Synthesis and Structure of a Seven-Membered Cyclic Cumulene

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Johnson and co-workers have reported the smallest isolated cyclic cumulene (cyclonona-1,2,3-triene)[2a] and the smallest example to be generated and trapped *in situ* (cyclohexa-1,2,3-triene).[2b] Herein we report the synthesis and X-ray crystal structure determination of the seven-membered cyclic cumulene[2c,d] 2,4,7-tris(trimethylsilyl)-3-((trimethylsilylethynyl)zirconacyclohepta-2,4,5,6-tetraene (**4**).[3]

In an attempt to prepare zirconaradialene **1** (Scheme I), 1,4-bis(trimethylsilyl)buta-1,3-diyne (**2**) was added at −78 °C to dibutylzirconocene (a precursor to the zirconocene complex of *n*-butene **3**).[4] The reaction mixture was warmed to room temperature and stirred overnight. From the reaction mixture, two compounds were isolated: **4** (a 1:2 adduct of Cp_2Zr and **2**) and **5** (a 2:1 adduct of Cp_2Zr and **2**). The yield of **4** was optimized by performing the reaction using a 1:2.5 ratio of the zirconocene reagent and **2**. Under these conditions, **4** was isolated in 66% yield after recrystallization from diethyl ether at low temperature. Compound **5**, the result of the cleavage of the carbon–carbon single bond in **2**, was identified by X-ray crystallography. The preparation and X-ray structure determination of an analogous complex has previously been reported by Erker and co-workers.[5]

Description of **4** as a distorted cumulene, rather than as the isomeric zirconacyclopentadiene **6**, follows from its X-ray crystal structure; the ORTEP diagram and selected bond lengths and angles for **4** are shown in Figure 1. For example, the bond lengths for C13–C14 [1.337(6) Å], C14–C15 [1.298(6) Å], and C15–C16 [1.279(6) Å] indicate that these are of roughly similar bond order. Certainly the C14–C15 distance is incompatible with its description as a C–C single bond.[3a] The bond angles for **4** are also consistent with its formulation as a cumulene but indicate a great deal of distortion from linearity, as would be expected in order to minimize ring strain. For example, the C13–C14–C15 angle [160.1(5)°] is significantly perturbed from the idealized value of 180°.[6] Moreover, the C14–C15–C16 angle [148.8(5)°] reflects an even more drastic deviation and is midway between that expected for sp and sp² hybridization at C15. These angles are similar to the value of 155.4(3)° reported by Wojicki and co-workers for the related d⁰ allene complex $Cp_2Zr(CH_3)(\eta^3\text{-}C(Ph){=}C{=}CH_2)$.[3a] In contrast, the Cβ-Cα-C1′ angle for structure **6** would be expected to be ~125° in comparison with two relevant structurally characterized zirconacyclopentadienes.[7] A further interesting structural feature is that the metallacyclic portion of **4** is essentially planar.[8]

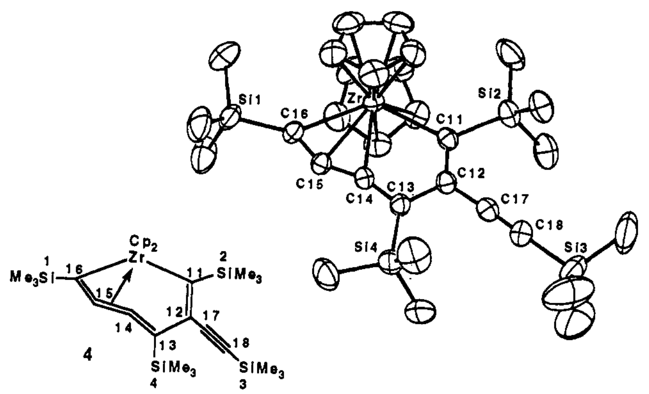
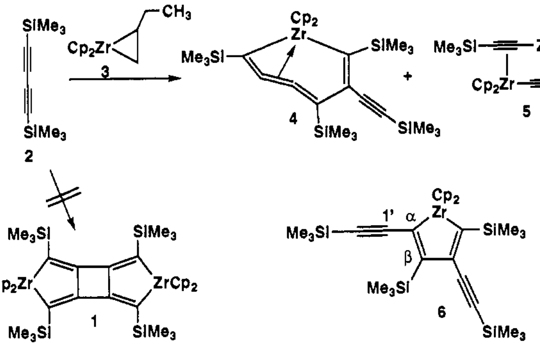


