

Review

Organolanthanide catalyzed regio- and stereoselective dimerization of terminal alkynes and polymerization of aromatic diynes

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Abstract

This mini review describes recent advances in the application of organolanthanide complexes toward dimerization of terminal alkynes and polymerization of aromatic diynes. The regio- and stereoselectivity in these reactions can be controlled by tuning the ancillary ligands and the central metals of the catalysts.

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1. Introduction

Catalytic dimerization of terminal alkynes is an atom economic and straightforward method for the synthesis of conjugated enynes, which are important building blocks for organic synthesis and significant components in various biologically active compounds [1]. Moreover, the application of this reaction to aromatic terminal diynes could provide an efficient route to poly(aryleneethynylene)s, a new type of π -conjugated polymer which could have potential applications in advanced materials with electroluminescence properties [2]. Various organometallic complexes are known to catalyze the dimerization of terminal alkynes [3–6]. In many cases, however, a mixture of regio (head-to-head versus head-to-tail)- and stereo (*E/Z*-head-to-head)-isomer products was obtained. The regio- and stereoselectivity of these reactions highly depend on the substituents in the alkynes and the nature of the catalysts. By appropriately tuning the metals and the ligands, the reactions could be achieved regio- and stereoselectively. This article is intended to give a brief overview on the organolanthanide catalyzed dimerization of terminal alkynes and its application to the polymerization of aromatic diynes.

2. Dimerization of terminal alkynes

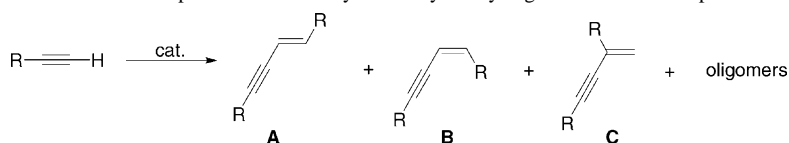
As shown in Table 1 and Scheme 1, the dimerization of $\text{MeC}\equiv\text{CH}$ by the scandium metallocene complex **1** afforded selectively the head-to-tail dimerization product **C** (entry 1) [5f], while in the case of the analogous lanthanum (**2b**) (entry 4) and cerium (**2c**) (entry 7) complexes, higher oligomers were also formed in addition to the dimerization product **C** [5d]. The bulkier alkyne $\text{Me}_3\text{CC}\equiv\text{CH}$ could be generally dimerized selectively into the corresponding head-to-tail product **C**, by the metallocene complexes **2a–2c** (entries 2, 5 and 8) [5d] and the amidinate-coordinated yttrium complexes **5a** or **5b** (entry 12). In contrast, $\text{Me}_3\text{SiC}\equiv\text{CH}$ was dimerized exclusively in the (*E*)-head-to-head fashion to give the 1,4-disubstituted (*E*)-1,3-enyne product **A**, by **5a,b** (entry 13) [5b] and the $\text{C}_5\text{Me}_5/\text{OC}_6\text{H}_3\text{Bu}_2$ -2,6-ligated yttrium complex **4** (entry 10) [5c]. Under the similar conditions the metallocene complexes **2a–2c** showed lower selectivity for $\text{Me}_3\text{SiC}\equiv\text{CH}$ (entries 3, 6 and 9) [5d]. The dimerization of 1-octyne $\text{C}_6\text{H}_{13}\text{C}\equiv\text{CH}$ by the silylene-linked cyclopentadienyl-anilido lutetium alkynide complex **7e** took place selectively in a head-to-tail manner in toluene (entry 14) [5a]. In THF, however, the head-to-head (*Z*)-dimerization occurred selectively to give the 1,4-disubstituted (*Z*)-1,3-enyne **B** in 95% yield (entry 15).

