The First Titanacyclic Five-Membered Cumulene. Synthesis, Structure, and Reactivity

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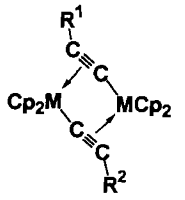
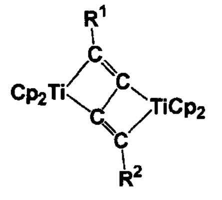
The first five-membered titanacyclic cumulene $Cp_2Ti-C(tBu)=C=C=C(tBu)$ (**5**) was prepared by treatment of the titanocene generator $Cp_2Ti(Me_3SiC_2SiMe_3)$ with the di-*tert*-butylbutadiyne in a molecular one-to-one ratio. The reaction of **5** with "Cp_2Zr" or of the analogous complex $Cp_2ZrC(tBu)=C=C=C(tBu)$ with "Cp_2Ti" leads to cleavage of the central C–C bond in the metallacyclocumulene complexes to afford the same product, the heterodimetallic σ,π-alkynyl-bridged titanocene-zirconocene complex $Cp_2Zr(\mu\text{-}\eta^1{:}\eta^2\text{-}C{\equiv}CtBu)Cp_2Ti(\mu\text{-}\eta^1{:}\eta^2\text{-}C{\equiv}CtBu)$ (**6**), in which each alkynyl group is σ-bonded to one and π-bonded to the other metal as shown by X-ray diffraction studies. In solution the two alkynyl groups become equivalent. The coupling reaction of "Cp_2Ti" with bis(trimethylsilyl)butadiyne in a one-to-two molecular ratio leads to the unsymmetrically substituted titanacyclopentadiene $Cp_2Ti-C(SiMe_3)=C(C{\equiv}CSiMe_3)-C(SiMe_3)=C(C{\equiv}CSiMe_3)$ (**7**).

In cyclizations of unsaturated compounds using the metallocene fragments "Cp_2M" (M = Ti or Zr)[1], which are frequently employed preparatively, little is known about reactions with 1,4-disubstituted 1,3-butadiynes[2].

Recently, we have found that two equivalents of the titanocene complex $Cp_2Ti(Me_3SiC_2SiMe_3)$[3], an excellent titanocene source, react with one equivalent of disubstituted butadiynes to give dinuclear complexes of type **1**[4] or **2**[5]. The obtained types of complexes are well-known[6], but we have found a new way of preparation in which, depending on different substituents, the central C–C single bond of the starting butadiyne is cleaved.

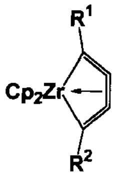


1 a: M = Ti, $R^1 = R^2 = SiMe_3$
b: M = Zr, $R^1 = R^2 = SiMe_3$
c: M = Zr, $R^1 = SiMe_3$, $R^2 = {}^tBu$

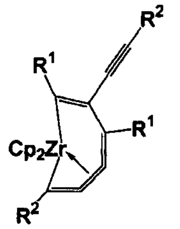


2 a: $R^1 = R^2 = {}^tBu$
b: $R^1 = SiMe_3$, $R^2 = {}^tBu$

With the complex $Cp_2Zr(THF)(Me_3SiC_2SiMe_3)$[7a] as zirconocene synthon the cleavage reaction to complexes of type **1**[7b] is more favoured, but when $Cp_2Zr(Py)(Me_3SiC_2SiMe_3)$ (Py = pyridine)[8a] was used five- (**3**) and seven-membered (**4**) zirconacyclic cumulene complexes were formed, depending as well on the substituents[8b]. However, analogous cumulene complexes of titanocene have been unknown so far.



3 $R^1 = R^2 = {}^tBu$

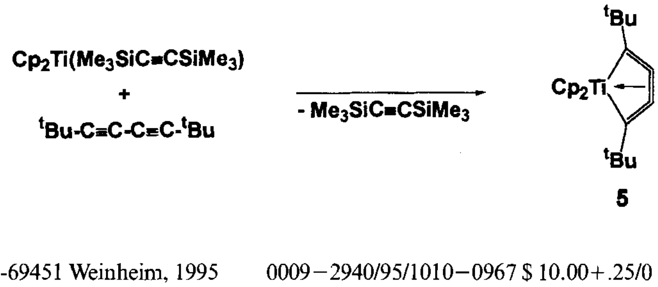


4 a: $R^1 = R^2 = SiMe_3$
b: $R^1 = SiMe_3$, $R^2 = {}^tBu$

In the present paper we report on the synthesis, spectral characteristics, and some chemical properties of the first five-membered metallacyclic cumulene complex of titanocene which can act as an intermediate in the cleavage reaction of diynes.

