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Synthesis and Structure of Seven-Membered Metallacyclic Alkynes

Noriyuki Suzuki,[*,†] Naoto Aihara,[‡] Masakazu Iwasaki,[‡] Masahiko Saburi,[‡] and Teiji Chihara[†]

RIKEN, Wako, Saitama 351-0198, Japan, and Department of Applied Chemistry, Faculty of Engineering, Saitama Institute of Technology, Okabe, Saitama 369-0293, Japan

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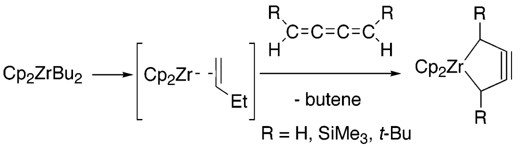
Summary: The zirconocene−ethylene complex and (Z)-1,4-bis(trimethylsilyl)-1,2,3-butatriene reacted to give a mixture of 1-zirconacyclopent-3-yne and 1-zirconacyclohept-3-yne. A zirconocene−alkyne complex gave, on the other hand, 1-zirconacyclohept-2-en-5-yne, which was structurally characterized as the major product along with a lesser amount of 1-zirconacyclopent-3-yne.

The synthesis and isolation of small cyclic alkynes have long attracted organic chemists.[1] We recently reported the synthesis and structure of five-membered metallacyclic alkynes that were prepared from 1,2,3-butatrienes and low-valent zirconocenes (eq 1).[2,3] These



(1)

compounds could be isolated as crystalline solids despite being small cyclic alkynes, and the structures were unambiguously determined. With regard to other cycloalkynes, some examples of isolable seven-membered cyclic alkynes have been reported.

Hydrocarbyl cycloheptynes,[4] as well as heterocyclic alkynes such as 1-thiacyclohept-4-ynes[5] and 1-silacyclohept-4-ynes, have been isolated and spectroscopically characterized.[1a] However, examples that have been structurally characterized by X-ray diffraction are very rare.[6−8] Also, to the best of our knowledge, there are no examples of 1-metallacyclohept-3-ynes.

Buchwald and Rosenthal independently reported the seven-membered metallacyclic cumulenes derived from a low-valent zirconocene and two 1,3-diyne molecules (vide infra).[9] This prompted us to pursue the synthesis of seven-membered metallacyclic alkynes by the reaction of a butatriene and a transition-metal complex. We report here the synthesis and structure of 1-zirconacyclohept-3-ynes.

In earlier work,[2a] the 1-zirconacyclopent-3-yne **2** was prepared by reaction of (*Z*)-1,4-bis(trimethylsilyl)-1,2,3-butatriene (**1**)[10] and Cp_2ZrBu_2 (Negishi reagent),[11] which forms Cp_2Zr(but-1-ene) in situ. Ligand exchange between the butatriene and butene predominated to the exclusion of their coupling. In the present study **1** was treated with Cp_2Zr(ethylene) derived from Cp_2ZrEt_2.[12] Interestingly, NMR spectroscopic examination of the solution indicated that the seven-membered metallacyclic product **3** was formed in 29% yield, accompanied by **2** (46% yield) after 18 h at room temperature (Scheme 1).[13] In the ^{13}C NMR spectrum signals due to two quaternary carbon atoms were observed at 96.36 and 104.05 ppm. The alkyne carbon signals appeared downfield, which suggests an interaction with the metal. Complex **2** was obtained as a mixture of cis and trans isomers, although **1** was of *Z* form ($\geq$98%). Judging from the NMR spectra of the reaction mixture, only one stereoisomer of **3** was predominantly formed and isomerization was not observed. Although its stereochemistry has not been determined, it was probably the syn form,

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[*] To whom correspondence should be addressed. E-mail: nsuzuki@riken.jp.

[†] RIKEN.

[‡] Saitama Institute of Technology.

