This paper describes the first preparation and X-ray crystal structure determination of a zirconacyclcopropene-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.
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. These species are often available via transmetallation of a zirconacycle precursor. Molecular structure appear to have superior packing properties in that zirconacycle 2 would be a useful precursor to 1. Treatment of 1 (Scheme I) with an equivalent reducing agent, unexpectedly failed to give 2, and instead, orange crystals.

**Scheme I**

![Scheme I](image)

a. Cp₂ZrCl₂/2 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. 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-d₅). 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 metalloocene complexes of
alkynes (metallacyclopropenes) in 4 at 1620 cm\(^{-1}\) and 5 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.

<table>
<thead>
<tr>
<th>Compound</th>
<th>C(_2)-C(_1)-Si bond angles °</th>
<th>C(_1)-C(_2)-C(_3) bond angles °</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>140.2(3)</td>
<td>154.8(4)</td>
</tr>
<tr>
<td>4</td>
<td>148.2(2)</td>
<td>141.0(2)</td>
</tr>
<tr>
<td>5</td>
<td>140.8(3)</td>
<td>151.9(3)</td>
</tr>
<tr>
<td>6</td>
<td>--</td>
<td>135.8(3)</td>
</tr>
</tbody>
</table>

Figure 2

The reactions of 3 are also consistent with the above structural description (Scheme II).
For example, treatment of 3 with I₂ produces zirconocene diiodide and reforms 1 in 88% yield. Treatment of 3 with aqueous sulfuric acid gives enyne 7, in 92% yield. 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.12

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

**Acknowledgment.** We thank the Office of Naval Research for partial support of this research. SLB acknowledges additional support received as an Alfred P. Sloan Fellow (1988-92) and a Camille & Henry Dreyfus Teacher-Scholar. We thank Dr. William Nugent for helpful discussions.

**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.
Footnotes:


(6) The initial reaction mixture also includes (as determined by 1H 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.


Figure 1. ORTEP diagram of 3 with selected bond distances and angles. Selected Bond Distances (Å): Zr₁-C₁, 2.346(4); Zr₁-C₂, 2.390(4); Si₁-C₁, 1.854(4); C₁-C₂, 1.255(5); C₂-C₂', 2.319(7); C₂-C₃, 1.460(5). Selected Bond Angles (°): Si₁-C₁-C₂, 140.0(3); C₁-C₂-C₃, 55.2(4); C₂-C₃-C₃', 108.9(2); Zr₁-C₁-C₂, 76.6(2); Zr₁-C₂-C₁, 72.7(2); C₁-Zr₁-C₂, 30.7(1). Primed atoms are at -x, y, 1/2-z.
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