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This paper describes the first preparation and X-ray crystal structure determination of a zirconacyclopropene-alkyne (bis-alkyne) complex. Species of this type have been proposed as intermediates in the zirconocene-mediated reductive coupling of two alkynes to form a zirconacyclopentadiene.

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Synthesis and X-Ray Structure of a Zirconacyclopropene-Alkyne Complex: On The Mechanism of Zirconium-Mediated Reductive Coupling of Alkynes

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Synthesis and X-ray Structure of a Zirconacyclopropene-Alkyne Complex: On the Mechanism of Zirconium-Mediated Reductive Coupling of Alkynes

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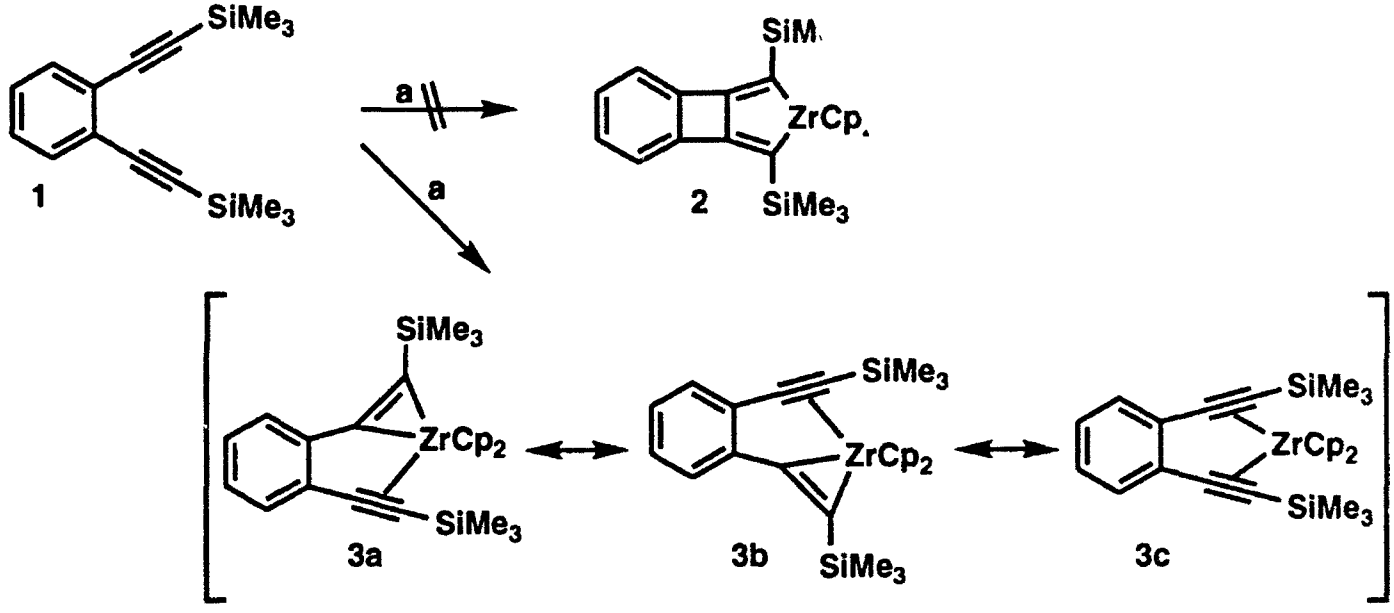
ABSTRACT

The zirconocene-mediated reductive coupling of alkynes has been proposed to proceed *via* an intermediate zirconacyclopropene-alkyne (bis-alkyne) complex. Herein, we report the first preparation and X-ray crystal structure determination of such a zirconacyclopropene-alkyne (bis-alkyne) complex.

For several years we have been interested in the synthesis and the study of the structural properties of main group metallacycles[1]. These species are oft- ently available *via* transmetallation of a zirconacycle precursor[2]. Mole- anar structure appear to have superior packing properties in " that zirconacycle **2** would be a useful precursor to t- Treatment of **1**[3] (Scheme I) with an equivalent c er agent[4], unexpectedly failed to give **2**[4,5], and inste orange crystals[6].

