

Reaction of Disubstituted 1,3-Butadiynes $R^1C\equiv CC\equiv CR^2$ with Zirconocene Complexes: Cleavage of the Central C—C Single Bond To Form Symmetrically and Unsymmetrically Doubly Acetylide-Bridged Metallocene Complexes

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Summary: It has been shown that the zirconocene complex $Cp_2Zr(THF)(Me_3SiC_2SiMe_3)$ readily reacts with disubstituted butadiynes $R^1C\equiv CC\equiv CR^2$ ($R^1 = R^2 = SiMe_3$; $R^1 = SiMe_3$, $R^2 = tBu$ or Ph) to form the dimeric symmetrical complex $[Cp_2Zr(\mu-\eta^1:\eta^2-C\equiv CSiMe_3)]_2$ (2) and doubly acetylide-bridged, unsymmetrical complexes $[Cp_2Zr(\mu-\eta^1:\eta^2-C\equiv CSiMe_3)(\mu-\eta^1:\eta^2-C\equiv C^tBu)ZrCp_2]$ (3) and $[Cp_2Zr(\mu-\eta^1:\eta^2-C\equiv CSiMe_3)(\mu-\eta^1:\eta^2-C\equiv CPh)ZrCp_2]$ (4), respectively. The structure of the products has been established by X-ray structure analyses.

Recently we have reported the first reaction of the titanocene complex $Cp_2Ti(Me_3SiC_2SiMe_3)$ with the disubstituted butadiyne $Me_3SiC\equiv CC\equiv CSiMe_3$ in which the starting butadiyne is split by the generated "titanocene" to yield the dinuclear complex $[Cp_2Ti(\mu-\eta^1:\eta^2-C\equiv CSiMe_3)]_2$ (1) of well-known Type A¹ ($M = Ti$, $R^1 = R^2 = SiMe_3$, Chart 1).^{2,3} Later we could show that the reaction mode of disubstituted butadiynes $R^1C\equiv CC\equiv CR^2$ with titanocene "Cp₂Ti" depends strongly on the nature of the substituents R^1 and R^2 .⁴ In all other investigated cases with $R^1 = R^2 = Ph$, tBu and $R^1 = SiMe_3$, $R^2 = Ph$ or tBu the reaction products are binuclear complexes with intact 1,4-substituted μ -(1-3 η :2-4 η -*trans,trans*-butadiene) units between two titanium centers (Type B,⁵ Chart 1).

On the other hand, zirconium complexes of Type A are also well-known.⁶ The recently published example in this series $[Cp_2Zr(\mu-\eta^1:\eta^2-C\equiv CSiMe_3)]_2$ (2) is an analogue of the titanium complex 1. Complex 2 was prepared in 1% yield by the reaction of Cp_2ZrCl_2 with nBuLi followed by the addition of $Me_3SiC\equiv CH^7$ and was characterized by an X-ray structure analysis. However, the mechanism of the formation remained unclear and there was only a very small amount of the compound available for characterization.

Later di-*n*-butylzirconocene (a precursor to the zirconocene complex of *n*-butene⁸) was described to react with $Me_3SiC\equiv CC\equiv CSiMe_3$ to yield 2, but no data were

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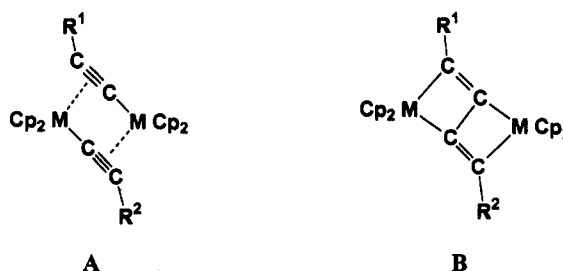
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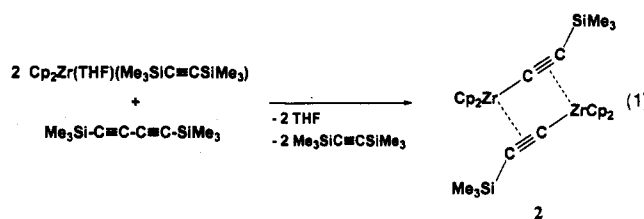
Chart 1



available.⁹ Prompted by these reports we wish to disclose results concerning our method to split the central C—C bond of butadiynes by use of zirconocene complexes to prepare 2 and the similar compounds 3 and 4. The latter are the first examples of an unsymmetrically bridged type A.

