



Ring expansion reactions of ethyl cyclopropylideneacetate and benzosilacyclobutenes: formal σ bond cross metathesis

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ABSTRACT

The ring expansion reaction of ethyl cyclopropylideneacetate (**1**) with benzosilacyclobutenes proceeded smoothly in the presence of Ni(cod)₂-TOPP (tribiphenyl-2-yl phosphite) to give benzosilacycloheptenes in good yields. This formal σ bond metathesis reaction proceeded in a selective manner. The Ni-catalyzed reaction of **1** with biphenylenes was also examined.

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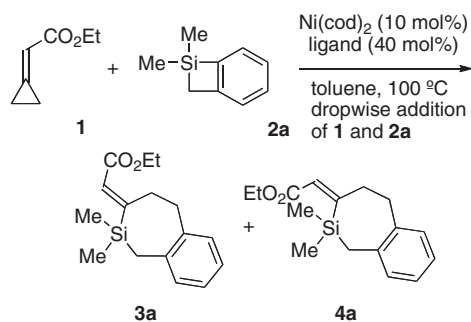
The strained C–Si and C–C bonds of four-membered cyclic compounds are reactive σ bonds and many attractive reactions have been reported. The transition metal-catalyzed reactions of these compounds generally involve the cleavage of the four-membered ring, and five-membered metalacycles are considered as the key intermediates. For example, the ring expansion reactions of benzosilacyclobutenes proceeded in the presence of Pd,¹ Ni,² or Co³ catalysts, and the intermediacy of the five-membered metalacyclic compounds has been established in some reactions.^{3,4} The ring expansion reactions of biphenylene were also catalyzed and/or mediated by the Ni,⁵ Rh,⁶ or other metal complexes,⁷ and these reactions would also proceed via similar metalacyclic intermediates.

We have been showing interest in the reactivity of ethyl cyclopropylideneacetate (**1**) in the presence of Ni(0) catalyst and have developed new methods for the synthesis of medium-sized carbocyclic compounds. The [3+2+2] cycloaddition of **1** with alkynes gave substituted cycloheptadienes⁸ and the [4+3] cycloaddition of **1** with 1,3-dienes gave cycloheptenes.⁹ Dienynes also turned out to be good substrates, and the [4+3+2] cycloaddition reaction of **1** with dienynes proceeded efficiently to yield the bicyclic cyclononadiene derivatives.¹⁰ We assumed that nickelacycles such as nickelacyclopentadiene were initially formed by the reaction of the Ni(0) species with alkynes, which further reacted with **1** to give the product.

Since very similar metalacycles have been postulated as the intermediates in the transition metal-catalyzed reactions of benzosilacyclobutenes as well as the nickel-catalyzed reactions of **1** and alkynes, we expected that benzosilacyclobutenes would be suitable substrates for the Ni-catalyzed reaction of **1**. In this Letter, we report the nickel-catalyzed ring expansion reaction of **1** and benzosilacyclobutenes. The reaction of **1** with biphenylenes, which are structurally similar compounds, was also examined.

The Ni-catalyzed ring expansion reaction of **1** with 1,1-dimethyl-2,3-benzo-1-sila-2-cyclobutene (**2a**) was examined under various reaction conditions and the results are summarized in Table 1. Compound **1** reacted with **2a** in the presence of Ni(cod)₂ (10 mol%) and PPh₃ (40 mol%). When a solution of **1** (1 equiv) and **2a** (1.2 equiv) in toluene was slowly added to a solution of the nickel catalyst at 100 °C over 5 h, compounds **3a** and **4a** were isolated in 44% combined yield (entry 1).¹¹ The ratio of **3a** to **4a** was close to unity. The yields of the product decreased when PBu₃ (**L2**) was used as the ligand for this reaction (entry 2). The reaction did not proceed efficiently when the reaction was carried out in the presence of tris(2-biphenyl)phosphine (**L3**, entry 3) or triphenylphosphite (**L4**, entry 4). On the other hand, bulky phosphite ligands turned out to be suitable for this reaction. For example, the combined yield of **3a** and **4a** was 39% when the reaction was carried out in the presence of tris[2,4-di(*tert*-butyl)phenyl]phosphite (**L5**, entry 5). The combined yield increased to 61% when the reaction was catalyzed by Ni(cod)₂-TOPP¹² (tribiphenyl-2-yl phosphite, **L6**, entry 6). The highest yield of the product was achieved when a solution of the substrates was slowly added to a mixture of the catalyst in toluene over

