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Interaction of the Buchwald Seven-Membered Zirconacyclocumulene Complex with Carbonyl Compounds

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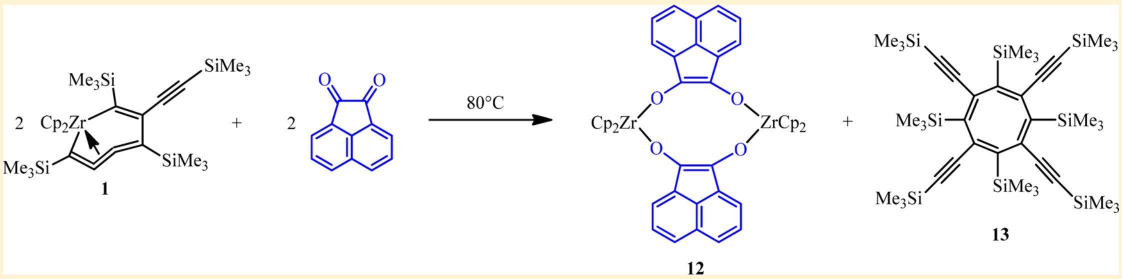
Supporting Information

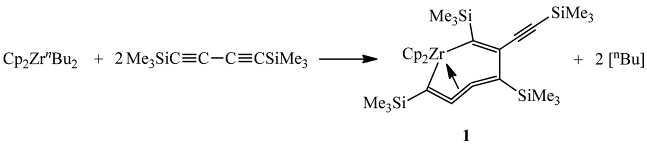


ABSTRACT: The interaction of the Buchwald seven-membered zirconacyclocumulene $Cp_2Zr[\eta^4\text{-}Me_3SiC_4(SiMe_3)\text{−}C(C_2SiMe_3){=}CSiMe_3]$ (**1**) with a 2-fold excess of benzophenone in toluene at 100 °C for 20 h results in the formation of $Me_3SiC{\equiv}C\text{−}C{\equiv}CSiMe_3$ and a nine-membered dioxazirconacycle $Cp_2Zr[\eta^2\text{-}OC(Ph)_2C(SiMe_3)C_2C(SiMe_3)C(Ph)_2O]$ (**5**) containing [3]cumulene group in the ring. Analogous metallacycle (**6**) is formed on heating of **1** with fluorenone in toluene at 100 °C. A treatment of **5** with HCl in dioxane at 20 °C affords Cp_2ZrCl_2 and *cis*-[3]cumulenic diol $Ph_2(HO)C(Me_3Si)\text{-}CC_2C(SiMe_3)C(OH)Ph_2$ (**7**) in 85% yield. The reaction of **1** with benzil $(PhCO)_2$ at 80 °C in benzene proceeds differently than with benzophenone and fluorenone. In this case, a nine-membered dioxazirconacycle $Cp_2Zr[\eta^2\text{-}Me_3SiC{=}C(C_2SiMe_3)\text{−}C(SiMe_3){=}C(C_2SiMe_3)OC(Ph){=}C(Ph)O]$ (**10**) is produced. The nature of products formed in the interaction of **1** with acenaphthenequinone proved to be temperature dependent. Thus, on carrying out the reaction at 20 °C, an 11-membered trioxazirconacycle (**11**) containing three C═C bonds in the ring was isolated from the mixture, whereas at 80 °C the reaction gave a ten-membered tetraoxadizirconacycle (**12**) and octasubstituted cyclooctatetraene $[(Me_3Si)C{=}C(C{\equiv}CSiMe_3)]_4$ (**13**). The structures of **5**−**7** and **10**−**13** have been determined by X-ray diffraction. The mechanism of the reactions found is discussed.

INTRODUCTION

In the last decades, there has been increasing interest in the chemistry of strained metallacycles containing a triple C≡C bond or cumulated double C═C bonds in the ring (see, e.g., refs 1−24). A remarkable property of these metallacycles is their surprisingly high thermal stability compared with the corresponding purely organic analogues. The first compound of such a type, $Cp_2Zr[\eta^4\text{-}Me_3SiC_4(SiMe_3)\text{−}C(C_2SiMe_3){=}CSiMe_3]$ (**1**), containing a [3]cumulene group in the seven-membered zirconacycle, was described in 1993 by Buchwald and co-workers.[1] The complex was prepared by the interaction of the Negishi reagent $Cp_2Zr^nBu_2$ with 1,4-bis(trimethylsilyl)butadiyne $Me_3SiC{\equiv}C\text{−}C{\equiv}CSiMe_3$ (Scheme 1), and its structure was determined by an X-ray diffraction study.

Scheme 1



Subsequently, a series of similar seven-membered zirconacyclocumulene complexes of zirconocene was synthesized and fully characterized (see review[25] and recent papers cited in refs 26−32), which provided the basis for a wide application of such cumulene complexes in organic synthesis and catalysis and, in particular, for the synthesis of functionalized purely organic [3]cumulenes and their testing in a drag design and as advanced materials (see papers cited in ref 33).

According to X-ray diffraction data, the central C(2)═C(3) bond of the cumulene moiety in these seven-membered

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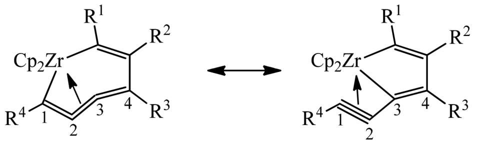
zirconacycles is coordinated with the zirconium atom and its terminal C(1)=C(2) bond (see Scheme 2) is intermediate between the double and triple bonds. This latter fact allowed one to suggest that the electronic structure of seven-membered zirconacyclocumulenes is essentially contributed by a resonance form of the five-membered zirconacyclopentadiene with the α-alkynyl group coordinated with zirconium (Scheme 2).[30−32]

Scheme 2



Data on reactivity of the presently known seven-membered zirconacyclocumulene complexes are limited by those for the Buchwald zirconacyclocumulene. For this metallacycle, its thermal isomerization leading to a novel seven-membered zirconacyclocumulene $Cp_2Zr[\eta^4\text{-}Me_3SiC_4(SiMe_3)\text{−}C(SiMe_3)\text{=}C(C_2SiMe_3)]$[32] as well as the reactions with acetylenes,[32] nitriles,[34,35] *N*-benzylideneaniline,[34,36] and S_2Cl_2[37] have been described. Especially interesting transformations were observed in the interaction of **1** with acetylenes and nitriles. Thus, in the reactions of **1** with acetylenes at 100 °C, new seven-membered zirconacyclocumulenes were produced as main products (Scheme 3).[32]

Under similar conditions, the reaction of **1** with acetonitrile gave dimeric zirconaazacyclopentadiene metallacycle **2** and $Me_3SiC{\equiv}C\text{−}C{\equiv}CSiMe_3$, whereas the interaction of **1** with benzonitrile afforded tetrasubstituted pyrimidine **3** (Scheme 4), in the presence of excess benzonitrile and $Me_3SiC{\equiv}C\text{−}C{\equiv}CSiMe_3$, the process of the synthesis of **3** acquiring a catalytic character.[34]

Finally, from the reaction of **1** with phenylacetonitrile in toluene at 100 °C, unusual tricyclic zirconocene complex **4**, containing four-, five-, and six-membered rings and the Zr−N coordination bond, was isolated (Scheme 5).[35]

In the present article, the reactions of **1** with various carbonyl compounds are described in detail. The results of this study show that with respect to such unsaturated substrates zirconacyclocumulene **1** demonstrates a quite different type of reactivity.

■ RESULTS AND DISCUSSION

If **1** is heated at 100 °C in toluene solution with a 2-fold excess of benzophenone for 20 h, the formation of free $Me_3SiC{\equiv}C\text{−}C{\equiv}CSiMe_3$ and a nine-membered dioxazirconacycle **5**, containing butatrienyl group in the ring, occurs (Scheme 6). The complex was isolated from the solution in 58% yield and fully characterized. Under similar conditions, the interaction of **1** with fluorenone afforded an analogous dioxazirconacycle **6** in 40% isolated yield.

Acetone, benzaldehyde, acetophenone, and cyclohexanone also react with **1** on heating, but our attempts to isolate any individual compounds from these reactions failed.