Results and Discussion

The reaction of $Cp_2Ti(Me_3SiC_2SiMe_3)$ with equimolar amounts of $tBuC{\equiv}C{-}C{\equiv}CtBu$ in hexane at room temperature affords green solutions from which the metallacyclic cumulene **5** can be isolated by cooling to −40 °C. Also small amounts of the dinuclear complex **2a** are formed after a reaction time of 1 to 2 days.



5

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Complex **5** is a green crystalline solid with m.p. 172–173 °C (dec.), decomposing in the presence of air or moisture.

In the IR spectrum of **5** in nujol suspension as well as in THF solution no absorption is observed in the region characteristic of the stretching vibrations for coordinated (1700–1800 cm^{-1}) or free C–C triple bonds (2050–2200 cm^{-1}).

The ^{1}H-NMR spectrum (400 MHz, [D$_8$]THF) of **5** displays only two singlets of methyl protons (δ = 1.60) and of cyclopentadienyl protons (δ = 5.05) in the theoretically expected intensity ratio for **5** (18:10). The ^{13}C{^{1}H}-NMR spectrum of **5** shows, in addition to signals at δ = 33.5 (CH$_3$), 38.1 (*C*CH$_3$), and 103.8 (Cp), two singlets at δ = 94.7 (*C*C*t*Bu) and 181.9 (C*C**t*Bu).

The mass spectrum of **5** exhibits a molecular ion peak at *m*/*z* 340 [M$^+$], indicative of a mononuclear complex.

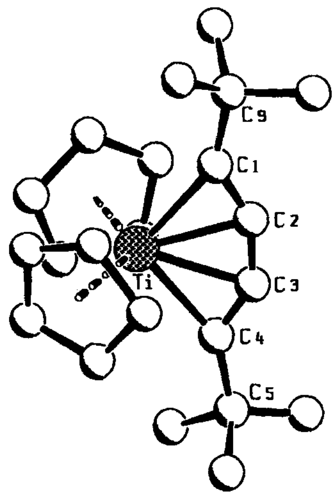
An X-ray diffraction study of **5** (Figure 1) shows a highly strained titanacyclocumulene, being isostructural with the zirconocene complex **3**[8b,c]. The structure, which is different from metallacyclopentadienes, has three bond lengths for C1–C2 1.243(13), C2–C3 1.339(13), and C3–C4 1.276(11) Å showing double bond[9] order. The atoms Ti, C1, C2, C3, and C4 are coplanar. All four ring C atoms have p orbitals perpendicular to the plane of the cumulene, and the sp-hybridized internal C2 and C3 atoms possess additional p orbitals lying in a plane. The central C=C bond is coordinated to the Ti center showing quite shorter distances between the β-carbon atoms and the titanium atom [Ti–C2 2.209(9), Ti–C3 2.213(9) Å] than to the α-carbon atoms [Ti–C1 2.298(10), Ti–C4 2.252(9) Å]. By this interaction the deviation of the cumulene unit from linearity [C1–C2–C3 150.0(10), C2–C3–C4 147.8(10)°] is reduced, but differs markedly from 180°, being not so large as in the calculated 1,2,3-cyclopentatriene (116.37°)[10].

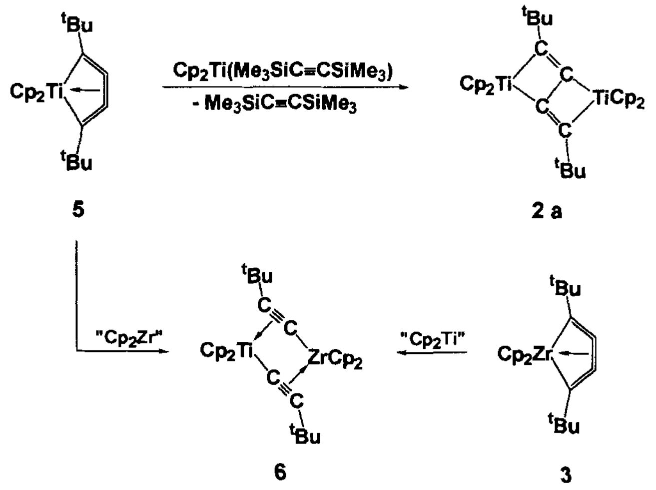
In the analogous zirconocene complex **3** the bond lengths of the double bonds C1–C2 1.28(1), C2–C3 1.31(1), C3–C4 1.29(1) Å, the distances of the β-carbon atoms [Zr–C2 2.303(5), Zr–C3 2.306(5) Å] and α-carbon atoms to zirconium [Zr–C1 2.357(5), Zr–C4 2.307(5) Å] reflect a more symmetrical and not so strained structure compared to **5**, which can be traced back to the larger atomic radius of zirconium. Surprisingly, the deviation of the cumulene unit from linearity is in the zirconium complex almost identical as found for **5** [C1–C2–C3 150.0(5), C2–C3–C4 147.2(5)°].

