

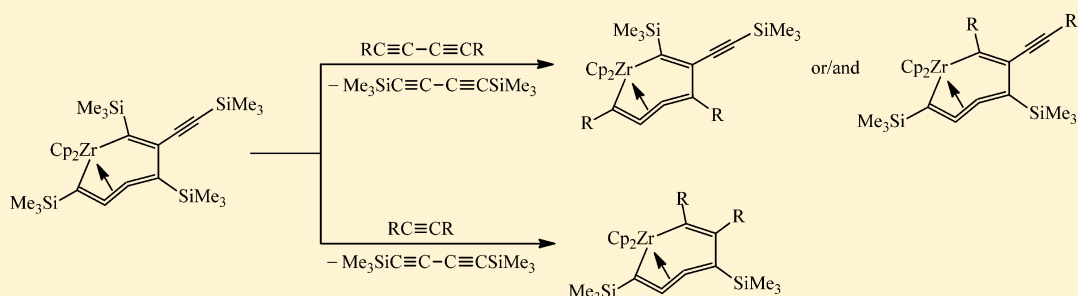
# Thermal Isomerization of the Buchwald Seven-Membered Zirconacyclocumulene and Its Interaction with Acetylenes. Synthesis and Structures of Novel Seven-Membered Zirconacyclocumulene Complexes

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## Supporting Information



**ABSTRACT:** On prolonged heating of the Buchwald seven-membered zirconacyclocumulene  $\text{Cp}_2\text{Zr}[\eta^4\text{-Me}_3\text{SiC}_4(\text{SiMe}_3)\text{-C}(\text{C}_2\text{SiMe}_3)=\text{CSiMe}_3]$  (**1**) in toluene at 100 °C, the isomerization of **1** takes place with the formation of a seven-membered zirconacyclocumulene complex,  $\text{Cp}_2\text{Zr}[\eta^4\text{-Me}_3\text{SiC}_4(\text{SiMe}_3)\text{-C}(\text{SiMe}_3)=\text{C}(\text{C}_2\text{SiMe}_3)]$  (**8**), containing the  $\text{Me}_3\text{SiC}\equiv\text{C}$  group in  $\alpha$ -position and the  $\text{SiMe}_3$  group in  $\beta$ -position with respect to the Zr atom. A remarkable peculiarity of complex **8** is its ability to undergo a rapid degenerate rearrangement at room temperature in toluene solution, as a result of which only two rather than four singlets of the  $\text{Me}_3\text{Si}$  groups are observed in the  $^1\text{H}$  NMR spectrum of **8** under such conditions. At temperatures below 200 K, the rate of this rearrangement decreases and, as a consequence, the  $^1\text{H}$  NMR spectrum of **8** acquires the normal view. If **1** is heated at 100 °C in the presence of acetylenes such as 1,4-bis(*tert*-butyl)butadiyne ( $t\text{BuC}\equiv\text{C-C}\equiv\text{C}t\text{Bu}$ ) and tolane, the corresponding seven-membered zirconacyclocumulenes, viz.,  $\text{Cp}_2\text{Zr}[\eta^4\text{-}t\text{BuC}_4(t\text{Bu})\text{-C}(\text{C}_2\text{SiMe}_3)=\text{CSiMe}_3]$  (**7**) and  $\text{Cp}_2\text{Zr}[\eta^4\text{-Me}_3\text{SiC}_4(\text{SiMe}_3)\text{-C}(\text{Ph})=\text{CPh}]$  (**14**), are formed along with free  $\text{Me}_3\text{SiC}\equiv\text{C-C}\equiv\text{CSiMe}_3$ . The interaction of **1** with 1,4-diphenylbutadiyne ( $\text{PhC}\equiv\text{C-C}\equiv\text{CPh}$ ) at 100 °C leads to the formation of a mixture of products, from which a zirconacyclopentadiene metallacycle,  $\text{Cp}_2\text{Zr}[\eta^2\text{-PhC}=\text{C}(\text{C}_2\text{Ph})\text{-C}(\text{C}_2\text{Ph})=\text{CPh}]$  (**10**), as well as seven-membered zirconacyclocumulenes  $\text{Cp}_2\text{Zr}[\eta^4\text{-PhC}_4(\text{Ph})\text{-C}(\text{C}_2\text{SiMe}_3)=\text{CSiMe}_3]$  (**11**),  $\text{Cp}_2\text{Zr}[\eta^4\text{-Me}_3\text{SiC}_4(\text{SiMe}_3)\text{-C}(\text{C}_2\text{Ph})=\text{CPh}]$  (**12**), and  $\text{Cp}_2\text{Zr}[\eta^4\text{-PhC}_4(\text{Ph})\text{-C}(\text{C}_2\text{Ph})=\text{CPh}]$  (**13**) were isolated. The structures of **8**, **9**, **10**, **12**, and **14** have been established by X-ray crystallography. The mechanism of the reactions found is discussed.

## INTRODUCTION

Seven-membered zirconacyclocumulene complexes of zirconocene, containing a butatrienyl unit in the ring, are of considerable interest because of their surprisingly high thermal stability and successful application in organometallic and organic synthesis.<sup>1–11</sup> In spite of a strong deviation of the butatrienyl moiety in the cycle from linearity, these unusual metallacycles remain in the solid state practically unchanged for an indefinitely long time at room temperature under Ar. This remarkable feature of seven-membered zirconacyclocumulenes, differing them from their unstable purely organic cyclic analogues (see, for example, ref 12), can be due to the

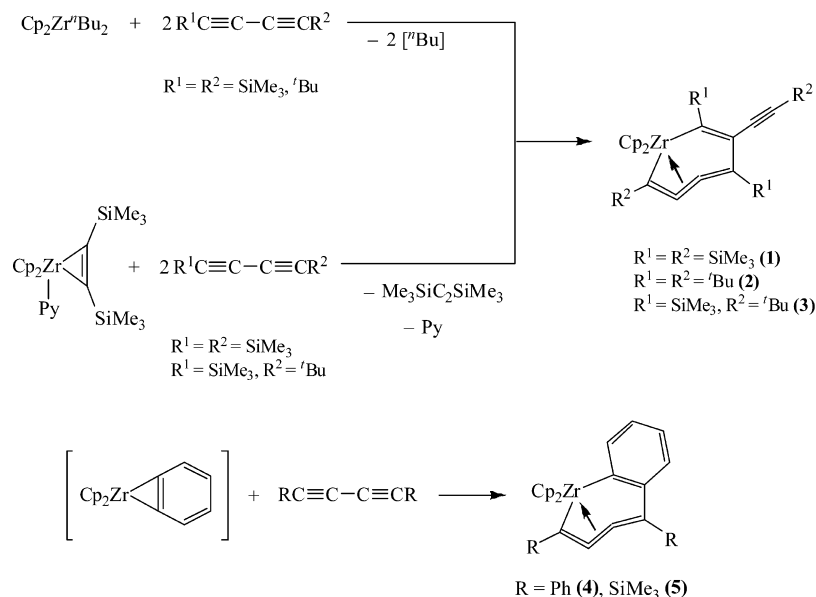
coordination of the central  $\text{C}=\text{C}$  double bond of the butatrienyl fragment with the zirconium atom. An analogous interaction of the butatrienyl  $\text{C}=\text{C}$  bond with the metal is apparently the reason for an abnormally high stability of the corresponding five-membered titana-, zircona-, and hafnacyclocumulenes,<sup>3,13–22</sup> representing the smallest cyclic [3]cumulenes known up to now.

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Scheme 1



The first seven-membered metallacyclocumulene complex,  $\text{Cp}_2\text{Zr}[\eta^4\text{-Me}_3\text{SiC}_4(\text{SiMe}_3)\text{-C}(\text{C}_2\text{SiMe}_3)=\text{CSiMe}_3]$  (**1**), was described in 1993 by Buchwald and co-workers.<sup>1</sup> The complex was synthesized by the reaction of the Negishi reagent  $\text{Cp}_2\text{Zr}''\text{Bu}_2$  with 1,4-bis(trimethylsilyl)butadiyne ( $\text{Me}_3\text{SiC}\equiv\text{C}-\text{C}\equiv\text{CSiMe}_3$ ) (Scheme 1) and structurally characterized. The use of  $\text{tBuC}\equiv\text{C}-\text{C}\equiv\text{CtBu}$  instead of  $\text{Me}_3\text{SiC}\equiv\text{C}-\text{C}\equiv\text{CSiMe}_3$  in this reaction leads to the formation of the corresponding *tert*-butyl-substituted seven-membered zirconacyclocumulene  $\text{Cp}_2\text{Zr}[\eta^4\text{-tBuC}_4(\text{tBu})\text{-C}(\text{C}_2\text{tBu})=\text{CtBu}]$  (**2**).<sup>2</sup> Zirconacycle **1** can also be obtained by the interaction of  $\text{Me}_3\text{SiC}\equiv\text{C}-\text{C}\equiv\text{CSiMe}_3$  with the bis(trimethylsilyl)acetylene complex of zirconocene,  $\text{Cp}_2\text{Zr}(\text{Me}_3\text{SiC}_2\text{SiMe}_3)(\text{Py})$ .<sup>3</sup> If  $\text{Me}_3\text{SiC}\equiv\text{C}-\text{C}\equiv\text{CtBu}$  rather than  $\text{Me}_3\text{SiC}\equiv\text{C}-\text{C}\equiv\text{CSiMe}_3$  is applied in this reaction, the seven-membered zirconacyclocumulene complex  $\text{Cp}_2\text{Zr}[\eta^4\text{-tBuC}_4(\text{SiMe}_3)\text{-C}(\text{C}_2\text{tBu})=\text{CSiMe}_3]$  (**3**) is produced.<sup>4</sup> The interaction of  $\text{PhC}\equiv\text{C}-\text{C}\equiv\text{CPh}$  and  $\text{Me}_3\text{SiC}\equiv\text{C}-\text{C}\equiv\text{CSiMe}_3$ , respectively, with the transient benzyne complex of zirconocene  $\text{Cp}_2\text{Zr}(\text{C}_6\text{H}_4)$  formed in the course of the thermal decomposition of  $\text{Cp}_2\text{ZrPh}_2$  at 80 °C also yields seven-membered zirconacyclocumulenes (**4** and **5**; see Scheme 1).<sup>5,6</sup>

Recently, we have reported<sup>2,7</sup> the first examples of the synthesis of seven-membered zirconacyclocumulene metallacycles by the interaction of five-membered zirconacyclocumulene  $\text{Cp}_2\text{Zr}(\eta^4\text{-tBuC}_4\text{tBu})$  (**6**)<sup>3</sup> with conjugated diacetylenes (Scheme 2).

