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Synthesis and X-ray Structure of a Zirconocene Complex of Two Alkynes

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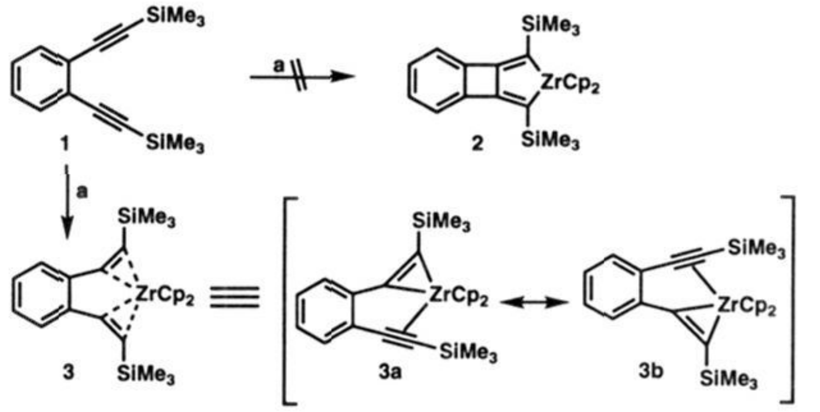
For several years we have been interested in the synthesis and the study of the structural properties of main group metallacycles.[1] These species are often conveniently available *via* transmetalation of a zirconacycle precursor.[2] Molecules possessing a planar structure appear to have superior packing properties in the solid state. We therefore felt that zirconacycle **2** would be a useful precursor to the molecules in which we were interested. Treatment of **1**[3] (Scheme 1) with 1 equiv of dibutylzirconocene, as a zirconocene transfer agent,[4] unexpectedly failed to give **2**,[4,5] and instead, complex **3** was isolated in 55% yield as air-sensitive, orange crystals.[6]

The nature of **3** is best described by the molecular orbital picture[5a,7] where there are three alkyne to metal interactions, two of which involve donation from the alkynes' π-systems to the metal ($a_1 + \pi$, $b_2 + \pi$), and one of which is back-bonding from the metal to the π^* system of the alkynes ($a_1 + \pi^*$) (Figure 1). One ramification of this orbital description is that each alkyne possesses full σ-bonding to the zirconium center, but there is only half the normal π-back-bonding that is seen in the more conventional metallacyclopropenes; the two electrons in the $a_1 + \pi^*$ orbital are shared equally between the two alkynes. This π-back-bonding is manifested in the characteristics of the identical alkynyl ligands, both of which display spectroscopic and structural features almost exactly halfway between those of free alkynes and zirconacyclopropenes. A consequence of this data (*vide infra*) is that **3** is difficult to describe by a single Lewis structure. Complex **3** can be best represented as the superposition of the degenerate resonance contributors **3a** and **3b**, each of which implies a Zr(IV) with one dative alkyne ligand and one zirconacyclopropene moiety.[8] That we were unable to "freeze out" any discrete zirconacyclopropene–alkyne complex by either low-temperature NMR or solid-phase IR supports the notion that **3a** and **3b** are equivalent resonance forms and not in rapid equilibrium.

Scheme 1[a]



[a] (a) $Cp_2ZrCl_2/2$ *n*-BuLi/THF/−78 °C to room temperature, then hexane to 70 °C (55%).

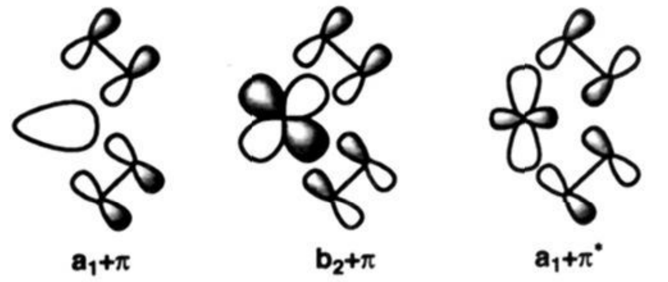


Figure 1. Molecular orbital description of a metallocene with two η^2 alkyne ligands.[5a,7]