Complex **5** is stable in hexane solution at room temperature under Ar for a long time, but the addition of an equimolar amount of complex Cp$_2$Ti(Me$_3$SiC$_2$SiMe$_3$) as generator for "Cp$_2$Ti" to its solution gives the well-known dinuclear complex **2a**[5] in high yield.

An analogous reaction of complex **5** with Cp$_2$Zr(THF)(Me$_3$SiC$_2$SiMe$_3$) at room temperature affords in a low yield the dimeric heterodimetallic titanocene-zirconocene derivative **6**, containing bridging σ,π-acetylide groups. This complex can be synthesized also by the reaction of the zirconocene cumulene complex **3** with Cp$_2$Ti(Me$_3$SiC$_2$SiMe$_3$). Complex **6** is a yellow-brown crystalline substance (m.p. 307–308 °C under argon, dec.) which was characterized by analytical and spectroscopical methods.

Figure 1. Molecular structure of **5**. Selected bond distances [Å] and angles [deg]: C1–C2 1.243(13), C2–C3 1.339(13), C3–C4 1.276(11), Ti–C1 2.298(10), Ti–C2 2.209(9), Ti–C3 2.213(9), Ti–C4 2.252(9); C1–Ti–C4 100.4(4), C9–C1–C2 139.2(10), C1–C2–C3 150.0(10), C2–C3–C4 147.8(10), C3–C4–C5 138.1(9)



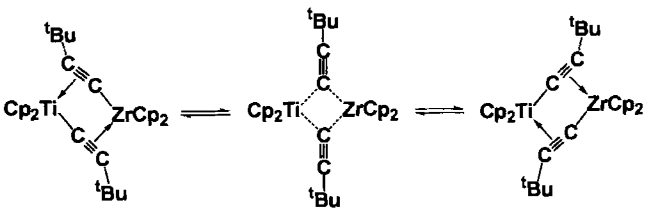


The mass spectrum of **6** exhibits a parent ion peak at *m*/*z* 560 and characteristic peaks of fragmental ions at *m*/*z* 382 [Cp$_2$Zr(CC*t*Bu)$_2$], 301 (Cp$_2$ZrCC*t*Bu), 220 (Cp$_2$Zr), and 178 (Cp$_2$Ti). No peaks for homodimetallic complexes were observed.

In the IR spectrum of **6** in nujol suspension the two different absorptions at 1780 (m) and 1865 (w) cm^{-1} are in the typical region of σ,π-alkynyl-bridged complexes, e.g. in Me$_3$Si-analogous homodimetallic titanocene **1** at 1798 cm^{-1}[4] and in the zirconocene complex at 1755 cm^{-1}[7a,11].

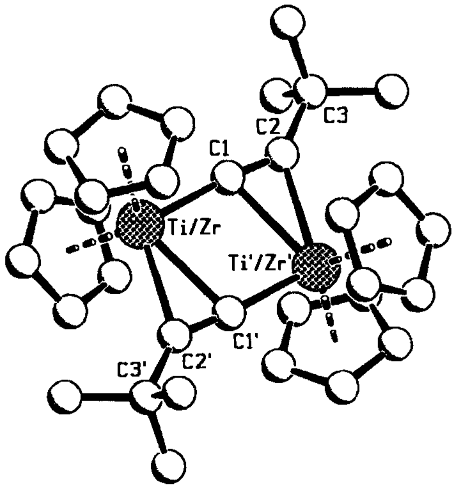
The ^{1}H-NMR spectrum of **6** in C$_6$D$_6$ shows only one resonance of the *t*Bu groups at δ = 1.39 and two resonances of the Cp protons (δ = 5.03 and 5.32). The ^{13}C{^{1}H}-NMR spectrum exhibits two signals of Cp groups at δ = 101.8 and 103.4 and four resonances of two equivalent alkynyl groups at δ = 33.4 (CH$_3$), 37.1 (*C*CH$_3$), 159.1 (C*C**t*Bu) and

215.2 (*C*C*t*Bu). The observed equivalence of the alkynyl groups in the ^{1}H- and ^{13}C{^{1}H}-NMR spectra indicate a dynamical behavior of **6** in solution at room temperature. This can be explained by highly fluxional alkynyl groups which undergo rapid intramolecular migration between the two metal centers[6e].