The process proceeds in toluene solution at 100 °C. In the case of  $\text{tBuC}\equiv\text{C}-\text{C}\equiv\text{CtBu}$ , the reaction is reversible and results in the formation of the above-mentioned complex **2**. When  $\text{Me}_3\text{SiC}\equiv\text{C}-\text{C}\equiv\text{CSiMe}_3$  is used, a novel seven-

membered zirconacyclocumulene, viz.,  $\text{Cp}_2\text{Zr}[\eta^4\text{-tBuC}_4(\text{tBu})\text{-C}(\text{C}_2\text{SiMe}_3)=\text{CSiMe}_3]$  (**7**), is obtained, and the reaction is irreversible. It should be noted that monoacetylenes such as tolane and phenylacetylene do not form seven-membered zirconacyclocumulenes in the interaction with **6** at 100 °C. Under these conditions, the corresponding zirconacyclopentadiene metallacycles are produced in good yields.<sup>7</sup>

In the present paper, data obtained on studying the interaction of acetylenes ( $\text{PhC}\equiv\text{CPh}$ ,  $\text{tBuC}\equiv\text{C}-\text{C}\equiv\text{CtBu}$ ,  $\text{PhC}\equiv\text{C}-\text{C}\equiv\text{CPh}$ ) with the Buchwald seven-membered zirconacyclocumulene complex **1** in toluene at 100 °C are presented. The results of this study have shown that in all the cases new seven-membered zirconacyclocumulene metallacycles are formed in the course of the reactions along with other products. The thermal isomerization of **1**, taking place at 100 °C in the absence of acetylenes, is also reported.

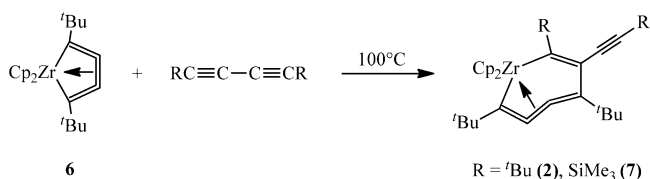
For recent works on five-, six-, and seven-membered metallacycloallenes, seven-membered azametallacycloallenes, and azazirconacyclocumulenes, see refs 23–28.

## RESULTS AND DISCUSSION

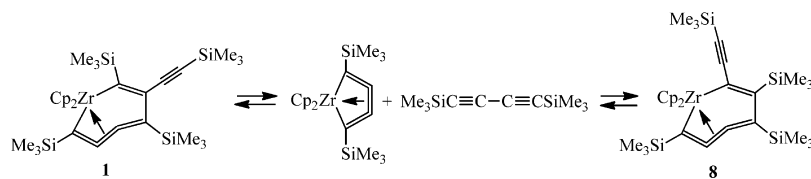
On heating of complex **1** in toluene-*d*<sub>8</sub> at 100 °C under Ar, the intensity of a singlet of Cp protons of the starting **1** at 5.32 ppm in the <sup>1</sup>H NMR spectrum (at 297 K) slowly diminishes and a singlet signal at 5.44 ppm, belonging to a novel complex (**8**), appears in the spectrum. The intensity of this new singlet gradually increases with time, and after 30 days the ratio of **8** to **1** in the solution becomes equal to 71:29.

On carrying out the reaction for 3 weeks at 110 °C in toluene, the resulting complex **8** was isolated from the mixture in an analytically pure state in 43% yield. According to X-ray crystallography, the isolated compound represents also a seven-membered zirconacyclocumulene but containing, in contrast to **1**, the  $\text{Me}_3\text{SiC}\equiv\text{C}$  group in the α-position and the SiMe<sub>3</sub> group in the β-position with respect to the zirconium atom. One may assume that the process of the isomerization of **1** to **8** proceeds via the reversible formation of the intermediate five-membered zirconacyclocumulene  $\text{Cp}_2\text{Zr}(\eta^4\text{-Me}_3\text{SiC}_4\text{SiMe}_3)$  and free diyne  $\text{Me}_3\text{SiC}\equiv\text{C}-\text{C}\equiv\text{CSiMe}_3$  (see Scheme 3).

Scheme 2

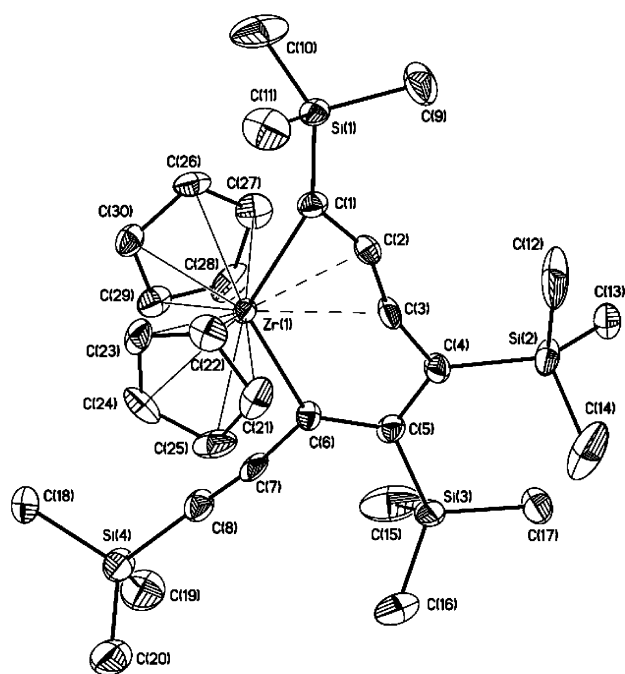


Scheme 3



Apparently, complex 1 is thermodynamically less stable than 8, which just leads to its isomerization.

The molecular structure of 8 is shown in Figure 1; only one of the molecules of the asymmetric unit is depicted. The asymmetric unit contains one and two half-molecules close in their geometrical parameters.



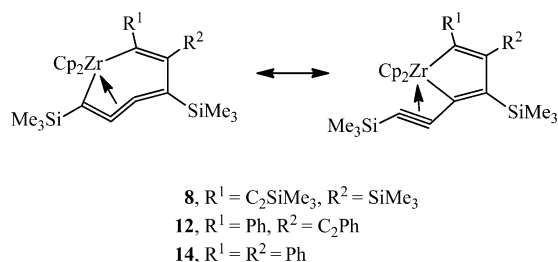
**Figure 1.** ORTEP representation of the molecular structure of 8 (only one of the molecules of the asymmetric unit is shown) with thermal ellipsoids drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): C(1)–C(2) 1.287(8), C(2)–C(3) 1.315(8), C(3)–C(4) 1.349(9), C(4)–C(5) 1.493(8), C(5)–C(6) 1.393(8), C(7)–C(8) 1.217(8), Zr(1)–C(1) 2.442(6), Zr(1)–C(2) 2.407(5), Zr(1)–C(3) 2.419(6), Zr(1)–C(6) 2.390(6), C(1)–C(2)–C(3) 150.7(6), C(2)–C(3)–C(4) 160.5(6), C(3)–C(4)–C(5) 113.0(5), C(4)–C(5)–C(6) 111.7(5), C(5)–C(6)–C(7) 123.98(15), C(6)–C(7)–C(8) 171.1(7), C(7)–C(8)–Si(4) 178.5(6).

In its structure, complex 8 is similar to 1 and other earlier synthesized seven-membered zirconacyclocumulenes (see above). The central C(2)–C(3) bond in the butatrienyl moiety of each independent molecule of 8 (1.315(8), 1.303(12), and 1.330(11) Å; av 1.32 Å) is elongated as compared to the corresponding central C=C bond (1.241–1.276 Å; av 1.26 Å) in usual, purely organic uncoordinated butatrienes,<sup>29–33</sup> which suggests the coordination of this C(2)–C(3) bond with the zirconium atom. The Zr(1)–C(1) and Zr(1)–C(6) bond lengths in the three molecules of 8 are equal to 2.394(8)–2.442(6) Å (av 2.42 Å) and 2.390(6)–2.397(8) Å (av 2.39 Å), respectively, and are comparable with the Zr(1)⋯C(2) and Zr(1)⋯C(3) distances (2.389(8)–2.407(5) Å; av 2.40 Å and 2.375(9)–2.438(8) Å; av 2.41 Å), which is consistent with the

assumption of the involvement of the C(2)–C(3) bond in the interaction with the zirconium center.

