



Five-membered zircona- and titanacycloallenes; their diverse reactivity depending upon the position of substituents[☆]

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ABSTRACT

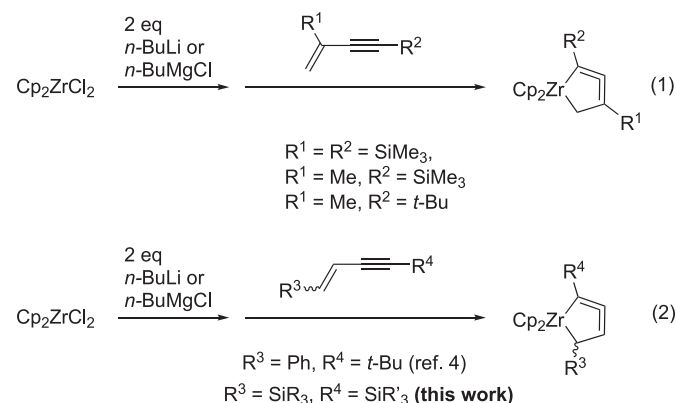
Five-membered metallacycloallene compounds that are 2,5-disubstituted 1-zirconacyclopenta-2,3-dienes were prepared from (*E*)-1,4-bis(trialkylsilyl)but-1-en-3-yne in good yields. The structures of these compounds were determined by X-ray diffraction study. Contrary to our previous study on 2,4-disubstituted 1-zirconacyclopenta-2,3-dienes, which gave alkynyl alcohols by the reaction with ketones after hydrolysis, the 2,5-bis(trialkylsilyl) complexes reacted with ketones to afford allenyl alcohols. Reactions with a nitrile gave a pyrrole compound probably via the formation of seven-membered 1-aza-2-zirconacyclohepta-3,4,7-triene ring structures. When the (*E*)-1,4-bis(trialkylsilyl)but-1-en-3-yne were treated with titanium isopropoxide/*n*-butyllithium followed by reaction with nitriles, the corresponding alkynyl ketones were obtained.

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1. Introduction

Allene compounds of a cyclic structure are normally volatile particularly if they have a five-membered ring structure, because allene compounds must have three carbon atoms linearly aligned. An all carbon cycloallene derivative was first reported as an extremely unstable species by Balci and coworkers in 2002, and the derivative could be confirmed only by being trapped as a cycloaddition product [1,2]. Our group, and Erker and coworkers independently reported that metallacyclic structures, 1-zircona- and 1-titanacyclopenta-2,3-diene, provided stable five-membered cycloallenes. Subsequently, it was reported that a few 2,4-disubstituted but-1-en-3-yne were effective for the synthesis of 2,4-disubstituted 1-zirconacyclopenta-2,3-diene complexes (eq. 1) [3–6]. Erker and coworkers reported that reductive elimination from zirconium alkenyl alkynyl species gave 2,5-disubstituted 1-zirconacyclopenta-2,3-diene complexes [7]. Rosenthal and coworkers first reported nitrogen-containing five-membered cycloallenes, 1-aza-2-titana- and 1-aza-2-zirconacyclopenta-3,4-diene compounds [8–10], and subsequently other nitrogen- [11] and sulfur-containing [12] five-membered metallacycloallenes were

also reported.



Although we have attempted to synthesize 1-zirconacyclopenta-2,3-dienes with various 1,3-enyne compounds, most of our attempts have resulted in low yield and selectivity. This is presumably because of a concomitant dimerization reaction of 1,3-enynes on the zirconium center [13–17]. Indeed, there have been only a few successful examples of the synthesis of 2,4-disubstituted 1-zirconacyclopenta-2,3-dienes from 2,4-disubstituted but-1-en-3-yne (eq. 1) [3–6]. Moreover, to the best of our knowledge, there has been only one example for the

[☆] This paper is dedicated to Prof. Atsushi Fukuoka (Institute for Catalysis, Hokkaido University) on the occasion of his 60th birthday.

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synthesis of five-membered metallacycloallene compounds from 1,4-disubstituted 1-en-3-yne, reported by Erker and coworkers (eq. 2) [4]. Nevertheless, attractive reactivities of these metallacycloallene compounds have been reported with various reagents such as $B(C_6F_5)_3$ [18], dihydrogen [19], Grignard reagent [20], carbon dioxide [7], alkyne (enyne) [5], nitrile [4,6,21] and isonitrile [5].

We have previously reported selective insertion of C=O and C≡N groups into the Zr–Csp³ bond on the 2,4-bis(trimethylsilyl)-1-zirconacyclopenta-2,3-diene **1** to afford seven-membered oxo- and azazirconacyclic allene compounds. These compounds afforded the corresponding alkynyl alcohols and ketones after hydrolysis (Scheme 1) [3]. It would be of interest if the same electrophiles afford different kinds of products depending upon the structure of the starting 1-zirconacyclopenta-2,3-diene compounds. Here, we report the diverse reactivity of 1-zirconacyclopenta-2,3-dienes towards ketones and nitriles in relation to the position of silyl substituents. A related reaction involving titanium isopropoxide is also discussed.

