

Synthesis and Structure of 1-Zirconacyclopent-3-yne Complexes without Substituents Adjacent to the Triple Bond

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Small cyclic alkynes are usually unstable because of ring strain, and much effort has been devoted to their preparation and isolation.¹ Generally, substituents adjacent to a triple bond decrease the reactivity of cycloalkynes and make them more stable. For example, 3,3,7,7-tetramethylcycloheptyne (**1**, Figure 1) was isolated,² whereas the nonsubstituted cycloheptyne (C₇H₁₀) has not been obtained in a pure form.³ 1,2,3,4-Tetrasilacyclohex-5-yne (**2**), which are isolable six-membered cycloalkynes, also have alkyl groups on all silicon atoms.⁴ Cyclooctyne is the smallest nonsubstituted cycloalkyne that has been isolated.⁵

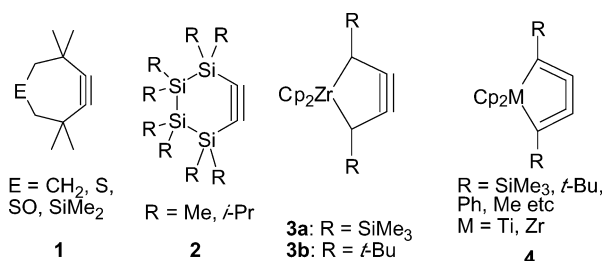
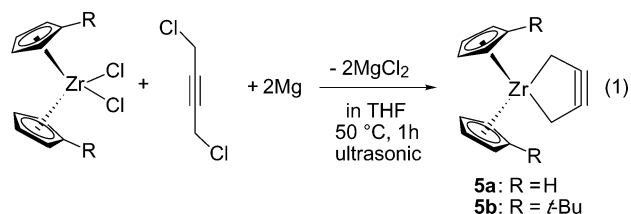


Figure 1. Isolable small cycloalkynes and related compounds.

We recently reported preparation and structural characterization of organozirconium complexes (**3**) by the reaction of Cp₂Zr(*n*-Bu)₂ (Negishi reagent, Cp = η⁵-C₅H₅) and 1,4-disubstituted-1,2,3-butatrienes.⁶ These compounds could be considered a 1-zirconacyclopent-3-yne, that is, the smallest ever isolated cyclic alkyne.⁷ They have bulky substituents (R = Me₃Si, *t*-Bu) at the carbons adjacent to the triple bond. The suggestion was made that these may contribute to the stability of **3**.^{6,8} Five-membered metallacyclocumulene complexes (**4**) were reported by Rosenthal and co-workers.⁹ The molecular structure of **3** was found to be similar to those of **4**. They synthesized a variety of related compounds and extensively studied their reactivity.¹⁰ However, a five-membered metallacyclocumulene without substituents (R = H in **4**) has not been prepared so far, although it was studied theoretically.¹¹ Thus it is challenging and intriguing to pursue the possibility of “nonsubstituted” metallacyclopentynes. We herein report the synthesis and characterization of 1-zirconacyclopent-3-yne compounds (**5**) that have no substituents adjacent to the triple bond.

The reduction of zirconocene dichloride and 1,4-dichlorobut-2-yne using magnesium in tetrahydrofuran (THF) gave **5a** in good yield (eq 1).¹² The ¹H NMR spectrum showed two singlets at 4.99 and 2.73 ppm assignable to the cyclopentadienyl rings and Zr-CH₂, respectively. In the ¹³C NMR spectrum, a signal for quaternary carbons appeared at 102.45 ppm. The alkynyl carbon observed downfield is a characteristic of zirconacyclopent-3-yne compounds.⁶ IR absorption of C≡C stretching was observed at 2018 cm⁻¹, which

is close to that of **3**.¹³ Elemental analysis also satisfied the structure **5a**.