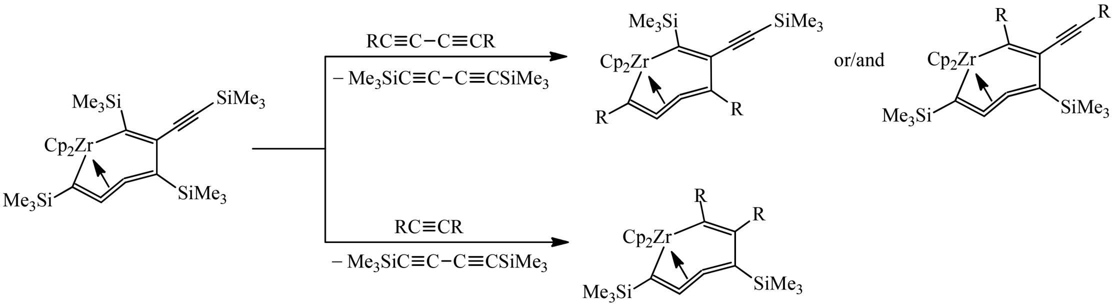
The molecular structure of complex **5** is shown in Figure 1. The asymmetric unit of **5** contains one and two half-molecules close in their geometrical parameters, and in Figure 1, only one of the molecules of the asymmetric unit is depicted. The complex consists of a bent $(\eta^5\text{-}C_5H_5)_2Zr$ sandwich and nine-membered dioxazirconacycle containing the butatrienyl group in the bisector plane of the dihedral angle between the $\eta^5\text{-}C_5H_5$ rings. The geometry of the butatrienyl moiety in **5**, in contrast to that in **1**, is close to linear (the C2−C3−C4 and C3−C4−C5 bond angles are 173.3(11) and 173.5(10)°, respectively) and the central C3−C4 bond of this moiety, as in usual uncoordinated acyclic butatrienes, is considerably shorter (1.264(14) Å) than the typical C=C double bond (av. 1.331 Å). In the starting **1**, the central C=C bond of the [3]cumulene group is essentially elongated (to 1.298(6) Å),[1] which is due to its coordination with the Zr atom. Thus, in complex **5**, in contrast to **1**, the central C=C bond of the butatrienyl unit does not interact with the zirconium. The lengths of the terminal C2−C3 and C4−C5 bonds of the butatrienyl fragment in **5** are 1.331(13) and 1.323(13) Å, respectively.

In accordance with its structure, complex **5** readily reacts with HCl in dioxane at room temperature to give Cp_2ZrCl_2 and *cis*-[3]cumulenic diol **7** (Scheme 7) in 85% isolated yield.

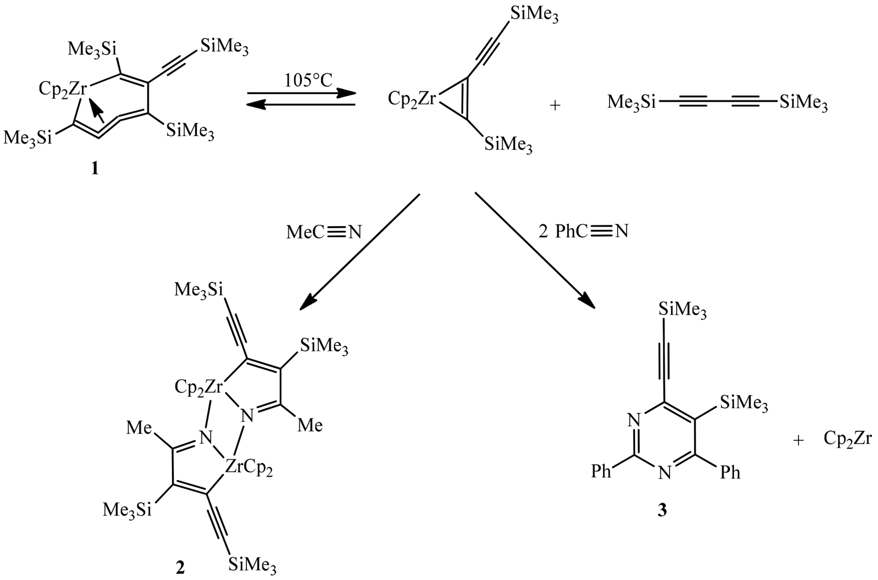
According to an X-ray analysis (Figure 2), the [3]cumulene group in this diol, as in **5**, has a practically linear geometry (the C2−C3−C4 and C3−C4−C5 bond angles are 173.49 (13) and 175.45(13)°, respectively), whereas the C2−C3, C3−C4 and C4−C5 bond distances in **7** (1.3254(17), 1.2690(18), 1.3284(17) Å) are close to those in **5**. The Raman spectrum of **7** exhibits the ν(C=C=C=C) band of the cumulene moiety at 2026 cm^{-1}. The corresponding ν(C=C=C=C) band in the Raman spectrum of complex **5** is observed at 2042 cm^{-1}.

An X-ray diffraction study of complex **6** (in a form of a solvate $6{\cdot}0.5C_6H_6$) has shown that its structure is similar to that of **5** (Figure 3). As in **5**, the butatrienyl fragment in **6** is close to linear (the C2−C3−C4 and C3−C4−C5 bond angles are 176.17(14) and 176.43(14)°, respectively) and its central C3−C4 bond (1.2686(18) Å) is again significantly shorter than the typical C=C double bond, thus indicating the

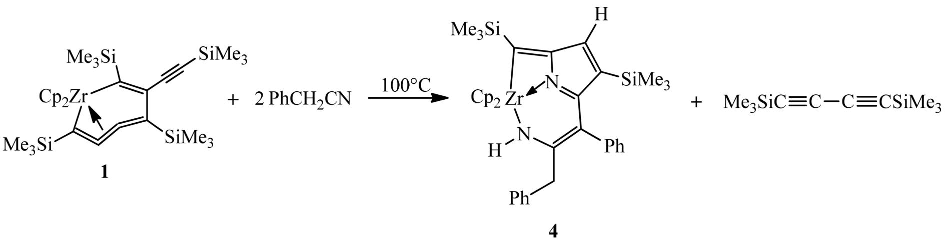
Scheme 3



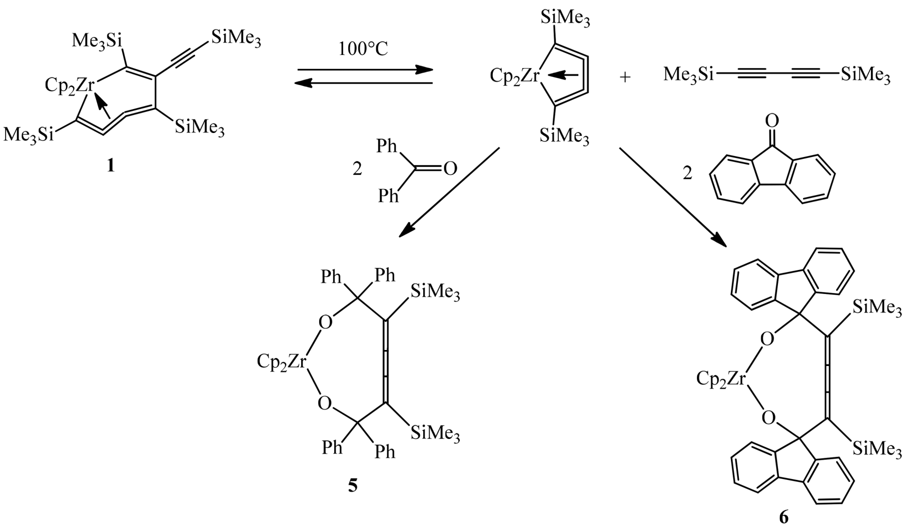
Scheme 4



Scheme 5



Scheme 6



absence of any interaction between this C3═C4 bond in **6** and the Zr center. The C2−C3 and C4−C5 bond lengths in **6** are equal to 1.3205(17) and 1.3233(17) Å, respectively. The Raman spectrum of **6** is characterized by a ν(C═C═C═C) band at 2058 cm^{-1}.

