

NbCl₃-Catalyzed Three-Component [2 + 2 + 2] Cycloaddition Reaction of Terminal Alkynes, Internal Alkynes, and Alkenes to 1,3,4,5-Tetrasubstituted 1,3-Cyclohexadienes

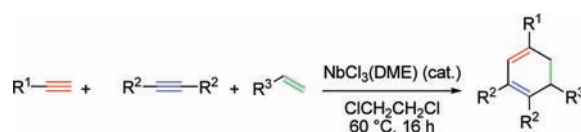
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ABSTRACT



Three-component [2 + 2 + 2] cycloaddition of terminal alkynes, internal alkynes, and terminal alkenes is achieved using an NbCl₃(DME) catalyst, leading to 1,3,4,5-substituted 1,3-cyclohexadienes in excellent yields with high chemo- and regioselectivity.

Transition-metal-catalyzed [2 + 2 + 2] cycloaddition of unsaturated compounds has been extensively studied for the formation of various aromatic and unsaturated cyclic compounds.¹ In general, this protocol is selectively accomplished by intramolecular reactions using diynes and dienes as substrates. Chemo- and stereocontrolled *intermolecular* [2 + 2 + 2] cycloadditions, in particular from *three different substrates*, are, therefore, highly desirable and a challenging target. To date, several examples of chemoselective transition-metal-catalyzed or -mediated alkyne cyclotrimerizations from three different alkynes,

leading to multisubstituted aromatic compounds, have been reported.^{2,3}

1,3-Cyclohexadiene derivatives are an important class of compounds and are widely used in organic and polymer chemistry.^{4,5} Among the various synthetic methods for the synthesis of 1,3-cyclohexadienes reported so far,⁶

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transition-metal-catalyzed [2 + 2 + 2] cycloaddition from easily accessible unsaturated compounds, such as simple alkynes and alkenes, is the most favorable. However, in contrast to the case of cycloaddition by alkyne trimerization, only a limited amount of work on the synthesis of 1,3-cyclohexadienes by intermolecular cycloaddition of alkynes and alkenes has been reported because of the difficulty in controlling the chemo- and regioselectivity.^{7,8}

NbCl₃(DME) is a thermally stable low-valent early transition-metal complex, which has been used as a reagent in the reactions of alkynes with several electrophiles.^{9–12} We recently reported that NbCl₃(DME) serves as an efficient catalyst for intermolecular cycloaddition of two molecules of terminal alkynes and one alkene or α,ω -diene molecule to afford 1,4,5-trisubstituted-1,3-cyclohexadiene derivatives.¹³

In this paper, we report the *three-component* [2 + 2 + 2] cycloaddition of terminal alkynes, internal alkynes, and terminal alkenes, catalyzed by NbCl₃(DME), leading to 1,3,4,5-tetrasubstituted 1,3-cyclohexadienes in excellent yields with high chemo- and regioselectivity. This reaction provides an unprecedented, selective, and atom-economic methodology for the formation of tetrasubstituted 1,3-cyclohexadienes from three different simple unsaturated feedstocks via intermolecular [2 + 2 + 2] cycloaddition.

The reaction of trimethylsilylacetylene (**1a**), 5-decyne (**2a**), and styrene (**3a**) was chosen as a model reaction and was carried out under various conditions (Table 1).

For instance, **1a** (2 mmol) was allowed to react with **2a** (1 mmol) and **3a** (4 mmol) under the influence of