Scheme I



a. Cp_2ZrCl_2/2 nBuLi/THF/-78° C to RT, then hexane to 70° C (55%)

[Figure 1]

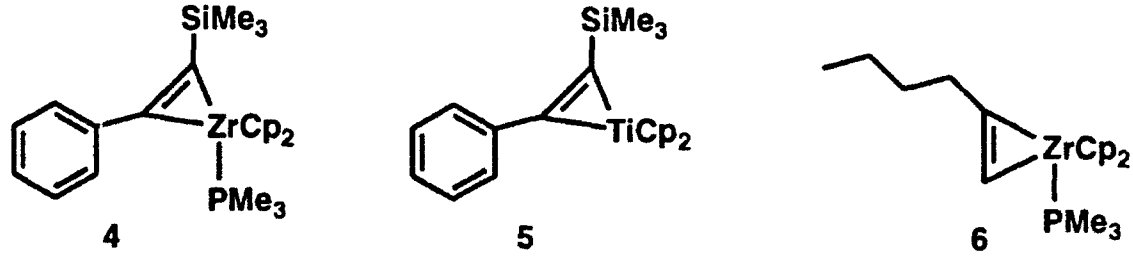
The three most plausible resonance structures for **3** are shown in Scheme I. Both the spectroscopic and crystallographic data which we have collected indicate that **3a** and **3b** are the major resonance forms, and that **3c** is a minor contributor.[7] Consistent with this representation, no change, other than slight broadening, is observed in the ^1H NMR spectrum at temperatures as low as -92 °C (toluene-d_8). The IR spectrum exhibits only a single stretch in the alkyne region at 1816 cm^{-1}. This signal is approximately mid-way between that observed for **1** at 2161 cm^{-1}, and that seen in normal group 4 metallocene complexes of

alkynes (metallacyclopropenes) in **4**[8] at 1620 cm^{-1} and **5**[9] at 1686 cm^{-1}. Similarly, in the ^{13}C NMR spectrum of **3**, signals for only two alkynyl carbons are present at 143.3 and 154.2 ppm. These resonances are roughly equidistant from those observed for their counterparts in **1** (98.4 and 103.3 ppm), and **4** (177.4 and 181.0 ppm) and **5** (213.0 and 219.6 ppm). An ORTEP of the structure resulting from an X-ray diffraction determination is shown in Figure 1. The effects of π-backbonding are manifested by the fact that the C_1-C_2 bond distance of 1.258(5) Å in **3** is substantially longer than the value of 1.195(3) Å seen in hexakis(trimethylsilylethynyl)benzene[10]. This longer bond length is close to that displayed by other zirconacyclopropenes, such as **6**[11a], in which the corresponding carbon-carbon bond length is 1.286(5) Å. Further, in **3** the C_2-C_1-Si and C_1-C_2-C_3 bond angles are similar to the analogous angles in **4**, **5** and **6** (Table 1). Taken together, the spectroscopic and crystallographic data both support the conclusion that **3** is best described as a zirconacyclopropene-alkyne complex.

Table 1: Comparison of selected bond angles of compounds **3-6**.

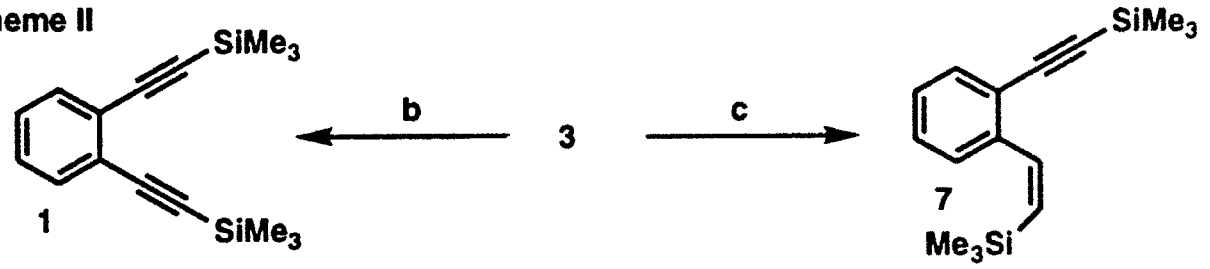
Compound	C_2-C_1-Si bond angles °	C_1-C_2-C_3 bond angles °
3	140.2(3)	154.8(4)
4	148.2(2)	141.0(2)
5	140.8(3)	151.9(3)
6	--	135.8(3)

Figure 2



The reactions of **3** are also consistent with the above structural description (Scheme II).