The proposed mechanism of the formation of complexes **5** and **6** includes the steps of double-insertion of the molecules of the carbonyl compound into the Zr−C bonds of the intermediate five-membered zirconacyclocumulene $Cp_2Zr(\eta^4\text{-}Me_3SiC_4SiMe_3)$, which is, apparently, in the equilibrium with **1** at 100 °C (see Scheme 6). The existence of such an equilibrium has been postulated previously in ref 32. For the synthesis and structure of stable five-membered titana-, zircona-, and hafnacyclocumulenes of the type $Cp_2M(\eta^4\text{-}{}^tBuC_4{}^tBu)$, where M is Ti, Zr, and Hf, see refs 2−8. It has also been shown that the above zirconacyclocumulene complex $Cp_2Zr(\eta^4\text{-}{}^tBuC_4{}^tBu)$ synthesized by the interaction of the Negishi reagent $Cp_2Zr^nBu_2$ with ${}^tBuC{\equiv}C{-}C{\equiv}C^tBu$, i.e.,

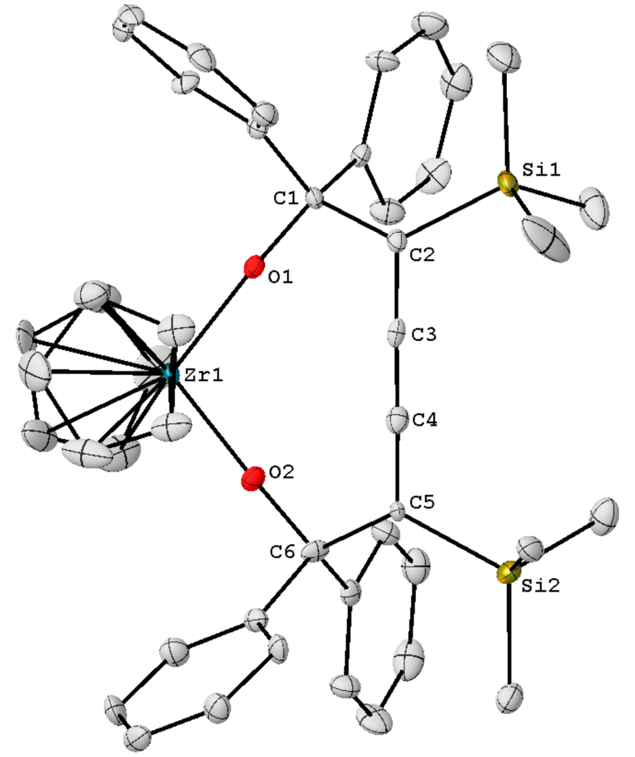
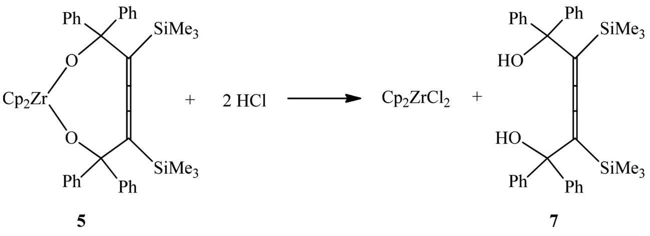


Figure 1. ORTEP representation of the molecular structure of complex **5** (only one of the molecules of the asymmetric unit is shown) with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Zr1–O1 1.971(6), C1–O1 1.394(10), C1–C2 1.550(12), C2–C3 1.331(13), C3–C4 1.264(14), C4–C5 1.323(13), C5–C6 1.554(12), C6–O2 1.410(11), Zr1–O2 1.958(6), O1–Zr1–O2 104.2(3), Zr1–O1–C1 161.8(6), O1–C1–C2 110.5(7), C1–C2–C3 115.8(8), C2–C3–C4 173.3(11), C3–C4–C5 173.5(10), C4–C5–C6 115.9(8), C5–C6–O2 109.6(7), Zr1–O2–C6 165.3(6).

Scheme 7



in manner described in refs 29 and 30 reacts readily with 4-chlorobenzaldehyde in toluene at 80 °C to yield *cis*-[3]cumulenic diol **8** after quenching of the mixture with HCl (Scheme 8).[38]

Evidently, the final product of this reaction before quenching is the corresponding dioxazirconacycle **9** (analogous to **5** and **6**), which, however, was not isolated by the authors from the mixture. A similar procedure based on the interaction of aldehydes with the products of the reactions of the Negishi reagent with a number of other 1,4-disubstituted butadiynes $RC{\equiv}C{-}C{\equiv}CR$ ($R{=}Si^tBuMe_2$, Si^tBuPh_2, Si^iPr_3) was successfully applied for the preparation of a wide range of various *cis*-[3]cumulenic diols (see also ref 33). Here too, the organozirconium products preceding the final diols, i.e., formed before quenching, were not isolated. For the synthesis and structure of the nine-membered dioxauranacycles (analogous to **5** and **6**) by the reaction of $Cp^*_2U(\eta^4\text{-}Me_3SiC_4SiMe_3)$ with carbonyl compounds (benzophenone, acetophenone, and others), see ref 9.

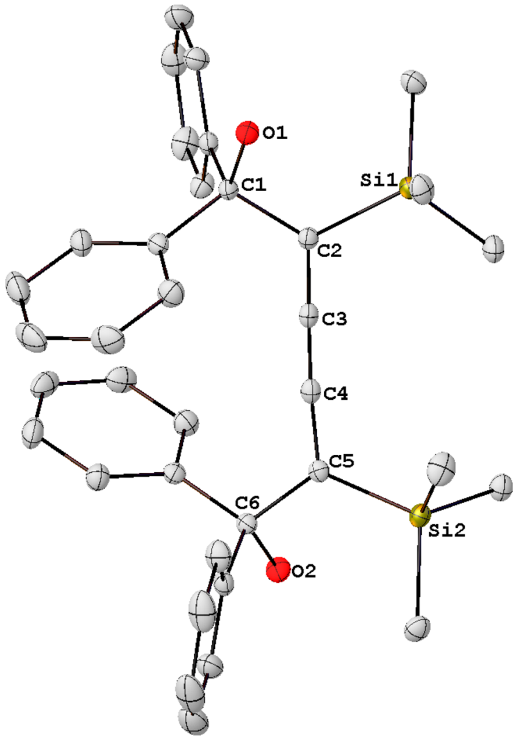


Figure 2. ORTEP representation of the molecular structure of **7** with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): C2–C3 1.3254(17), C3–C4 1.2690(18), C4–C5 1.3284(17), C1–C2–Si1 119.16(8), Si1–C2–C3 118.80(9), C1–C2–C3 121.97(11), C2–C3–C4 173.49(13), C3–C4–C5 175.45(13), C4–C5–Si2 115.06(9), C4–C5–C6 121.23(11), C6–C5–Si2 123.199(8).

The reactions of **1** with 1,2-diketones proceed quite differently than with benzophenone and fluorenone. Thus, it turned out that in the interaction with benzil $(PhCO)_2$ at 80 °C in benzene, the starting **1** reacts in its zirconacyclopentadiene rather than in zirconacyclocumulene resonance form, and in the course of this process, the molecule of benzil is inserted by both its CO groups into the Zr–C bond of the five-membered zirconacycle of this resonance form (Scheme 9). As a result, a zirconocene complex (**10**), containing a nine-membered dioxazirconacycle, is produced. On carrying out the reaction of **1** with a 3-fold excess of benzil at 80 °C for 30 h in benzene, the yield of **10** reaches 85% (based on **1**) according to ^1H NMR spectrum. However, the yield of the complex after a multiple recrystallization of crude **10** did not exceed 5%. Single crystals of complex **10** contained one molecule of cocrystallized benzil per two molecules of **10**.

According to X-ray diffraction data, the nine-membered dioxazirconacycle in **10**·0.5$(PhCO)_2$ is nonplanar and contains two conjugated C=C double bonds (C1–C2 1.364(2) Å, C3–C4 1.341(2) Å) and one isolated C=C bond (C5–C6 1.355(2) Å) connected with two oxygen atoms and two phenyl rings (Figure 4). The C≡C distances in the $Me_3SiC{\equiv}C{-}$ groups of **10** are 1.213(2) Å (C7–C8) and 1.207(2) Å (C9–C10), and the bond angles at the sp-hybridized carbon atoms in both cases are close to 180° (172.72(12) – 176.63(12)°).