The terminal C(3)–C(4) bond length in the butatrienyl fragment of 8 is 1.338(12)–1.349(9) Å (av 1.34 Å), which corresponds to the length of the typical C=C double bond (av 1.331 Å). However, the terminal C(1)–C(2) bond of this fragment (1.268(11)–1.287(8) Å; av 1.28 Å) is considerably shorter than the typical C=C double bond. This fact can be explained by the supposition that the electronic structure of 8 is essentially contributed by a resonance form of the five-membered zirconacyclopentadiene (see Scheme 4) wherein

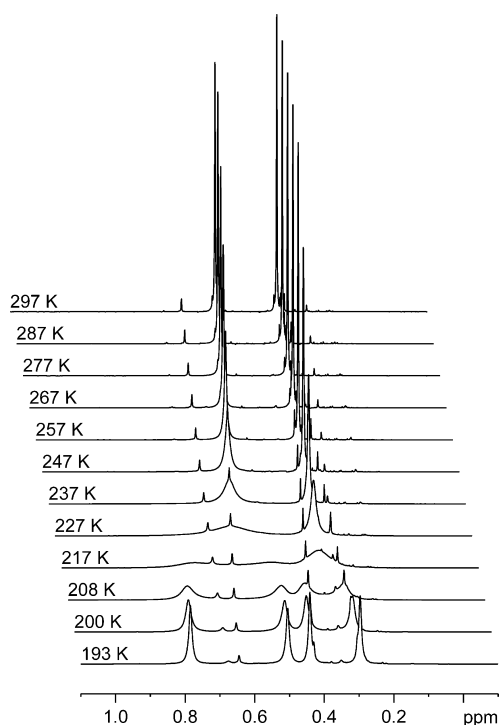
Scheme 4



the  $\alpha$ -alkynyl group deviates toward the Zr atom and coordinates with it. Similar resonance forms were earlier proposed<sup>2,7</sup> for the explanation of the structure of 1 and other presently known seven-membered zirconacyclocumulenes.

The <sup>1</sup>H NMR spectrum of the isolated 8 in toluene-*d*<sub>8</sub> at temperatures below 200 K displays a singlet of Cp protons at 5.50 ppm and singlets of four nonequivalent SiMe<sub>3</sub> groups (at 0.30, 0.44, 0.51, and 0.78 ppm) in the theoretical intensity ratio (10:9:9:9:9). However, with a rise in temperature, the observed SiMe<sub>3</sub> singlet signals gradually broaden, and at 297 K the <sup>1</sup>H NMR spectrum of 8 shows only two singlets of Me<sub>3</sub>Si groups (at 0.33 and 0.51 ppm) as well as the above singlet of Cp protons (at 5.44 ppm) in 18:18:10 ratio (Figure 2). Signals of quaternary carbon atoms in the <sup>13</sup>C NMR spectrum of 8 are not observed at 297 K due to strong line broadening; however the required number of lines (eight) appears at 193 K. Heating the sample up to 353 K brings about four signals with averaged chemical shifts (at 110.4, 144.7, 173.7, and 198.2 ppm). Coalescence for the <sup>1</sup>H and <sup>13</sup>C signals of the silyl groups occurs in the region 215–220 K; the free enthalpy of activation for the exchange process in that region may be estimated to be about 43 kJ mol<sup>−1</sup>. The resonances assigned to the Cp groups are not affected by the temperature changes at all.

The results obtained suggest that at room temperature a rapid degenerate rearrangement of complex 8 proceeds in toluene solution (see Scheme 5). A driving force of this rearrangement could be a significant contribution of the aforementioned zirconacyclopentadiene resonance form (8a) to the electronic structure of 8. In accordance with such an assumption about the electronic structure of 8, the protolysis of



**Figure 2.** Temperature dependence of chemical shifts and line shapes of SiMe<sub>3</sub> groups in the <sup>1</sup>H NMR spectrum (400.13 MHz) of complex **8** in toluene-*d*<sub>8</sub>. The small peaks (largely unaffected by temperature variation) are due to residual starting complex **1**.

this complex with HCl in dioxane at 22 °C affords Cp<sub>2</sub>ZrCl<sub>2</sub> and 1,4,5,8-tetra(trimethylsilyl)octa-3,5-diene-1,7-diyne (**9**).

An alternative mechanism of the above-described degenerate rearrangement could consist in the rapid and reversible transformation of **8** into the corresponding genuine zirconacyclopentadiene derivative (Scheme 6).

However, to date, there are no data that would provide evidence for the presence of such a five-membered zirconacycle in toluene solution of **8** at room temperature in any detectable amounts.

The structure of **9** has been established by X-ray diffraction (Figure 3). The C(1)–C(2) and C(7)–C(8) distances in **9** are equal to 1.205(2) and 1.203(2) Å, respectively, which is close to the length of the typical triple C≡C bond, whereas the

C(3)–C(4) and C(5)–C(6) distances in **9** are 1.342(2) Å, which corresponds to the length of the double C=C bond. The bond angles at the sp-hybridized C(1), C(2), C(7), and C(8) atoms in the molecule of **9** are close to 180°, and the bond angles at the sp<sup>2</sup>-hybridized C(3), C(4), C(5), and C(6) atoms are close to 120°.

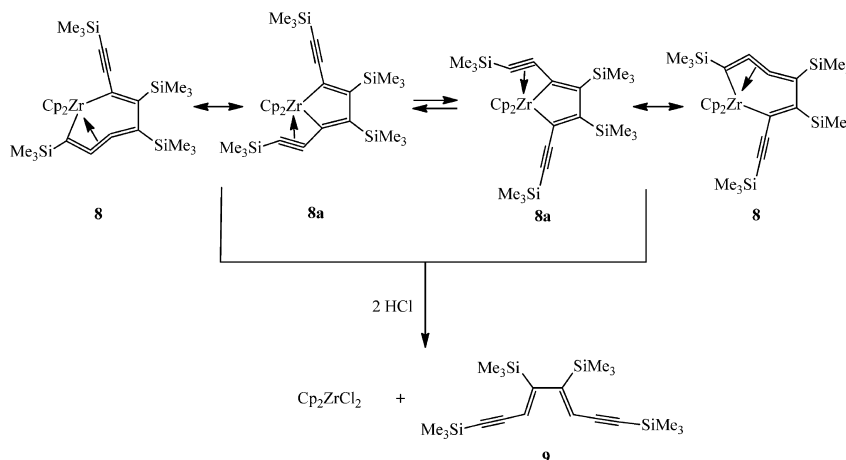
If **1** is heated at 100 °C in toluene solution in the presence of 1,4-bis(*tert*-butyl)butadiyne (<sup>*t*</sup>BuC≡C–C≡C<sup>*t*</sup>Bu) for 35 days, the replacement of the butatrienyl fragment Me<sub>3</sub>SiC<sub>4</sub>SiMe<sub>3</sub> in the molecule of **1** by the <sup>*t*</sup>BuC<sub>4</sub><sup>*t*</sup>Bu fragment occurs and the previously described seven-membered zirconacyclocumulene complex **7** (see ref 7 and Scheme 2) is produced along with free Me<sub>3</sub>SiC≡C–C≡CSiMe<sub>3</sub> (Scheme 7).

The complex was isolated from the solution and identified by <sup>1</sup>H and <sup>13</sup>C NMR spectra. The mechanism of this novel reaction includes apparently the reversible transformation of **1** into the above-mentioned intermediate five-membered zirconacyclocumulene Cp<sub>2</sub>Zr(η<sup>4</sup>-Me<sub>3</sub>SiC<sub>4</sub>SiMe<sub>3</sub>) and then into the transient acetylene complex Cp<sub>2</sub>Zr(Me<sub>3</sub>SiC<sub>2</sub>C≡CSiMe<sub>3</sub>) having a zirconacyclopentadiene structure. Subsequent insertion of <sup>*t*</sup>BuC≡C–C≡C<sup>*t*</sup>Bu into the Zr–C(C≡CSiMe<sub>3</sub>) bond of this zirconacyclopentadiene derivative gives the final **7** (Scheme 8).