Table 1. NbCl₃-Catalyzed [2 + 2 + 2]-Cycloaddition of Trimethylsilylacetylene (**1a**), 5-Decyne (**2a**), and Styrene (**3a**)^a

entry	catalyst	solvent	yield (%)		
			4a ^b	5a ^c	6a ^d
1	NbCl ₃ (DME)	Cl(CH ₂) ₂ Cl	quant (97)	trace	nd ^e
2 ^f	NbCl ₃ (DME)	Cl(CH ₂) ₂ Cl	62	5	trace
3 ^g	NbCl ₃ (DME)	Cl(CH ₂) ₂ Cl	56	trace	trace
4 ^h	NbCl ₃ (DME)	Cl(CH ₂) ₂ Cl	72	9	12
5	NbCl ₃ (DME)	Cl(CH ₂) ₄ Cl	82	5	8
6	NbCl ₃ (DME)	toluene	77	trace	10
7 ⁱ	NbCl ₃ (DME)	dioxane	58	trace	trace
8	NbCl ₃ (DME)	THF	3	nd ^e	trace
9	NbCl ₃ (DME)	DME	nd ^e	nd ^e	nd ^e
10	TaCl ₃ (DME)	Cl(CH ₂) ₂ Cl	nd ^e	nd ^e	nd ^e
11	NbCl ₅	Cl(CH ₂) ₂ Cl	trace	13	6
12	Cp ₂ NbCl ₂	Cl(CH ₂) ₂ Cl	nd ^e	nd ^e	nd ^e

^a Reaction conditions: **1a** (2 mmol), **2a** (1 mmol), **3a** (4 mmol), and catalyst (0.2 mmol) in solvent (1 mL) at 60 °C for 16 h. ^b Determined by GC based on **2a** used. The number in parentheses shows isolated yield. ^c Determined by GC based on **1a** used. Compound **5a** was exclusively obtained as 1,4,5-adduct. ^d Determined by GC based on **1a** used. Compound **6a** was exclusively obtained as 1,4,5-adduct. ^e Not detected by GC. ^f Reaction was performed using NbCl₃(DME) (0.2 mmol), **1a** (1 mmol), **2a** (1 mmol), and **3a** (1 mmol). ^g Reaction was performed using NbCl₃(DME) (0.2 mmol), **1a** (2 mmol), **2a** (2 mmol), and **3a** (2 mmol). ^h Reaction was performed using NbCl₃(DME) (0.2 mmol), **1a** (4 mmol), **2a** (2 mmol) and **3a** (2 mmol). ⁱ The reaction was performed at 80 °C.

NbCl₃(DME) (0.2 mmol) in 1,2-dichloroethane (1 mL) at 60 °C for 16 h. 1-Trimethylsilyl-3,4-*n*-dibutyl-5-phenyl-1,3-cyclohexadiene (**4a**) was obtained in quantitative yield with excellent chemo- and regioselectivity (Table 1, entry 1). It is noteworthy that the reaction led exclusively to intermolecular three-component cross-cycloaddition products from three different substrates, in preference to the cyclotrimerization of terminal alkynes (leading to **6a**)¹¹ and cross-cycloaddition reactions of terminal alkynes with alkenes (leading to **5a**).^{7,8,13}

The substrates ratio markedly influenced the selectivity and yield of the desired product **4a**. On screening the reaction, we found that the optimized reaction ratio of **1a**:**2a**:**3a** is 2:1:4 (entry 1). Nevertheless, even if **1a**, **2a**, and **3a** were allowed to react in a stoichiometric ratio (**1a**:**2a**:**3a** = 1:1:1), the yield of the product was still acceptable (62%) (entry 2). In addition, chemoselective (entry 3) and high-yield formation (entry 4) of **4a** was achieved by tuning the ratio of the substrates (**1a**:**2a**:**3a**) with smaller amounts (10 mol %) of NbCl₃ catalyst. With regard to the solvent, **4a** was obtained in high yields when halogenated solvents such as 1,2-dichloroethane and 1,4-dichlorobutane were

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Table 2. NbCl₃-Catalyzed Reactions of Various Terminal Alkynes **1**, Internal Alkynes **2**, and Alkenes **3** Leading to 1,3,4,5-Tetrasubstituted 1,3-Cyclohexadienes **4**^a

entry	4 (yield) ^b		
1	 4a (97%) ^c	2	 4b (85%) ^c
4	 4d (89%) ^{d,e,f} (71%) ^g	5	 4e (56%) ^{d,h} (40%) ^g
7	 4g (99%) ^f	8	 4h (91%) ^c (4h : 4h' = 1 : 1)
9	 4i (92%) ^{c,i}	10	 4j (72%) ^{c,k}
11	 4k (97%) ^{c,l}		