The dimerization of phenylacetylene by various organolanthanide catalysts is summarized in Table 2. As in the case

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Table 1
Dimerization of aliphatic terminal alkynes catalyzed by organolanthanide complexes^a

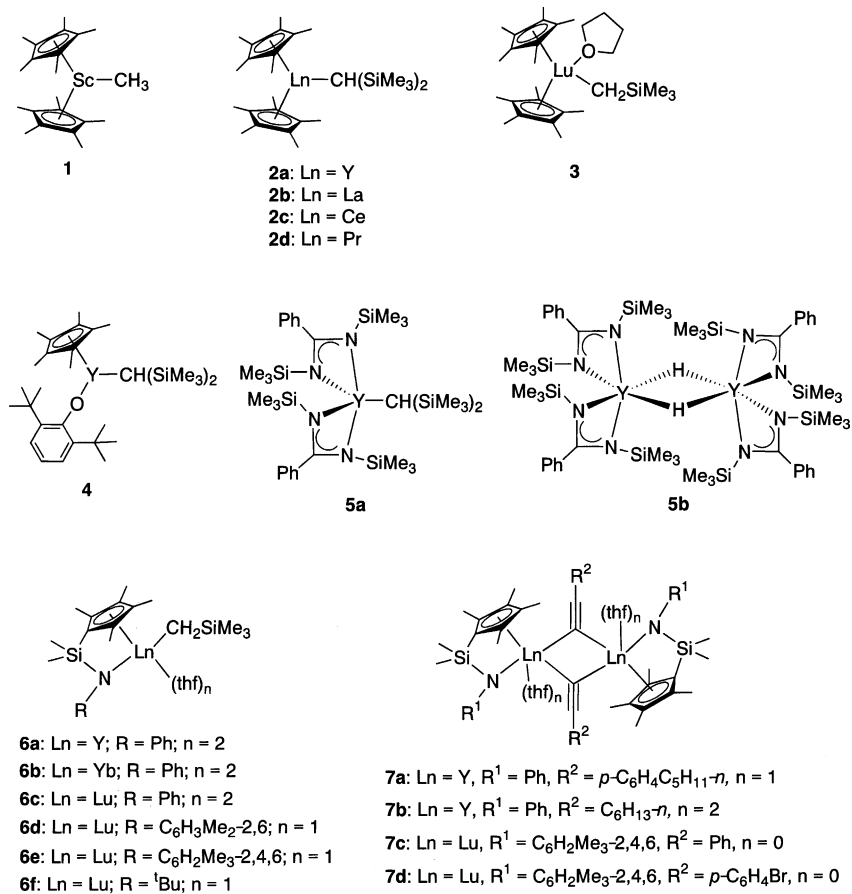


Entry	Catalyst	R	A	B	C	Oligomers	Reference
1	1	Me			100		[5f]
2	2a	CMe ₃			100		[5d]
3		SiMe ₃	80		20		[5d]
4	2b	Me			78	21	[5d]
5		CMe ₃			100		[5d]
6		SiMe ₃	45		4	51	[5d]
7	2c	Me			74	25	[5d]
8		CMe ₃			100		[5d]
9		SiMe ₃	61		7	32	[5d]
10	4	SiMe ₃	100				[5c]
11	5a or 5b	Me			100		[5b]
12		CMe ₃			100		[5b]
13		SiMe ₃	100				[5b]
14	7e	C ₆ H ₁₃ ^b		4	96		[5a]
15		C ₆ H ₁₃ ^c		95	5		[5a]
16	6e	C ₆ H ₁₃ ^c		95	5		[5a]

^a The reactions were carried out in benzene, unless otherwise noted.

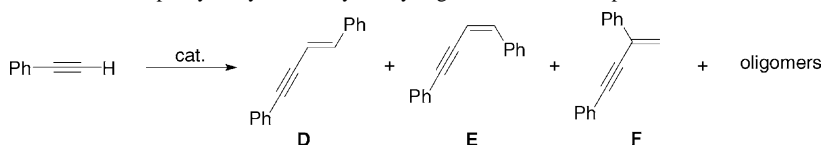
^b The reaction was carried out in toluene.

^c The reaction was carried out in THF.



Scheme 1.