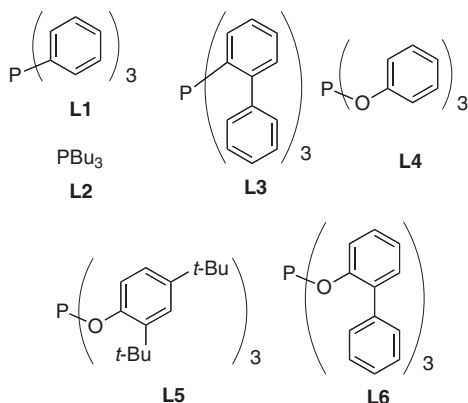
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Table 1
Nickel-catalyzed ring expansion reaction of **1** with **2a**

Entry	Ligand	Addition time (h)	Yield (%) (3a + 4a)	Ratio ^a (3a : 4a)
1	L1	5	44	47:53
2	L2	5	14	50:50
3	L3	5	0	—
4	L4	5	Trace	—
5	L5	5	39	56:44
6	L6	5	61	50:50
7	L6	2	63	52:48
8	L6	1	53	49:51

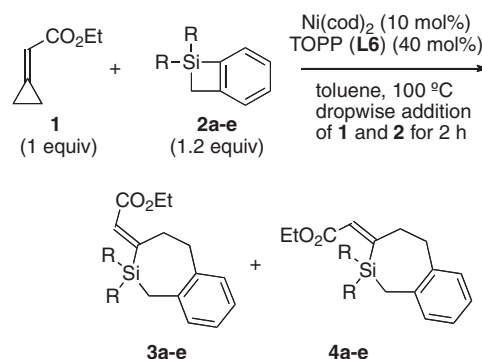
^a The ratio was determined by the isolated yields of **3a** and **4a**.

2 h (entry 7). The yields of **3a** and **4a** decreased when the addition time was 1 h (entry 8).



The scope of this reaction was studied under the optimized reaction conditions and the results are summarized in Table 2. The ring expansion reaction proceeded smoothly when other alkyl groups such as ethyl group (entry 2) or *n*-butyl group (entry 3) were introduced to the silicon atom of the benzosilyclobutene. The yield of the products decreased when the phenyl group was introduced (entry 4). In this reaction, however, the *E*-isomer (**3d**) was isolated as the major isomer. The introduction of a more bulky isopropyl group resulted in the significant decrease of the yield and the predominant formation of the *E*-isomer (entry 5).

Encouraged by the successful conversion of benzosilyclobutenes, we examined the Ni-catalyzed reaction of **1** with biphenylenes (**5a–c**). The results are summarized in Table 3. To a mixture of Ni(cod)₂ (10 mol%) and PPh₃ (40 mol%) in toluene was slowly added a solution of **1** and biphenylene (**5a**) in toluene at 100 °C, and the ring expansion product (**6a**) was isolated in 70% yield (entry 1). In contrast to the reaction of **1** with **2a**, no isomeric compound was isolated. The proper selection of the ligand was critical for the progress of this reaction, and PPh₃ (**L1**) turned out to be the best ligand: the yield of **6a** decreased when TOPP (**L6**) was used (entry 2).¹³ This reaction proceeded smoothly with other biphenylene derivatives such as **5b** and **5c** (entries 3 and 4).¹⁴ In the reaction of **5c**, the selective cleavage of the less sterically hindered

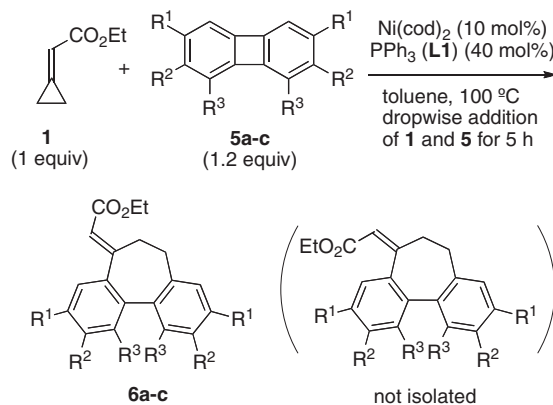
Table 2
Nickel-catalyzed ring expansion reaction of **1** with **2a–e**

Entry	Compd	Yield (%) (3 + 4)	Ratio ^a (3 : 4)
1	2a (R = Me)	63	52:48
2	2b (R = Et)	69	55:45
3	2c (R = <i>n</i> -Bu)	58	50:50
4	2d (R = Ph)	47	83:17 ^b
5	2e (R = <i>i</i> -Pr)	8	>95:<5 ^c

^a The ratio was determined by the isolated yields of **3** and **4**, unless otherwise noted.

^b The ratio was determined by the NMR spectrum of the mixture of **3d** and **4d**.

^c The minor isomer was not detected by NMR analysis.