(1) (a) Krebs, A.; Wilke, J. *Top. Curr. Chem.* **1983**, *109*, 189−233. (b) Gleiter, R.; Merger, R. In *Modern Acetylene Chemistry*; Stang, P. J., Diederich, F., Eds.; VCH: Weinheim, Germany, 1995; Chapter 8. (c) Meier, H. *Adv. Strain Org. Chem.* **1991**, *1*, 215−272.

(2) (a) Suzuki, N.; Nishiura, M.; Wakatsuki, Y. *Science* **2002**, *295*, 660−663. (b) Suzuki, N.; Aihara, N.; Takahara, H.; Watanabe, T.; Iwasaki, M.; Saburi, M.; Hashizume, D.; Chihara, T. *J. Am. Chem. Soc.* **2004**, *126*, 60−61. A 1-titanacyclopent-3-yne complex has been reported very recently: (c) Burlakov, V. V.; Arndt, P.; Baumann, W.; Spannenberg, A.; Rosenthal, U.; Parameswaran, P.; Jemmis, E. D. *Chem. Commun.* **2004**, 2074−2075. (d) Suzuki, N.; Watanabe, T.; Hirose, T.; Chihara, T. *Chem. Lett.* **2004**, *33*, 1488−1489.

(3) There has been discussion of the structures of these compounds; see: (a) Jemmis, E. D.; Phukan, A. K.; Jiao, H.; Rosenthal, U. *Organometallics* **2003**, *22*, 4958−4965. (b) Jemmis, E. D.; Phukan, A. K.; Giju, K. T. *Organometallics* **2002**, *21*, 2254−2261. (c) Lam, K. C.; Lin, Z. *Organometallics* **2003**, *22*, 3466−3470. (d) Rosenthal, U. *Angew. Chem., Int. Ed.* **2004**, *43*, 3882−3887.

(4) Krebs, A.; Kimling, H. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 509−510.

(5) Krebs, A.; Kimling, H. *Tetrahedron Lett.* **1970**, *11*, 761−764.

(6) 1-Thiacyclohept-4-yne 1,1-dioxide: (a) Bartsch, H.-H.; Colberg, H.; Krebs, A. *Z. Kristallogr.* **1981**, *156*, 10−12. 1,2,3,4,5-Pentasilacylohept-6-yne: (b) Ando, W.; Nakayama, N.; Kabe, Y.; Shimizu, T. *Tetrahedron Lett.* **1990**, *31*, 3597−3598.

(7) The structure of 1-argenta-2,7-dithacyclohept-4-yne, which contains Ag−S dative bonds, has been reported. Gleiter, R.; Rockel, H.; Nuber, B. *Chem. Ber.* **1996**, *129*, 581−584.

(8) There have been reports of metal-coordinated cycloheptynes: Bennett, M. A.; Schwemlein, H. P. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1296−1320 and references therein.

(9) (a) Hsu, D. P.; Davis, W. M.; Buchwald, S. L. *J. Am. Chem. Soc.* **1993**, *115*, 10394−10395. (b) Rosenthal, U.; Ohff, A.; Baumann, W.; Kempe, R.; Tillack, A.; Burlakov, V. V. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1605−1607. See also: (c) Bredeau, S.; Delmas, G.; Pirio, N.; Richard, P.; Donnadieu, B.; Meunier, P. *Organometallics* **2000**, *19*, 4463−4467.

(10) (a) Wakatsuki, Y.; Yamazaki, H.; Kumegawa, N.; Johar, P. S. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 987−989. (b) Wakatsuki, Y.; Yamazaki, H.; Kumegawa, N.; Satoh, T.; Satoh, J. Y. *J. Am. Chem. Soc.* **1991**, *113*, 9604−9610.

(11) Negishi, E.; Cederbaum, F. E.; Takahashi, T. *Tetrahedron Lett.* **1986**, *27*, 2829−2832.