Table 2
Dimerization of phenylacetylene catalyzed by organolanthanide complexes



Catalyst	D	E	F	Oligomers	Reference
2a	11		89		[5d]
2b	86			14	[5d]
2c	82			18	[5d]
2d	73			27	[7]
3	4		96		[7]
5a or 5b			100		[5b]
6a		89	6	5	[5a]
6b		92		8	[5a]
6c		100			[5a]
6d		100			[5a]
6e		100			[5a]
6f		72	13	15	[5a]

of aliphatic alkynes described above, the selectivity of phenylacetylene dimerization is also extremely susceptible to the ancillary ligands and the character of the metals. The yttrium (**2a**) [5d] and lutetium (**3**) [7] metallocene complexes afforded the head-to-tail dimerization product **F** as a dominant product (89 and 96%, respectively) with the head-to-head (*E*)-dimerization product **D** as a minor one. In contrast, the analogous lanthanum (**2b**), cerium (**2c**), and praseodymium (**2d**) complexes resulted in formation of the head-to-head (*E*)-dimerization product **D** as a major product (73–86% yield) with higher oligomers as minor products. The amidinate-supported yttrium complexes **5a,b** showed excellent selectivity (100%) for the head-to-tail dimerization [5b]. On the other hand, the half-metallocene lanthanide complexes, in particular the silylene-linked cyclopentadienyl–anilido lutetium complexes **6c–6e**, showed extremely high (*Z*)-head-to-head selectivity to give (*Z*)-1,4-diphenyl-1-buten-3-yne (**E**) exclusively [5a], which represents the first example of (*Z*)-selective head-to-head dimerization of an aromatic alkyne.

Various aromatic terminal alkynes could be cleanly dimerized into the corresponding 1,4-disubstituted (*Z*)-1,3-enynes by the lutetium half metallocene complexes such as **6c–6e**. Some representative results are summarized in Table 3 [5a]. Aromatic C–Cl, C–Br, and C–I bonds, which are known to be extremely susceptible to reductive cleavage by transition metals, survived in these reactions. The corresponding dimeric alkyne species such as **7c,d** (Fig. 1) were confirmed to be the true catalysts. These alkyne complexes were thermally stable and soluble at the reaction temperatures (80–110°C), but precipitated upon cooling to room temperature after completion of the reaction. Therefore, these catalyst systems worked homogeneously but could be easily separated and reused (Scheme 2), which thus constitutes the first example of a recyclable catalyst system for the dimerization of terminal alkynes [5a]. This is

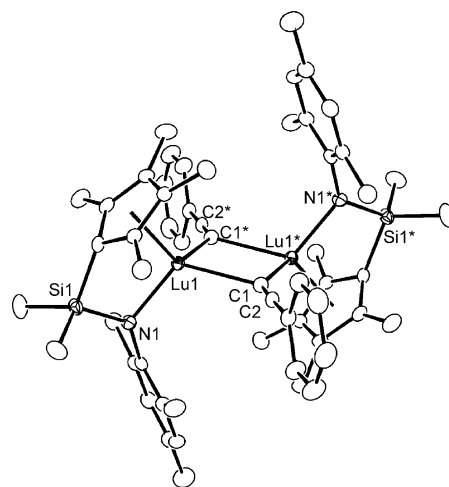
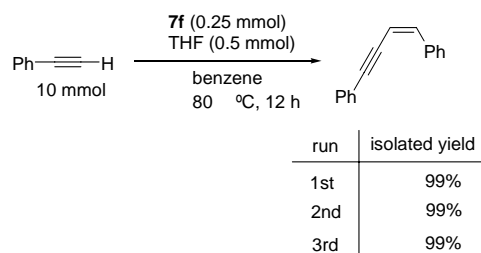


Fig. 1. ORTEP drawing of **7c**.

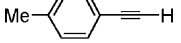
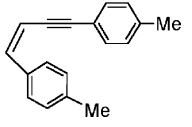