Results and Discussion

We found that 2 mol of $Cp_2Zr(THF)(Me_3SiC_2SiMe_3)$ ¹⁰ react with $Me_3SiC\equiv CC\equiv CSiMe_3$ in THF at room temperature to give, after workup under argon, complex 2 in 45% yield (eq 1).



Complex 2 is an orange crystalline solid (mp 270–271 °C under argon, lit 210 °C dec⁷) which was characterized by IR and NMR spectroscopy. The C≡C triple bond stretching frequency for 2 (1755 cm⁻¹; lit. 1751 cm⁻¹) is in the expected region of σ,π -alkynyl-bridged complexes (1: 1798 cm⁻¹ ³).

The ¹H ($\delta = 0.41$ (Me), 5.22 (Cp)) and ¹³C NMR spectra ($\delta = 1.8$ (Me), 102.5 (Cp), 151.4 (C≡CSi), 245.2 (C≡CSi)) show equivalent alkynyl groups and are identical with the limited data in ref 7 where not all ¹³C NMR resonances

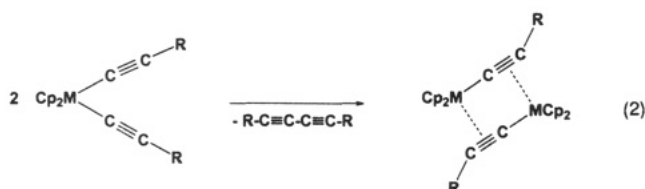
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were detected. A characteristic feature of dinuclear complexes of this type (A) is the extended low-field shift and signal separation of the acetylenic carbon atoms in the ^{13}C NMR spectrum. Thus we are quite sure that complex 2 prepared by us is identical to the product described in ref 7, which has been characterized in its structure.

Furthermore, complex 2 has apparently been obtained also by a third group. ^{13}C NMR data reported¹¹ for a compound believed to be $\text{Cp}_2\text{Zr}(\text{C}\equiv\text{CSiMe}_3)_2$ are identical to the data of dinuclear 2. It is most likely that the complex 2 is the product of the reductive elimination of butadiyne from $\text{Cp}_2\text{Zr}(\text{C}\equiv\text{CSiMe}_3)_2$ (eq 2).

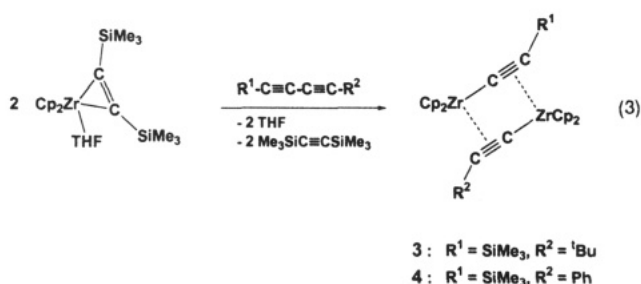


The reductive elimination reaction could be the reason for the instability of the metallocene(IV) acetylide complexes and gives an explanation concerning the mechanism of the formation of 2 in low yield in ref 7. It is reasonable to assume that the $\text{Me}_3\text{SiC}\equiv\text{CH}$ is partially metalated by $n\text{BuLi}$ to afford $\text{Me}_3\text{SiC}\equiv\text{CLi}$ which reacts with Cp_2ZrCl_2 giving the unstable zirconium(IV) complex $\text{Cp}_2\text{Zr}(\text{C}\equiv\text{CSiMe}_3)_2$. In the last step this intermediate converts into 2 by the reductive elimination of butadiyne.