(12) (a) Takahashi, T.; Seki, T.; Nitto, Y.; Saburi, M.; Rousset, C. J.; Negishi, E. *J. Am. Chem. Soc.* **1991**, *113*, 6266−6268. (b) Takahashi, T.; Suzuki, N.; Kageyama, M.; Nitto, Y.; Saburi, M.; Negishi, E. *Chem. Lett.* **1991**, 1579−1582. (c) Alt, H. G.; Denner, C. E.; Thewalt, U.; Rausch, M. D. *J. Organomet. Chem.* **1988**, *356*, C83−C85.

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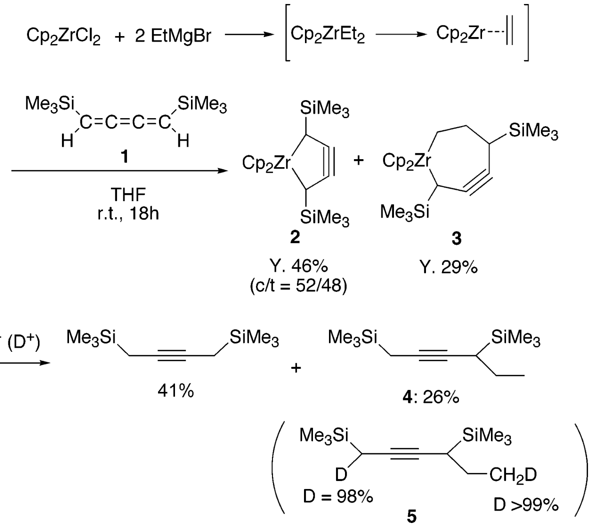
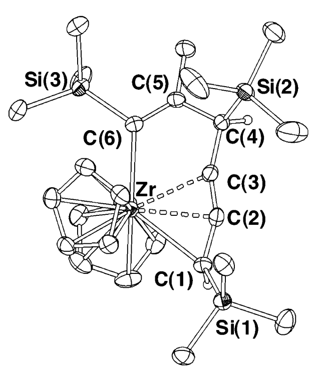
Scheme 1. Formation of a Seven-Membered Metallacyclic Alkyne



considering the results of compound **7** (vide infra). Hydrolysis of the reaction mixture with aqueous HCl gave the corresponding alkyne **4** (26% yield based on total Zr atoms), as well as 1,4-bis(trimethylsilyl)but-2-yne (41% yield based on Zr).[2a] Deuteriolysis gave **5** with 98% and >99% D incorporation at the 1- and 6-positions, respectively. These results supported the seven-membered structure of **3**. Although **3** was satisfactorily characterized by NMR spectroscopy in solution except for stereochemistry, our attempt to isolate it has been unsuccessful. The low yield of **3** is due to the ligand exchange between ethylene and **1** that competes with the coupling reaction. This led us to study the reaction using an alkyne complex instead of the ethylene complex. The zirconocene−alkyne complex $Cp_2Zr(Me_3SiC{\equiv}CMe)(PMe_3)$ (**6**),[14] was prepared and reacted with **1** (Scheme 2). After heating at 80 °C for 1 h, the formation of **7** in 62% yield was detected by NMR spectroscopy. The ligand exchange was suppressed, and **2** was formed only in low yield (19% by ^1H NMR) along with a small amount of unidentified products.[15] Hydrolysis of **7** by acidic media gave the 1,4-enyne **8** in good yield.[16] When **2** was treated with 1-(trimethylsilyl)-1-propyne or ethylene, formation of **7** or **3** was not observed.

Recrystallization of the reaction mixture of **7** from hexane gave single crystals. X-ray diffraction analysis showed that the molecule has a distorted seven-membered metallacyclic structure (Figure 1). The stereochemistry of the two trimethylsilyl groups was syn.