Scheme II

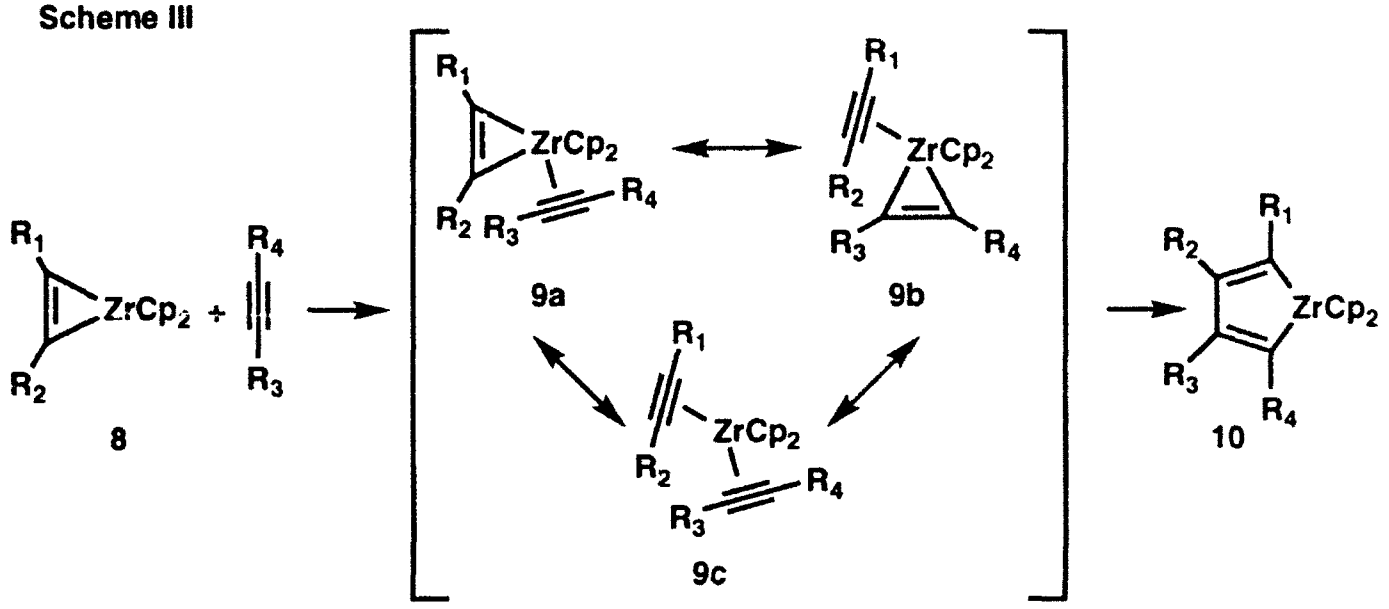


b. I_2/THF/-78° C (88%) c. H_2SO_4/H_2O/THF (92%)

For example, treatment of **3** with I_2 produces zirconocene diiodide and reforms **1** in 88% yield[12]. Treatment of **3** with aqueous sulfuric acid gives enyne **7**, in 92% yield[5a,12]. This result is similar to that seen by Nugent, where hydrolysis of the product of the reaction of "titanocene" and 2,6-octadiyne yielded *Z*-6-octene-2-yne[5a].

Group 4 metallocene-induced reductive coupling of alkynes have been proposed to proceed as shown in scheme III[5a,13]. The zirconocene-alkyne complex **8**, best described as a zirconacyclopropene[5a,11,13b], reacts with a second alkyne to form **9a (9b)**[5a,13], an 18 electron intermediate which has also been described as a bis-alkyne complex **9c**[5a,13a]. Insertion of the alkyne into the zirconium-carbon bond produces a zirconacyclopentadiene **10**. Other metal-mediated reductive coupling reactions have been proposed to proceed via similar mechanisms[14], and some intermediate species have been isolated[14b-d]. While several examples of zirconacyclopropenes[11] and zirconacyclopentadienes[5a,13a] have been isolated and structurally characterized, complex **3** represents, to our knowledge, the first example of the intermediate zirconacyclopropene-alkyne (bis-alkyne) complex.

Scheme III



In summary, we have isolated and structurally characterized a zirconacyclopropene-alkyne complex. Treatment of **1** with zirconocene-butene does not proceed to the zirconacyclopentadiene, but instead yields **3**. This demonstrates, for the first time, the viability of such a complex, which has been proposed as an intermediate in the zirconocene-induced reductive coupling of alkynes. We are continuing to examine the factors that affect these cyclizations, and their use in the synthesis of main group metallacycles with interesting physical properties.