For titanium the titanocene " Cp_2Ti " cleaves the butadiyne $\text{RC}\equiv\text{CC}\equiv\text{CR}$ only in the case of $\text{R} = \text{SiMe}_3$ to give complex 1.³ In all other reactions with disubstituted diynes $\text{R}^1\text{C}\equiv\text{CC}\equiv\text{CR}^2$ the C_4 -unit remains intact as a "zigzag-butadiyne" bound between two titanium centers.⁴

Using the zirconocene generator $\text{Cp}_2\text{Zr}(\text{THF})(\text{Me}_3\text{SiC}_2\text{SiMe}_3)$,¹⁰ the cleavage is favored in all cases. Only for $\text{R}^1 = \text{R}^2 = t\text{Bu}$ we did not find complexes of Type A or B but the binuclear zirconium σ -alkenyl complex $\{\text{Cp}[\mu-(\eta^1:\eta^5-\text{C}_5\text{H}_4)]\text{Zr}[\text{C}(\text{SiMe}_3)=\text{CH}(\text{SiMe}_3)]_2\}$ ¹⁰ together with another yet unidentified product.

$\text{Me}_3\text{SiC}\equiv\text{CC}\equiv\text{C}^t\text{Bu}$ reacts with 2 mol of $\text{Cp}_2\text{Zr}(\text{THF})(\text{Me}_3\text{SiC}_2\text{SiMe}_3)$ to give complex 3 in a 39% yield (eq 3, $\text{R}^1 = \text{SiMe}_3$, $\text{R}^2 = t\text{Bu}$). Complex 3 is an orange-brown crystalline solid (mp 277–278 °C under argon dec) which was characterized by IR and NMR spectroscopy.



In the IR spectra the absorptions of 3 at 1770 and 1820 cm^{-1} are in the typical region for the $[\text{Cp}_2\text{Zr}(\mu-\eta^1:\eta^2-\text{C}\equiv\text{C}-\text{C}\equiv\text{C})_2]$ complexes⁶ and indicate π -complexed alkynyls. Complex 3 is the first example of a complex in which two different alkynyl groups act as bridging ligands between two zirconocene units $\text{Cp}_2\text{Zr}(\mu-\eta^1:\eta^2-\text{C}\equiv\text{C}-\text{C}\equiv\text{C})(\mu-\eta^1:\eta^2-$

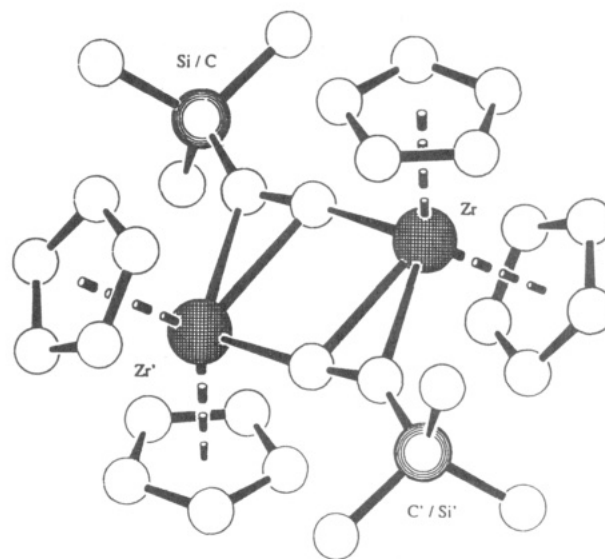


Figure 1. Molecular structure of complex 3.

$\text{C}\equiv\text{CR}^2$) ZrCp_2 . To assign the IR bands to the different alkynyl substituents we considered that a decrease in the $\nu(\text{C}\equiv\text{C})$ IR stretching frequency is observed upon attaching a SiMe_3 group to a triple bond, due to the canonical form $\text{RC}^{(+)}=\text{C}=\text{Si}^{(-)}\text{Me}_3$.¹² Therefore, the band at 1770 cm^{-1} should be assigned to the $\nu(\text{C}\equiv\text{C})$ stretching frequency of the $\text{C}\equiv\text{CSiMe}_3$ moiety and the band at 1820 cm^{-1} to the $\text{C}\equiv\text{C}^t\text{Bu}$ unit.