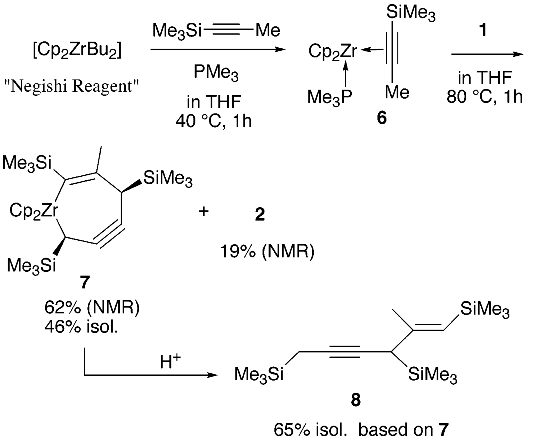


Zr-C(1)	2.580(2)
Zr-C(2)	2.417(2)
Zr-C(3)	2.425(2)
Zr-C(6)	2.424(2)
C(1)-C(2)	1.383(3)
C(2)-C(3)	1.239(3)
C(3)-C(4)	1.465(3)
C(4)-C(5)	1.512(3)
C(5)-C(6)	1.358(3)

Zr-C(1)-C(2)	67.5(1)
Zr-C(3)-C(4)	125.1(1)
C(3)-Zr-C(6)	65.8(1)
C(1)-C(2)-C(3)	156.1(2)
C(2)-C(3)-C(4)	159.3(2)
C(3)-C(4)-C(5)	106.6(2)
C(4)-C(5)-C(6)	120.2(2)
C(6)-C(5)-C(7)	127.7(2)

Figure 1. Molecular structure of **7**, drawn with 50% probability ellipsoids. Hydrogen atoms are partly omitted for clarity.

Scheme 2. Preparation of the 1-Zirconacyclohept-2-en-5-yne 7



The formation of the anti isomer was negligible, judging from the NMR spectra of the reaction mixture. The length of the Zr−C(1) bond (2.580(2) Å) demonstrates the existence of a metal−carbon bond. The C(2)−C(3)

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[13] To a solution of dichlorobis(cyclopentadienyl)zirconium(IV) (292 mg, 1.0 mmol) in THF (5 mL) was added ethylmagnesium bromide (0.89 M THF solution, 2.0 mmol) dropwise at −78 °C. Then **1** (196 mg, 1.0 mmol) was added and the mixture was warmed to room temperature and stirred overnight. The formation of **3** in 29% yield was observed by ^1H NMR at this stage, accompanied by zirconacyclopentyne compounds **2** in 46% yield (cis/trans = 52/48). After dioxane (0.2 mL) was added to precipitate magnesium salts, the volatiles were removed in vacuo and the residue was dissolved in C_6D_6 to measure NMR spectra without separation. NMR yields were determined by using pyrene as an internal standard. The NMR signals of **3** were assigned by subtracting the signals of **2**[2a] from the spectra of the mixture. Attempts to isolate **3** by recrystallization have been unsuccessful.

[14] For examples of Cp_2Zr(alkyne) complexes, see: (a) Buchwald, S. L.; Lum, R. T. *J. Am. Chem. Soc.* **1986**, *108*, 7441−7442. (b) Takahashi, T.; Swanson, D. R.; Negishi, E. *Chem. Lett.* **1987**, 623−626. (c) Buchwald, S. L.; Nielsen, R. B. *Chem. Rev.* **1988**, *88*, 1047−1058. (d) Wagenen, B. C. V.; Livinghouse, T. *Tetrahedron Lett.* **1989**, *30*, 3495−3498. See also ref 11.