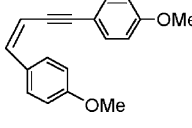
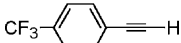
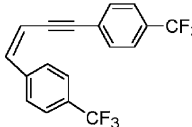
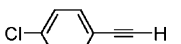
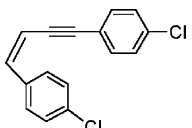
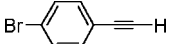
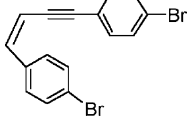
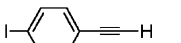
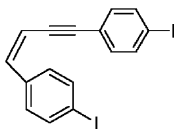
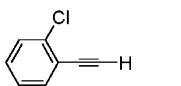
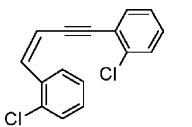
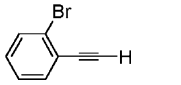
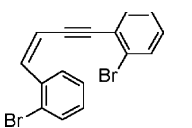
in striking contrast with what was observed in the case of the analogous metallocene or benzamidinate-ligated lanthanide alkyne complexes, which rapidly decomposed or coupled into trienediyl derivatives such as $[\text{Cp}^*_2\text{Ln}][\mu\text{-}\eta^2\text{:}\eta^2\text{-PhC=C=C=CPh}]$ upon heating [5b,8].

The (*Z*)-selective dimerization reaction catalyzed by the half-metallocene complexes such as **6c–e** or **7c–f** could



Scheme 2.

Table 3
Dimerization of aromatic terminal alkynes catalyzed by **6e**^a

Substrate	Product	Solvent	Conversion (%) ^b	Selectivity (%) ^b
		Toluene-d ₈	>99	>99
		Toluene-d ₈ + THF ^c	>99	>99
		Toluene-d ₈	97	95 ^d
		C ₆ D ₆	>99	>99
		C ₆ D ₆	>99	>99
		C ₆ D ₆	>99	>99
		C ₆ D ₆	>99	>99
		C ₆ D ₆	>99	>99

^a Conditions: substrate (1 mmol), **6e** (0.02–0.05 mmol), temperature 80–110 °C, reaction time 2–14 h.

^b Determined by ¹H NMR and GC-MS.

^c THF: 2 equiv per **6e**. In THF-free toluene, 2,4-bis(4-nethoxyphenyl)but-1-ene-3-yne (33%) was also formed.

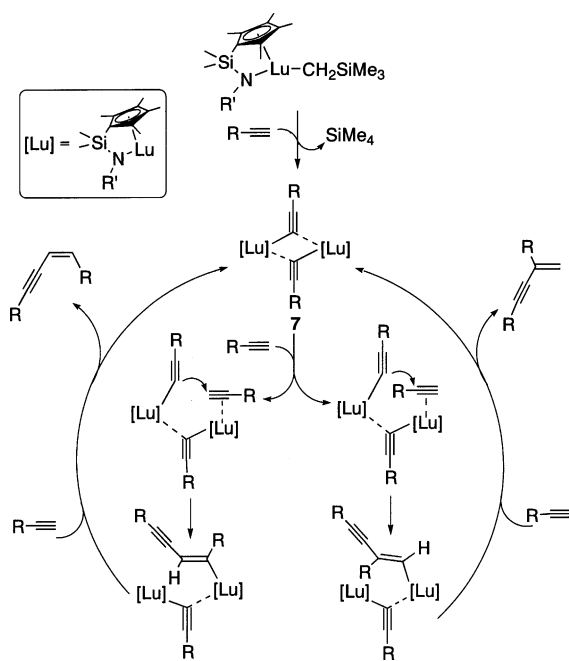
^d 1,4,6-Tris[4-(trifluoromethyl)phenyl]hex-1-yne-3,5-diene (5%) was also formed.

be explained by the mechanism shown in Scheme 3 [5a]. The alkynide-bridged dimeric intermediates such as **7c–f**, which lead to “intermolecular” addition of an alkynide to an alkyne, obviously play a critically important role in the present (*Z*)-selective dimerization. This is in sharp contrast with the analogous reactions catalyzed by metallocene or benzamidinate-ligated catalysts, in which the addition of an alkynide to an alkyne took place in an “intramolecular” fashion at a monomeric alkynide/alkyne intermediate, and thus always yielded the (*E*)-enyne products whenever the head-to-head reaction occurred (Scheme 4) [5b–f,8]. The regioselectivity to determine either head-to-head or head-to-tail dimerization could be influenced by the inter-

