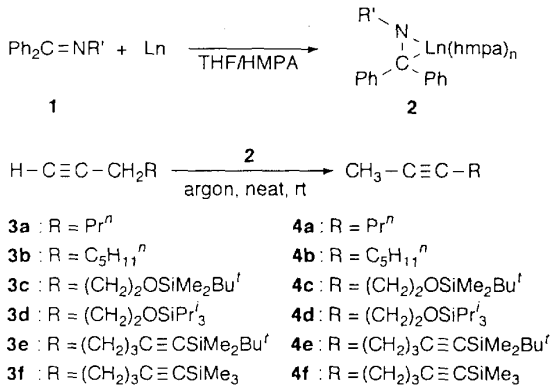
Much attention has been paid to the characteristic reactivities of lanthanoids and many synthetic reactions have been established by using lanthanoid reagents and catalysts for the last 15 years [1]. Especially, metallic samarium and ytterbium are stable and can be handled in open air and have been used as starting materials for divalent lanthanoid compounds such as lanthanoid(II) halides [2], bis(cyclopentadienyl)lanthanoid(II) derivatives [3], and lanthanoid(II) thiolates [4].

We have studied the chemistry of lanthanoid(II)-ketone derivative complexes and we have found unique chemical properties leading to various synthetic reactions. For example, metallic ytterbium causes the umpolung [5] of the cationic carbonyl carbon into anionic and affords ytterbium-diaryl ketone dianionic complexes [6], one of which is isolated and structurally characterized by X-ray analysis [7]. These ketone moieties in the complexes react with ketone epoxides, esters, and carbon dioxide to provide unsymmetrical pinacols, 1,3-diols, α-hydroxyketones, and α-hydroxycarboxylic acids, respectively. In addition, a μ-oxo-μ-alkylidene complex is generated by further treatment of ytterbium-diaryl ketone with excess metallic ytterbium via a reductive C–O bond cleavage [7a]. Similarly diaryl thioketone–ytterbium intermediates are formed from the reaction of diaryl thioketone and metallic ytterbium, and each diarylmethanethiol, diarylmethane, or tetraarylethene can be selectively obtained by proper treatment of the intermediates [8]. *C,C*-diarylimines are also reduced with metallic ytterbium to generate ytterbium-imine complexes **2**, which afford α-amino acids by reacting with carbon dioxide [9]. We have studied the application of those ytterbium-imine complexes as catalysts of organic reactions and found that catalytic amounts of ytterbium-imine complexes **2** cause isomerization of terminal alkynes **3** into alk-2-ynes **4** (scheme 1). Here we report these results.

Results and discussion

The results of the isomerization of 1-hexyne **3a** in the presence of catalytic amounts (10 mol%) of various lanthanoid-imine complexes **2**, prepared in situ from metallic ytterbium and imines **1**, are summarized in table I. In the case of ytterbium–$Ph_2C{=}NPh$ complex **2a**, 2-hexyne **4a** was obtained in 89% yield (entry 1). Samarium can be used instead of ytterbium to afford **4a** in 83% yield (entry 2). With respect to the substituent of the nitrogen atom of the imine moiety, phenyl- and

* Correspondence and reprints



Scheme 1

p-Me and Cl substituted phenyl groups showed good results (entries 1–4) whereas bulkiness of the substituent of *o,o'*-carbons in the aromatic ring suppressed the catalytic activity on the isomerization (entries 5 and 6). *N*-Benzylimine (entry 7) and benzophenone imine complexes (entry 8) were inactive towards isomerization. In addition, the ytterbium–benzophenone dianionic complex $[Yb(Ph_2CO)(HMPA)_2]_2$ [7] did not work.

Table I. Isomerization of 1-hexyne **3a** catalyzed by lanthanoid-imine complex **2**[a].

Entry	*Imine* **1**	*R'*	*Ln*	*Complex* **2**	*Yield of* **4a**[b] *(%)*
1	**1a**	Ph	Yb	**2a**	89
2	**1b**	Ph	Sm	**2b**	83
3	**1c**	C_6H_4Me-*p*	Yb	**2c**	88
4	**1d**	C_6H_4Cl-*p*	Yb	**2d**	85
5	**1e**	$C_6H_3Me_2$-*o,o'*	Yb	**2e**	10
6	**1f**	$C_6H_3Pr^i_2$-*o,o'*	Yb	**2f**	0
7	**1g**	Bn	Yb	**2g**	0
8	**1h**	H	Yb	**2h**	0

[a] Conditions: Yb (0.25 mmol); **1** (0.25 mmol); HMPA (1.0 mmol); **3a** (2.5 mmol); room temperature; 17 h. For the preparation of **2**, see the experimental section. [b] GC yield.