At ambient temperature the SiMe_3 and $t\text{Bu}$ groups and the Cp-rings cause singlets in the ^1H NMR spectrum. The ^{13}C NMR spectrum shows, in addition to the signals of the SiMe_3 and $t\text{Bu}$ groups, two broadened peaks for Cp ($\delta = 102.1$ and 102.6 ppm) and singlets of four alkynyl carbon atoms ($\delta = 148.6$ ($\text{C}\equiv\text{CSi}$), 170.7 ($\text{C}\equiv\text{C}^t\text{Bu}$), 224.4 ($\text{C}\equiv\text{C}^t\text{Bu}$), 241.2 ($\text{C}\equiv\text{CSi}$)). The more extended low-field shift of the signal at 241.2 ppm is explained by the β -Si-effect of the SiMe_3 group which causes the positivation of the β -carbon atom and the assignment of that signal to the $\text{C}\equiv\text{CSiMe}_3$ alkynyl group and that at 224.4 ppm to the $t\text{Bu}$ moiety.

At higher temperatures complex 3 exhibits in the ^{13}C NMR spectrum only one Cp-signal due to a dynamic process of the complex (see below).

An X-ray structure analysis of complex 3 (Figure 1)¹³ confirms a dinuclear alkynyl zirconium complex $[\text{Cp}_2\text{Zr}(\mu-\eta^1:\eta^2-\text{C}\equiv\text{C}-\text{C}\equiv\text{C})_2]$. SiMe_3 and $t\text{Bu}$ groups are disordered. Thus, the structural details are not discussed further.

When the unsymmetrically substituted butadiyne $\text{Me}_3\text{SiC}\equiv\text{CC}\equiv\text{CPh}$ is applied in the reaction, complex 4 is formed in 32% yield (eq 3, $\text{R}^1 = \text{SiMe}_3$, $\text{R}^2 = \text{Ph}$). Complex 4 is an orange crystalline substance (mp 232–233 °C under argon) which is readily soluble in benzene and THF. The structure of 4 has been determined by IR, NMR spectroscopy, and X-ray structure analysis.

The data are similar to those of the analogous complex 3. As for 3 in the IR spectra of 4, the absorption at 1749 cm^{-1} is assigned to the $\text{C}\equiv\text{CSiMe}_3$ and that at 1820 cm^{-1} to the $\text{C}\equiv\text{CPh}$ moiety. The ^1H and ^{13}C NMR spectra show the signals of the SiMe_3 and Ph group and of two nonequivalent Cp-rings. The ^{13}C NMR signals of the four alkynyl carbon atoms appear at 147.7 ($\text{C}\equiv\text{CSi}$), 158.5 ($\text{C}\equiv\text{CPh}$), 232.5 ($\text{C}\equiv\text{CPh}$), and 238.6 ($\text{C}\equiv\text{CSi}$) ppm.

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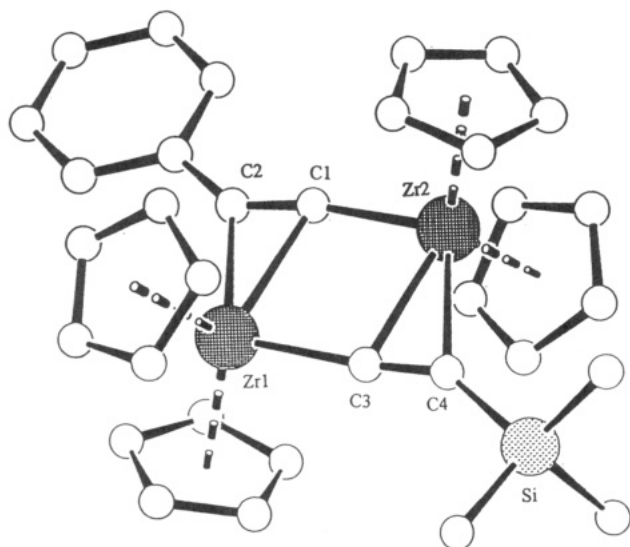