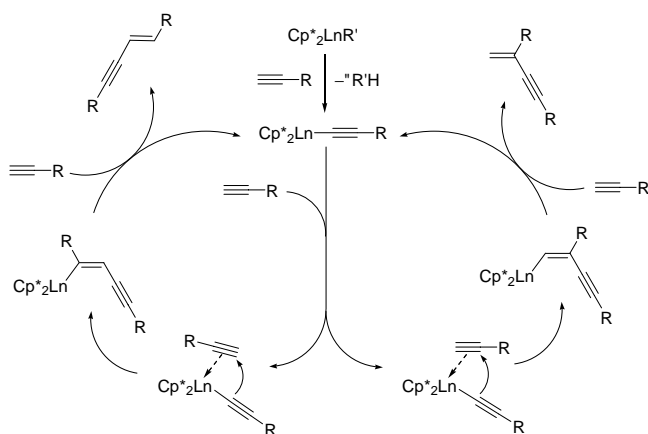
play of the electronic and steric effects of both the substrates and the catalysts.

3. Polymerization of aromatic diynes

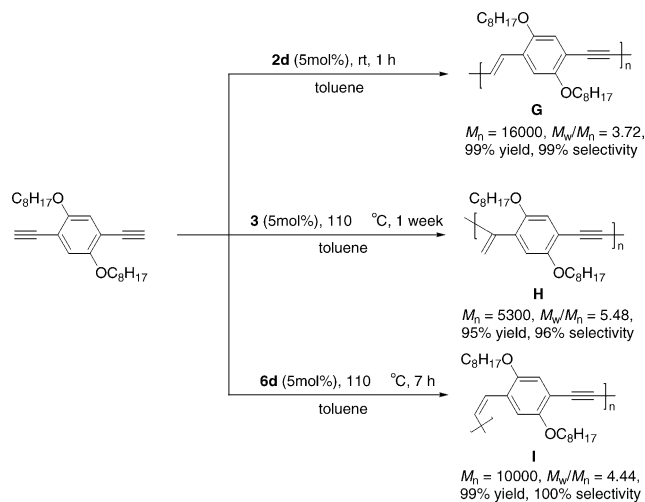
Aromatic diynes such as 1,4-diethynyl-2,5-alkoxybenzene could be polymerized regio- and stereoselectively to give the corresponding π -conjugated polyenyynes by choosing appropriate catalysts. Some examples are shown in Scheme 5 [9]. The lutetium half-metallocene alkyl complex **6d**, which acted as a novel catalyst precursor for the (*Z*)-selective head-to-head dimerization of



Scheme 3.



Scheme 4.



Scheme 5.

phenylacetylene as described above, showed excellent selectivity also for the (*Z*)-head-to-head polymerization of 1,4-diethynyl-2,5-octyloxybenzene to give solely the corresponding (*Z*)-polyenyne **I**. Similarly, the lutetium metallocene complex **3**, which showed high selectivity for the head-to-tail dimerization of phenylacetylene, also served as a good catalyst precursor for the head-to-tail polymerization of 1,4-diethynyl-2,5-octyloxybenzene to give polymer **H** with 96% selectivity. Interestingly, the praseodymium metallocene complex **2d** showed excellent selectivity (99%) for the (*E*)-head-to-head polymerization of 1,4-diethynyl-2,5-octyloxybenzene to give polymer **G**, although its selectivity for the head-to-head (*E*)-dimerization of phenylacetylene was poor (73%) [9]. The amidinate complex **5a** showed high head-to-head (*E*)-selectivity for the polymerization of 1,4-diethynyl-2,5-octyloxybenzene [9], although excellent head-to-tail selectivity was observed in the dimerization of phenylacetylene [5b]. These results again demonstrate that the regio- and stereoselectivity in the present reactions are strongly influenced by the steric and electronic effects of both the catalysts and the substrates.

4. Conclusion

By tuning the ancillary ligands and the metal centers of organolanthanide complexes, the regio- and stereoselective dimerization of various terminal alkynes have been achieved. Some of these reactions such as the *Z*-selective head-to-head dimerization of aromatic alkynes are unique to the lanthanides. Application of these reactions to aromatic diynes has resulted in formation of a new family of π -conjugated polymers. The lanthanide catalysts seemed superior to transition metal catalysts in terms of selectivity, activity, and the molecular weight of the resulting polymers [10].

Acknowledgements

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