It is noteworthy that the additive which exists in the catalytic system determines whether the isomerization proceeds or not: only hexamethylphosphoramide (HMPA) is effective among these additives investigated. In the reaction of **3a** as described under entry 1 in table I, the presence of other additives like 1,3-dimethyl-2-imidazolidinone (DMI), *N,N,N',N'*-tetramethylurea, pyridine, and *N,N,N',N'*-tetramethylethylenediamine (TMEDA) instead of HMPA did not cause isomerization. With respect to the amount of HMPA, 1 and 2 equiv of HMPA to **2a** gave inferior yields; 41 and 67% respectively. On the other hand, **4a** was provided in 89 and 88% yields respectively when 8 and 16 equiv of HMPA were used. Thus it is found that not less than 4 equiv to **2a** are necessary to obtain the product **4a** in high yield. In the reaction of **3a** (2.5 mmol) catalyzed by **2a** (10 mol%) using HMPA, addition of 0.5 mL of solvents such as THF, toluene, and *n*-hexane suppressed the yield; only 23, 7, and 6% of **4a** were obtained respectively when the reaction time was limited to 2 h whereas **4a** was afforded in 75% yield in the absence of these solvents. However, in the 17 h reaction the yields were 86% (THF), 87% (toluene), and 86% (*n*-hexane) respectively.

Table II shows the effect of the amount of **2a** on the yield of **4a** in the isomerization reaction of **3a**. The highest yield of **4a** was obtained when 10 mol% of **2a** was used (entry 4) and, interestingly, the yield decreased as the amount of **2a** was increased (entries 1–3). The isomerized alk-2-yne **4a** was obtained in only 66% yield when 5 mol% of **2a** was used (entry 5), however, the yield was improved (95%) by adding 4 equiv of HMPA to the catalyst (entry 6). The effect of adding HMPA is to enhance the polarity of the reaction mixture. In fact, addition of 4 equiv of DMI, which was itself ineffective to the isomerization, instead of HMPA gave almost the same results (entry 7). However, **4a** was not obtained in the presence of only 1 mol% of **2a**, even if those polar additives were added (entries 8 and 9).

Table II. Effect of the amount of ytterbium–imine complex **2a** on the isomerization of 1-hexyne **3a**[a].

Entry	***1a*** *(mol%)*	*Yield of* **4a**[b] *(%)*
1	100	28
2	50	60
3	25	78
4	10	89
5	5	66
6	5[c]	95
7	5[d]	91
8	1	0
9	1[c]	0

[a] Complex **2a** was prepared in situ using Yb (0.25 mmol), imine **1a** (0.25 mmol), and HMPA (1.0 mmol) and the isomerization of **3a** was carried out using **2a** thus formed, at room temperature for 17 h. [b] GC yield. [c] Added further 4 equiv of HMPA to **2a**. [d] Added 4 equiv of DMI.

The isomerization reaction of various terminal alkynes **3** catalyzed by the ytterbium-imine complex **2a** has been carried out (table III). Simple alkynes **3a** and **3b** underwent isomerization to internal alkynes **4a** and **4b** in high yields (entries 1 and 2). On the other hand, the starting alkyne was quantitatively recovered in the reaction of internal alkynes **4a** (entry 3). Reaction of alkyne **3c** having *tert*-butyldimethylsilyloxy group, afforded the isomerized product **4c**, however, the yield was moderate (entry 4). Using 20 mol% of **2a** improved the yield of **4c** to 67% (entry 5). Similar results were obtained in the reaction of **3d** (entries 6 and 7). In the reaction of monosilylated bisalkyne **3e**, the desired **4e** was obtained in 78% yield (entry 8). On the contrary, **4f** was obtained in 25% yield only together with 1,8-bis(trimethylsilyl)-1,7-octadiyne **5f** (24%) as a byproduct when **3f** was reacted (entry 9). The hydrogen-silyl exchange of terminal alkynes was observed in the reaction of **3b** and 1-trimethylsilyl-1-hexyne **5a** to afford **4b** (42%), 1-trimethylsilyl-1-octyne **5b** (43%), **3a** (10%), and **4a** (34%), but silicon-alkynyl carbon fission did not occur in the reaction of **2a** with 1-trimethylsilyl-1-hexyne in the

