Synthetic Methods

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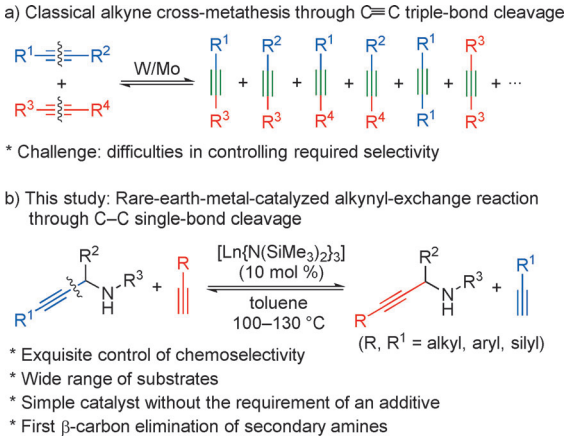
Lanthanide-Catalyzed Reversible Alkynyl Exchange by Carbon–Carbon Single-Bond Cleavage Assisted by a Secondary Amino Group

*Yinlin Shao, Fangjun Zhang, Jie Zhang, and Xigeng Zhou**

Abstract: *Lanthanide-catalyzed alkynyl exchange through C–C single-bond cleavage assisted by a secondary amino group is reported. A lanthanide amido complex is proposed as a key intermediate, which undergoes unprecedented reversible β-alkynyl elimination followed by alkynyl exchange and imine reinsertion. The in situ homo- and cross-dimerization of the liberated alkyne can serve as an additional driving force to shift the metathesis equilibrium to completion. This reaction is formally complementary to conventional alkyne metathesis and allows the selective transformation of internal propargylamines into those bearing different substituents on the alkyne terminus in moderate to excellent yields under operationally simple reaction conditions.*

The functionalization of unstrained carbon–carbon bonds is one of the most desirable reactions in organic synthesis. Alkyne metathesis has shown great promise over the past three decades for the synthesis of natural products, macrocycles, and polymers.[1,2] However, there have been many challenging issues in terms of the availability and performance of catalysts,[3] substrate compatibility,[4] and selectivity control.[5] In particular, the lack of predictability of selectivity in intermolecular alkyne cross-metathesis severely limits its practical use (Scheme 1 a). The development of a predictive model for cross-metathesis between two different alkynes is highly desired.

Metal-catalyzed β-carbon elimination and the retroallylation of secondary and tertiary alcohols as a strategy for the cleavage of unstrained C–C single bonds has been nicely applied in organic synthesis.[6–8] However, no such method for the C–C cleavage of primary and secondary amines has been reported, mainly owing to the more facile β-H elimination pathways available for metal amides[9] and the potential thermodynamic disadvantages. Currently, successful metal-catalyzed processes are limited to tertiary amines and β-carbon elimination.[10] Although alkoxide and amido complexes of early transition metals are quite common, they have been neglected for a long time as key intermediates in catalytic β-carbon elimination processes, possibly because of the general belief that C–C bond cleavage would be difficult owing to unfavorable M–C bond formation at the expense of a stronger M–O(N) bond.[6b] Herein, we report the first metal-catalyzed β-carbon elimination of secondary amines and its application in alkynyl exchange (Scheme 1 b).



Scheme 1. Alkyne cross-metathesis reactions.

Organolanthanide catalysis exhibits distinct performance when compared to transition-metal catalysis.[11–13] Thus, preliminary studies examined the feasibility of the lanthanide-catalyzed alkynyl exchange of propargylamines with terminal alkynes. It was found that the reaction of **2k** with **1a** in toluene in the presence of [Lu{N(SiMe$_3$)$_2$}$_3$] (**Lu-1**; 10 mol %) at 120–130 °C afforded the desired product **2a** in 85 % yield (see the Supporting Information).