2. Results and discussion

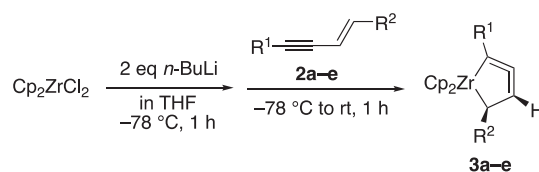
2.1. Synthesis of 1-zirconacyclopenta-2,3-dienes from 1,4-bis(trialkylsilyl)but-1-en-3-yne

Here we employed (*E*)-1,4-bis(trialkylsilyl)but-1-en-3-yne **2a–e** for the preparation of 1-zirconacyclopenta-2,3-diene complexes. The 1-en-3-yne **2** reacted with Negishi reagent at rt to provide the corresponding 2,5-bis(trialkylsilyl)-1-zirconacyclopenta-2,3-dienes **3a–e** in good yields (Table 1). It should be noted that bulky silyl groups such as *tert*-butyldimethylsilyl and triisopropylsilyl groups could be applied to the synthesis of the complex **3**.

Erker and coworkers have synthesized **3a** via an alternative approach and determined its molecular structure by X-ray diffraction analysis [7]. NMR data of **3b–e** resembled those reported for **3a**, supporting their “1-zirconacyclopenta-2,3-diene” structures. The ¹H NMR spectra showed two CH signals at 4.0 and 0.1 ppm being coupled to each other (*J* = 15 Hz) and inequivalent Cp signals at 5.4 and 5.1 ppm. In the ¹³C NMR spectra the central quaternary carbon of the “allene” moieties appeared in higher field (135–139 ppm) compared with normal allene compounds. We structurally characterized **3b** and **3c**, and the molecular structure of **3b** is shown in Fig. 1, while a disordered structure was found in **3c**. The bond lengths and angles are similar to those reported for 1-zirconacyclopenta-2,3-diene compounds [4,7,21–24], showing that complex **3b** has the “cycloallene” structure.

It should be noted that we successfully synthesized the 1-titanacyclopenta-2,3-diene **4c**. The molecular structure of **4c** was determined by X-ray diffraction analysis (Fig. 2). Titanacycloallenes that contain a nitrogen or sulfur atom as a ring-member have been

Table 1
Synthesis of 2,5-disilyl-1-zirconacyclopenta-2,3-dienes **3**.



Entry	Product	R ¹	R ²	Yield/% ^a
1	3a	SiMe ₃	SiMe ₃	88 (22)
2	3b	SiMe ₂ (<i>t</i> -Bu)	SiMe ₃	80 (40)
3	3c	SiMe ₂ (<i>t</i> -Bu)	SiMe ₂ (<i>t</i> -Bu)	90 (21)
4	3d	SiEt ₃	SiMe ₃	96 (20)
5	3e	Si(<i>i</i> -Pr) ₃	SiMe ₃	67 (9)

^a Determined by ¹H NMR, isolated yield in parentheses.

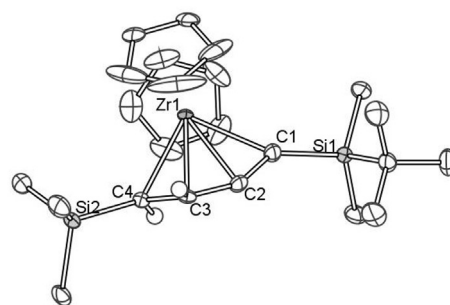


Fig. 1. The molecular structure of **3b**. Selected bond lengths (Å) and angles (°) are listed in Table 2.

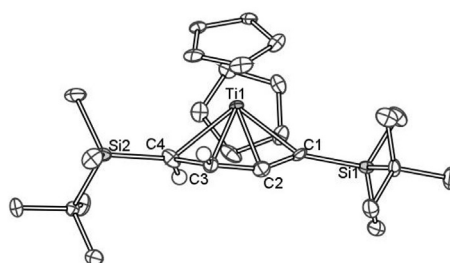
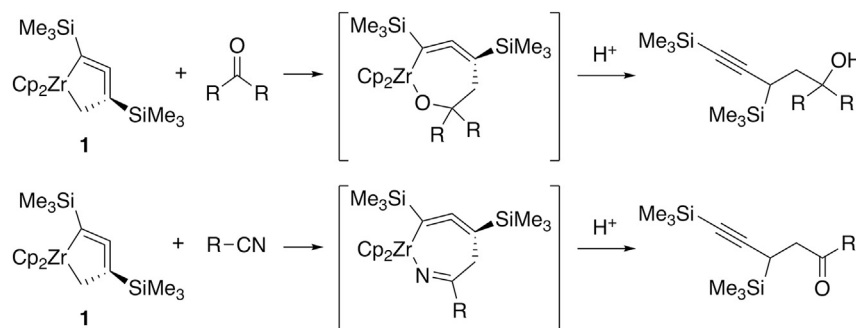


Fig. 2. The molecular structure of **4c**. Selected bond lengths (Å) and angles (°) are summarized in Table 2.

reported [8,11,12]. To our knowledge, this is the first example of a 1-titanacyclopenta-2,3-diene compounds in which the cycloallene



Scheme 1. Insertion of C=O and nitrile into the Zr–Csp³ bond in 2,4-bis(trimethylsilyl)-1-zirconacyclopenta-2,3-diene **1** and the hydrolysis products.

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