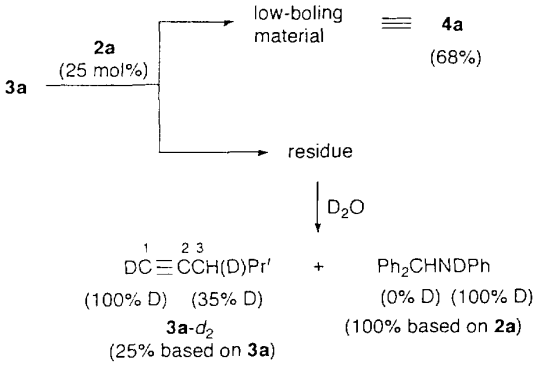
presence of HMPA additive. These results show that the exchange takes place between alkynylytterbium, formed in situ, and alkynylsilane moiety in the substrate. The reaction of the terminal alkynes such as ethyl 4-pentynoate **3g**, 4-cyano-1-butyne **3h**, and 1-(*tert*-butyldimethylsilyl)-2-propyne **3i** resulted in a recovery of the starting **3**.

Table III. Isomerization of various terminal alkynes **3** catalyzed by the complex **2a**[a].

Entry	*Alkyne*	**2a** *(mol%)*	*Product*	*Yield*[b] *(%)*
1	**3a**	10	**4a**	89
2	**3b**	10	**4b**	89
3	**4a**	10	–[c]	–
4	**3c**	10	**4c**	59
5	–	20	**4c**	67
6	**3d**	10	**4d**	34
7	–	20	**4d**	63
8	**3e**	20	**4e**	78
9	**3f**	20	**4f**	25[d]

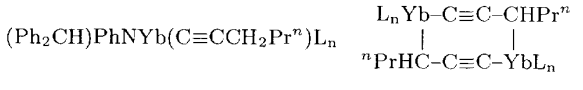
[a] Conditions: Yb (0.25 mmol); **1** (0.25 mmol); HMPA (1.0 mmol); room temperature; 17 h. [b] GC yield. [c] The starting **4a** was recovered quantitatively. [d] 1,8-Bis(trimethylsilyl)-1,7-octadiyne **5f** was also formed in 24% yield.

To investigate the active species of the isomerization, the following control experiment was performed. After the reaction of **3a** catalyzed by 25 mol% of **2a** in the presence of HMPA additive, the low-boiling material was evaporated in vacuo, and the residue was quenched with D_2O as shown in scheme 2. It was revealed that the low-boiling material was pure **4a** (68% isolated yield), which was formed by the isomerization of **3a** with **2a**. From the residue treated with D_2O, deuterated **3a** was obtained in 25% yield. Interestingly, the alkynyl proton was completely deuterated whereas only 35% D was incorporated at the propargylic carbon. Moreover, the imine carbon of the imine dianion was not deuterated although *N*-(diphenylmethyl)aniline was obtained quantitatively.



Scheme 2

These results indicate that the ytterbium monoacetylide **A** should be formed by the reaction of **2a** with 1 equiv of **3a**. The nitrogen anion of **A** would be stabilized with the phenyl group and still exists without reacting with another molecule of **3a**. 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** or other oligomers, which would lead to production of **3a** through allenyl- and propargyl anion-ytterbium [10a].