Figure 1. Selected bond lengths and angles for **4**. Lengths (Å): Zr–C11 2.416(5), Zr–C14 2.396(5), Zr–C15, 2.423(5), Zr–C16 2.442(5), C13–C14, 1.337(6), C14–C15, 1.298(6), C15–C16, 1.279(6), C17–C18, 1.205(7), C12–C17, 1.452(7). Angles (deg): C11–C12–C17, 124.9(5), C13–C14–C15, 160.1(5), Si1–C16–C15, 143.6(4), Si3–C18–C17, 176.3(6), C14–C15–C16, 148.8(5), C12–C17–C18, 177.9(6), C11–Zr–C16, 128.6(2), C15–Zr–C16, 30.5(2).

Scheme I



To date, we have not examined the reaction chemistry of **4** in detail, but we have shown that it survives, largely unchanged, heating as a benzene solution at 75 °C for 3 days. If the thermolysis is carried out in the presence of excess PMe_3, no conversion to a characterizable product is seen; only slow decomposition of **4** is observed.

While the route by which **4** is formed is unclear, it is reasonable to invoke the intermediacy of **6**. Severe in-plane steric interactions between the ring substituents[9] could induce the zirconocene unit to migrate from C14 to C16.[3a] Several reasons for the relative stability of **4** are likely. First, coordination of the central double bond of the cumulene produces a coordinately saturated zirconium center. Such intramolecular coordination of olefins in related systems is well precedented.[10] The π-system of the central double

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(2) (a) Angus, R. O., Jr.; Johnson, R. P. *J. Org. Chem.* **1984**, *49*, 2880–2883. (b) Shakespeare, W. C.; Johnson, R. P. *J. Am. Chem. Soc.* **1990**, *112*, 8578–8579. (c) Szeimies and co-workers have reported the generation of transient 1,2,3-cycloheptatriene and its trapping with a variety of reagents: Zoch, H.-G.; Szeimies, G.; Römer, R.; Germain, G.; Declercq, J.-P. *Chem. Ber.* **1983**, *116*, 2285–2310. (d) Lead references can be found in a recent review, cf.: Johnson, R. P. *Chem. Rev.* **1989**, *89*, 1111–1124.

(3) Several fascinating and relevant publications have recently appeared: (a) Blosser, P. W.; Galluci, J. C.; Wojicki, A. *J. Am. Chem. Soc.* **1993**, *115*, 2994–2995 and references therein. (b) Yin, J.; Abboud, K. A.; Jones, W. M. *J. Am. Chem. Soc.* **1993**, *115*, 3810–3811. (c) Pang, Y.; Petrich, S. A.; Young, V. G., Jr.; Gordon, M. S.; Barton, T. J. *J. Am. Chem. Soc.* **1993**, *115*, 2534–2536. (d) Lin, J.; Pang, Y.; Young, V. G., Jr.; Barton, T. J. *J. Am. Chem. Soc.* **1993**, *115*, 3794–3795. (e) Rappert, T.; Nürnberg, O.; Werner, H. *Organometallics* **1993**, *12*, 1359–1364.

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

(5) (a) Erker, G.; Frömberg, W.; Benn, R.; Mynott, R.; Angermund, K.; Krüger, C. *Organometallics* **1989**, *8*, 911–920 and references therein. (b) Details of the structure and formation of **5** are described in the Ph.D. thesis of D. P. Hsu, Massachusetts Institute of Technology, 1991.

(6) The energetic cost of distorting a cumulene from 180 to 160° has been calculated to be ~4 kcal/mol per unit: Diederich, F.; Rubin, Y.; Knobler, C. B.; Whetten, R. L.; Schriver, K. E.; Houk, K. N.; Li, Y. *Science* **1989**, *245*, 1088–1090.