^a Reaction conditions: **1** (2 mmol), **2** (1 mmol), **3** (4 mmol), and NbCl₃(DME) (0.2 mmol) in 1,2-dichloroethane (1 mL) at 60 °C, 16 h. ^b Isolated yields unless otherwise noted. ^c Compound **4** was obtained exclusively as the 1,3,4,5-adducts. ^d Regioisomers (entries 4–6) of **4** were identified by GC and GC–MS, and the yields were determined by GC. The structures of the major regioisomers (1,3,4,5-adducts) are shown in the table. The products were isolated as a mixture of **4**–**6** due to difficulty in completely separating them. ^e The major regioisomer (1,3,4,5-adduct) of **4d** was isolated in 63% yield. ^f In addition to the product **4d**, **5d** (12%) and **6d** (4%) were formed. ^g Regioselectivity (%) of the 1,3,4,5-adducts in the total regioisomers of **4**. The regiochemistry of the other isomers was not determined. ^h In addition to the product **4e**, **6e** (18%) was formed. ⁱ In addition to the product **4f**, **5f** (8%) and **6f** (59%) were formed. ^j In addition to the product **4i**, **5i** (8%) and **6i** (12%) were formed. ^k In addition to the product **4j**, **6j** (13%) was formed. ^l In addition to the product **4k**, **5k** (8%) and **6k** (10%) were formed.

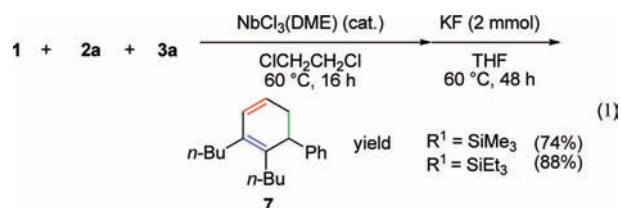
used (entries 1–5). However, toluene and dioxane were tolerated as solvents (entries 6 and 7). The catalyst precursor significantly influenced the reaction activity: the low-valent Nb(III) complex, NbCl₃(DME), is highly efficient (entry 1). When the Ta(III) analogue, TaCl₃(DME), was used as a catalyst, all the substrates were evidently converted in the course of the reaction, but only an intractable mixture of oligomeric products was obtained under these conditions (entry 10). Other Nb(IV), Nb(V), and V(III) complexes,

such as NbCl₅ and Cp₂NbCl₂, were totally ineffective as catalysts for the cycloaddition reactions (entries 11 and 12).

Under the optimized conditions shown in Table 1, entry 1, the reactions of various terminal alkynes **1**, internal alkynes **2**, and alkenes **3** were examined (Table 2). The chemo- and regioselectivities of the adducts were significantly influenced by the bulkiness of the substituents on the terminal alkynes **1** used in the reaction. Thus, reactions using trialkylsilylacetylenes, such as trimethylsilylacetylene (**1a**), triethylsilylacetylene (**1b**), and dimethylphenylsilylacetylene (**1c**), provide the corresponding 1,3,4,5-tetrasubstituted-1,3-cyclohexadiene derivatives **4a**–**c** in excellent yield, as the sole product, and with excellent chemo- and regioselectivity (entries 1–3). *tert*-Butylacetylene was also a good substrate for the formation of three-component cycloaddition products in high yield, along with the formation of **5d** (12%) and **6d** (4%) as byproduct. The regioselectivity for the 1,3,4,5-adduct **4d** was good but not completely selective (71%) (entry 4). The use of less bulky terminal acetylenes such as phenylacetylene and 1-octyne did not give the desired three-component coupling product selectively, but alkyne cyclotrimerization products were obtained in considerable yields (entries 5 and 6).