A B

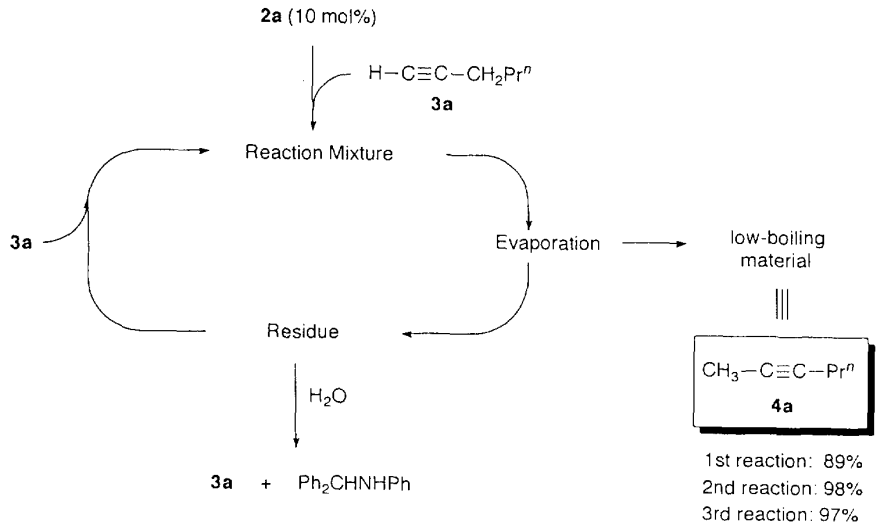
The information obtained also suggests that **3a**, the recovered alk-1-yne after the treatment of the mixture with H_2O or D_2O, exists as the ytterbium acetylides **A** and **B** when the reaction is completed, and that **4a** may exist as a free alk-2-yne. In fact, **4a** could be isolated by simple trap-to-trap distillation from the mixture after the reaction of **3a** with 10 mol% of **2a** at room temperature for 17 h (1st reaction in scheme 3). It is interesting that the isomerization reaction again proceeds by adding **3a** to the residue to afford **4a** in almost quantitative yields under similar conditions (second and third runs in scheme 3). Thus the catalytic system is reusable, when kept free from oxygen and moisture.

In conclusion, the ytterbium-imine dianionic complexes have been found to act as effective catalysts in the isomerization reaction of terminal alkynes to afford alk-2-ynes in good yields. Since most of the isomerization reactions or terminal alkynes catalyzed by base catalysts, for example sodium alkoxides and potassium *tert*-butoxide/dimethyl sulfoxide, have been documented to be reversible and to afford 1,2- and/or 2,4-dienes as byproducts [10], the present ytterbium-imine complex catalyst should be useful for the isomerization of terminal alkynes due to their higher selectivity and mild reaction conditions [11]. In addition, the chemical behavior is quite different from that of group 4 transition-metal–imine complexes which undergo the addition of imine carbon to alkynes [12]. Although there have been many lanthanoid-catalyzed reactions, this is the first example of isomerization of terminal alkynes by lanthanoid–imine complex catalysts [13]. Further synthetic application of **2** is presently being investigated.

Experimental section

All melting points were measured on a Yanagimoto micro melting point apparatus, and uncorrected. IR spectra were recorded on Perkin-Elmer 1600-FTIR and HITACHI 260-30 spectrometers. ^{1}H- and ^{13}C-NMR spectra were obtained on a JEOL JNM-EX270 (270 MHz) spectrometer, and chemical shifts were reported in parts per million on the δ scale from tetramethylsilane. GC analyses were performed on a Shimadzu GC-14B equipped with a FID by using 1 m × 3.2 mm id column of 5% Silicon OV-17 on 60–80 mesh Uniport HP. Peak areas were obtained on a Shimadzu Chromatopac C-R5A. Mass spectra were obtained on a Shimadzu GC-MS QP1000 at 70 eV by using 1 m × 3.2 mm id column of 2% Silicon OV-17 on 60–80 Uniport HP. Elemental analyses were performed on a Yanagimoto MT-2 CHN corder.

Materials were used without further purification unless stated otherwise. THF, toluene, *n*-hexane were dried



Scheme 3

and deoxygenated over benzophenone ketyl under argon and distilled prior to use. HMPA, DMI, *N,N,N',N'*-tetramethylurea, pyridine, and TMEDA were dried over calcium hydride and distilled. Ytterbium (40-mesh, Shiga Rare Metal) and samarium (20-mesh) were washed with *n*-hexane, dried in vacuo. Imines **1a–h** [14], terminal alkynes **3g** [15], **3h** [16], and **3i** [17] were obtained according to the literature method.