[15] To a solution of Cp_2ZrCl_2 (292 mg, 1.0 mmol) in THF (5 mL) was added *n*-butyllithium (1.54 M in hexane, 2.0 mmol) dropwise at −78 °C. Then 1-(trimethylsilyl)-1-propyne (112 mg, 1.0 mmol) and trimethylphosphine (91.3 mg, 1.2 mmol) were added, and the mixture was warmed to room temperature. The solution was stirred at 40 °C for 1 h. The quantitative formation of $Cp_2Zr(Me_3SiC{\equiv}CMe)(PMe_3)$ (**6**) was observed by ^1H NMR. To this solution was added **1** (196 mg, 1.0 mmol), and the mixture was stirred at 80 °C for 1 h. At this stage, the formation of **7** in 62% yield was observed by ^1H NMR spectroscopy along with **2** (19% yield, cis/trans = 42/58). The NMR yield was determined by using pyrene as an internal standard. Volatiles were removed in vacuo, and the residue was dissolved in hexane and the solution filtered. The filtrate was concentrated, and cooling at −20 °C gave 243 mg of yellow crystals of **7** in 46% isolated yield. The mother liquid contained a considerable amount of **2**. **7**: ^1H NMR (C_6D_6) δ 0.17 (s, 3H), 0.27 (s, 3H), 0.51 (s, 3H), 1.95 (d, $^4J_{H-H}$ = 0.7 Hz, 3H), 2.17 (d, ^5J = 5.2 Hz, 1H), 3.68 (dd, ^5J = 5.2 Hz, ^4J = 0.7 Hz, 1H), 5.52 (s, 5H), 5.64 (s, 5H); ^{13}C NMR (C_6D_6) δ −1.02, 1.39, 5.61, 26.23, 38.84, 52.12, 101.36, 105.60, 107.29, 110.05, 162.41, 172.50; IR 2028 cm^{-1}; mp 108−109 °C dec (in Ar). Anal. Calcd for $C_{26}H_{42}Si_3Zr$: C, 58.91; H, 7.99. Found: C, 58.75; H, 7.98. Crystal data of **7**: $C_{26}H_{42}Si_3Zr$, FW = 530.09, monoclinic, space group = *C*2/*c*, *a* = 11.041(1) Å, *b* = 19.729(3) Å, *c* = 25.440(4) Å, β = 98.759(6)°, *V* = 5477(1) Å^3, *Z* = 8, D_{calcd} = 1.29 g/cm^3, *R* = 0.040, R_w = 0.135, GOF = 1.61.

[16] The isolated compound **7** (304 mg, 0.524 mmol) was dissolved in THF (2 mL), and H_2O (1 mL) was added at room temperature. After it was stirred for 3 min, the mixture was extracted with diethyl ether (10 mL × 3). The organic layers were combined and dried over magnesium sulfate. The solution was filtered, and the solvent was removed in vacuo. The yellow oily residue was dissolved in hexane, and purification by column chromatography using silica gel (deactivated with 10 v/v % of water) and hexane as an eluent gave 105.8 mg of pure **8** as a colorless liquid in 65% yield based on **7**. Hydrolysis with aqueous HCl resulted in higher yield (97% by GC), although it caused desilylation of the product during the purification.

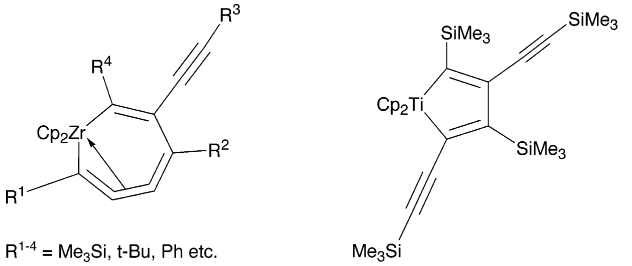
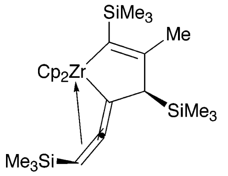


Figure 2. Zirconacyclocumulene vs α-alkynyltitanacyclopentadiene.