Figure 2. Molecular structure of complex 4.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 4

Zr1-C1	2.416(3)	Zr1-C2	2.354(3)
Zr1-C3	2.216(3)	Zr2-C1	2.157(3)
Zr2-C3	2.448(3)	Zr2-C4	2.442(3)
C1-C2	1.267(4)	C1-C3	2.986(6)
C3-C4	1.246(5)		
C1-Zr1-C2	30.8(1)	C1-Zr1-C3	80.3(1)
C3-Zr2-C4	29.5(1)	C1-Zr2-C3	85.0(2)
C2-C1-Zr2	171.5(3)	C1-C2-C10	141.2(3)
C4-C3-Zr1	173.3(3)	C3-C4-Si	144.6(3)

The structure of complex 4 is dynamic, as observed for 3. At higher temperatures there is only one Cp-signal in ^1H and ^{13}C NMR spectra. This can be explained by highly fluxional alkynyl groups which undergo rapid intramolecular migration between the two zirconium centers.^{6b}

The structure of complex 4, as determined by an X-ray analysis (Figure 2), is similar to that of 3. Positional parameters and selected bond lengths and angles of 4 are given in Tables 1 and 2.

Complexes 2-4 are formally zirconium(III) species and, therefore, exhibit paramagnetism. But nevertheless the compounds are diamagnetic at room temperature. The reason should be an antiferromagnetic coupling directly between the zirconium centers or an electronic coupling between the zirconium atoms via the bridging alkynyl groups. It was found that a decrease of the M-M distance increases the antiferromagnetic coupling.² Because of the long Zr1-Zr2 distance in 4 (3.528(2) Å), we propose an electronic coupling via the unsaturated bridging groups like in $[\text{Cp}_2\text{Zr}(\mu\text{-}\eta^1\text{:}\eta^2\text{-C}\equiv\text{CR})_2]$ complexes.⁶

Some spectroscopic and structural parameters of complexes 1-4 are listed in Table 3 to compare the influence of metals and substituents on the complexation of alkynyl groups.

Replacing Ti in 1³ by Zr in 2⁷ results in a decrease of the $\nu(\text{C}\equiv\text{C})$ bond vibration in the IR-absorption and an extended low-field coordination shift of the acetylenic carbon atoms in the ^{13}C NMR spectrum. The SiMe_3 substituent (in comparison to $\text{R} = \text{Ph}$ or ^tBu) diminishes the $\nu(\text{C}\equiv\text{C})$ bond vibration and causes a larger low-field shift of the metal bonded $\alpha\text{-C}$ atoms of the alkynyl moiety.

However, according to the X-ray structural analyses the distances and angles of the complexes 1-4 are similar, except for the metal-C $_{\alpha}$ (alkynyl) bond length. The largest

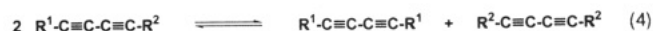
Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{Å}^2 \times 10^3$) for 4