Preparation of 1-[(tert-Butyldimethylsilyl)oxy]-4-pentyne ***3c***

In a round-bottomed flask containing a solution of 4-pentyn-1-ol (5.0 g, 60 mmol) and *tert*-butyldimethylchlorosilane (60 mmol) were added triethylamine (6.1 g, 60 mmol) and 4-(dimethylamino)pyridine (56 mg, 0.45 mmol). The mixture was stirred for one day at room temperature and filtered off. The filtrate was diluted with 300 mL of ether and washed with 2 N aqueous NH_4Cl (200 mL) and saturated aqueous NaCl (200 mL). The organic layer was dried over anhydrous Na_2SO_4. After the solvent was evaporated in vacuo, the silylated product **3c** was purified by distillation to give 9.1 g (46 mmol, 77%) yield as colorless liquid. Bp 42 °C/5 mmHg. This product was identified by comparison of its spectra with the reported data [18].

IR (neat): 2 120, 1 253 cm^{-1}.

^1H NMR ($CDCl_3$, 270 MHz): δ 0.09 (s, 6H), 0.89 (s, 9H), 1.72 (tt, J = 6.9, 6.9 Hz, 2H), 1.92 (t, J = 2.6 Hz, 1H), 2.27 (dt, J = 2.9, 6.9 Hz, 2H), 3.69 (t, J = 6.9 Hz, 2H).

^{13}C NMR ($CDCl_3$, 68 MHz): δ 5.1, 14.8, 18.3, 25.9, 31.5, 61.4, 68.2, 84.2.

MS (EI, 70 eV): m/z 141 ($M^+ - Bu^t$).

Synthesis of 1-[(Triisopropylsilyl)oxy]-4-pentyne ***3d***

Obtained in 3.6 g (15 mmol, 59%) yield in a similar manner from triisopropylchlorosilane in a 25 mmol scale as colorless liquid. Bp 82 °C/3 mm Hg.

IR (neat): 2 121, 1 247, 1 110 cm^{-1}.

^1H NMR ($CDCl_3$, 270 MHz): δ 1.01–1.13 (m, 21H), 1.75 (tt, J = 6.2, 7.0 Hz, 2H), 1.92 (t, J = 2.6 Hz, 1H), 2.31 (dt, J = 2.9, 7.0 Hz, 2H), 3.77 (t, J = 6.2 Hz, 2H).

^{13}C NMR ($CDCl_3$, 68 MHz): δ 12.0, 14.9, 18.0, 31.8, 61.7, 68.1, 84.2.

MS (EI, 70 eV): m/z 198 ($M^+ - Pr^i$).

Anal calc for $C_{14}H_{28}OSi$: C, 69.93; H, 11.74. Found: C, 69.93; H, 11.51.

Preparation of 1-(tert-Butyldimethylsilyl)-1,7-octadiyne ***3e***

A solution of ethyl bromide (5.45 g, 50 mmol) in THF (40 mL) was added dropwise to a mixture of magnesium turnings (1.2 g, 50 mmol) and THF (20 mL) in a round-bottomed flask. To the resulting solution, 1,7-octadiyne (6.4 mL, 50 mmol) and THF were slowly added at 0 °C. Then a solution of (*tert*-butyldimethyl)chlorosilane (7.4 g, 50 mmol) in THF (30 mL) was added, and the mixture was stirred for 30 min. The clean solution was treated with saturated aqueous NH_4Cl (20 mL) followed by adding of anhydrous $MgSO_4$ (20 g). The mixture was filtered off and concentrated in vacuo. The desired 1-(*tert*-butyldimethylsilyl)-1,7-octadiyne **3e** was purified by distillation to give in 4.4 g (20 mmol, 40%). Bp 70 °C/3 mm Hg.

IR (neat): 2 173, 1 250 cm^{-1}.

^1H NMR ($CDCl_3$, 270 MHz): δ 0.07 (s, 6H), 0.92 (s, 9H), 1.64 (m, 4H), 1.94 (t, J = 2.6 Hz, 1H), 2.22 (m, 4H).

^{13}C NMR ($CDCl_3$, 68 MHz): δ −4.5, 16.5, 17.9, 19.3, 26.1, 27.5, 27.6, 68.4, 81.2, 84.1, 107.4.

MS (EI, 70 eV): m/z 163 ($M^+ - Bu^t$).

Anal calc for $C_{14}H_{24}Si$: C,76.28; H, 10.97. Found: C, 76.63; H, 11.15.