A zirconocene bearing *tert*-butyl groups on Cp rings also gave 1-zirconacyclopent-3-yne **5b** in a similar manner. The molecular structure of **5b** is shown in Figure 2.¹⁴ The structure of the metallacyclopent-3-yne moiety was fundamentally the same as that observed in the moiety bearing trimethylsilyl groups in **3a**. It should be noted, however, that there are a few slight differences. The bond length C2–C3 (1.237(3) Å) is slightly longer than the corresponding bond of **3a** (1.206(7) Å), while C1–C2 and C3–C4 are in the same range (1.415(7) and 1.400(6) Å in **3a**). The angles C1–C2–C3 and C2–C3–C4 are smaller than those in **3a** (156 and 155°). The slightly longer triple bond is consistent with more strained C–C≡C angles. These structural data are in good correspondence with the calculated results.¹¹

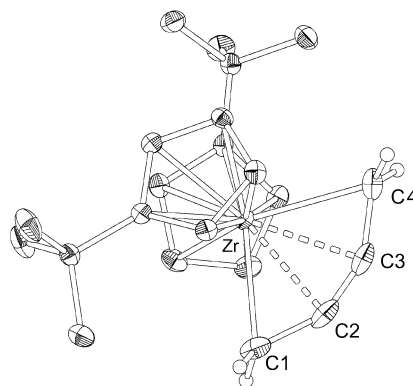


Figure 2. Molecular structure of **5b**. Drawn with 50% probability. Hydrogens are partly omitted for clarity. Selected bond lengths (Å) and angles (deg): Zr–C1 2.414(2), Zr–C2 2.311(2), Zr–C3 2.305(2), Zr–C4 2.433(2), C1–C2 1.418(3), C2–C3 1.237(3), C3–C4 1.417(3); C1–Zr–C4 100.6(1), Zr–C1–C2 68.6(1), C1–C2–C3 150.8(2), C2–C3–C4 152.3(2), Zr–C4–C3 67.7(1).

These results showed that metallacyclopentynes are stable enough to be isolated in a pure form, even though they have no substituents adjacent to the triple bond. Complexes **5a,b** can be stored at room temperature under an inert atmosphere for at least a month as well as **3**.

When **5a** was treated with an equimolar amount of Cp₂Zr-(but-1-ene)(PME₃),¹⁵ a ligand exchange between but-1-ene and **5a**

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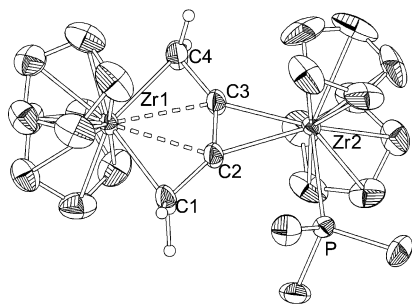
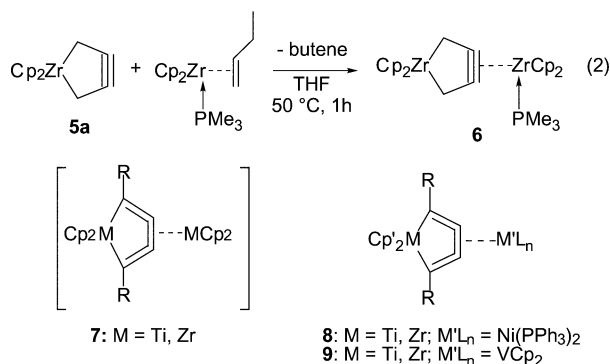


Figure 3. Molecular structure of **6**. Drawn with 50% probability. Hydrogen atoms are partly omitted for clarity. Selected bond lengths (Å) and angles (deg): Zr1–C1 2.279(4), Zr1–C2 2.495(3), Zr1–C3 2.461(3), Zr1–C4 2.270(3), Zr2–C2 2.292(3), Zr2–C3 2.221(3), C1–C2 1.490(4), C2–C3 1.336(4), C3–C4 1.480(4); C1–Zr1–C4 103.3(1), C1–C2–C3 136.7(3), C2–C3–C4 140.6(3).

took place to give a bimetallic complex **6** in excellent yield (eq 2).¹⁶ Figure 3 shows the molecular structure of **6**.