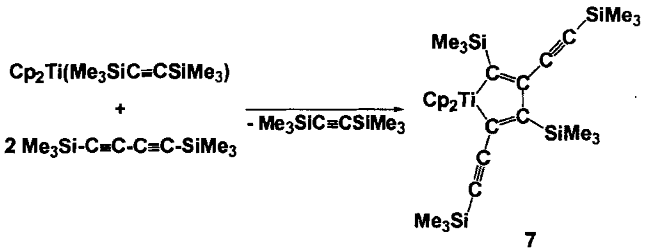


An X-ray structure analysis of compound **6** (Figure 2) confirms the presence of a heterodinuclear σ,π-alkynyl-bridged complex in which the titanium and zirconium atoms are disordered. Thus, the structural details are not discussed further.

Figure 2. Molecular structure of **6**



The reaction of the titanocene-alkyne complex $Cp_2Ti(Me_3SiC_2SiMe_3)$ with two equivalents of bis(trimethylsilyl)butadiyne leads to the titanacyclopentadiene complex **7**.



7

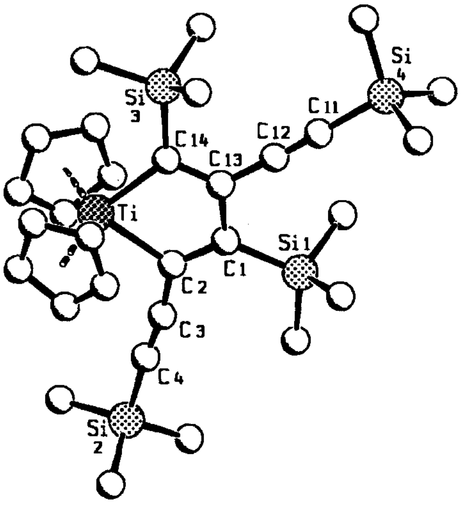
The two diyne molecules are coupled by one molecule of titanocene giving in contrast to zirconium the unsymmetrically substituted titanacyclopentadiene **7** and not a seven-membered cyclocumulene complex of type **4**. When this reaction was carried out in a 1:1 ratio of the titanocene complex and the diyne a mixture of complexes **1** and **7** was isolated.

Complex **7** crystallizes as red-brown prisms, which melt with decomposition at 162–163 °C. The IR spectrum of **7** exhibits within the range of 1600–2300 cm^{-1} three bands at 2052, 2081, and 2124 cm^{-1}, which can be assigned to stretching vibrations of uncomplexed alkynyl groups.

The ^{1}H-NMR spectrum of complex **7** in [D$_8$]THF displays four resonances at $\delta = 0.04, 0.10, 0.13$, and 0.24 assigned to the $SiMe_3$ groups and one resonance of the η^5-cyclopentadienyl protons at $\delta = 6.30$. The ^{13}C{^{1}H}-NMR spectrum of this complex shows four resonances of the $SiMe_3$ groups ($\delta = -0.2, 0.2, 1.2, 2.2$), a singlet of Cp ($\delta = 115.0$), and eight resonances of inequivalent diyne C atoms [$\delta = 91.5, 122.1, 157.0, 245.6$ (C*C*–SiMe$_3$) and 106.6, 109.9, 130.4, 198.4 [*C*CSiMe$_3$].

Complex **7** was additionally characterized by an X-ray crystal structure analysis (Figure 3), which confirms the existence of an unsymmetrically substituted five-membered titanacyclopentadiene with only one bulky trimethylsilyl group in α position to the metal. Usually, both trimethylsilyl groups are bound in the α position and take advantage of the sterically free lateral sectors in the central plane of the bent metallocene unit[12]. The explanation for the unusual regiochemistry in **7** is the neighborhood to the alkynyl group, demanding only little space in the β positions of the molecule.