Synthesis of 1-Trimethylsilyl-1,7-octadiyne ***3f*** *[19]*

Obtained in 4.5 g (25 mmol, 50%) in a similar method from trimethylchlorosilane (6.4 mL, 50 mmol) as colorless liquid. Bp 117 °C/30 mm Hg.

IR (neat): 2 160, 2 105, 1 238 cm^{-1}.

^1H NMR ($CDCl_3$, 270 MHz): δ 0.07 (s, 9H), 1.56–1.59 (m, 4H), 1.88 (t, J = 2.6 Hz, 1H), 2.14–2.18 (m, 4H).

Preparation of 1-Trimethylsilyl-1-hexyne ***5a*** *[20]*

Obtained in 5.5 g (36 mmol, 71%) in a similar method from trimethylchlorosilane (6.4 mL, 50 mmol) and **3a** (4.1 g, 50 mmol) as colorless liquid. Bp 63 °C/25 mm Hg.

IR (neat): 2 255, 1 238 cm^{-1}.

^1H NMR ($CDCl_3$, 270 MHz): δ 0.13 (s, 9H), 0.90 (t, J = 7.3 Hz, 3H), 1.35–1.52 (m, 4H), 2.21 (t, J = 6.9 Hz, 2H).

^{13}C NMR ($CDCl_3$, 68 MHz): δ 0.1, 13.6, 19.5, 21.9, 30.7, 84.2, 107.7.

MS (EI, 70 eV): m/z 139 (M^+ – Me).

General procedure for isomerization of terminal alkynes **3** *catalyzed by the lanthanoid–imine complex* **2**

All reactions were carried out under argon. THF (0.5 mL), HMPA (179 mg, 1.0 mmol), and methyl iodide (0.5 μL) were successively added into a Schlenk tube containing a lanthanoid metal (0.25 mmol) and an aromatic imine **1** (0.25 mmol), and the mixture was stirred at room temperature for 4 h to give lanthanoid–imine complex **2** [21]. After THF was removed in vacuo, a proper amount of terminal alkyne **3** was added, and the mixture was stirred for a proper period. The resulting mixture was treated with H_2O (0.1 mL). Yields of products were determined by GC. The alk-2-yne **4** was isolated by trap-to-trap distillation or column chromatography (SiO_2, *n*-hexane/diethyl ether = 100:1).

• *2-Hexyne* **4a**

Obtained in 89% yield from **3a** as colorless liquid. This compound was identified by comparison of its IR and ^1H- and ^{13}C-NMR spectra with those of an authentic sample commercially available.

IR (neat): 2 070 cm^{-1}.

^1H NMR ($CDCl_3$, 270 MHz): δ 0.97 (t, J = 7.3 Hz, 3H), 1.50 (m, 2H), 1.78 (t, J = 2.6 Hz, 3H), 2.10 (tq, J = 7.3, 2.6 Hz).

^{13}C NMR ($CDCl_3$, 68 MHz): δ 3.3, 13.4, 20.7, 22.5, 75.4, 79.1.

MS (EI, 70 eV): m/z 82 (M^+).

• *2-Octyne* **4b**

Obtained in 89% yield from **3b** as colorless liquid. This compound was identified by comparison of its IR and ^1H- and ^{13}C-NMR spectra with those of an authentic sample commercially available.

IR (neat): 2 140 cm^{-1}.

^1H NMR ($CDCl_3$, 270 MHz): δ 0.90 (t, J = 7.0 Hz, 3H), 1.27–1.34 (m, 4H), 1.43–1.50 (m, 2H), 1.78 (t, J = 2.6 Hz, 3H), 2.10 (tq, J = 6.9, 2.6 Hz, 2H).

^{13}C NMR ($CDCl_3$, 68 MHz): δ 3.4, 13.9, 18.7, 22.2, 28.8, 31.1, 75.2, 79.3.

MS (EI, 70 eV): m/z 110 (M^+).

• *1-[(tert-Butyldimethylsilyl)oxy]-3-pentyne* **4c**

Obtained in 67% yield from **3c** as colorless liquid, using Yb–imine complex **2a** as the catalyst prepared from Yb (0.5 mmol), **1a** (0.5 mmol), and HMPA (2.0 mmol).