Table 3
Nickel-catalyzed ring expansion reaction of **1** with biphenylenes

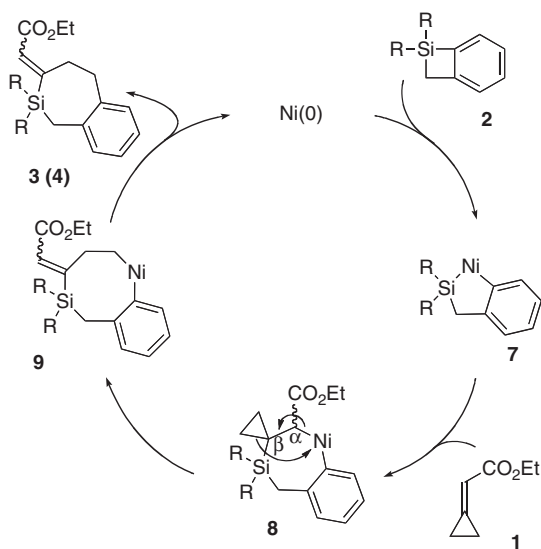
Entry	Compd	R ¹	R ²	R ³	Yield (%)
1	5a	H	H	H	70
2 ^a	5a	H	H	H	(16) ^b
3	5b	Me	Me	H	74
4	5c	H	H	Me	56

^a TOPP (**L6**) was used as the ligand.

^b The product was not isolated in pure form.

C–C bond proceeded to give the ring expansion product **6c** exclusively.

A possible mechanism of the ring expansion reaction of **2** is presented in Scheme 1. Since the insertion of Pd and Pt complex to the silacyclobutane ring has been reported in the literature,^{3,4} we assume that the insertion of the Ni(0) species to the silacyclobutane ring of **2** would proceed, leading to the formation of **7**. The more reactive Si–Ni bond would react with **1**, and a seven-membered nickelacycle would be formed. The cyclopropylmethyl-butenyl rearrangement¹⁵ and reductive elimination would proceed to give **3** and **4** as the final products. We assume that the regiochemistry of the product is determined when the cyclopropylmethyl-butenyl rearrangement (i.e., the formation of **9** from



Scheme 1. Proposed mechanism.

8) proceeds. The *E*-isomer (**3**) would be isolated preferentially when a large steric hindrance exists between the ethoxycarbonyl group and the substituent (R), and/or the *s*-trans conformation^{8d,10} of the C(carbonyl)–C(α)–C(β)–Si bond is preferred.

The Ni-catalyzed reaction of **5** would proceed via a similar pathway. In the reaction of **5**, however, the conformation of the seven-membered metalacyclic intermediate, which corresponds to **8**, would be restricted so that the *E*-isomer is isolated exclusively.

In summary, we developed a new Ni-catalyzed ring expansion reaction of **1** and benzosilacyclobutenes (**2**). The formal σ bond cross metathesis proceeded in a selective manner, and seven-membered silacyclic compounds were isolated. The Ni-catalyzed reaction of **1** and biphenylenes (**5**) proceeded smoothly as well. The study provided a new method for the synthesis of cyclic seven-membered compounds in a selective manner. Further extension of this study is on going.

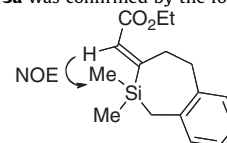
Supplementary data

Supplementary data (experimental procedures, characterization data, and copies of NMR spectra of **3**, **4**, and **6**.) associated with this article can be found, in the online version, at [doi:10.1016/j.tetlet.2010.09.031](https://doi.org/10.1016/j.tetlet.2010.09.031).

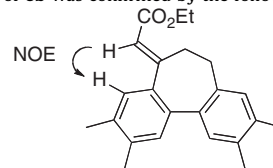
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- The stereochemistry of **3a** was confirmed by the following NOE experiment.



- This ligand was used for the [4+3] cycloaddition of **1** with 1,3-dienes. See, Ref. 9.
- The reactivity of the Ni(cod)₂-TOPP catalyst was low in the [3+2+2] cycloaddition of **1** with alkynes (Ref. 8d). In the reaction of **1** with benzosilacyclobutene, the Ni(cod)₂-TOPP complex, which would be a weaker π donor, might insert selectively to the reactive C–Si bond of benzosilacyclobutene. As a result, product might be isolated in higher yield by suppressing the possible dimerization of **1**. In most reactions of **1**, Ni(cod)₂-PPh₃ complex was the best catalyst among the catalyst we tested. For the dimerization of **1**, see, Kawasaki, T.; Saito, S.; Yamamoto, Y. *J. Org. Chem.* **2002**, *67*, 4911–4915.
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