	x	y	z	U(eq)
Zr(1)	3511(1)	3909(1)	6296(1)	31(1)
Zr(2)	6545(1)	3483(1)	6166(1)	34(1)
Si	7868(1)	4401(1)	9160(1)	46(1)
C(1)	4596(3)	3372(1)	5082(4)	37(1)
C(2)	3428(3)	3363(1)	4460(4)	34(1)
C(3)	5504(3)	4036(1)	7420(4)	37(1)
C(4)	6663(3)	4078(1)	7931(4)	41(1)
C(5)	9052(4)	4101(1)	10545(5)	63(1)
C(6)	8715(5)	4715(1)	7804(6)	74(1)
C(7)	6986(6)	4745(2)	10379(7)	95(2)
C(10)	2548(3)	3149(1)	3235(4)	34(1)
C(11)	1252(3)	3227(1)	2916(4)	47(1)
C(12)	453(4)	3005(1)	1762(5)	60(1)
C(13)	947(5)	2711(1)	887(5)	62(1)
C(14)	2243(5)	2631(1)	1169(5)	60(1)
C(15)	3031(4)	2845(1)	2321(4)	47(1)
C(20)	7325(5)	3171(1)	8919(5)	66(1)
C(21)	8130(4)	3025(2)	7869(6)	70(1)
C(22)	7418(5)	2775(1)	6722(6)	69(1)
C(23)	6203(5)	2762(1)	7043(6)	68(1)
C(24)	6127(5)	3003(1)	8395(6)	68(1)
C(30)	7252(5)	4027(1)	4287(5)	61(1)
C(31)	8328(4)	3811(2)	4951(6)	68(1)
C(32)	8204(5)	3417(2)	4320(7)	77(2)
C(33)	7043(5)	3389(2)	3326(5)	72(1)
C(34)	6456(4)	3772(2)	3299(5)	61(1)
C(40)	2959(4)	3358(1)	8254(5)	56(1)
C(41)	1822(5)	3509(2)	7459(6)	71(1)
C(42)	1721(5)	3906(2)	7950(6)	81(2)
C(43)	2806(6)	4008(1)	9020(5)	71(1)
C(44)	3581(4)	3659(1)	9222(4)	56(1)
C(5)	1916(4)	4330(1)	4433(5)	58(1)
C(51)	2425(5)	4586(1)	5663(5)	65(1)
C(52)	3680(5)	4650(1)	5589(6)	70(1)
C(53)	3976(5)	4435(2)	4232(7)	72(1)
C(54)	2850(5)	4236(1)	3527(5)	65(1)

distances of this bond are given by Zr as the central metal and SiMe_3 as the alkynyl substituent.

Complexes 1-4 exemplify one more time that the differences in C-C triple bond complexation are better described by spectroscopic methods than by structural details of the bonding.

The method to prepare the doubly acetylide-bridged complexes as $[\text{Cp}_2\text{Zr}(\mu\text{-}\eta^1\text{:}\eta^2\text{-C}\equiv\text{CSiMe}_3)(\mu\text{-}\eta^1\text{:}\eta^2\text{-C}\equiv\text{C-}^t\text{Bu})\text{ZrCp}_2]$ (3) and $[\text{Cp}_2\text{Zr}(\mu\text{-}\eta^1\text{:}\eta^2\text{-C}\equiv\text{CSiMe}_3)(\mu\text{-}\eta^1\text{:}\eta^2\text{-C}\equiv\text{CPh})\text{ZrCp}_2]$ (4) by splitting disubstituted butadiynes by zirconocene is the basic reaction to study the yet unknown "single bond metathesis" (eq 4).



Experimental Section

General Considerations. All operations were carried out in an inert atmosphere (argon) with standard Schlenk techniques. Solvents were freshly distilled from sodium tetraethylaluminate under argon prior to use. Deuterated solvents were treated with sodium or sodium tetraethylaluminate, distilled, and stored under argon. The following spectrometers were used: NMR, Bruker ARX 300; IR, Nicolet Magna 550 (Nujol mulls using KBr plates); MS, AMD 402. Melting points were measured in sealed capillaries on a Büchi 535 apparatus.

$[\text{Cp}_2\text{Zr}(\mu\text{-}\eta^1\text{:}\eta^2\text{-C}\equiv\text{CSiMe}_3)]_2$ (2). To 0.624 g (1.34 mmol) of $\text{Cp}_2\text{Zr}(\text{THF})(\text{Me}_3\text{SiC}_2\text{SiMe}_3)$ dissolved in 15 mL of THF was added 0.131 g (0.67 mmol) of 1,4-bis(trimethylsilyl)-1,3-butadiyne in THF (10 mL). The orange mixture was stirred at room temperature for 8 h and evaporated to dryness. The remaining product was dissolved in hexane and filtered at 60 °C. On standing at room temperature for 3 days orange crystals deposited. The crystals were washed with cold hexane (2 \times 5 mL) and dried in vacuo.