The zirconacyclopentene coordinates to the other metal with its alkyne moiety. The two metals and C1–C2–C3–C4 are almost coplanar, and the plane is nearly perpendicular (85°) to the (Cp centroid)–Zr2–(Cp centroid) plane. The C2–C3 bond length (1.336(4) Å) is significantly longer than the triple bonds in known Zr–cyclopentene (1.296 Å)¹⁷ and Zr–cyclohexyne complexes (1.30, 1.32 Å).¹⁸ The ¹³C NMR chemical shifts of C2 and C3 (133.06, 154.64 ppm) are observed upfield compared with them.¹⁹ Although the reason for these findings on the C2/C3 is still vague, it might be because Zr1 also interact with them. The bonds C1–C2 and C3–C4 can be regarded as single bonds, showing that the metallacycle moiety is a “flat” 1-zirconacyclopent-3-ene.²⁰ It should be emphasized that **5** behaved as an alkyne to form a metal–cycloalkyne complex,²¹ supporting its cycloalkyne character. In metallacyclocumulenes **4**, similar complexes **7** were proposed as intermediates in further transformation.^{10,22} However, homobimetallic **7** has not been isolated to date, although heterobimetallic analogues **8**²³ and **9**²⁴ have been reported. The similarity between **6** and **9** is of interest in understanding the reactivity of these compounds. Further study on the related compounds is now in progress.

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Supporting Information Available: Synthetic procedures and spectroscopic data for **5** and **6**; crystallographic data (PDF and CIF)

for **5b** and **6**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (12) To a suspension of dry magnesium powder (72.9 mg, 3 mmol) in THF (5 mL) were added Cp₂ZrCl₂ (292 mg, 1.0 mmol) and 1,4-dichlorobut-2-yne (123 mg, 1.0 mmol). The mixture was sonicated at 50 °C for 1 h. The formation of **5a** in 70–80% yield was observed by ¹H NMR. The volatiles were removed in vacuo and the residue was dissolved in hexane and filtered. The filtrate was concentrated and cooled at –20 °C. A white microcrystalline solid of **5a** was obtained (40%). ¹H NMR (C₆D₆): δ 2.73 (s, 4H), 4.99 (s, 10H). ¹³C NMR (C₆D₆): δ 38.64, 102.45, 103.10. IR (KBr): 2018 cm^{–1} (weak, ν_{C≡C}). Anal. Calcd for C₁₄H₁₄Zr: C, 61.49; H, 5.16. Found: C, 61.23; H, 5.14.
- (13) It is known that even symmetrical cycloalkynes usually exhibit a weak IR absorption of C≡C stretching at 2100–2200 cm^{–1}, see ref 1a.
- (14) **5b**. Yield 76% by NMR, 52% isol. ¹H NMR (C₆D₆): δ 1.23 (s, 18H), 2.82 (s, 4H), 4.88 (t, J = 2.7 Hz, 4H), 5.01 (t, J = 2.7 Hz, 4H). ¹³C NMR (C₆D₆): δ 32.16, 32.46, 41.36 (CH₂), 101.93, 104.29 (C≡C), 104.63, 130.65. IR (KBr): 2018 cm^{–1} (weak, ν_{C≡C}). Anal. Calcd for C₂₇H₃₀Zr: C, 68.51; H, 7.84. Found: C, 68.46; H, 7.89. Crystal data: C₂₇H₃₀Zr, FW = 385.68, monoclinic, space group = P₂/n, a = 26.7687(11), b = 8.7564(3), c = 8.0887(4) Å, β = 91.063(2)°, V = 1895.64(14) Å³, Z = 4, D_{calc} = 1.351 g/cm³, R = 0.0303, wR = 0.0688, GOF = 1.151. See the Supporting Information for details.
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- (16) **6**. Yield 96% by ¹H NMR, 65% isol. ¹H NMR (THF-*d*₆, Me₄Si): δ 1.15–1.17 (m, 2H), 1.55–1.57 (m, 2H), 1.57 (d, J_{p-H} = 5.9 Hz, 9H), 5.14 (d, J_{p-H} = 1.6 Hz, 10H), 5.32 (s, 10H). ¹³C NMR (THF-*d*₆, Me₄Si): δ 17.48 (J_{C-P} = 16 Hz), 27.71, 30.67, 102.60, 104.26, 133.06 (J_{p-C} = 17.9 Hz), 154.64 (J_{p-C} = 8.4 Hz). Anal. Calcd for C₂₇H₃₂ZrP: C, 56.80; H, 5.83. Found: C, 56.82; H, 6.11. Crystal data: C₂₇H₃₂ZrP, FW = 570.97, monoclinic, space group = P₂/c, a = 10.5259(2), b = 33.0858(4), c = 8.2256(1) Å, β = 105.6613(5)°, V = 2758.28(7) Å³, Z = 4, D_{calc} = 1.375 g/cm³, R = 0.041, wR = 0.132, GOF = 1.71. See the Supporting Information for details.
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