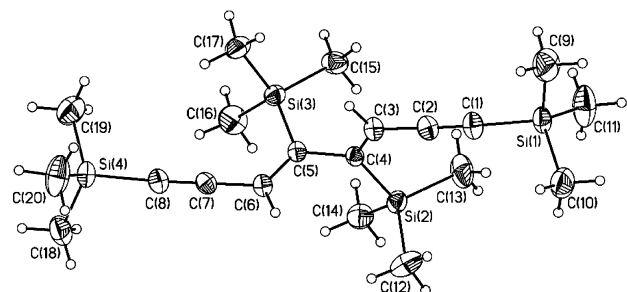
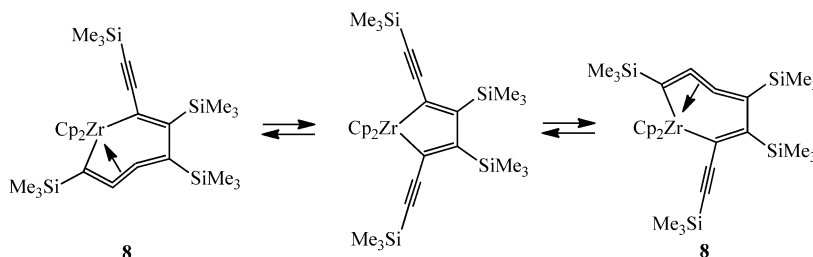
A considerably more complicated picture is observed in the interaction of **1** with 1,4-diphenylbutadiyne PhC≡C–C≡CPh in toluene at 100 °C. When this reaction is conducted under such conditions for 36 days, the <sup>1</sup>H NMR spectrum of the resulting mixture shows, besides a singlet at 5.32 ppm of unreacted **1**, seven other singlets of Cp rings (at 5.26, 5.35, 5.45, 5.55, 5.63, 5.84, and 5.85 ppm) belonging apparently to seven new complexes. The ratio of these complexes (in mol %) is 37:8:19:13:4:10:6 (the amount of unreacted **1** is 3%). The process is accompanied also by the formation of free Me<sub>3</sub>SiC≡C–C≡CSiMe<sub>3</sub>. Repeated recrystallization of the above product mixture from *n*-hexane allowed the isolation of four complexes, viz., **10** (δ 5.85 ppm), **11** (δ 5.45 ppm), **12** (δ 5.26 ppm), and **13** (δ 5.35 ppm) in an individual state.

Complex **10** was obtained in 4% isolated yield and was fully characterized. An X-ray diffraction study of **10** has shown that it represents a zirconacyclopentadiene derivative formed by a Cp<sub>2</sub>Zr species and two molecules of PhC≡C–C≡CPh. The Ph groups in the molecule of **10** are disposed in α-positions with respect to the zirconium atom, whereas the PhC≡C groups are disposed in β-positions (Figure 4). The C≡C

## Scheme 5



Scheme 6



**Figure 3.** ORTEP representation of the molecular structure of **9** with thermal ellipsoids drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): C(1)–C(2) 1.205(2), C(2)–C(3) 1.424(2), C(3)–C(4) 1.342(2), C(4)–C(5) 1.491(2), C(5)–C(6) 1.342(2), C(6)–C(7) 1.430(2), C(7)–C(8) 1.203(2), Si(1)–C(1)–C(2) 177.69(17), C(1)–C(2)–C(3) 177.63(18), C(2)–C(3)–C(4) 125.84(15), C(3)–C(4)–C(5) 117.89(13), C(4)–C(5)–C(6) 119.04(14), C(5)–C(6)–C(7) 123.98(15), C(6)–C(7)–C(8) 178.29(18), C(7)–C(8)–Si(4) 177.17(16).

distances in the  $\text{PhC}\equiv\text{C}$  substituents of **10** are 1.202(3) and 1.204(3) Å, and the lengths of the conjugated double bonds C(1)–C(2) and C(3)–C(4) in the zirconacycle are 1.369(3) and 1.368(2) Å. The bond angles at the  $\text{sp}$ -hybridized carbon atoms of the  $\text{PhC}\equiv\text{C}$  groups are in the range 172.3(2)–176.4(2)°.

Thus, both  $\text{Me}_3\text{SiC}_4\text{SiMe}_3$  fragments in the starting **1** are replaced by two  $\text{PhC}_4\text{Ph}$  fragments as a result of the formation of **10** from **1** and  $\text{PhC}\equiv\text{C}-\text{C}\equiv\text{CPh}$  (Scheme 9).

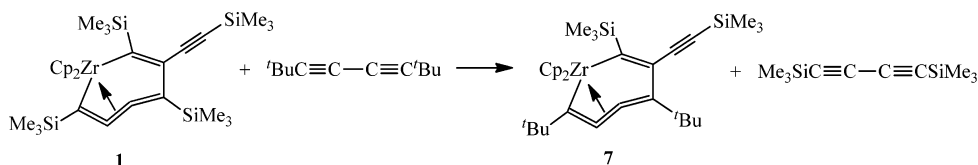
Complex **11** was isolated from the mixture in 3% yield. In contrast to **10**, this compound could not be obtained as crystals suitable for an X-ray analysis, but its structure was unequivocally established by elemental analysis and  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra. According to these data, the isolated complex is a seven-membered zirconacyclocumulene in which the Ph groups are located at the terminal carbon atoms of the butatrienyl moiety while the  $\text{Me}_3\text{Si}$  and  $\text{Me}_3\text{SiC}\equiv\text{C}$  substituents are disposed at the  $\alpha$ - and  $\beta$ -carbon atoms, respectively, of the olefinic  $\text{C}=\text{C}$  bond of the zirconacycle. The mechanism of this transformation is analogous to that of the above-discussed reaction of **1** with  $^t\text{BuC}\equiv\text{C}-\text{C}\equiv\text{C}^t\text{Bu}$  and includes the reversible conversion of **1** first into the aforementioned five-membered zirconacyclocumulene  $\text{Cp}_2\text{Zr}$ -

( $\eta^4\text{-Me}_3\text{SiC}_4\text{SiMe}_3$ ) and then into the intermediate acetylene complex  $\text{Cp}_2\text{Zr}(\text{Me}_3\text{SiC}_2\text{C}\equiv\text{CSiMe}_3)$ . Subsequent insertion of  $\text{PhC}\equiv\text{C}-\text{C}\equiv\text{CPh}$  into the  $\text{Zr}-\text{C}(\text{C}\equiv\text{CSiMe}_3)$  bond of this acetylene complex, which has a zirconacyclopentadiene structure, affords **11** (Scheme 10). The ability of acetylene complexes of zirconocene to form seven-membered zirconacyclocumulenes in the interaction with conjugated diacetylenes has earlier been demonstrated.<sup>2,5,6</sup>

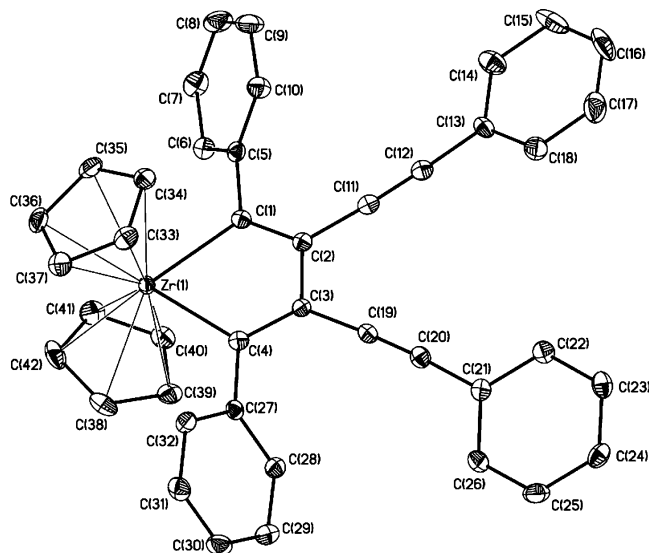
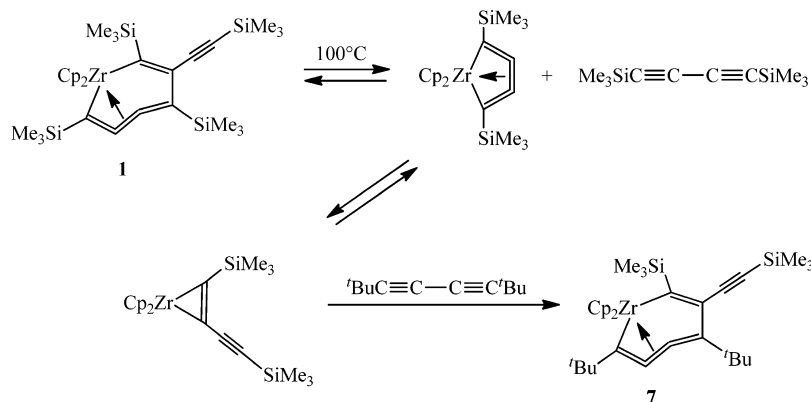
Complex **12** is dominant (37%) in the product mixture and was obtained in an analytically pure state in 17% yield. According to X-ray diffraction data, it represents an isomer of **11** and contains the  $\text{Me}_3\text{Si}$  groups rather than the Ph groups at the terminal carbon atoms of the butatrienyl fragment. Correspondingly, the  $\alpha$ - and  $\beta$ -carbon atoms of the olefinic  $\text{C}=\text{C}$  bond of the zirconacycle in **12** are linked with the Ph and  $\text{PhC}\equiv\text{C}$  substituents, respectively, rather than with the  $\text{Me}_3\text{Si}$  and  $\text{Me}_3\text{SiC}\equiv\text{C}$  groups as in the case of **11**. Such an arrangement of the substituents in **12** suggests that this complex is formed through the step of insertion of one of the  $\text{C}\equiv\text{C}$  bonds of the starting  $\text{PhC}\equiv\text{C}-\text{C}\equiv\text{CPh}$  into the  $\text{Zr}-\text{C}$  bond of the above-mentioned intermediate five-membered zirconacyclocumulene derivative  $\text{Cp}_2\text{Zr}(\eta^4\text{-Me}_3\text{SiC}_4\text{SiMe}_3)$  arising, apparently, from **1** in the course of heating (Scheme 10). A similar mechanism was previously proposed for the formation of compound **7** in the interaction of the individual five-membered zirconacyclocumulene complex **6** with  $\text{Me}_3\text{SiC}\equiv\text{C}-\text{C}\equiv\text{CSiMe}_3$  at 100 °C (see Scheme 2 and ref 7).