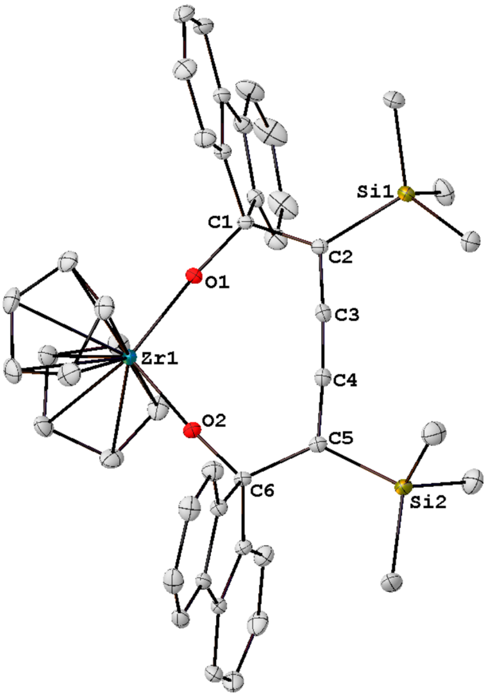
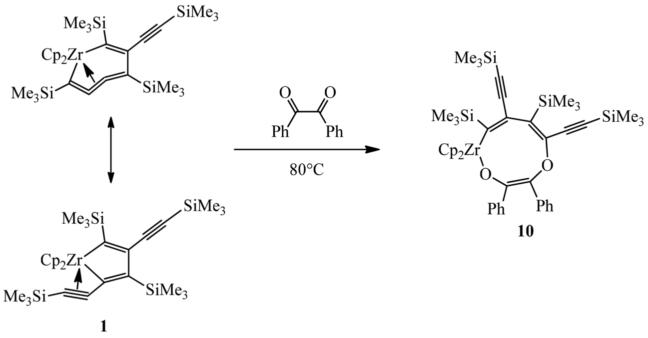


Figure 3. ORTEP representation of the molecular structure of complex **6** with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Zr1−O1 1.9623(9), C1−O1 1.3891(14), C1−C2 1.5382(18), C2−C3 1.3205(17), C3−C4 1.2686(18), C4−C5 1.3233(17), C5−C6 1.5467(17), C6−O2 1.3993(15), Zr1−O2 1.9558(9), O1−Zr1−O2 103.79(4), Zr1−O1−C1 173.65(8), O1−C1−C2 110.74(10), C1−C2−C3 116.25(11), C2−C3−C4 176.17(14), C3−C4−C5 176.43(14), C4−C5−C6 116.35(11), C5−C6−O2 111.19(10), Zr1−O2−C6 174.63(8).

In the interaction of **1** with a 2-fold excess of acenaphthenequinone in toluene at room temperature, the starting zirconacyclocumulene also reacts in its zirconacyclopentadiene resonance form. However, in this case, two rather than one molecules of the dicarbonyl compound are inserted into the Zr−C bonds of the five-membered zirconacycle of the aforementioned resonance form. Interestingly, while in one of these acenaphthenequinone molecules both its carbonyl groups are involved in the insertion, in the other one a single CO group takes part in this process. As a result of the reaction, a zirconocene derivative (**11**), containing an 11-membered trioxazirconacycle, is formed in 70% isolated yield after 30 days (Scheme 10).

Figure 5 shows the structure of **11**. The trioxazirconacyclic fragment in the molecule of **11** is also nonplanar and contains three C═C bonds in the cycle (C1−C2 1.365(9), C3−C4 1.347(8), C5−C6 1.347(9) Å). The lengths of the triple C8−

Scheme 9



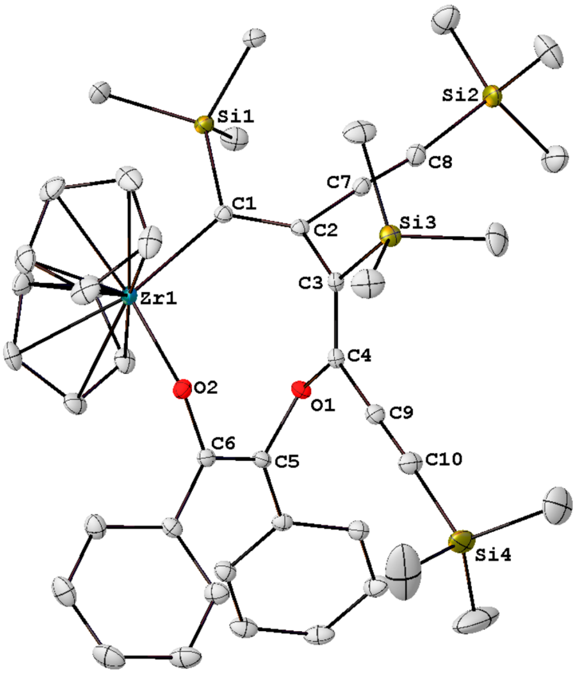
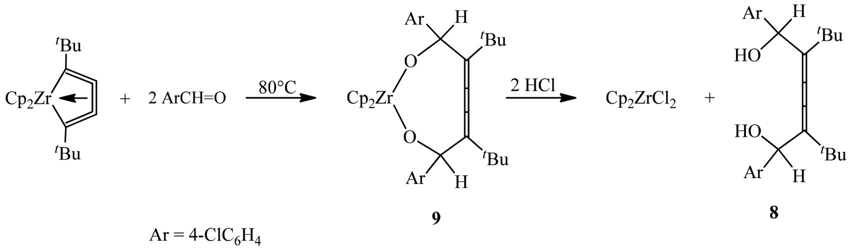
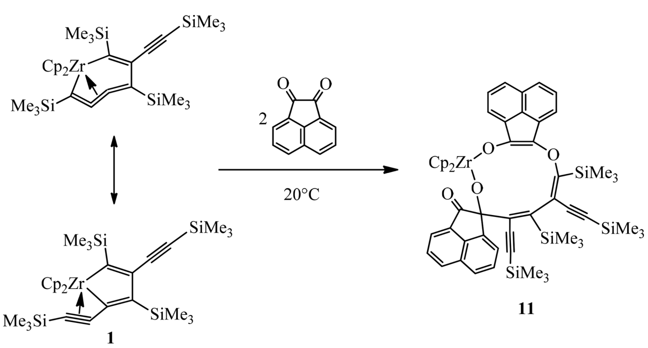


Figure 4. ORTEP representation of the molecular structure of complex **10** with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Zr1−C1 2.319(1), C1−C2 1.364(2), C2−C3 1.506(2), C3−C4 1.341(2), C4−O1 1.398(1), C5−O1 1.407(1), C5−C6 1.355(2), C6−O2 1.354(2), Zr1−O2 2.018(1), C7−C8 1.213(2), C9−C10 1.207(2), C1−Zr1−O2 107.88(4), Zr1−C1−C2 120.74(8), C1−C2−C3 128,70(11), C2−C3−C4 120.8(1), C3−C4−O1 120.65(11), C4−O1−C5 112.96(9), O1−C5−C6 117.1(1), C5−C6−O2 119.7(1), C6−O2−Zr1 134.43(8), C2−C7−C8 176.60(13), C7−C8−Si2 172.72(12), C4−C9−C10 174.64(14), C9−C10−Si4 176.63(12).

Scheme 8



Scheme 10



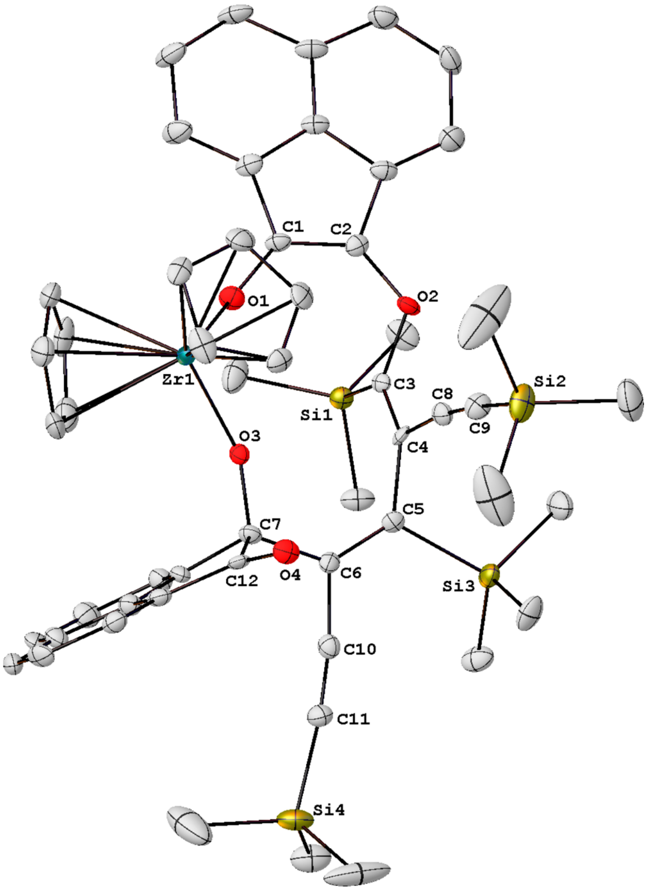


Figure 5. ORTEP representation of the molecular structure of complex **11** with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Zr1−O1 1.978(4), C1−O1 1.326(8), C1−C2 1.365(9), C2−O2 1.390(7), C3−O2 1.432(7), C3−C4 1.347(8), C4−C5 1.500(8), C5−C6 1.347(9), C6−C7 1.531(8), C7−O3 1.400(7), Zr1−O3 1.975(4), C8−C9 1.205(10), C10−C11 1.204(9), C7−C12 1.581(8), C12−O4 1.206(8), O1−Zr1−O3 94.35(18), Zr1−O1−C1 150.3(4), O1−C1−C2 128.5(6), C1−C2−O2 1.390(7), C2−O2−C3 116.6(5), C4−C3−O2 113.9(5), C3−C4−C5 127.4(6), C4−C5−C6 124.8(6), C5−C6−C7 130.4(6), C6−C7−O3 115.7(5), Zr1−O3−C7 156.4(4), C8−C9−Si2 172.1(6), C4−C8−C9 171.6(7), C6−C10−C11 172.6(7), C10−C11−Si4 173.3(6).