Having optimized the reaction conditions, we proceeded to explore the utility of these conditions for transformations of different substrate combinations (Scheme 2). The treatment of various internal propargylamines with excess **1a** afforded **2a** in good to excellent yields, but the use of terminal propargylamine **2m** resulted in a low yield. Noticeably, the reaction of **2h** with **1a** gave a small amount of enyne by-products that resulted from dimerization of the liberated PhC≡CH with **1a**, or with itself,[14] along with the formation of **2a** in excellent yield, thus indicating that such a transformation of the liberated alkyne could potentially enable the amount of alkyne substrate used to be decreased and improve synthetic efficiency. However, the dimerization of aliphatic alkynes is much less facile under the current conditions. For example, only a trace amount enyne by-products was observed in the reaction of **1a** with **2d** (see Scheme S1 in the Supporting Information). A variety of other aliphatic alkynes, **1b–f**, reacted with internal propargylamines to give the corresponding alkynyl-exchange products in 52–97 % yield. The reaction of **2a** with **1e** also proceeded at 100 °C or

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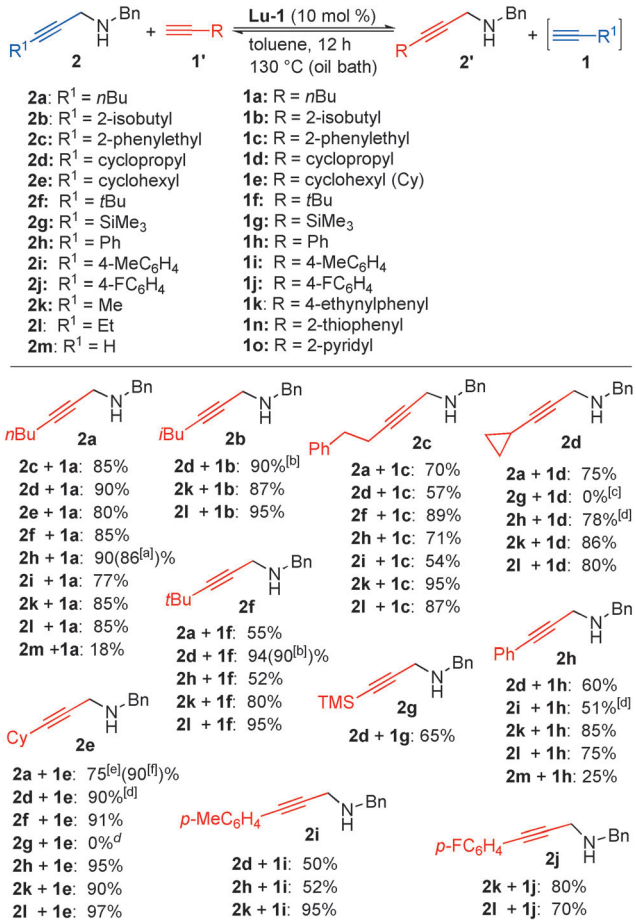


Scheme 2. Lutetium-catalyzed reversible alkynyl exchange of propargylamines with terminal amines. Reaction conditions: **1** (0.30 mmol), **2** (1.50 mmol), **Lu-1** (0.030 mmol), toluene (3 mL), sealed Schlenk tube equipped with a Teflon cap under N_2, 130 °C, 12 h. Yields are for the isolated product. [a] The reaction was carried out with 3 equivalents of **1**. [b] The reaction was carried out at 120 °C. [c] Recovery of **2g**. [d] The reaction was carried out with 10 equivalents of **1**. [e] The reaction was carried out with 2 equivalents of **1**. [f] The reaction was carried out at 100 °C for 48 h. Bn = benzyl, TMS = trimethylsilyl.

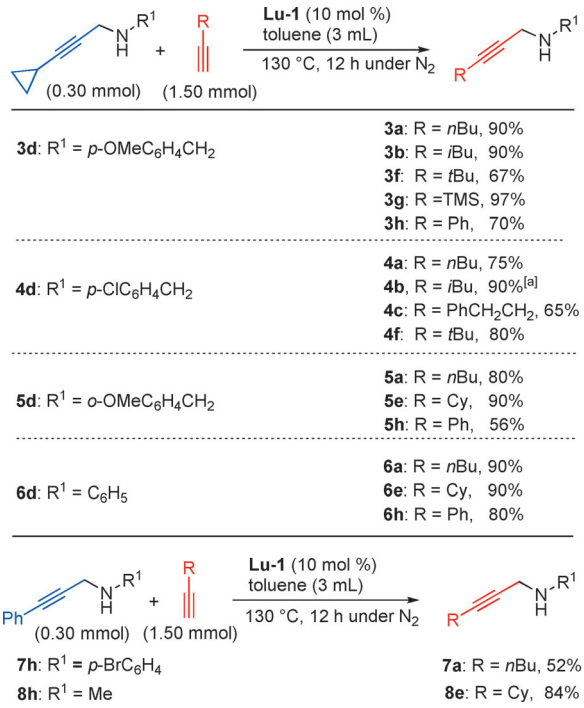
even with a substrate ratio of 1:2. Significantly, a cyclopropyl group survived the catalytic conditions, which is not possible in metal-catalyzed unstrained C–C single-bond cleavage by oxidative addition.[6,15] When **1g** was employed as a metathesis partner, the Me_3Si-substituted propargylamine **2g**, which is valuable as a precursor to terminal propargylamines[16a] and as a synthetic intermediate,[16b,c] was obtained in 65% yield. However, when **2g** was used as the substrate, the alkynyl exchange did not proceed under the same reaction conditions.