The structure of complex **12** is shown in Figure 5. Here too, the central C(2)–C(3) bond of the butatrienyl fragment (1.318(3) Å) is considerably longer than that in usual organic butatrienes (see above), and the  $\text{Zr}(1)\cdots\text{C}(2)$  and  $\text{Zr}(1)\cdots\text{C}(3)$  distances (2.4378(19) and 2.431(2) Å) are comparable with the  $\text{Zr}(1)-\text{C}(1)$  and  $\text{Zr}(1)-\text{C}(6)$  bond lengths (2.451(2) and 2.4264(18) Å), thus indicating the coordination of this C(2)–C(3) bond with the zirconium atom. On the other hand, the terminal C(1)–C(2) bond in the butatrienyl moiety of **12** (1.282(3) Å) is again significantly shorter than the typical  $\text{C}=\text{C}$  double bond, which can be explained, as in the case of **8**, by an essential contribution of the resonance form of the corresponding zirconacyclopentadiene, containing the coordinated  $\alpha$ -alkynyl group, to the electronic structure of the complex (see Scheme 4).

Scheme 7



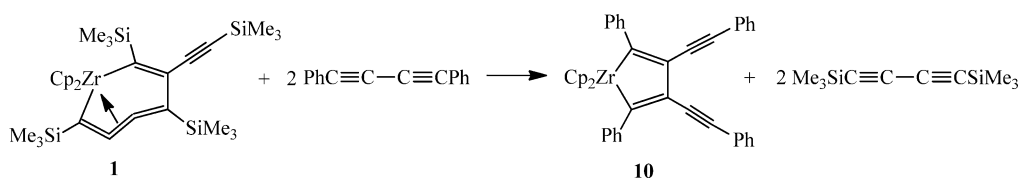
Scheme 8



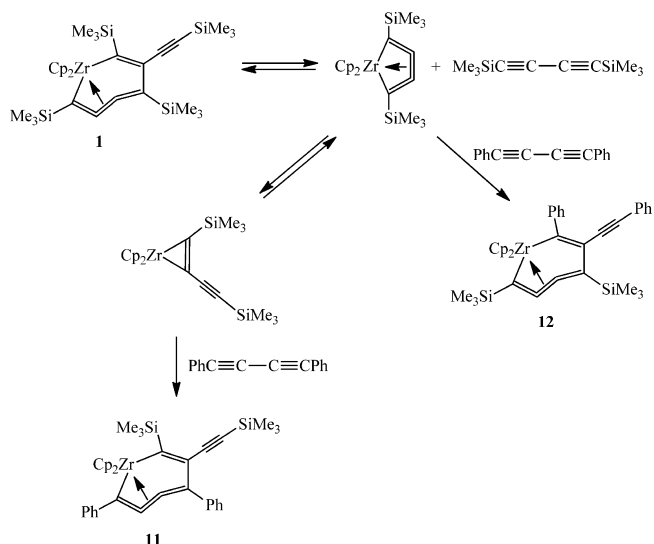
**Figure 4.** ORTEP representation of the molecular structure of **10** with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): C(1)–C(2) 1.369(3), C(2)–C(3) 1.500(2), C(3)–C(4) 1.368(2), C(11)–C(12) 1.204(3), C(19)–C(20) 1.202(3), Zr(1)–C(1) 2.2721(18), Zr(1)–C(4) 2.2795(18), Zr(1)–C(1)–C(2) 111.42(13), C(1)–C(2)–C(3) 119.59(16), C(2)–C(3)–C(4) 119.89(16), C(3)–C(4)–Zr(1) 110.99(12), C(1)–Zr(1)–C(4) 77.80(6), C(2)–C(11)–C(12) 174.7(2), C(11)–C(12)–C(13) 172.3(2), C(3)–C(19)–C(20) 175.22(19), C(19)–C(20)–C(21) 176.4(2).

Complex **13** was isolated from the reaction mixture in 2.9% yield. According to analytical and spectral data, it represents a seven-membered zirconacyclocumulene containing four Ph groups in its structure instead of four SiMe<sub>3</sub> groups as in the starting **1** (Scheme 11). Thus, as in the formation of **10**, both Me<sub>3</sub>SiC<sub>4</sub>SiMe<sub>3</sub> fragments in zirconacycle **1** are replaced by two PhC<sub>4</sub>Ph fragments in the course of the formation of **13**.

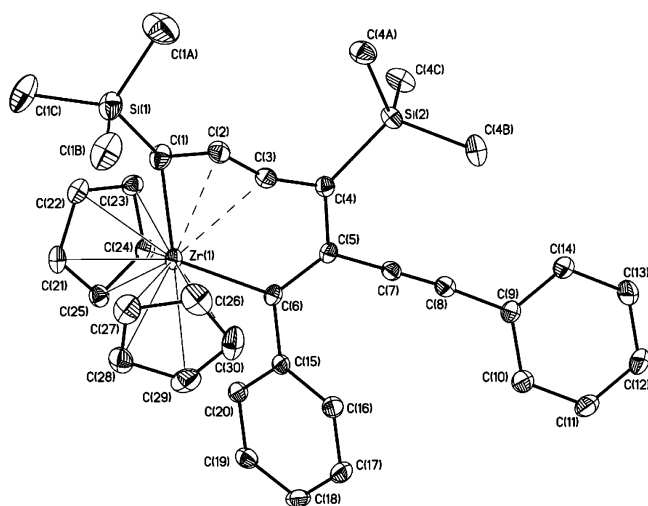
Scheme 9



Scheme 10



The interaction of **1** with toluene in toluene at 100 °C also results in the formation of a seven-membered zirconacyclocumulene (**14**). The reaction was carried out for 16 days. Under these conditions, complex **14** was obtained in 47% isolated yield. The structure of **14** has been determined by an X-ray diffraction study, which showed that the Me<sub>3</sub>Si substituents in **14**, as in **12**, are bound to the terminal carbon atoms of the butatrienyl unit, whereas the Ph groups are connected with the carbon atoms of the olefinic C=C bond of the metallacycle. Thus, one may conclude that the mechanism of the formation of **14** from **1** and PhC≡C–C≡CPh is similar to that of the formation of **12** from **1** and PhC≡C–C≡CPh and includes the step of insertion of toluene into the Zr–C bond of the above-noted intermediate five-membered zirconacyclocumulene derivative Cp<sub>2</sub>Zr(η<sup>4</sup>-Me<sub>3</sub>SiC<sub>4</sub>SiMe<sub>3</sub>) (Scheme 12).



**Figure 5.** ORTEP representation of the molecular structure of **12** with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): C(1)–C(2) 1.282(3), C(2)–C(3) 1.318(3), C(3)–C(4) 1.337(3), C(4)–C(5) 1.480(3), C(5)–C(6) 1.379(3), C(7)–C(8) 1.199(3), Zr(1)–C(1) 2.451(2), Zr(1)–C(2) 2.4378(19), Zr(1)–C(3) 2.431(2), Zr(1)–C(6) 2.4264(18), C(1)–C(2)–C(3) 149.4(2), C(2)–C(3)–C(4) 160.9(2), C(3)–C(4)–C(5) 111.99(17), C(4)–C(5)–C(6) 118.55(17), C(1)–Zr(1)–C(6) 127.46(7), Zr(1)–C(1)–C(2) 74.24(12), Zr(1)–C(6)–C(5) 119.23(13), C(5)–C(7)–C(8) 175.8(2), C(7)–C(8)–C(9) 172.1(2).

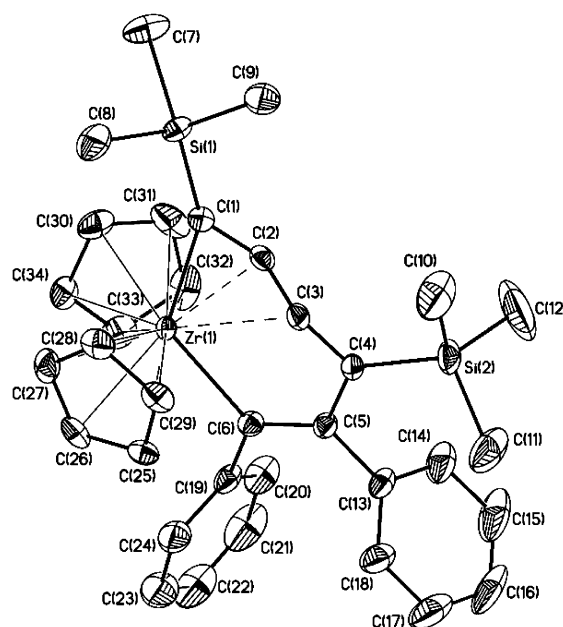
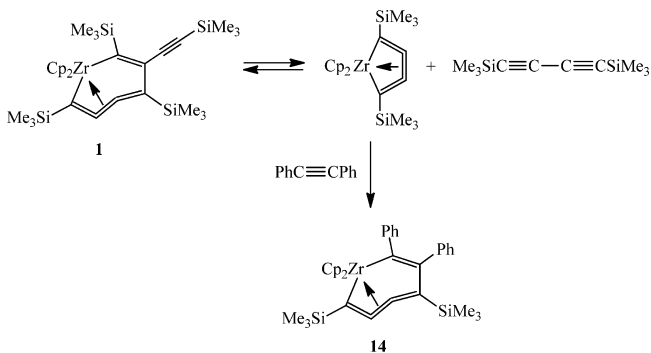
As in **8** and **12**, the central C(2)–C(3) bond of the butatrienyl unit in **14** interacts with the Zr center (Figure 6), which is evidenced by the length of this bond (1.310(3) Å) as well as by the closeness of the Zr(1)⋯C(2) and Zr(1)⋯C(3) separations (2.419(2) and 2.433(2) Å) to the Zr(1)–C(1) and Zr(1)–C(6) bond lengths (2.432(2) and 2.425(2) Å). The C(1)–C(2) bond distance in complex **14** (1.280(3) Å) is very close to the corresponding values in **8** (1.268(11)–1.287(8) Å; av 1.28 Å) and **12** (1.282(3) Å), which allows one to propose for this complex an analogous resonance description of its electronic structure (see Scheme 4).