C9 and C10−C11 bonds of the $Me_3SiC{\equiv}C$ substituents in the ring are 1.205(10) and 1.204(9) Å, respectively, and the corresponding bond angles at the sp-hybridized carbon atoms are in the range of 171.6(7)−173.3(6)°. The length of the C(12)−O(4) bond of the carbonyl C=O group in **11** is equal to 1.206(8) Å. In the IR spectrum of **11**, the bands of the stretching vibrations of the C≡C and C=O bonds are observed at 2135 ($\nu_{C\equiv C}$), 2122 ($\nu_{C\equiv C}$), and 1728 ($\nu_{C=O}$) cm^{-1}.

Unexpected results were obtained on carrying out the reaction of **1** with acenaphthenequinone in toluene for 1 h at 80 °C. It turned out that under such conditions two new products, namely, a tetraoxadizirconacycle **12** and octasubstituted cyclooctatetraene $[(Me_3Si)C{=}C(C{\equiv}CSiMe_3)]_4$ (**13**), are formed in 39 and 30% isolated yield, respectively (Scheme 11), along with **11**. The both compounds were characterized by analytical and spectral means, and their structures were determined by an X-ray diffraction study.

Complex **12** occupies in the crystal a special position on an inversion center and represents a binuclear ten-membered metallacycle formed by two $(\eta^5\text{-}C_5H_5)_2Zr$ groups and two 1,2-acenaphthilenedioxy moieties (Figure 6). The metallacycle in **12** has a chair conformation and contains in the ring two zirconium and four oxygen atoms as well as two acenaphthilene C=C double bonds. The Zr−O distances in **12** are equal to 1.997(3) Å and the C=C bond lengths in the zirconacycle are 1.384(7) Å.

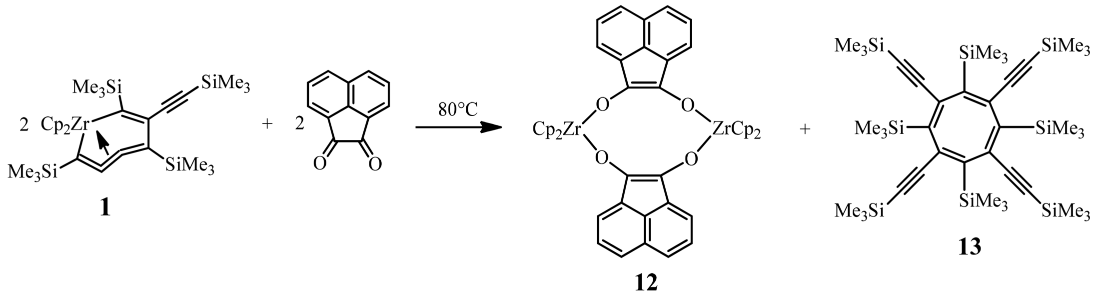
The cyclooctatetraene ring in **13** (Figure 7), as that in nonsubstituted cyclooctatetraene,[39] is nonplanar and has a saddle conformation. The C=C distances in the ring of **13** span the range of 1.327(5) − 1.342(6) Å and the C−C bond lengths are 1.514(6) − 1.520(5) Å. The C≡C separations in the $Me_3SiC{\equiv}C$ substituents range from 1.196(6) to 1.211(6) Å and the bond angles at the acetylene carbon atoms are close to 180°.

The synthesized **13** can be formally considered as a product of cyclotetramerization of 1,4-bis(trimethylsilyl)butadiyne $Me_3SiC{\equiv}C{-}C{\equiv}CSiMe_3$ which, in its turn, could form, in principle, from the starting **1**. However, we have found that no **13** is obtained even in trace amounts on heating the toluene solution of **1** at 80 °C for 30 h. Thus, one may conclude that the presence of acenaphthenequinone in the mixture with **1** is necessary for the formation of **13** in this process. The following mechanism of the reaction of **1** with acenaphthenequinone at 80 °C can be proposed (see Scheme 12).

In the first stage, the starting **1** in its zirconacyclopentadiene resonance form reacts with acenaphthenequinone to give a 1:1 complex (**14**) of the corresponding zirconacyclopentadiene metallacycle with one of the oxygen atoms of the quinone. Then, the homolytic splitting of the Zr−C bonds of the zirconacycle followed by the electron transfer from the zirconium to the coordinated quinone molecule takes place. This leads to the formation of the tetrasubstituted cyclobutadiene $[(Me_3Si)C{=}C(C{\equiv}CSiMe_3)]_2$ and the biradical acenaphthilenedioxy $Cp_2Zr(III)$ derivative (**15**). The subsequent cyclic dimerization of this cyclobutadiene species (via the intermediate Diels−Alder dimer[40]) affords cyclooctatetraene **13**, whereas the cyclic dimerization of **15** gives rise to zirconacycle **12**.

The intermediate formation of the tetrasubstituted cyclobutadiene in this process is confirmed by the experiments, wherein the interaction of **1** with acenaphthenequinone was carried out in the presence of an 8-fold excess of cyclopentadiene for 2 h at 60 °C. It turned out that under such conditions the arising cyclobutadiene is trapped by cyclopentadiene (Scheme 13) to yield the corresponding Diels−Alder adduct (**16**).

Scheme 11



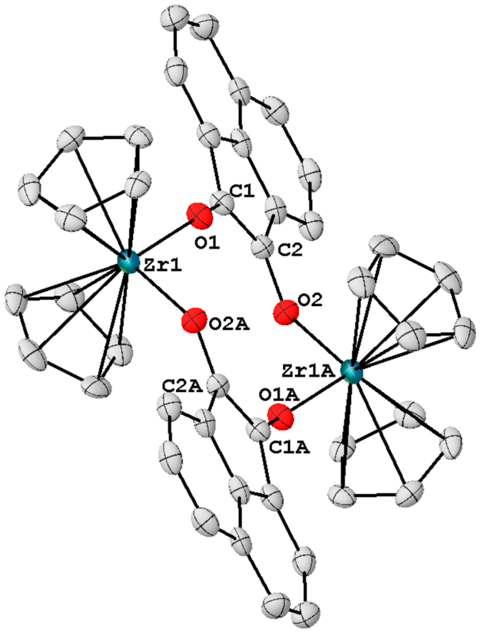


Figure 6. ORTEP representation of the molecular structure of complex **12** with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Zr1−O1 1.997(3), O1−C1 1.327(6), C1−C2 1.384(7), C2−O2 1.329(6), O1−Zr1−O2A 99.75(13), Zr1−O1−C1 149.0(3), O1−C1−C2 127.4(4), C1−C2−O2 127.4(4). Symmetry transformation−x+1, − y+1, − z+1 was used to generate equivalent atoms.

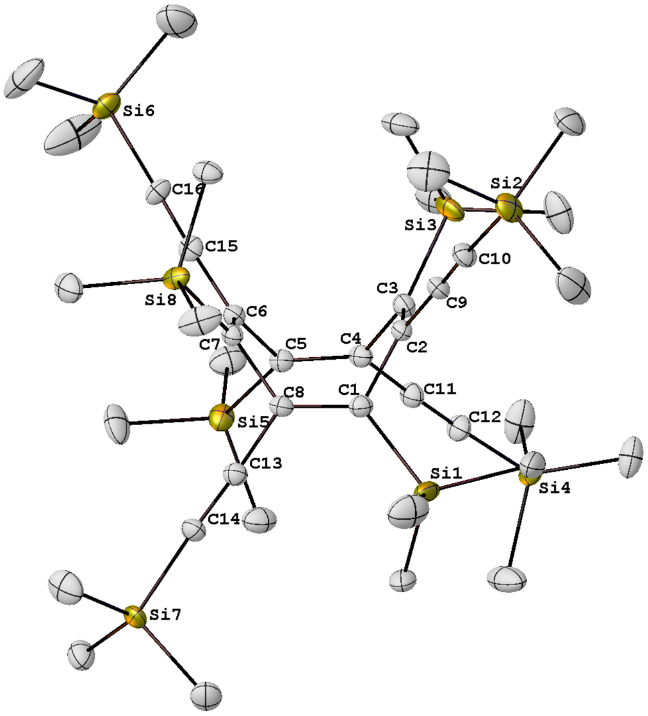


Figure 7. ORTEP representation of the molecular structure of **13** with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): C1−C2 1.514(6), C2−C3 1.339(6), C3−C4 1.514(6), C4−C5 1.335(6), C5−C6 1.520(5), C6−C7 1.327(5), C7−C8 1.516(5), C8−C1 1.342(6), C9−C10 1.196(6), C11−C12 1.209(6), C13−C14 1.206(6), C15−C16 1.211(6).