Figure 3. Molecular structure of **7**. Selected bond distances [Å] and angles [deg]: Ti–C2 2.166(5), Ti–C14 2.147(6), C1–C2 1.374(7), C13–C14 1.375(7), C1–C13 1.487(7); Ti–C2–C1 113.8(4), Ti–C14–C13 110.5(4), C14–C13–C1 121.5(5), C2–C1–C13 114.3(5), C2–Ti–C14 80.0(2)



The bond distances and angles of the central five-membered metallacycle in **7** are typical of the known examples of such titanacyclopentadiene complexes, e.g. in the tetraphenylated analogon $Cp_2\overline{Ti-C(Ph)=C(Ph)-C(Ph)=C}(Ph)$[13].

An analogous zirconacyclopentadiene complex was assumed to be the intermediate in the synthesis of the seven-membered cyclocumulene complex of type **4**[2a]. For titanium the reaction stops at the metallacyclopentadiene stage. Because titanium is smaller than zirconium no further complexation or insertion of the external triple bond in the α position of **7** occurs yielding a seven-membered cyclocumulene.

Table 1 summarizes the reaction products observed in reactions of disubstituted butadiynes with titanocene and zirconocene.

Table 1. Products of reactions of butadiynes $R{-}C{\equiv}C{-}C{\equiv}C{-}R$ with metallocenes "Cp_2M"

M	R	Stoichiometry 2 : 1	1 : 1	1 : 2
Ti	$SiMe_3$	σ,π-alkynyl-bridged compl. **1a**	**1a** and **7**	metallacyclo-pentadiene **7**
Ti	^tBu	*trans,trans*-diene compl. **2a**	five-memb. cyclocumulene **5**	unreacted butadiyne and **5**
Zr	$SiMe_3$	σ,π-alkynyl-bridged compl. **1b**	**1b** and **4a**	seven-memb. cyclocumulene **4a**
Zr	^tBu	unreacted zirconocene and **3**	five-memb. cyclocumulene **3**	unreacted butadiyne and **3**

Conclusions

The results obtained show clearly that the product distribution in reactions of metallocene complexes with 1,4-disubstituted butadiynes $RC{\equiv}C{-}C{\equiv}CR$ ($R = SiMe_3$, *t*Bu) depends strongly on the substituents of diynes, the metals and the used stoichiometry.

As in the case of zirconium the electronical stabilization by the substituent is essential for the coordination as a cumulene which is favored for R = *t*Bu over cleavage or coupling reactions (as found for $R = SiMe_3$, showing a withdrawal of electron density).

Compared to the zirconacyclic cumulene **3** the titanium analog **5** is less stable (lower yield in preparation). Both complexes react with titanocene, but only **5** with zirconocene. The reaction of complex $Cp_2\overline{Ti{-}C(tBu){=}C{=}C{=}C}(tBu)$ (**5**) with "Cp_2Zr" as well as of complex $Cp_2\overline{Zr{-}C(tBu){=}C{=}C{=}C}(tBu)$ (**3**) with "Cp_2Ti" gives an identical product, the heterodimetallic σ,π-alkynyl-bridged titanocene-zirconocene complex $Cp_2Zr(\mu\text{-}\eta^1{:}\eta^2\text{-}C{\equiv}CtBu)Cp_2Ti(\mu\text{-}\eta^1{:}\eta^2\text{-}C{\equiv}CtBu)$ (**6**). The reaction of **5** with "Cp_2Ti" yields complex **2a**. These reactions suggest, that the cleavage reactions of butadiynes[4,11] proceeds via metallacyclocumulenes, which react with an excess of metallocene to yield, depending on the diyne substituents, complexes of type **1**[4,11] or **2**[5].

Experimental

All operations were carried out under argon with standard Schlenk techniques. Solvents were freshly distilled from sodium tetraethylaluminate under argon prior to use. – NMR: Bruker ARX 400. – IR: Nicolet Magna 550 (Njuol mulls using KBr plates). – MS: AMD 402. – Melting points: sealed capillaries, Büchi 535 apparatus.