The seven-membered metallacycle in **8**, **12**, and **14** is virtually planar. The butatrienyl group in these complexes deviates strongly from linearity (the endocyclic C(1)–C(2)–C(3) and C(2)–C(3)–C(4) bond angles are 148.2(10)–151.3(8)° and 158.0(9)–161.4(8)° in **8**, 149.3(2)° and 160.89(19)° in **12**, and 149.4(2)° and 160.9(2)° in **14**) and has a transoid configuration. The C(7)≡C(8) distances in **8** and **12** are 1.208(11)–1.217(8) and 1.199(3) Å, respectively, and the bond angles at the sp-hybridized carbon atoms in both compounds are close to 180°.

## CONCLUSION

The results of our study revealed an unusual reactivity of the Buchwald seven-membered zirconacyclocumulene **1** under

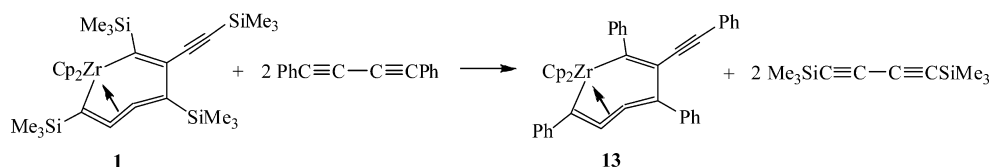
**Scheme 12**



**Figure 6.** ORTEP representation of the molecular structure of **14** with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): C(1)–C(2) 1.280(3), C(2)–C(3) 1.310(3), C(3)–C(4) 1.338(3), C(4)–C(5) 1.475(3), C(5)–C(6) 1.364(3), Zr(1)–C(1) 2.432(2), Zr(1)–C(2) 2.419(2), Zr(1)–C(3) 2.433(2), Zr(1)–C(6) 2.425(2), C(1)–C(2)–C(3) 150.2(2), C(2)–C(3)–C(4) 162.8(2), C(3)–C(4)–C(5) 112.56(19), C(4)–C(5)–C(6) 118.24(19), C(1)–Zr(1)–C(6) 127.34(7), Zr(1)–C(1)–C(2) 74.14(13), Zr(1)–C(6)–C(5) 119.71(15).

conditions of its prolonged heating in toluene at 100 °C. When this process is conducted in the presence of acetylenes (tolane, conjugated diacetylenes), new seven-membered zirconacyclocumulene metallacycles together with free  $\text{Me}_3\text{SiC}\equiv\text{C}-\text{C}\equiv\text{CSiMe}_3$  are produced as main products. In the absence of acetylenes, the starting **1** is converted into the isomeric seven-membered zirconacyclocumulene complex

**Scheme 11**



differing from **1** by the mutual arrangement of the  $\text{Me}_3\text{Si}$  and  $\text{Me}_3\text{SiC}\equiv\text{C}$  substituents at the carbon atoms of the olefinic  $\text{C}=\text{C}$  bond of the zirconacycle. The mechanism of these transformations becomes understandable if we assume the existence of an equilibrium at 100 °C between **1**, the corresponding five-membered zirconacyclocumulene  $\text{Cp}_2\text{Zr}(\eta^4\text{-Me}_3\text{SiC}_4\text{SiMe}_3)$ , and  $\text{Me}_3\text{SiC}\equiv\text{C}-\text{C}\equiv\text{CSiMe}_3$  as well as between the arising  $\text{Cp}_2\text{Zr}(\eta^4\text{-Me}_3\text{SiC}_4\text{SiMe}_3)$  and the acetylene complex  $\text{Cp}_2\text{Zr}(\text{Me}_3\text{SiC}_2\text{C}\equiv\text{CSiMe}_3)$ . The reactions found open new possibilities for the synthesis of seven-membered zirconacyclocumulenes.

## EXPERIMENTAL SECTION

Experiments were carried out under Ar with careful exclusion of air and moisture using standard Schlenk techniques. The starting seven-membered zirconacyclocumulene **1** was prepared according to the published procedure.<sup>1</sup> Commercial  $\text{Me}_3\text{SiC}\equiv\text{C}-\text{C}\equiv\text{CSiMe}_3$ ,  $^t\text{BuC}\equiv\text{C}-\text{C}\equiv\text{C}^t\text{Bu}$ ,  $\text{PhC}\equiv\text{C}-\text{C}\equiv\text{CPh}$ , and toluene were purchased from Sigma-Aldrich and used without additional purification. A 4 M solution of HCl in dioxane was also purchased from Sigma-Aldrich. Solvents (toluene, *n*-hexane) were purified by conventional methods and freshly distilled prior to use over metallic sodium or sodium tetraethylaluminate under Ar. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on Bruker AMX-400 and AV-400 spectrometers. Chemical shifts ( $^1\text{H}$ ,  $^{13}\text{C}$ ) are given relative to  $\text{SiMe}_4$  and are referenced to signals of benzene- $d_6$  ( $\delta_{\text{H}}$  7.16 ppm,  $\delta_{\text{C}}$  128.0 ppm) or the methyl group of toluene- $d_8$  ( $\delta_{\text{H}}$  2.08 ppm,  $\delta_{\text{C}}$  20.4 ppm) as solvents. Signal assignment was done by homo- and heteronuclear chemical shift correlation (COSY, HMBC) and  $^1\text{H}$  NOE experiments. The IR spectra were measured on Carl Zeiss M-82 and Nicolet Magna IR-750 FTIR spectrometers. The Raman spectra were registered on a JY LABRAM 300 spectrometer (He-Ne laser, 632.8 nm). The mass spectra were recorded on a MAT 95-XP instrument.

**Thermal Isomerization of Complex 1.** Complex **1** (3.860 g, 6.325 mmol) was dissolved in 15 mL of toluene, and the resulting brownish-orange solution was heated at 110 °C for 21 days. Then, the reaction mixture was cooled to room temperature and evaporated in vacuo to dryness. The red-orange residue was extracted with 20 mL of *n*-hexane at -30 °C, and the obtained cold extract was filtered and evaporated to dryness in vacuo to give 2.434 g of a red-orange solid representing a mixture of **8** (93%) and **1** (7%). Repeated recrystallization of this solid from *n*-hexane gave red-orange crystals of complex **8**. Yield of **8**: 1.645 g (43%). Mp: 148–151 °C under Ar. Anal. Calcd for  $\text{C}_{30}\text{H}_{46}\text{Si}_4\text{Zr}$ : C, 59.04; H, 7.60. Found: C, 59.11; H, 7.48.  $^1\text{H}$  NMR (297 K, toluene- $d_8$ ,  $\delta$ , ppm): 0.33 (s, 18H,  $\text{SiMe}_3$ ); 0.51 (s, 18H,  $\text{SiMe}_3$ ); 5.44 (s, 10H, Cp).  $^{13}\text{C}$  NMR (193 K, toluene- $d_8$ ,  $\delta$ , ppm): 0.30 (s, 9H, C(1)- $\text{SiMe}_3$ ); 0.43 (s, 9H, C(8)- $\text{SiMe}_3$ ); 0.51 (s, 9H, C(4)- $\text{SiMe}_3$ ); 0.78 (s, 9H, C(5)- $\text{SiMe}_3$ ); 5.50 (s, 10H, Cp).  $^{13}\text{C}$  NMR (297 K, toluene- $d_8$ ,  $\delta$ , ppm): 0.9, 2.2 ( $\text{SiMe}_3$ ); 106.9 (Cp); signals of quaternary carbon atoms are not observed at this temperature.  $^{13}\text{C}$  NMR (193 K, toluene- $d_8$ ,  $\delta$ , ppm): 0.4 (C(8)- $\text{SiMe}_3$ ); 1.0 (C(1)- $\text{SiMe}_3$ ); 1.7 (C(4)- $\text{SiMe}_3$ ); 2.5 (C(5)- $\text{SiMe}_3$ ); 102.4 (C(2)); 106.6 (Cp); 115.3 (C(7)); 122.6 (C(8)); 161.9 (C(4)); 166.7 (C(1)); 183.2 (C(5)); 191.8 (C(3)); 204.9 (C(6)).  $^{29}\text{Si}$  NMR (193 K, toluene- $d_8$ ,  $\delta$ , ppm): -7.8 (C(1)- $\text{SiMe}_3$ ); -9.7 (C(4)- $\text{SiMe}_3$ ); -13.7 (C(5)- $\text{SiMe}_3$ ); -20.8 (C(8)- $\text{SiMe}_3$ ) (for the numbering scheme, see Figure 1). Raman spectrum ( $\nu$ ,  $\text{cm}^{-1}$ ): 1855 ( $\text{C}=\text{C}=\text{C}=\text{C}$ ), 2065 ( $\text{C}\equiv\text{C}$ ). MS (EI, 70 eV,  $m/z$ ): 608 [ $\text{M}$ ] $^+$ .