(7) Nugent, W. A.; Thorn, D. L.; Harlow, R. L. *J. Am. Chem. Soc.* **1987**, *109*, 2788–2796. These values were calculated using the positional parameters given in the supplementary material of this reference.

(8) Additional views of **4** are included in the supplementary material.

(9) (a) Buchwald, S. L.; Nielsen, R. B. *J. Am. Chem. Soc.* **1989**, *111*, 2870–2874 and references therein. (b) Buchwald, S. L.; Nielsen, R. B. *Chem. Rev.* **1988**, *88*, 1047–1058. The manifestation of this sort of stabilization for the preparation of zirconocene complexes of strained cycloallenes has recently been reported by Jones and co-workers.[3b]

(10) Cf.: Erker, G.; Krüger, C.; Müller, G. *Adv. Organomet. Chem.* **1985**, *24*, 1–39.

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bond is in the metallacyclic plane, facilitating its interaction with the Zr-centered LUMO.[11] We note that **4** is different from the many zirconocene complexes of strained unsaturated organic molecules which we have reported.[9b] In these molecules, the strain is attenuated by back-bonding from a d^2 zirconium center; such a means of stabilization is obviously not available for this d^0 complex. Second, Zr–C bond lengths (Figure 1) are significantly longer than C–C bond lengths, which mitigates the ring strain.[2c,3c] In addition, Zr–C bonds in which the carbon center has a trimethylsilyl substituent possess increased stability.[9a] Finally, the thermal stability of **4** is not entirely surprising; the bulky trimethylsilyl substituents at C13 and C16, as well as the enormous zirconocene unit, sterically protect the cumulene moiety. This minimizes the likelihood of bimolecular reactions of **4**,[2d] whether they be dimerization or nucleophilic attack.

In summary, we have prepared the smallest ring cyclic cumulene to be structurally characterized.[12] The results reported herein indicate that the combination of transition metals and serendipity can lead to unexpected and interesting new chemistry.

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Supplementary Material Available: Crystallographic data and procedures, ORTEP and PLUTO diagrams of **4**, tables of bond distances and angles for **4**, and a table of final positional and thermal parameters for **4** (27 pages); table of structure factors for **4** (53 pages). Ordering information is given on any current masthead page.

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(11) Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729–1742.

(12) Experimental procedure for the preparation of **4**: to a solution of zirconocene dichloride (0.292 g, 1 mmol) in ether (20 mL) at –78 °C, under an argon atmosphere, was added a solution of *n*-butyllithium (1.14 M in hexane, 1.75 mL, 2 mmol) dropwise. After 30 min, a solution of 1,4-bis(trimethylsilyl)-1,3-butadiyne (0.488 g, 2.5 mmol) in ether (10 mL) was added, the cold bath was removed, and the reaction was allowed to be stirred overnight at room temperature. At this point, the solution was cannula-filtered, and the volatiles were removed *in vacuo* to give a crude product which was recrystallized from diethyl ether at –80 °C to yield **4** as a yellow solid (0.401 g, 66%): ^{1}H NMR (300 MHz, C_6D_6) δ 5.38 (s, 10 H), 0.66 (s, 9 H), 0.58 (s, 9 H), 0.35 (s, 9 H), 0.31 (s, 9 H); ^{13}C NMR (75 MHz, C_6D_6) δ 229.2, 187.8, 162.7, 161.4, 152.3, 110.0, 105.3, 101.0, 91.6, 3.3, 1.3, –0.1, –0.2; IR (KBr) 2955, 2894, 2123, 1875, 1649, 1441, 1438, 1397, 1265, 1250, 1244, 1080, 1018, 989, 840, 812, 805, 799, 794, 755, 693, 679, 669, 634, 628, 484, 437, and 431 cm^{-1}. A sample of **4** from a separate experiment was characterized by elemental analysis. Anal. Calcd for $C_{30}H_{46}Si_4Zr$: C, 59.05; H, 7.6. Found: C, 58.94; H, 7.44.