Table 3. Selected Spectroscopic and Structural Parameters of Complexes $[\text{Cp}_2\text{M}(\mu\text{-}\eta^1\text{:}\eta^2\text{-C}\equiv\text{CR}^1)\text{Cp}_2\text{M}(\mu\text{-}\eta^1\text{:}\eta^2\text{-C}\equiv\text{CR}^2)]$ 1–4

	1: R ¹ = SiMe ₃ , R ² = SiMe ₃ , M = Ti ^b	2: R ¹ = SiMe ₃ , R ² = SiMe ₃ , M = Zr ^c	3: R ¹ = SiMe ₃ , R ² = CMe ₃ , M = Zr ^c	4: R ¹ = SiMe ₃ , R ² = Ph, M = Zr ^c
IR [cm ⁻¹]				
$\nu(\text{C}\equiv\text{CR}^1)$	1798	1755	1770	1749
$\nu(\text{C}\equiv\text{CR}^2)$			1820	1820
¹³ C NMR [ppm]				
$\delta(\text{C}\equiv\text{CR}^1)$	237.5	245.4	241.2	238.6
$\delta(\text{C}\equiv\text{CR}^2)$			224.4	232.5
$\delta(\text{C}\equiv\text{CR}^1)$	142.8	151.5	148.6	147.7
$\delta(\text{C}\equiv\text{CR}^2)$			170.7	158.5
X-ray distances [Å]				
d(C–CR ¹)	1.244(3)	1.249(7)	<i>b</i>	1.246(5)
d(C–CR ²)	–	1.260(7)	–	1.267(4)
d(M–C ₂ R ¹)	2.069(1)	2.191(5)	–	2.216(3)
d(M–C ₂ R ²)	–	–	–	2.157(3)
angle [deg]				
C–C–R ¹	141.5(2)	142.5(4)	–	144.6(3)
C–C–R ²	–	–	–	141.2(3)
M–C–C(R ¹)	176.4(1)	172.7(4)	–	173.3(3)
M–C–C(R ²)	–	–	–	171.5(3)

^a This work. ^b 3 is disordered in respect to the SiMe₃ and the ^tBu groups.

Yield: 0.193 g (45%) of 2, mp 270–271 °C. MS: *m/z* = 636 (M⁺). IR (Nujol mull): 1755 cm⁻¹ ($\nu_{\text{C}\equiv\text{C}}$). ¹H NMR (C₆D₆): δ = 0.41 (s, 18 H, Me), 5.22 (s, 20 H, Cp). ¹³C NMR (C₆D₆): δ = 1.8 (s, SiMe₃), 102.5 (s, Cp), 151.4 (s, C=C–SiMe₃), 245.2 (s, C=C–SiMe₃). Anal. Calcd for C₃₀H₃₈Si₂Zr₂: C, 56.55; H, 6.01. Found: C, 57.25; H, 6.19.

$[\text{Cp}_2\text{Zr}(\mu\text{-}\eta^1\text{:}\eta^2\text{-C}\equiv\text{CSiMe}_3)\text{Cp}_2\text{Zr}(\mu\text{-}\eta^1\text{:}\eta^2\text{-C}\equiv\text{CCMe}_3)]$ (3). To a solution of 0.799 g (1.72 mmol) of Cp₂Zr(THF)(Me₃SiC₂SiMe₃) in 20 mL of THF was added 0.153 g (0.86 mmol) of 1-(trimethylsilyl)-4-(*tert*-butyl)-1,3-butadiyne in THF (10 mL). The mixture was stirred at 50 °C for 10 h and THF was removed in vacuo. The remaining solid was extracted with hexane and filtered at 60 °C. After 3 days at room temperature the solution afforded orange-brown crystals, which were washed with cold hexane and dried in vacuo.

Yield: 0.206 g (38.5%) of 3, mp 277–278 °C. MS: *m/z* = 620 (M⁺). IR (Nujol mull): 1770, 1820 cm⁻¹ ($\nu_{\text{C}\equiv\text{C}}$). ¹H NMR (C₆D₆): δ = 0.41 (s, 9 H, SiMe₃), 1.44 (s, 9 H, CMe₃), 5.22 (s, 20 H, Cp). ¹³C NMR (C₆D₆): δ = 1.8 (s, SiMe₃), 33.5 (s, C(CH₃)₃), 37.8 (s, CMe₃), 102.1, 102.6 (s, Cp), 148.6 (s, C=C–SiMe₃), 170.7 (s, C=CCMe₃), 224.4 (s, C=CCMe₃), 241.2 (s, C=C–SiMe₃). Anal. Calcd for C₃₁H₃₉Si₂Zr₂: C, 59.94; H, 6.17. Found: C, 59.65; H, 6.38.