Aryl acetylenes underwent the transformation, but the yields varied depending on the propargylamine employed. The reactions of **1h–j** with internal propargylamines (**2d**, **2k**, **2l**, **2h**, and **2i**) gave **2h–j** in moderate to excellent yields. The major by-products formed in these reactions result from di- and oligomerization of the starting aryl acetylene (see Scheme S1), which will decrease the amount of alkynyl-exchange products or suppress the alkyne-exchange process. The treatment of **2k** with 2-thiophenyl- and 2-pyridylacetylene gave only trace amounts of the alkynyl-exchange products.

A significant challenge in the development of metal-catalyzed functionalization reactions of C–C single bonds is the control of reversibility. In most cases, the reactions are irreversible.[6,15] Interestingly, many of the present reactions can be reversed by a simple change in the molar ratio of the reactants. For example, the reaction between **2a** and aliphatic alkynes **1c–f** is reversible. The same trend was observed in the exchange between two different aryl acetylenes (e.g., **2h** vs. **2i**). Moreover, the reversal of the aliphatic/aromatic alkynyl exchange of **2h** with **1d** was also feasible. This unusual reversibility will extend the changeability of the end-capping groups of propargylic amines.

This reaction also appears to be general with regard to secondary propargylamines containing various N-substituents. A number of synthetically useful N-substituents, such as alkyl, aryl, and benzyl groups, were found to be compatible with the reaction conditions (Scheme 3). The treatment of diyne **1k** with 0.1 equivalent of **2k** afforded the mono-alkynyl-exchange product **9k**, whereas the reaction of **1k** with 2 equivalents of **2d** or **2k** afforded the double-alkynyl-exchange product **10k** (Scheme 4). Moreover, this procedure is amenable to the gram-scale synthesis of **2a** from **2d** (74% yield). The structure of **2h**·HCl was confirmed by X-ray crystal diffraction analysis (see Figure S1 in the Supporting Information).[17]

Propargylamines are versatile building blocks in organic synthesis and a structural feature of many biologically active compounds and natural products.[18,19] Although many methods for the synthesis of propargylamines have been devel-



Scheme 3. Effect of the N-substituent on the lutetium-catalyzed alkynyl exchange. Yields are for the isolated product. [a] The reaction was carried out with 10 equivalents of **1b**.

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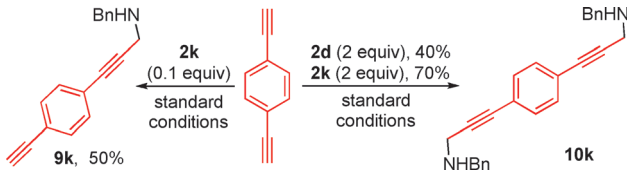
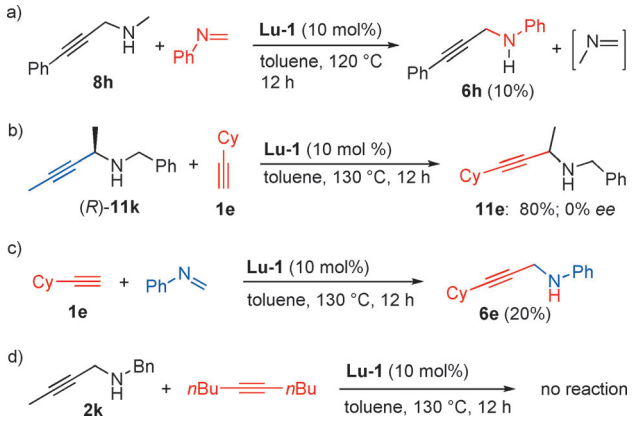


Scheme 4. Double alkynyl exchange.

oped,[20] they require the use of stoichiometric quantities of Lewis acids and bases or show limited substrate generality in some cases. Clearly, the present reaction provides an efficient way to convert readily accessible propargylamines into those bearing a different substituent on the alkyne terminus.