IR (neat): 2 130, 1 242, 1 090 cm^{-1}.

^1H NMR ($CDCl_3$, 270 MHz): δ 0.08 (s, 6H), 0.90 (s, 9H), 1.77 (t, J = 2.5 Hz, 3H), 2.34 (tq, J = 7.2, 2.5 Hz, 2H), 3.69 (t, J = 7.2 Hz, 2H).

^{13}C NMR ($CDCl_3$, 68 MHz): δ –5.3, 3.4, 18.3, 23.1, 25.9, 62.3, 76.1.

MS (EI, 70 eV): m/z 141 (M^+ – Bu^t).

Anal calc for $C_{11}H_{22}OSi$: C, 66.60; H, 11.17. Found: C, 66.56; H, 10.93.

• *1-[(Triisopropylsilyl)oxy]-3-pentyne* **4d**

Obtained in 63% yield from **3d** as colorless liquid, using Yb–imine complex **2a** as the catalyst prepared from Yb (0.5 mmol), **1a** (0.5 mmol), and HMPA (2.0 mmol).

IR (neat): 2 172, 1 248, 1 107 cm^{-1}.

^1H NMR ($CDCl_3$, 270 MHz): δ 0.96–1.07 (m, 21H), 1.55 (t, J = 2.5 Hz, 3H), 2.37 (tq, J = 6.8, 2.5 Hz, 2H), 3.80 (t, J = 6.6 Hz, 2H).

^{13}C NMR ($CDCl_3$, 68 MHz): δ 11.3, 16.3, 18.6, 32.2, 63.1, 74.4, 80.1.

MS (EI, 70 eV): m/z 198 (M^+ – Pr^i).

Anal calc for $C_{14}H_{28}OSi$: C, 69.93; H, 11.74. Found: C, 70.00; H, 11.53.

• *1-(tert-Butyldimethylsilyl)-1,6-octadiyne* **4e**

Obtained in 78% yield from **3e** as colorless liquid, using Yb–imine complex **2a** as the catalyst prepared from Yb (0.5 mmol), **1a** (0.5 mmol), and HMPA (2.0 mmol).

IR (neat): 2 173, 1 250 cm^{-1}.

^1H NMR ($CDCl_3$, 270 MHz): δ 0.07 (s, 6H), 0.92 (9H, s), 1.69 (tt, J = 6.9, 7.3 Hz, 2H), 1.77 (t, J = 2.5 Hz, 3H), 2.21–2.27 (m, 2H), 2.33 (t, J = 7.1 Hz, 2H).

^{13}C NMR ($CDCl_3$, 68 MHz): δ –4.5, 3.5, 16.5, 17.6, 19.0, 26.1, 28.2, 68.4, 76.0, 83.0, 107.1.

MS (EI, 70 eV): m/z 163 (M^+ – Bu^t).

Anal calc for $C_{14}H_{24}Si$: C, 76.28; H, 10.97. Found: C, 76.04; H, 10.77.

• *1-Trimethylsilyl-2,6-octadiyne* **4f**

Obtained in 25% yield from **3f** as colorless liquid, using Yb–imine complex **2a** as the catalyst prepared from Yb (0.5 mmol), **1a** (0.5 mmol), and HMPA (2.0 mmol).

IR (neat): 2 150, 1 238 cm^{-1}.

^1H NMR ($CDCl_3$, 270 MHz): δ 0.18 (s, 9H), 1.67 (tt, J = 7.3, 7.3 Hz, 2H), 1.76 (t, J = 2.3 Hz, 3H), 2.19–2.26 (m, 2H), 2.31 (t, J = 7.3 Hz, 2H).

^{13}C NMR ($CDCl_3$, 68 MHz): δ 0.1, 3.4, 17.8, 19.0, 28.1, 76.1, 78.2, 84.9, 106.6.

MS (EI, 70 eV): m/z 163 (M^+ – Me), 73 (Me_3Si^+).

HRMS (EI, 20 eV) calc for $C_{11}H_{18}Si$: 178.1177. Found: 178.1202.

• *1,8-Bis(trimethylsilyl)-1,7-octadiyne* **5f** *[22]*

Obtained in 24% yield from **3f** as colorless liquid, using Yb–imine complex **2a** as the catalyst prepared from Yb (0.5 mmol), **1a** (0.5 mmol), and HMPA (2.0 mmol).