$[\text{Cp}_2\text{Zr}(\mu\text{-}\eta^1\text{:}\eta^2\text{-C}\equiv\text{CSiMe}_3)\text{Cp}_2\text{Zr}(\mu\text{-}\eta^1\text{:}\eta^2\text{-C}\equiv\text{CPh})]$ (4). A volume of 0.18 mL (0.82 mmol) of 1-(trimethylsilyl)-4-phenyl-1,3-butadiyne in THF (5 mL) was added to a solution of 0.746 g (1.65 mmol) of Cp₂Zr(THF)(Me₃SiC₂SiMe₃) in 20 mL of THF. The mixture was stirred at ambient temperature for 36 h and the solvent was replaced by hexane. After filtration at 60 °C and standing at room temperature for 3 days, orange crystals were obtained. The mother liquor was decanted and the product was washed with hexane (2 × 5 mL) and dried in vacuo.

Yield: 0.17 g (32%) of 4, mp 232–233 °C. MS: *m/z* = 640 (M⁺). IR (Nujol mull) 1749, 1820 cm⁻¹ ($\nu_{\text{C}\equiv\text{C}}$). ¹H NMR (C₆D₆): δ = 0.40 (s, 9 H, SiMe₃), 5.23, 5.28 (s, 10 H, Cp), 7.21–7.79 (m,

5 H, Ph). ¹³C NMR (C₆D₆): δ = 1.8 (s, SiMe₃), 102.6, 102.8 (s, Cp), 126.7, 128.9, 131.2, 137.4 (s, Ph), 147.7 (s, C=C–SiMe₃), 158.5 (s, C=C–Ph), 232.5 (s, C=C–Ph), 238.6 (s, C=C–SiMe₃). Anal. Calcd for C₃₈H₃₄Si₂Zr₂: C, 61.82; H, 5.35. Found: C, 61.56; H, 5.69.

X-ray Crystallographic Study of $[\text{Cp}_2\text{Zr}(\mu\text{-}\eta^1\text{:}\eta^2\text{-C}\equiv\text{CSiMe}_3)\text{Cp}_2\text{Zr}(\mu\text{-}\eta^1\text{:}\eta^2\text{-C}\equiv\text{CPh})]$ (4). Diffraction data were collected on a CAD4 diffractometer using Mo K α radiation. The structure was solved by direct methods (Shelxs-86, Sheldrick, G. M. *Acta Crystallogr. Sect. A* 1990, 46, 467) and refined by full-matrix least-square techniques against *F*² (Shelxl-93, G. M. Sheldrick, Göttingen, Germany, 1993); structural representation: SCHAKAL 92, E. Keller, University Freiburg, 1992; molecular weight: 641.13 g mol⁻¹; space group: *P*2₁/*c*; *a* = 10.608(1), *b* = 32.992(4), *c* = 8.316(1) Å, β = 98.848(8)°, *V* = 2875.8(6) Å³, crystal dimensions 0.5 × 0.4 × 0.1 mm, *Z* = 4, *D*_c = 1.481 g/cm³, μ = 0.786 mm⁻¹; θ range: 1.23–27.45°; number of collected data at 293 K: 8010; number of unique data: 6586; number of observed data with *I* > 2 σ (*I*): 5264; hydrogen atoms were included at calculated positions, non-hydrogen atoms were refined anisotropically; number of variables: 326; *R*₁ = 0.043, *wR*₂ = 0.102.

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Supplementary Material Available: SCHAKAL figures, complete positional and thermal parameters, anisotropic thermal parameters, bond distances and angles: (11 pages). Ordering information is given on any current masthead page.

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