**Protolysis of Complex 8.** To a red-orange solution of complex **8** (0.720 g, 1.18 mmol) in 10 mL of *n*-hexane was added at room temperature a 4 M solution (0.60 mL, 2.4 mmol) of HCl in dioxane. Immediately, the reaction mixture turned yellow and a colorless precipitate of  $\text{Cp}_2\text{ZrCl}_2$  was formed. After 15 min, the resulting  $\text{Cp}_2\text{ZrCl}_2$  was filtered, washed with *n*-hexane, and dried in vacuo. Yield of  $\text{Cp}_2\text{ZrCl}_2$ : 0.295 g (86%). The yellow *n*-hexane mother liquor, after the separation of  $\text{Cp}_2\text{ZrCl}_2$ , was evaporated, the oily residue was dissolved in 1 mL of *n*-hexane, and the obtained solution was allowed to stand at -78 °C. After 1 day, the precipitated colorless crystals of **9**

were separated by decanting of the mother liquor, washed with a small amount of cold *n*-hexane, and dried in vacuo. Yield of **9**: 0.231 g (50%). Mp: 48–49 °C under Ar. Anal. Calcd for  $\text{C}_{20}\text{H}_{38}\text{Si}_4$ : C, 61.46; H, 9.80. Found: C, 61.30; H, 9.71.  $^1\text{H}$  NMR (297 K, benzene- $d_6$ ,  $\delta$ , ppm): 0.18 (s, 18H,  $\text{SiMe}_3$ ); 0.29 (s, 18H,  $\text{SiMe}_3$ ); 5.82 (s, 2H,  $\text{C}=\text{CH}$ ).  $^{13}\text{C}$  NMR (297 K, benzene- $d_6$ ,  $\delta$ , ppm): -0.8, -0.2 ( $\text{SiMe}_3$ ); 99.5, 105.7 ( $\text{C}\equiv\text{C}$ ); 117.8 ( $\text{C}=\text{CH}$ ); 164.6 ( $\text{C}=\text{CSiMe}_3$ ). IR (ATR,  $\nu$ ,  $\text{cm}^{-1}$ ): 2119, 2161 ( $\text{C}\equiv\text{C}$ ). MS (EI, 70 eV,  $m/z$ ): 390 [ $\text{M}$ ] $^+$ , 375 [ $\text{M} - \text{Me}$ ] $^+$ .

**Synthesis of Complex 7.** To a mixture of complex **1** (1.016 g, 1.66 mmol) and  $^t\text{BuC}\equiv\text{C}-\text{C}\equiv\text{C}^t\text{Bu}$  (0.324 g, 2.00 mmol) was added 15 mL of toluene, and the resulting orange solution was heated at 100 °C for 35 days. Then, the orange solution formed was evaporated to dryness in vacuo, the residue was dissolved at 60 °C in 30 mL of *n*-hexane, and the obtained solution, after cooling to room temperature, was placed in dry ice. In 1 day, the precipitated yellow crystalline solid was separated, washed with cold *n*-hexane, and dried in vacuo to give 0.647 g of a cocrystallizate, containing ca. 90% of complex **7** and ca. 10% of the starting **1** according to X-ray crystallography (see ref 7) and  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra. Analytically pure **7** can be obtained by the reaction of the above cocrystallizate with an additional amount of  $^t\text{BuC}\equiv\text{C}-\text{C}\equiv\text{C}^t\text{Bu}$  in toluene at 100 °C for 7 days, as it has previously been described in ref 7.

**Synthesis of Complexes 10, 11, 12, and 13.** A mixture of complex **1** (0.180 g, 0.295 mmol) and  $\text{PhC}\equiv\text{C}-\text{C}\equiv\text{CPh}$  (0.060 g, 0.297 mmol) was dissolved in 1.5 mL of toluene- $d_8$ , after which a part of the solution obtained (ca. 0.7 mL) was placed in the NMR tube with a PTFE valve and heated at 100 °C for 36 days. The  $^1\text{H}$  NMR spectrum of the final reaction mixture has shown a singlet (at -0.01 ppm) of the  $\text{Me}_3\text{Si}$  group of free  $\text{Me}_3\text{SiC}\equiv\text{C}-\text{C}\equiv\text{CSiMe}_3$ , seven singlets of Cp protons (at 5.26, 5.35, 5.45, 5.55, 5.63, 5.84, and 5.85 ppm) belonging to novel complexes, and a singlet of Cp protons (at 5.32 ppm) of unreacted **1**. The intensity ratio of the observed eight singlets of Cp rings is 37:8:19:13:4:10:6:3, respectively.

In the other experiment, a mixture of complex **1** (1.629 g, 2.67 mmol) and  $\text{PhC}\equiv\text{C}-\text{C}\equiv\text{CPh}$  (0.554 g, 2.74 mmol) was dissolved in 15–20 mL of toluene, and the resulting orange solution was heated for 36 days at 105 °C. Then, the red-brown solution formed was evaporated in vacuo to dryness, and the residue was repeatedly recrystallized from *n*-hexane. As result of the recrystallization, complexes **10** ( $\delta(^1\text{H})$  5.85 ppm), **11** ( $\delta(^1\text{H})$  5.45 ppm), **12** ( $\delta(^1\text{H})$  5.26 ppm), and **13** ( $\delta(^1\text{H})$  5.35 ppm) were isolated in an analytically pure state from the above-mentioned product mixture.

Yield of the isolated **10**: 0.069 g (4%). Mp: 237–238 °C under Ar. Anal. Calcd for  $\text{C}_{42}\text{H}_{30}\text{Zr}$ : C, 80.59; H, 4.83. Found: C, 80.68; H, 4.90.  $^1\text{H}$  NMR (297 K, benzene- $d_6$ ,  $\delta$ , ppm): 5.84 (s, 10H, Cp); 6.97–6.88 (m, 6H, *m*-, *p*-Ph); 7.11 (m, 2H, *p*-Ph); 7.23 (m, 4H, *o*-Ph); 7.34 (m, 4H, *m*-Ph); 7.50 (m, 4H, *o*-Ph).  $^{13}\text{C}$  NMR (297 K, benzene- $d_6$ ,  $\delta$ , ppm): 90.8, 90.9 ( $\text{C}\equiv\text{C}$ ); 112.5 (Cp); 125.0, 127.4 (*p*-Ph); 127.0, 128.3, 128.4, 131.9 (*o*-, *m*-Ph); 124.2, 125.5, 148.3 (*i*-Ph and  $\text{Zr}-\text{C}=\text{C}$ ); 205.9 ( $\text{Zr}-\text{C}\equiv\text{C}$ ). Raman spectrum ( $\nu$ ,  $\text{cm}^{-1}$ ): 2196 ( $\text{C}\equiv\text{C}$ ).

Yield of the isolated **11**: 0.049 g (3%). Mp: 117–119 °C under Ar. Anal. Calcd for  $\text{C}_{36}\text{H}_{38}\text{Si}_2\text{Zr}$ : C, 69.96; H, 6.20. Found: C, 70.33; H, 6.42.  $^1\text{H}$  NMR (297 K, benzene- $d_6$ ,  $\delta$ , ppm): 0.22 (s, 9H, C(5)- $\text{C}_2\text{SiMe}_3$ ); 0.68 (s, 9H, C(6)- $\text{SiMe}_3$ ); 5.47 (s, 10H, Cp); 7.06 (m, 1H, C(1)-*p*-Ph); 7.18 (m, 1H, C(4)-*p*-Ph); 7.19 (m, 2H, C(1)-*m*-Ph); 7.32 (m, 2H, C(4)-*m*-Ph); 7.50 (m, 2H, C(1)-*o*-Ph); 8.12 (m, 2H, C(4)-*o*-Ph).  $^{13}\text{C}$  NMR (297 K, benzene- $d_6$ ,  $\delta$ , ppm): -0.3 (C(5)- $\text{C}_2\text{SiMe}_3$ ); 3.1 (C(6)- $\text{SiMe}_3$ ); 87.8 (C(2)); 94.8 (C(5)- $\text{C}\equiv\text{C}$ ); 108.7 (C(5)- $\text{C}\equiv\text{C}$ ); 106.4 (Cp); 127.7 (C(4)-*m*-Ph); 127.8 (C(4)-*p*-Ph); 128.4 (C(1)-*p*-Ph); 129.1 (C(1)-*m*-Ph); 129.5 (C(4)-*o*-Ph); 132.1 (C(1)-*o*-Ph); 134.0 (C(1)-*i*-Ph); 140.1 (C(4)-*i*-Ph); 147.1 (C(4)); 148.9 (C(5)); 154.0 (C(1)); 170.8 (C(3)); 225.1 (C(6)).  $^{29}\text{Si}$  NMR (297 K, benzene- $d_6$ ,  $\delta$ , ppm): -7.1 (C(6)- $\text{SiMe}_3$ ); -19.3 (C(5)- $\text{C}_2\text{SiMe}_3$ ) (the numbering scheme in the seven-membered ring of **11** is analogous to that for complex **12** in Figure 5). IR (ATR,  $\nu$ ,  $\text{cm}^{-1}$ ): 1869 ( $\text{C}=\text{C}=\text{C}=\text{C}$ ); 2067, 2122 ( $\text{C}\equiv\text{C}$ ). MS (70 eV,  $m/z$ ): 616 [ $\text{M}$ ] $^+$ ; 543 [ $\text{M} - \text{SiMe}_3$ ] $^+$ ; 414 [ $\text{M} - \text{PhC}_2\text{Ph}$ ] $^+$ ; 220 [ $\text{Cp}_2\text{Zr}$ ] $^+$ .