IR (neat): 2 160, 1 235 cm^{-1}.

^1H NMR ($CDCl_3$, 270 MHz): δ 0.14 (s, 18H), 1.61 (m, 4H), 2.24 (m, 4H).

^{13}C NMR ($CDCl_3$, 68 MHz): δ –0.3, 18.9, 27.2, 81.2, 106.6.

MS (EI, 70 eV): m/z 177 (M^+ – $SiMe_3$), 73 (Me_3Si^+).

Crossover experiment of 1-octyne **3b** *and 1-(trimethylsilyl)-1-hexyne* **5a** *in the presence of the ytterbium–imine complex* **2a**

After the preparation of **2a** from ytterbium (43 mg, 0.25 mmol), **1a** (64 mg, 0.25 mmol), and HMPA (179 mg, 1.0 mmol) as expressed in the general procedure, 1-trimethylsilyl-1-hexyne **5a** and 1-octyne **3b** were added, successively. The reaction mixture was stirred for 17 h and treated with 0.1 mL of H_2O. The products were analyzed by GC to find that **3a** (0.25 mmol, 10%), **4a** (0.85 mmol, 34%), **4b** (1.05 mmol, 42%), and **5b** (1.08 mmol, 43%) were formed. The authentic sample of **5b** was synthesized in a similar manner to **5a** from **3b** and trimethylchlorosilane.

• *1-(Trimethylsilyl)-1-octyne* **5b** *[23]*

IR (neat): 2 176, 1 249 cm^{-1}.

^1H NMR ($CDCl_3$, 270 MHz): δ 0.14 (s, 9H), 0.89 (t, J = 6.6 Hz, 3H), 1.29–1.54 (m, 8H), 2.21 (t, J = 6.9 Hz, 2H).

^{13}C NMR ($CDCl_3$, 68 MHz): δ 0.16, 14.0, 19.9, 22.5, 28.5, 28.6, 31.3, 84.2, 107.8.

MS (EI, 70 eV): m/z 167 (M^+ – Me), 73 (Me_3Si^+).

Evaporation of the reaction mixture and D_2O treatment of the residue obtained by the reaction of **3a** *and* **2a** *(25 mol%)*

After the reaction of **3a** (82 mg, 1.0 mmol) in the presence of **2a** prepared from ytterbium (43 mg, 0.25 mmol), **1a** (64 mg, 0.25 mmol), and HMPA (179 mg, 1.0 mmol) for 17 h, the low-boiling material was distilled in vacuo and trapped in a liquid N_2 bath. The trapped material was pure 2-hexyne **4a** (56 mg, 0.68 mmol). The residue flushed with argon was treated with D_2O (0.1 mL) and analyzed by ^1H NMR ($CDCl_3$, 250 MHz). The residue contained $Ph_2CHNDPh$ (0.25 mmol) and 1,3-dideuterio-1-hexyne (0.25 mmol), which was completely C1- and partly (35%) C3-deuteriated.

Reuse of the catalyst in the isomerization of **3a**

After the reaction of **3a** (82 mg, 1.0 mmol) in the presence of **2a** prepared from ytterbium (43 mg, 0.25 mmol), **1a** (64 mg, 0.25 mmol), and HMPA (179 mg, 1.0 mmol) for 17 h, the low-boiling material was distilled in vacuo and trapped in a liquid N_2 bath. The trapped material was pure 2-hexyne **4a** (182 mg, 89%). To the residue flushed with argon, **3a** (205 mg, 2.5 mmol) was added and the mixture was stirred for 17 h. The low-boiling material was again distilled and trapped to give **4a** in 200 mg (2.45 mmol, 98%) yield. A similar procedure afforded **4a** in 198 mg (2.43 mmol, 97%) yield.

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11 The isomerization of **3a** by 10 mol% of **2a** at room temperature for 2 h afforded **4a** and **3a** in 75 and 25%, respectively, but neither 1,2- nor 1,3-hexadiene has been detected on GC. In addition, no difference has been observed between 17 h (entry 1 in table III) and 40 h reactions. Thus the reaction time described in the text should be sufficient to complete the isomerization of **3a** and the catalytic reaction should kinetically proceed

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