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Supplementary Material Available: Full experimental procedures for the preparation of **3** and **7**. NMR, IR, and elemental analysis or HRMS characterization of compounds **3** and **7**, along with the crystallographic data and procedures, an ORTEP diagram of **3**, tables of bond distances and angles for **3**, and a table of final positional and thermal parameters for **3** (25

pages); table of structural factors for **3** (9 pages). Ordering information is given on any current masthead page.

Footnotes:

(1) (a) Buchwald, S.L.; Fisher, R.A.; Foxman, B.M. *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 771. (b) Buchwald, S.L.; Fisher, R.A.; Davis, W.M. *Organometallics* **1989**, *8*, 2082. (c) Fisher, R.A.; Nielsen, R.B.; Davis, W.M.; Buchwald, S.L. *J. Am. Chem. Soc.* **1991**, *113*, 165. (d) Spence, R.E.V.H.; Hsu, D.P.; Buchwald, S.L. *Organometallics* **1992**, *11*, 3492.

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(6) The initial reaction mixture also includes (as determined by ^{1}H NMR) the symmetrical zirconacyclopentadiene formed by coupling two equivalents of **1**. Upon heating the reaction products in hexane, this disproportionates into **1** and **3**. See Gesing, E.R.F. *J. Chem. Soc., Chem. Commun.* **1982**, 426.

(7) For a cogent discussion on the related question of whether metallacyclopropanes and metal-olefin complexes are resonance forms, cf: Bender, B.R.; Norton, J.R.; Miller, M.M.; Anderson, O.P.; Rappe, A.K. *Organometallics* **1992**, *11*, 3434.

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(9) Rosenthal, U.; Gorls, H.; Burlakov, V.V.; Shur, V.B.; Vol'pin, M.E. *J. Organomet. Chem.* **1992**, *426*, C53.

(10) Diercks, R.; Armstrong, J.C.; Boese, R.; Vollhardt, K.P.C. *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 268.

(11) (a) Buchwald, S.L.; Watson, B.T. *J. Am. Chem. Soc.* **1987**, *109*, 2544. (b) Buchwald, S.L.; Lum, R.T.; Dewan, J.C. *J. Am. Chem. Soc.* **1986**, *108*, 7441. (c) Buchwald, S.L.; Watson, B.T.; Huffman, J.C. *J. Am. Chem. Soc.* **1986**, *108*, 7411.

(12) Takagi, K.; Rousset, C.J.; Negishi, E. *J. Am. Chem. Soc.* **1991**, *113*, 1440.

(13) This mechanistic proposal was first suggested, to our knowledge, by Nugent, et al.[5a] For closely related mechanistic descriptions, cf: (a) Erker, G.; Zwettier, R.; Kruger, C.; Hyla-Kryspin, I.; Gleiter, R. *Organometallics.* **1990**, *9*, 524. (b) Buchwald, S.L.; Neilsen, R.B. *Chem. Rev.* **1988**, *88*, 1047 and references therein. (c) Yasuda, H.; Nakamura, A. *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 723. Similar associative mechanisms for alkyne-olefin coupling reactions are proposed in: (d) Negishi, E.; Holmes, S.J.; Tour, J.M.; Miller, J.A.; Cederbaum, F.E.; Swanson, D.R.; Takahashi, T. *J. Am. Chem. Soc.* **1989**, *111*, 3336. (e) Tidwell, J.H.; Senn, D.R.; Buchwald, S.L. *J. Am. Chem. Soc.* **1991**, *113*, 4685.

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Figure 1. ORTEP diagram of **3** with selected bond distances and angles. Selected Bond Distances (Å): Zr_1-C_1, 2.346(4); Zr_1-C_2, 2.390(4); Si_1-C_1, 1.854(4); C_1-C_2, 1.255(5); C_2-C_2', 2.319(7); C_2-C_3, 1.460(5). Selected Bond Angles (°): Si_1-C_1-C_2, 140.0(3); C_1-C_2-C_3, 55.2(4); C_2-C_3-C_3', 108.9(2); Zr_1-C_1-C_2, 76.6(2); Zr_1-C_2-C_1, 72.7(2); C_1-Zr_1-C_2, 30.7(1). Primed atoms are at -x, y, 1/2-z.

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