The adduct was isolated from the reaction mixture in 15% yield and identified by analytical and spectral means.

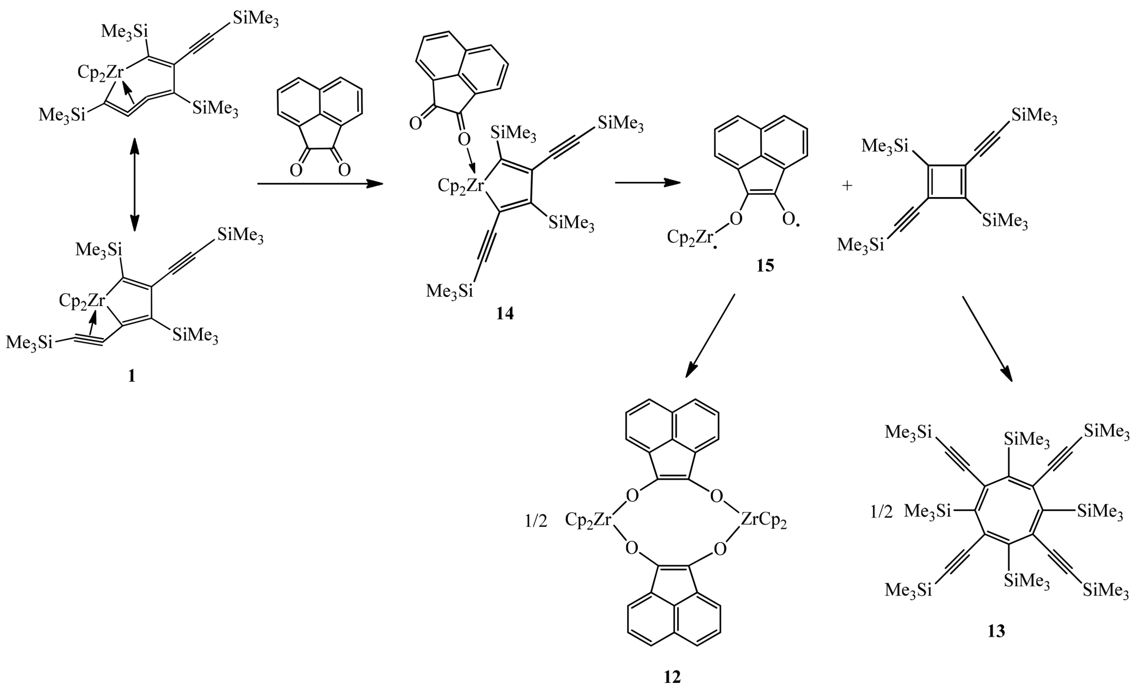
■ CONCLUSION

The results of our study show that the seven-membered zirconacyclocumulene **1** is capable of reacting with various mono- and dicarbonyl compounds to form products whose character is strongly dependent on the nature of a carbonyl derivative and reaction temperature. When diarylketones such as benzophenone and fluorenone are used in the reaction with **1**, the nine-membered dioxazirconacycles **5** and **6** are produced as a result of the insertion of the ketone molecules into two Zr−C bonds of the intermediate five-membered zirconacyclocumulene complex $Cp_2Zr(\eta^4\text{-}Me_3SiC_4SiMe_3)$ formed from **1**. The starting **1** reacts here as in the interaction with acetylenes[32] and nitriles[34,35] (see Schemes 3−5) in its [3]cumulene resonance form. A quite different type of the transformations of **1** is observed in the reactions with α-dicarbonyl compounds such as benzil and acenaphthenequinone. In these transformations, the starting **1** behaves as if it was in its zirconacyclopentadiene resonance form. The data obtained together with the earlier published data impressively demonstrate the surprising variety of chemistry of the Buchwald seven-membered zirconacyclocumulene.

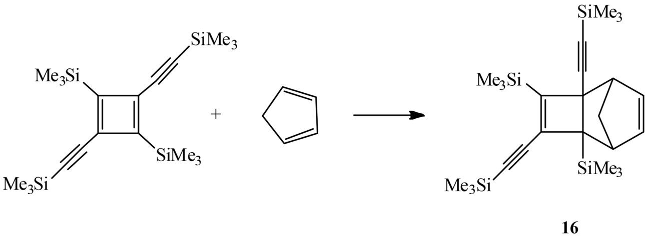
■ EXPERIMENTAL SECTION

Experiments were carried out under argon with careful exclusion of air and moisture using standard Schlenk techniques. The starting seven-membered zirconacyclocumulene **1** was synthesized according to the original procedure described below. Solvents (benzene, toluene, *n*-hexane, THF) were purified by conventional methods and twice distilled prior to use over metallic sodium under Ar. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AMX-400 spectrometer. Chemical shifts (^{1}H, ^{13}C) are given relative to $SiMe_4$ and are referenced to signals of benzene-d_6 (δ_H 7.16 ppm, δ_C 128.0 ppm) as solvent. The IR spectra were recorded on a Nicolet Magna 750 Series II Fourier spectrometer. The Raman spectra were registered on a JY LABRAM 300 spectrometer (He−Ne laser, 632.8 nm, 5 mW). The mass spectra were recorded on a Finnigan Polaris Q instrument.

Scheme 12



Scheme 13



Synthesis of Complex 1. To 2.000 g (6.84 mmol) of Cp_2ZrCl_2, 0.166 g (6.84 mmol) of magnesium turnings, and 2.660 g (13.68 mmol) of 1,4-bis(trimethylsilyl)butadiyne was added 20 mL of THF, and the reaction mixture was stirred at room temperature for 3 h. Then, the resulting green-brown solution was evaporated in vacuo to dryness, the residue was extracted with 30 mL of *n*-hexane at 60 °C, and the obtained extract was concentrated by an argon stream to 15 mL and allowed to stand at −40 °C. After 1 day, the precipitated yellow crystals of complex **1** were separated by decanting of the mother liquor, washed with cold *n*-hexane, and dried under vacuum. Yield of **1**: 3.484 g (92%). Mp: 187−188 °C (dec.) under Ar. Lit. Mp: 187−188 °C (dec.) under Ar.[2] The ^1H and ^{13}C NMR spectra of the synthesized **1** completely coincide with the literature data for **1**.[1]

Synthesis of Complex 5. Complex **1** (0.823 g,1.348 mmol) and 0.491 g (2.696 mmol) of benzophenone were dissolved in 15 mL of toluene, and the obtained solution was heated at 100 °C for 20 h. Then, the resulting bright yellow toluene solution was concentrated in vacuo to 1−1.5 mL and treated with 3 mL of *n*-hexane after which the mixture was allowed to stand at −20 °C. After 14 days, the precipitated colorless crystals of complex **5** were separated by decanting of the mother liquor, washed with cold *n*-hexane, and dried in vacuo. Yield of **5**: 0.610 g (58%). Mp: 194−196 °C (under Ar). Anal. Calcd for $C_{46}H_{48}O_2Si_2Zr$: C, 70.81; H, 6.20. Found: C, 71.15; H, 6.16. ^1H NMR (296 K, benzene-d_6, δ, ppm): 0.10 (s, 18H, $SiMe_3$); 5.60 (s, 10H, Cp); 7.15 (m, 4H, *p*-Ph); 7.25 (m, 8H, *m*-Ph); 7.62 (m, 8H, *o*-Ph). ^{13}C NMR (296 K, benzene-d_6, δ, ppm): 0.8 ($SiMe_3$); 94.7 ($\underline{C}Ph_2$); 111.8 (Cp); 127.5 (CH, *p*-Ph); 127.8, 129.9 (CH, *o*,*m*-Ph); 136.1 ($\underline{C}$=C−$SiMe_3$); 146.8 (C_q, arom.); 174.1 (C=$\underline{C}$−$SiMe_3$). Raman spectrum (ν, cm^{-1}): 2042 (C=C=C=C). MS (70 eV, *m*/*z*): 584 $[M-Me_3SiC_4SiMe_3]^+$; 402 $[M-Me_3SiC_4SiMe_3-Ph_2CO]^+$; 220 $[Cp_2Zr]^+$; 182 $[Ph_2CO]^+$. Single crystals of **5** suitable for X-ray diffraction study were not washed and were not dried under vacuum.