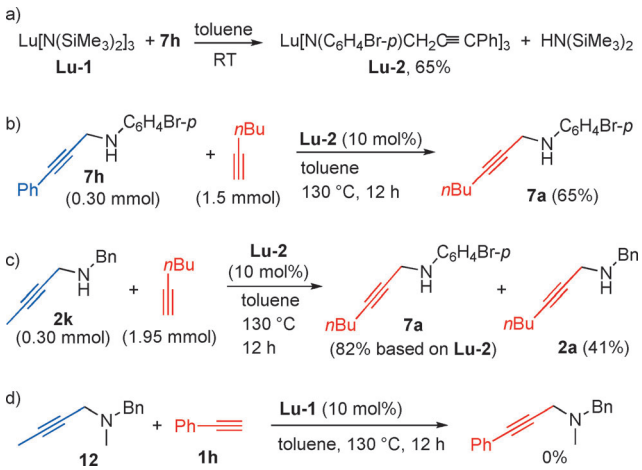
To clarify the mechanism, we investigated the reactions shown in Scheme 5. As expected, the reaction of **8h** with an



Scheme 5. Confirmation of C(sp)–C(sp^3) bond cleavage.

imine afforded the product of imine-fragment exchange **6h**, albeit in low yield (Scheme 5a). Furthermore, racemization was found with the optically active substrate (*R*)-**11k** (Scheme 5b). Compound **6e** was obtained in 20% yield upon the treatment of a mixture of **1e** with *N*-phenylmethanimine in the presence of **Lu-1** (10 mol%) in toluene at 130°C (Scheme 5c). When the terminal alkyne was replaced with an internal alkyne, however, no reaction occurred (Scheme 5d). These results suggest that the substitution involves the aminated carbon atom rather than the C≡C triple bond. ^{1}H NMR monitoring revealed that the addition of **Lu-1** (10 mol%) to a mixture of **1e** and **2k** in toluene at 120°C led to the complete liberation of the $(Me_3Si)_2N$ ligand (a new peak at 0.08 ppm) from the precatalyst,[12d] and **2k** was cleanly converted into **2e** (see Figure S2).

When we examined the stoichiometric reaction of **Lu-1** and **7h**, **Lu-2** was obtained in 65% yield (Scheme 6a). It was found that the activity of **Lu-2** for the catalytic alkynyl exchange of **7h** with **1a** was nearly same as that of **Lu-1** (Scheme 6b). Notably, the treatment of a mixture of **2k** and **1a** with **Lu-2** generated the product **7a** from β-alkynyl elimination of **Lu-2** (Scheme 6c). Moreover, heating of the solution of $[Lu\{N(Bn)CH_2C{\equiv}CPh)\}_3]$ in toluene at 130°C, followed by hydrolysis, afforded a significant amount of phenylacetylene (see Scheme S9), whereas small amounts of



Scheme 6. Confirmation of the involvement of lutetium amido intermediates.

an imine and an enyne could be detected when **Lu-1** was treated with a large excess of **2f** in toluene at 130°C (see Scheme S10). These results demonstrate that the formation and β-alkynyl elimination of lutetium–propargylamide intermediates are viable under the current conditions, and that the free alkyne and imine may compete for insertion into the lutetium–alkynyl bond. However, attempts to isolate or detect lutetium–alkynyl and lutetium–alkenyl complex intermediates by ^{1}H NMR spectroscopy failed. Instead, we found that $[Cp_2Er(C{\equiv}CtBu)]$[21] can also catalyze the alkynyl exchange of **2f** with **1a**. Furthermore, we examined the reaction of tertiary propargylamine **12** with **1h**, but no alkynyl-exchange product was obtained (Scheme 6d). This result excludes the involvement of iminium intermediates[10] and demonstrates that the deprotonation of propargylamines to form lutetium–propargylamide species might be an essential step for the alkynyl exchange.