Yield of the isolated **12**: 0.278 g (17%). Mp: 213–215 °C under Ar. Anal. Calcd for  $C_{36}H_{38}Si_2Zr$ : C, 69.96; H, 6.20. Found: C, 69.88; H, 6.13.  $^1H$  NMR (297 K, benzene- $d_6$ ,  $\delta$ , ppm): 0.36 (s, 9H, C(1)–SiMe<sub>3</sub>); 0.65 (s, 9H, C(4)–SiMe<sub>3</sub>); 5.31 (s, 10H, Cp); 6.91 (m, 1H, C≡C–*p*-Ph); 6.99 (m, 2H, C≡C–*m*-Ph); 7.19 (m, 1H, C(6)–*p*-Ph); 7.35 (m, 2H, C≡C–*o*-Ph); 7.39 (m, 2H, C(6)–*m*-Ph); 7.49 (m, 2H, C(6)–*o*-Ph).  $^{13}C$  NMR (297 K, benzene- $d_6$ ,  $\delta$ , ppm): –0.5 (C(4)–SiMe<sub>3</sub>); 1.4 (C(1)–SiMe<sub>3</sub>); 88.8 (C(5)–C≡C); 92.8 (C(5)–C≡C); 103.6 (C(2)); 106.2 (Cp); 124.3 (C(6)–*p*-Ph); 125.4 (C≡C–*i*-Ph); 126.4 (C(6)–*o*-Ph); 127.2 (C≡C–*p*-Ph); 127.9 (C(6)–*m*-Ph); 128.5 (C≡C–*m*-Ph); 131.2 (C≡C–*o*-Ph); 143.6 (C(5)); 155.9 (C(6)–*i*-Ph); 156.0 (C(4)); 162.6 (C(1)); 184.2 (C(3)); 225.0 (C(6)).  $^{29}Si$  NMR (297 K, benzene- $d_6$ ,  $\delta$ , ppm): –7.4 (C(1)–SiMe<sub>3</sub>); –8.9 (C(4)–SiMe<sub>3</sub>) (for the numbering scheme, see Figure 5). IR (ATR,  $\nu$ , cm<sup>–1</sup>): 1871 (C=C=C=C); 2188 (C≡C). MS (70 eV,  $m/z$ ): 616 [M]<sup>+</sup>; 414 [M – PhC<sub>2</sub>Ph]<sup>+</sup>; 220 [Cp<sub>2</sub>Zr]<sup>+</sup>.

Yield of the isolated **13**: 0.048 g (2.9%). Mp: 104–105 °C under Ar. Anal. Calcd for  $C_{36}H_{38}Si_2Zr$ : C, 80.59; H, 4.85. Found: C, 80.04; H, 5.11.  $^1H$  NMR (297 K, toluene- $d_8$ ,  $\delta$ , ppm): 5.35 (s, 10H, Cp); 6.89 (m, 1H, C≡C–*p*-Ph); 6.95 (m, 2H, C≡C–*m*-Ph); 7.08 (m, 1H, C(1)–*p*-Ph); 7.15 (m, 2H, C≡C–*o*-Ph); 7.17 (m, 1H, C(4)–*p*-Ph); 7.18 (m, 1H, C(6)–*p*-Ph); 7.22 (m, 2H, C(1)–*m*-Ph); 7.32 (m, 2H, C(4)–*m*-Ph); 7.39 (m, 2H, C(6)–*m*-Ph); 7.48 (m, 2H, C(6)–*o*-Ph); 7.59 (m, 2H, C(1)–*o*-Ph); 8.30 (m, 2H, C(4)–*o*-Ph).  $^{13}C$  NMR (297 K, toluene- $d_8$ ,  $\delta$ , ppm): 89.5 (C(2)); 91.6 (C(5)–C≡C); 92.0 (C(5)–C≡C); 106.7 (Cp); 124.5 (C(6)–*p*-Ph); 125.4 (C≡C–*i*-Ph); 126.7 (C(6)–*o*-Ph); 127.2 (C≡C–*p*-Ph); 127.9 (C(6)–*m*-Ph); 128.1 (C(4)–*m*-Ph); 128.2 (C(4)–*p*-Ph); 128.3 (C(1)–*p*-Ph); 128.3 (C≡C–*m*-Ph); 129.2 (C(1)–*m*-Ph); 129.2 (C(4)–*o*-Ph); 131.2 (C≡C–*o*-Ph); 132.5 (C(1)–*o*-Ph); 135.7 (C(1)–*i*-Ph); 139.5 (C(4)–*i*-Ph); 140.7 (C(5)); 141.3 (C(4)); 156.0 (C(6)–*i*-Ph); 158.5 (C(1)); 167.5 (C(3)); 220.2 (C(6)) (the numbering scheme in the seven-membered ring of **13** is analogous to that for complex **12** in Figure 5). IR (ATR,  $\nu$ , cm<sup>–1</sup>): 1865 (C=C=C=C). MS (70 eV,  $m/z$ ): 624 [M]<sup>+</sup>; 422 [M – PhC<sub>2</sub>Ph]<sup>+</sup>; 404 [M – Cp<sub>2</sub>Zr]<sup>+</sup>; 220 [Cp<sub>2</sub>Zr]<sup>+</sup>.

**Synthesis of Complex 14.** A mixture of **1** (1.118 g, 1.83 mmol) and toluene (0.351 g, 1.97 mmol) was dissolved in 20 mL of toluene, and the resulting yellow-orange solution was heated for 16 days at 100 °C. Then, the red-orange reaction mixture was evaporated in vacuo, the oily residue was dissolved at 60 °C in 20 mL of *n*-hexane, and the obtained solution, after cooling to room temperature and filtration, was placed in dry ice. After 1 day, the precipitated fine crystalline orange complex **14** was separated from the mother liquor by decanting, washed with cold *n*-hexane, and dried in vacuo. Yield of **14**: 0.515 g (47%). Mp: 212–213 °C under Ar. Anal. Calcd for  $C_{34}H_{38}Si_2Zr$ : C, 68.74; H, 6.45. Found: C, 68.53; H, 6.22.  $^1H$  NMR (297 K, benzene- $d_6$ ,  $\delta$ , ppm): 0.14 (s, 9H, C(4)–SiMe<sub>3</sub>); 0.39 (s, 9H, C(1)–SiMe<sub>3</sub>); 5.40 (s, 10H, Cp); 6.83 (m, 1H, C(6)–*p*-Ph); 6.93 (m, 1H, C(5)–*p*-Ph); 7.08 (m, 2H, C(5)–*m*-Ph); 7.10 (m, 2H, C(6)–*m*-Ph); 7.20 (m, 2H, C(6)–*o*-Ph); 7.26 (m, 2H, C(5)–*o*-Ph).  $^{13}C$  NMR (297 K, benzene- $d_6$ ,  $\delta$ , ppm): –0.1 (C(4)–SiMe<sub>3</sub>); 1.5 (C(1)–SiMe<sub>3</sub>); 104.0 (C(2)); 106.3 (Cp); 123.1 (C(6)–*p*-Ph); 125.8 (C(5)–*p*-Ph); 126.9 (C(6)–*o*-Ph); 127.4 (C(6)–*m*-Ph); 127.5 (C(5)–*m*-Ph); 130.6 (C(5)–*o*-Ph); 143.8 (C(5)–*i*-Ph); 155.0 (C(6)–*i*-Ph); 159.5 (C(4)); 162.5 (C(1)); 166.1 (C(5)); 185.0 (C(3)); 207.9 (C(6)).  $^{29}Si$  NMR (297 K, benzene- $d_6$ ,  $\delta$ , ppm): –7.5 (C(1)–SiMe<sub>3</sub>); –10.0 (C(4)–SiMe<sub>3</sub>) (for the numbering scheme, see Figure 6). Raman spectrum ( $\nu$ , cm<sup>–1</sup>): 1873 (C=C=C=C). MS (70 eV,  $m/z$ ): 592 [M]<sup>+</sup>; 220 [CpZr]<sup>+</sup>.

**X-ray Diffraction Study.** Diffraction data were collected on a Bruker APEX II CCD diffractometer using graphite-monochromated Mo K $\alpha$  radiation. The structures were solved by direct methods and refined by full-matrix least-squares procedures on  $F^2$  with the SHELXTL software package.<sup>34</sup> Crystallographic data for complexes **8**, **9**, **10**, **12**, and **14** are presented in the Supporting Information (Table 1).

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

Table of crystal data and structure refinement parameters for **8**, **9**, **10**, **12**, and **14**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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## ■ DEDICATION

Dedicated to the memory of Professor Michael F. Lappert.

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