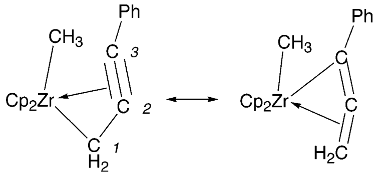
bond is short enough (1.239(3) Å) to be regarded as a triple bond. The alkyne moiety is bent toward the metal, showing its interaction with Zr. The angles C(1)−C(2)−C(3) and C(2)−C(3)−C(4) are 156.1(2) and 159.3(2)°, respectively. The short Zr−C(2) and Zr−C(3) distances also support metal−carbon interactions.

Rosenthal reported that the titanocene and 1,3-diynes formed an α-alkynyltitanacyclopentadiene, while zirconocene forms a seven-membered zirconacyclocumulene (Figure 2).[17] One might suggest, also in **7**, the possibility of an α-allenylidenezirconacyclopentene structure such as **7′**.[18]

The X-ray diffraction study of **7** showed that the C(2)−C(3) distance is significantly shorter than C(1)−C(2) (1.383(2) Å) and that the angle C(2)−C(3)−C(4) is much larger than 120°, suggesting the 1-metallacyclohept-2-en-5-yne structure. In the ^{1}H NMR spectrum, the methine proton at C(1) appeared at 2.17 ppm, showing its sp^3 character. The C(2) and C(3) signals appeared at 101.36 and 110.05 ppm in the ^{13}C NMR spectrum, which could be regarded as alkyne carbons. The signal for C(1) was observed at 38.8 ppm. In the infrared spectrum absorption due to the triple bond was observed at 2028 cm^{-1}. These results support the seven-membered enyne structure of **7**, although the C(1)−C(2) bond is too short to be regarded as a single bond.



7'



9 **9'**

Wojcicki et al. reported the synthesis and structure of $Cp_2Zr(Me)(CH_2C{\equiv}CPh)$ (**9**).[19] They suggested the contribution of the allenyl structure **9′**, taking into account the long $Zr-CH_2$ bond (2.658(4) Å) and a short Zr−CPh distance (2.361(3) Å). The propargyl moiety of **7** resembles that of **9**. However, the Zr−C(1) distance in **7** (2.580(2) Å) is shorter than $Zr-CH_2$ in **9**, and Zr−C(3) (2.425(2) Å) is longer than Zr−CPh in **9**. In addition, C(1)−C(2) in **7** is significantly longer than that of **9** (1.383(3) vs 1.344(5) Å), and C(2)−C(3) is shorter (1.239(3) vs 1.259(4) Å). Thus, we conclude that structures **7** and **7′** both contribute to the description of this complex, although the contribution of the former must be more important.

Finally, **7** is thermally stable and the crystals could be stored under an inert atmosphere for months, although it is sensitive toward air and moisture. Further studies of the reactivity of these compounds are in progress.

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Supporting Information Available: Text and figures giving synthetic procedures and spectroscopic data for **3**, **4**, and **6**−**8** and crystallographic data (CIF) for **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) Burlakov, V. V.; Ohff, A.; Lefeber, C.; Tillack, A.; Baumann, W.; Kempe, R.; Rosenthal, U. *Chem. Ber*. **1995**, *128*, 967−971.

(18) Resonance structures between α-vinylzirconacyclopentanes and seven-membered rings have been proposed. For example: (a) Nakamura, A. *J. Organomet. Chem*. **1990**, *400*, 35−48 and references therein. (b) Erker, G.; Engel, K.; Dorf, U.; Atwood, J. L.; Hunter, W. E. *Angew. Chem., Int. Ed. Engl*. **1982**, *21*, 914−915.

(19) (a) Blosser, P. W.; Gallucci, J. C.; Wojcicki, A. *J. Am. Chem. Soc*. **1993**, *115*, 2994−2995. See also: (b) Binger, P.; Langhauser, F.; Gabor, B.; Mynott, R.; Herrmann, A. T.; Krüger, C. *J. Chem. Soc., Chem. Commun*. **1992**, 505−506.