Protolysis of Complex 5 and Synthesis of Diol 7. Complex **5** (0.196 g, 0.251 mmol) was dissolved in 15 mL of *n*-hexane, and the resulting solution was treated with a 4.6 M solution (0.11 mL, 0.51 mmol) of HCl in dioxane. Immediately, the reaction mixture turned opaque and colorless precipitate of Cp_2ZrCl_2 was formed. Then, the precipitated Cp_2ZrCl_2 was filtered, and the obtained solution was evaporated in vacuo to dryness. The residue was dissolved in 10 mL of *n*-hexane at 60 °C, the resulting colorless solution was filtered and allowed to stand at −20 °C. The next day, the precipitated colorless crystals of diol **7** were separated by decanting of the mother liquor, washed with cold *n*-hexane, and dried in vacuo. Yield of **7**: 0.120 g (85%). Mp: 162−163 °C (under Ar). Anal. Calcd for $C_{36}H_{40}O_2Si_2$: C, 77.09; H, 7.19. Found: C, 77.00; H, 7.16. ^1H NMR (296 K, benzene-d_6, δ, ppm): 0.22 (s, 18H, $SiMe_3$); 2.18 (s, 2H, OH); 7.01 (m, 12H, *p*,*m*-Ph); 7.25 (d, 8H, *o*-Ph). ^{13}C NMR (296 K, benzene-d_6, δ, ppm): 1.0 ($SiMe_3$); 84.7 ($OCPh_2$); 127.4 (CH, *p*-Ph); 128.0, 128.3 (CH, *o*,*m*-Ph); 139.7 ($\underline{C}$=C−$SiMe_3$); 146.6 (C_q, Ph); 174.5 (C=$\underline{C}$−$SiMe_3$). Raman spectrum (ν, cm^{-1}): 2026 (C=C=C=C). MS (70 eV, *m*/*z*): 280 $[1/2M]^+$; 182 $[Ph_2CO]^+$.

Synthesis of Complex 6. Complex **1** (0.900 g , 1.622 mmol) and 0.584 g (3.244 mmol) of fluorenone were dissolved in 15 mL of toluene under Ar, and the resulting yellow-orange solution was heated at 100 °C for 20 h. Then, the obtained red-brown solution was evaporated to dryness in vacuo, the residue was washed twice with *n*-hexane at 65 °C and extracted with 15 mL of benzene at 70 °C. The warm extract was filtered and concentrated by an argon stream to 3−4 mL after which it was allowed to cool slowly to room temperature in a water bath. The next day, the precipitated colorless crystals of complex **6** were separated by decanting of the mother liquor, washed with cold *n*-hexane, and dried in vacuo. Yield of **6**: 0.513 g (40%). Mp: 254−256 °C (under Ar). Anal. Calcd for $C_{46}H_{44}O_2Si_2Zr$: C, 71.18; H, 5.71. Found: C, 71.20; H, 5.66. ^1H NMR (296 K, benzene-d_6, δ, ppm): − 0.12 (s, 18H, $SiMe_3$); 5.71 (s, 10H, Cp); 7.22 (m, 8H, CH, arom.); 7.49 (m, 4H, CH, arom.), 7.76 (m, 4H, CH, arom.). ^{13}C NMR (296 K, benzene-d_6, δ, ppm): − 0.1 ($SiMe_3$), 95.9 (O$\underline{C}$); 111.8 (Cp); 120.5, 126.0, 127.7, 129.1 (CH, arom.); 130.4 ($\underline{C}$=C−$SiMe_3$); 140.5, 149.8 (C_q, arom.); 175.9 (C=$\underline{C}$−$SiMe_3$). Raman spectrum (ν, cm^{-1}): 2058 (C=C=C=C). MS (70 eV, *m*/*z*): 580 [M−

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$\mathrm{Me_3SiC_4SiMe_3]^+}$; 402 $\mathrm{[M{-}Me_3SiC_4SiMe_3{-}fluorenone]^+}$; 220 $\mathrm{[Cp_2Zr]^+}$; 180 $\mathrm{[fluorenone]^+}$. Single crystals of **6** for the X-ray diffraction study were not washed and were not dried in vacuo and contained one benzene molecule per two molecules of **6**.

Synthesis of Complex 10. Complex **1** (0.500 g, 0.819 mmol) and 0.516 g (2.460 mmol) of benzil were dissolved in 20 mL of benzene, and the obtained mixture was heated at 80 °C for 30 h to afford complex **10** in 85% yield according to ^{1}H NMR spectrum. After carrying the reaction, the resulting solution was evaporated to dryness in vacuo, and the solid residue underwent a multiple recrystallization from a benzene/*n*-hexane (1:3) mixture to give yellow-green crystals of complex **10**, containing also small amounts of cocrystallized benzil as an admixture according to ^{1}H NMR spectrum (δ 6.95, 7.06, 7.89 ppm). Yield of the isolated **10**: 0.035 g (5%). Mp: 151−152 °C (dec.) (under Ar). Anal. Calcd for $\mathrm{C_{44}H_{56}O_2Si_4Zr}$: C, 64.41; H, 6.88. Found: C, 63.86; H, 6.72. Although these results are outside the range viewed as establishing analytical purity, they are provided to illustrate the best values obtained to date. ^{1}H NMR (296 K, benzene-d_6, δ, ppm): 0.04, 0.21, 0.52, 0.74 (s, 9H each, $\mathrm{SiMe_3}$); 6.06, 6.11 (s, 5H, Cp); 6.98 (m, 4H *m*-Ph); 7.12 (m, 2H, *p*-Ph); 7.45 (m, 4H, *o*-Ph). ^{13}C NMR (296 K, benzene-d_6, δ, ppm): − 0.5, − 0.2, 0.7, 3.7 ($\mathrm{SiMe_3}$); 94.7, 97.2, 103.3, 109.2 ($\mathrm{C{\equiv}C}$); 111.9, 112.3 (Cp); 127.2, 127.9, 128.1, 128.2, 128.7, 129.7 (CH arom.); 133.4, 135.8, 136.7, 138.0, 139.3, 139.9, 154.2 (C=C, $\mathrm{C_{ipso}}$); 208.2 ($\mathrm{C{=}\underline{C}{-}Zr}$). MS (70 eV, *m*/*z*): 430 $\mathrm{[M{-}2Me_3SiC_4SiMe_3]^+}$; 414 $\mathrm{[M{-}2Me_3SiC_4SiMe_3{-}O]^+}$; 220 $\mathrm{[Cp_2Zr]^+}$. Single crystals of **10** for the X-ray diffraction study were obtained by a multiple recrystallization of the above-mentioned solid residue from a benzene/*n*-hexane (1:1) mixture, were not washed and were not dried and contained one cocrystallized benzil molecule per two molecules of **10**.

Synthesis of Complex 11. Complex **1** (0.482 g, 0.79 mmol) was dissolved in 15 mL of toluene at room temperature and 0.287 g (1.58 mmol) of acenaphthenequinone was added to the solution. After 3 days, the reaction mixture became dark maroon. After 30 days, the solution was filtered and evaporated to dryness. The red-brown residue was washed with *n*-hexane and dissolved in 5 mL of toluene at 70 °C after which the obtained toluene solution was filtered and cooled to −40 °C. The next day, the precipitated bright-red crystals of complex **11** were separated by decanting of the mother liquor, washed with *n*-hexane, and dried in vacuo. Yield of **11**: 0.540 g (70%). Mp: 249−253 °C (dec.) under Ar. Anal. Calcd for $\mathrm{C_{54}H_{58}O_4Si_4Zr}$: C, 66.55; H, 6.00. Found: C, 66.43; H, 5.78. ^{1}H NMR (296 K, benzene-d_6, δ, ppm): − 0.44 (s, 9H, $\mathrm{SiMe_3}$); 0.30 (s, 9H, $\mathrm{SiMe_3}$); 0.46 (s, 9H, $\mathrm{SiMe_3}$); 0.72 (s, 9H, $\mathrm{SiMe_3}$); 5.42 (s, 5H, Cp); 6.48 (s, 5H, Cp); 7.26−7,44 (m, 7H, arom.); 7.51−7.56 (m, 2H, arom.); 7.66 (m, 1H, arom.); 7.97 (m, 1H, arom.); 7.99 (m, 1H, arom.). ^{13}C NMR (296 K, benzene-d_6, δ, ppm): − 1.2, 0.1, 0.9, 1.5 ($\mathrm{SiMe_3}$); 101.9, 104.3, 104.7, 106.6 ($\mathrm{C{\equiv}C}$); 112.2, 115.2, (Cp); 118.3, 119.7, 121.5, 121.6, 125.1, 125.2, 126.9, 127.3, 128.5, 129.0, 131.1 (CH, arom.); 95.9, 121.9, 122.5, 131.2, 132.7, 133.4, 135.3, 136.5, 137.2, 142.7, 144.1, 149.0, 149.7, 163.8 (Cq arom. and C=C); 201.3 (C=O), two signals of complex **11** are screened by a signal from $\mathrm{C_6D_6}$. IR (ν, cm^{-1}): 2135, 2122 ($\mathrm{C{\equiv}C}$), 1728 (C=O), 1574 (C=C). MS (70 eV, *m*/*z*): 570 $\mathrm{[M{-}acenaphthenequinone{-}Cp_2Zr]^+}$; 402 $\mathrm{[Cp_2Zr{+}acenaphthenequinone]^+}$; 220 $\mathrm{[Cp_2Zr]^+}$. Single crystals of **11** suitable for the X-ray diffraction study were not washed and were not dried in vacuo.