Our proposed catalytic cycle for this transformation is shown in Scheme 7. Initial deprotonation of propargylamine **2** by the metal species provides lanthanide amide **A**, which undergoes reversible β-alkynyl elimination to form the key intermediate **B**. The resulting alkynyl ligand of **B** is exchanged with terminal alkyne **1′** to afford alkynide **C**. Imine-fragment reinsertion into the Ln–C bond gives lanthanide amide **D**.[20a,b] Finally, the protonation of **D** by another propargylamine molecule affords the alkynyl-exchange product **2′** and regenerates the active intermediate **A**. β-Carbon elimination of metal amides is unprecedented. We note also that the β-carbon elimination of secondary propargylic amines would probably be more challenging because of the preponderance of the intermolecular hydroamination/cyclization under the conditions involved.[11c] Presumably, the major driving forces for the reaction are the kinetically and/or thermodynamically favorable alkynyl-ligand exchange and subsequent regeneration of stable C–C and Ln–N bonds. Similar β-alkynyl elimination was observed for related rhodium alkoxides.[7b] It is clear that the sluggish dimerization of the liberated alkyne with the starting alkyne or with itself in situ (side reaction (i)) can serve as an additional driving force to shift the metathesis equilibrium to completion,[14] whereas a competing homo-

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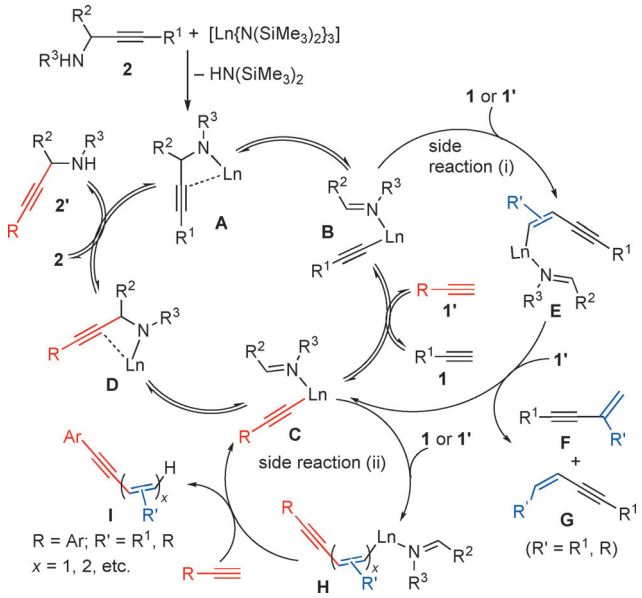

Scheme 7. Proposed mechanism for the alkynyl exchange.

dimerization and oligomerization of aryl acetylene substrates (side reaction (ii)) will disfavor the alkynyl exchange and consequently decrease the amount of alkynyl-exchange product formed or suppress the alkyne-exchange processes.

In conclusion, the first metal-catalyzed β-carbon elimination of secondary amines and its application in alkynyl exchange have been established, thus providing an efficient way to convert internal propargylamines into other propargylamines bearing different substituents on the alkyne terminus. Mechanistic studies have shed light on the possible reaction pathway. As a complementary approach to the reconstruction of alkynes, this reaction has significant advantages, such as wide scope, excellent control of selectivity and reversibility, and simple manipulation. The chemistry shown herein opens a door to a new class of early-transition-metal-catalyzed C–C bond-functionalization reactions that are not possible with conventional late-transition-metal catalytic systems. Further studies on synthetic applications are now in progress.

Experimental Section

General procedure**:** A mixture of [Lu{N(SiMe$_3$)$_2$}$_3$] (19.7 mg, 0.030 mmol), a propargylamine (0.30 mmol), a terminal alkyne (1.5 mmol), and toluene (3 mL) in a Teflon-valve-sealed Schlenk tube was heated at 100–130 °C (oil-bath temperature) under N_2. After completion of the reaction, the crude product was purified by flash column chromatography on silica gel with ethyl acetate/hexane as the eluent.

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Keywords: alkynes · amines · C–C bond cleavage · lanthanides · reaction mechanisms

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Synthetic Methods

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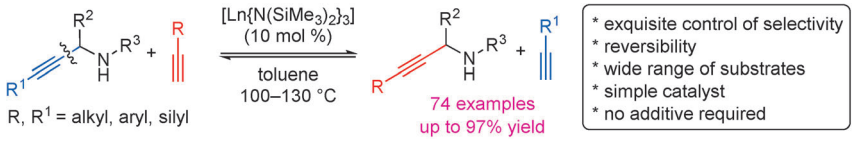

Lanthanide-Catalyzed Reversible Alkynyl Exchange by Carbon–Carbon Single-Bond Cleavage Assisted by a Secondary Amino Group

A good swap: Lanthanide-catalyzed alkynyl exchange through C—C single-bond cleavage enabled the selective transformation of internal propargylamines into differently substituted propargylamines in moderate to excellent yields. As an alternative to metathesis for the reconstruction of alkynes, this reaction has significant advantages, such as broad scope and excellent control of selectivity.

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