Similarly, 4-octyne and 1-phenyl-1-propyne were allowed to react with **1a** and **3a**, affording the corresponding 1,3,4,5-tetrasubstituted-1,3-cyclohexadiene derivatives **4g** and **4h** in excellent yields with excellent chemo- and regioselectivity (entries 7 and 8). In addition, the reaction tolerated the use of simple alkenes, such as 1-octene and 1-decene, giving the desired 1,3,4,5-substituted 1,3-cyclohexadienes in high yields with high regioselectivity (entries 9 and 10). It is noteworthy that the reactions of α,ω -dienes with **1a** and **2a** took place exclusively at one side, affording 5- ω -alkenyl-1,3,4,5-tetrasubstituted-1,3-cyclohexadienes in high yield with high regioselectivity (entry 11).

In addition, we found that 3,4,5-trisubstituted 1,3-cyclohexadienes have been synthesized by desilylation¹⁴ from the 1,3,4,5-tetrasubstituted 1,3-cyclohexadienes obtained in this study. Thus, addition of KF (2 mmol) and THF (1 mL) to a reaction mixture prepared under the reaction conditions shown in Table 1, entry 1, gave 3,4-di-*n*-butyl-5-phenyl-1,3-cyclohexadiene (**7**) in good isolated yields (74% with R¹ = SiMe₃ and 88% with R¹ = SiEt₃; eq 1). This one-pot and high-yield synthesis provides an efficient and versatile protocol for the synthesis of various 3,4,5-trisubstituted 1,3-cyclohexadienes.

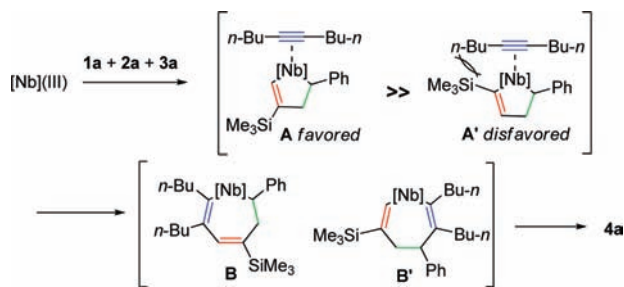


Although it is not possible to confirm a detailed reaction mechanism at this stage, the present three-component

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cycloaddition of **1a**, **2a**, and **3a** is thought to proceed by the following pathway (Scheme 1).

Scheme 1. Plausible Reaction Pathway



The reaction initiates oxidative cyclometalation of the terminal alkyne (**1a**) and terminal alkene (**3a**); coordination of the internal alkyne (**2a**) to the Nb center gives a niobacyclopentene intermediate (**A**). Bulky substituents such as a trimethylsilyl group would lead to preferential formation of **A** rather than the sterically congested form **A'**.¹⁵ Subsequently, divergent migratory insertion of the coordinated

internal alkyne **2a** into the Nb–vinyl bond or the Nb–alkyl bond occurs to form **B** and **B'**, respectively.^{15,16} Insertion into the less-hindered Nb–vinyl bonds would be favored, affording the niobacyclic intermediate **B**.¹⁷ **B** then exclusively produces the three-component coupling product 1,3,4,5-tetrasubstituted 1,3-cyclohexadiene **4a**.

In conclusion, we have found a new highly active catalytic system for chemo- and regioselective [2 + 2 + 2] intermolecular cycloaddition reactions of terminal alkynes, internal alkynes, and alkenes to 1,3,4,5-tetrasubstituted-1,3-cyclohexadiene derivatives. Further investigation with regard to the detailed reaction mechanism, scope, and applications of this reaction is currently in progress.

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Supporting Information Available. Experimental procedure and compound characterization data (¹H NMR, ¹³C NMR, HMQC, HMBC, IR, and MS spectra) of the compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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