Synthesis of 12 and 13. Complex **1** (0.816 g, 1.337 mmol) was dissolved in 30 mL of toluene at 80 °C and to the resulting solution was slowly added a warm solution of 0.300 g (1.646 mmol) of acenaphthenequinone in 20 mL of toluene. The mixture was heated at 80 °C for 1 h, and after cooling, the deposited dark red crystals of complex **12** were filtered, washed twice with *n*-hexane, then with THF, and dried in vacuo. Yield of **12**: 0.210 g (39% based on the starting **1**). The obtained dark-red filtrate was evaporated to dryness, the residue was washed with 20 mL of warm *n*-hexane, then with 50 mL of warm toluene, and dried in vacuo. The resulting toluene extract containing **11** was concentrated in vacuo to 5 mL and allowed to stand at −40 °C, which resulted in the deposition of **11**. Yield of **11**: 0.520 g (65% based on the starting acenaphthenequinone). The obtained *n*-hexane solution was passed through alumina, the resulting colorless solution was filtered and evaporated to dryness. The residue was dissolved in 5 mL of warm acetone, and the solution was filtered and allowed to stand at room temperature. The next day, the precipitated colorless crystals of cyclooctatetraene **13** were separated by decanting of the mother liquor, washed with cold acetone, and dried in vacuo. The subsequent sublimation in vacuo at 160 °C gave analytically pure **13**. Yield of **13**: 0.160 g (30% based on the starting **1**).

(**12**): Mp: > 300 °C. Anal. Calcd for $\mathrm{C_{44}H_{32}O_4Zr_2}$: C, 65.47; H, 4.00. Found: C, 65.60; H 4.19%. Because of very low solubility of complex **12** in conventional solvents, its NMR spectra could not be measured. MS (70 eV, *m*/*z*): 402 [1/2M]$^+$; 220 $\mathrm{[Cp_2Zr]^+}$; 182 [acenaphthenequinone]$^+$.

(**13**): Mp: 220−222 °C under Ar. Anal. Calcd for $\mathrm{C_{40}H_{72}Si_8}$: C, 61.78; H, 9.33. Found: C, 61.95; H 9.11. ^{1}H NMR (296 K, benzene-d_6, δ, ppm): 0.18 (s, 36H, $\mathrm{SiMe_3}$); 0.58 (s, 36H, $\mathrm{SiMe_3}$). ^{13}C NMR (296 K, benzene-d_6, δ, ppm): − 0.7 ($\mathrm{SiMe_3}$); − 0.4 ($\mathrm{SiMe_3}$); 101.4, 105.2 ($\mathrm{C{\equiv}C}$); 135.7, 151.5 (C=C). MS (70 eV, *m*/*z*): 673 $\mathrm{[M{-}SiMe_3\ {-}\ 2Me]^+}$; 615 $\mathrm{[M{-}2SiMe_3{-}Me]^+}$; 603 $\mathrm{[M{-}SiMe_3{-}4Me]^+}$; 585 $\mathrm{[M{-}2SiMe_3{-}3Me]^+}$; 527 $\mathrm{[M{-}3SiMe_3{-}2Me]^+}$; 453 $\mathrm{[M{-}4SiMe_3{-}2Me{+}H]^+}$; 73 $\mathrm{[SiMe_3]^+}$. Single crystals of **13** suitable for the X-ray diffraction study were grown from *n*-hexane and were not washed and were not dried in vacuo.

Synthesis of Diels−Alder Adduct 16. Complex **1** (0.873 g, 1.430 mmol) , 0.338 g (1.859 mmol) of acenaphthenequinone, and 0.94 mL (11.444 mmol) of cyclopentadiene were added to 20 mL of benzene, and the obtained mixture was heated under stirring at 60 °C for 2 h. Then, the resulting dark-red solution was filtered off and evaporated in vacuo to dryness. The solid residue was extracted with 40 mL of *n*-hexane, the obtained extract was passed through alumina, filtered, and evaporated to dryness. The residue was then sublimated in vacuo at 70 °C to afford colorless crystals of Diels−Alder adduct **16**. Yield of **16**: 0.098 g (15%). M.p.: 70−71 °C. Anal. Calcd for $\mathrm{C_{25}H_{42}Si_4}$: C, 66.00; H, 9.31. Found: C, 66.04; H, 9.26. ^{1}H NMR (296 K, benzene-d_6, δ, ppm): 0.13 (s, 9H, $\mathrm{SiMe_3}$); 0.19 (s, 9H, $\mathrm{SiMe_3}$); 0.31 (s, 9H, $\mathrm{SiMe_3}$); 0.44 (s, 9H, $\mathrm{SiMe_3}$); 1.83 (m, 1H, CH); 2.06 (m, 1H, CH); 2.76 (br., 1H, $\mathrm{CH_2}$); 2.85 (br., 1H, $\mathrm{CH_2}$); 5.90 (dd, *J*=5.2, 3.1 Hz, 1H, CH); 6.09 (dd, *J*=5.2, 3.0 Hz, 1H, CH). ^{13}C NMR (296 K, benzene-d_6, δ, ppm): −1.6 ($\mathrm{SiMe_3}$), −1.2 ($\mathrm{SiMe_3}$), −0.2 ($\mathrm{SiMe_3}$), 0.1 ($\mathrm{SiMe_3}$), 46.6, 52.7, 54.4 (CH and $\mathrm{CH_2}$); 50.4, 57.4 ($\mathrm{C_q}$); 88.5, 101.8, 102.3,110.6, ($\mathrm{C{\equiv}C}$), 131.8, 134.5 (=CH), 148.3, 160.7 (=C). MS (70 eV, *m*/*z*): 454 [M]$^+$; 439 [M−Me]$^+$; 381 $\mathrm{[M{-}SiMe_3]^+}$; 311 $\mathrm{[M{-}2SiMe_3]^+}$; 73 $\mathrm{[SiMe_3]^+}$.

X-ray Diffraction Study. Single-crystal X-ray diffraction experiments were carried out with a Bruker SMART APEX II diffractometer (graphite monochromated Mo−K$_\alpha$ radiation, λ = 0.71073 Å, ω-scan technique). The APEX II software[41] was used for collecting frames of data, indexing reflections, determination of lattice constants, integration of intensities of reflections, scaling, and absorption correction. All calculations (space group and structure determination, refinements, graphics, and structure reporting) were made using the SHELXTL2014[42] and OLEX2[43] program packages. The structures were solved by direct methods and refined by the full-matrix least-squares technique against F^2 with the anisotropic thermal parameters for all non-hydrogen atoms. Positions of hydrogen atoms were calculated, and all were included in the refinement by the riding model with $U_{\mathrm{iso}}(\mathrm{H}) = 1.5U_{\mathrm{eq}}(\mathrm{X})$ for hydrogen atoms of methyl groups and water molecules, and $U_{\mathrm{iso}}(\mathrm{H}) = 1.2U_{\mathrm{eq}}(\mathrm{X})$ for other atoms. Crystals of **5** and **10**−**12** were two-component twins; in each case, the intensities were separated into two domains using the PLATON package,[44] and the structures were then refined using BASF/HKLF 5 SHELXTL instructions. Crystallographic data for **5**−**7** and **10**−**13** are presented in Table S1.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.9b00190.

^1H NMR spectra of **5**−**7**, **10**, **11**, and **13** (PDF)

Accession Codes

CCDC 1884615−1884621 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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