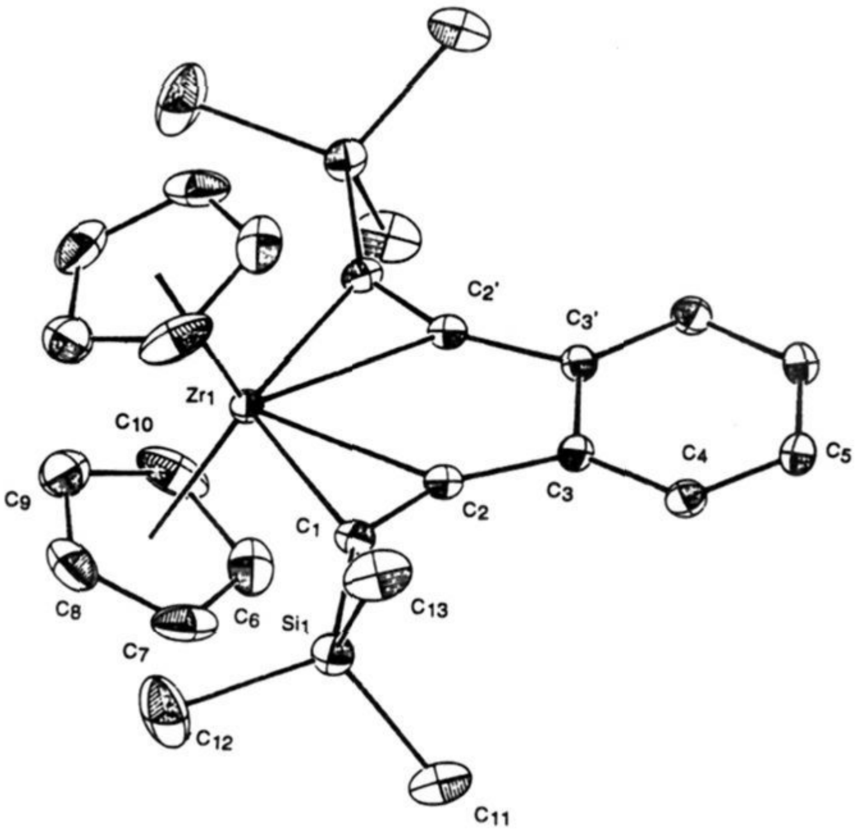


Figure 2. ORTEP diagram of **3** with selected bond distances and angles. Selected bond distances (Å): Zr_1–C_1, 2.346(4); Zr_1–C_2, 2.390(4); Si_1–C_1, 1.854(4); C_1–C_2, 1.255(5); C_2–C_2', 2.319(7); C_2–C_3, 1.460(5). Selected bond angles (deg): Si_1–C_1–C_2, 140.0(3); C_1–C_2–C_3, 155.2(4); C_2–C_3–C_3', 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, $^1/_2 - z$.

An ORTEP representation of the structure resulting from an X-ray diffraction determination is shown in Figure 2. The molecule possesses a crystallographic C_2 axis of symmetry. The effects of partial π-back-bonding are manifested by the fact that the C_1–C_2 bond distance of 1.258(5) Å in **3** is approximately halfway between the value of 1.195(3) Å seen in hexakis(trimethylsilylethynyl)benzene[9] and the length of 1.302(9) Å in zirconacyclopropene **6**[10] (Figure 3). Further, in **3** the C_2–C_1–Si and C_1–C_2–C_3 bond angles are similar to the analogous angles

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(6) The initial reaction mixture also includes (as determined by ^{1}H NMR) the symmetrical zirconacyclopentadiene formed by coupling 2 equiv of **1**. Upon heating of the reaction products in hexane, this disproportionates into **1** and **3**. See: Gesing, E. R. F. *J. Chem. Soc., Chem. Commun.* **1982**, 426.

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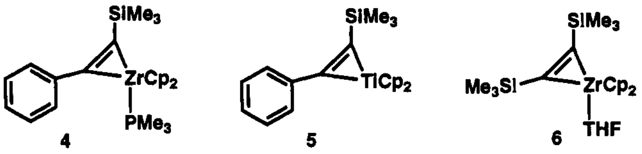
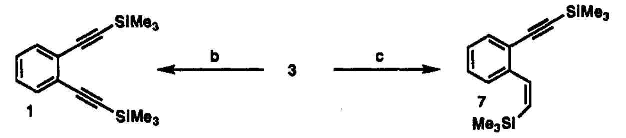


Figure 3.

Table 1. Comparison of Selected Bond Angles of Compounds 3–6

compd	bond angles, deg	
	C_2–C_1–Si	C_1–C_2–C_3
3	140.0(3)	155.2(4)
4	148.2(2)	141.0(2)
5	140.8(3)	151.9(3)
6	143.5(6)/134.4(6)	

Scheme 2[a]



[a] (b) I_2/THF/−78 °C (88%). (c) H_2SO_4/H_2O/THF (92%).

in **4**,[11] **5**,[12] and **6** (Table 1). Consistent with this representation, no change, other than slight broadening, is observed in the ^{1}H 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 midway between that observed for **1** at 2161 cm^{-1} and that seen in normal group 4 metallacyclopropenes as in **4** at 1620 cm^{-1}, **5** at 1686 cm^{-1}, and **6** at 1581 cm^{-1}.[13] 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), **5** (213.0 and 219.6 ppm), and **6** (212.9 ppm).[13]

The reactions of **3** are also consistent with the above structural description (Scheme 2). For example, treatment of **3** with I_2 produces zirconocene diiodide and re-forms **1** in 88% yield.[14] Treatment of **3** with aqueous sulfuric acid gives enyne **7**, in 92% yield.[5a,14] 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-octen-2-yne, while the corresponding zirconacycle was isolated and structurally characterized.[5a]

The structure and reactivity of compound **3** address the mechanism of zirconocene-mediated reductive coupling. This process is thought to have three principal intermediates,[5a,15] only two of which had been isolated: a zirconacyclopropene,[10,11,16] a postulated intermediate complex of the metal and two alkynes, and a zirconacyclopentadiene.[5a,15a] Molecular orbital calculations (shown in Figure 1)[5a,7] show that the intermediate complex possesses two σ-type metal–alkyne orbitals and one π-type orbital. The implication of this model is that each alkyne possesses full σ-bonding, but only partial π-back-bonding to the metal. Under normal circumstances this complex is unstable relative to the metallacyclopentadiene (Scheme 1), but in systems where the metallacyclopentadiene would be highly strained, the zirconacyclopropene–alkyne complex is stable.[5a] In accord with this proposal, **3** is not converted to **2** even when heated to 195 °C for 5 h.

In summary, we have prepared, for the first time, a complex where zirconocene is bound to two alkynyl ligands. The structural and spectroscopic data shows that this compound is best described as shown in Scheme 1 and Figure 1. Further, we have demonstrated the viability of such a complex, which has been proposed as an intermediate in the zirconocene-induced reductive coupling of alkynes.[5a] 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 analytical or HRMS data for 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); tables of structure factors for **3** (9 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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[15] This mechanistic proposal was first suggested, to our knowledge, by Nugent et al.[5a] For closely related mechanistic descriptions, cf.: (a) Erker, G.; Zwettler, 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 the following: (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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