Preparation of **5**: To a solution of 1.385 g (3.97 mmol) of $Cp_2Ti(Me_3SiC_2SiMe_3)$ in 3 ml of *n*-hexane was added 0.645 g (3.97 mmol) of 1,4-di-*tert*-butyl-1,3-butadiyne in *n*-hexane (7 ml). After standing at room temp. for 2 d the green solution was filtered from small amounts of **2a** which is insoluble in *n*-hexane and allowed to crystallize at −40 °C. Green crystals of **5** formed and were washed with cold *n*-hexane and dried in vacuo. Yield: 0.482 g (36%), m.p. 172–173 °C (dec.). – MS, *m/z*: 340 [M^+]. – ^1H NMR ([D_8]THF): δ = 1.60 (s, 18H, Me), 5.05 (s, 10H, Cp). – $^{13}C\{^1H\}$ NMR ([D_8]THF): δ = 35.5 (CH_3), 38.1 (CCH_3), 94.7 (*C*C*t*Bu), 103.8 (Cp), 181.9 (C*C**t*Bu). – $C_{22}H_{28}Ti$ (342.4): calcd. C 77.64, H 8.29; found C 77.57, H 8.41.

Crystal Data for **5**: *a* = 9.206(1), *b* = 14.179(1), *c* = 14.823(1) Å, *V* = 1934.9(2) Å^3, space group $P2_12_12_1$, *Z* = 4, mol. mass = 340.34 for $C_{22}H_{28}Ti$, *d*(calcd.) = 1.168 g/cm^3, λ = 0.71069 Å, measured reflections 1947, independent reflections 1947, observed reflections 996, refined parameters 193, $R_1 = 0.069$ [$I \geqslant 2\sigma(I)$] and $wR_2 = 0.179$ (all data)[14].

Reaction of **5** *with* $Cp_2Ti(Me_3SiC_2SiMe_3)$: A solution of 0.130 g (0.38 mmol) of complex **5** in 10 ml of *n*-hexane was added to 0.144 g (0.41 mmol) of $Cp_2Ti(Me_3SiC_2SiMe_3)$. The solution obtained was filtered. On standing at room temp. for 7 d dark-green crystals deposited. After decantion of the solution the crystals were washed with *n*-hexane and dried in vacuo. Yield: 0.174 g (88%) of **2a**, m.p. 272–273 °C (dec.), 277 °C[3]. Spectroscopical data of the product are identical with those given in ref.[3].

Preparation of **6**. – *Reaction of* **5** *with* $Cp_2Zr(THF)(Me_3SiC_2SiMe_3)$: To a solution of 0.157 g (0.46 mmol) of complex **5** in 10 ml of *n*-hexane was added 0.215 g (0.46 mmol) of $Cp_2Zr(THF)(Me_3SiC_2SiMe_3)$ in 5 ml of THF. After 2 d the green solution was evaporated to dryness in vacuo. NMR investigation revealed the residue to be a mixture of **6** and the starting materials (25% conversion). – *Reaction of* **3** *with* $Cp_2Ti(Me_3SiC_2SiMe_3)$: To a solution of 0.674 g (1.93 mmol) of $Cp_2Ti(Me_3SiC_2SiMe_3)$ in 5 ml of *n*-hexane was added 0.713 g (1.86 mmol) of **3** in 15 ml of *n*-hexane. The solution was filtered and allowed to stand under argon at room temp. After 1 d a yellow-brown crystalline solid started to form. After 8 d the mother liquor was decanted, and the product was washed with cold *n*-hexane and dried in vacuo. Yield: 0.715 g (68.5%) of **6**, m.p. 307–308 °C (dec.). – MS, *m/z*: 560 [M^+], 382 [$Cp_2Zr(CCtBu)_2$], 301 [$Cp_2ZrCCtBu$], 220 [Cp_2Zr], 178 [Cp_2Ti]. – IR (nujol mull): 1780 and 1865 cm^{-1} [ν(C≡C)]. – ^1H NMR (C_6D_6): δ = 1.39 (s, 18H, Me), 5.03 (s, 10H, Cp), 5.32 (s, 10H, Cp). – $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 33.4 (CH_3), 37.1 (CCH_3), 101.8, 103.4 (Cp), 159.1 (C*C**t*Bu), 215.2 (*C*C*t*Bu). – $C_{32}H_{38}TiZr$ (563.8): calcd. C 68.42, H 6.82; found C 68.45, H 6.93.

Crystal Data for **6**: *a* = 8.542(1), *b* = 10.687(1), *c* = 15.657(1) Å, *V* = 1367.1(2) Å^3, space group *P*-1, *Z* = 2, mol. mass = 561.74 for $C_{32}H_{38}TiZr$, *d*(calcd.) = 1.365 g/cm^3, λ = 0.71069 Å, measured reflections 5165, independent reflections 4811, observed reflections 3995, refined parameters 299, *R* = 0.045 [$I \geqslant 2\sigma(I)$] and $wR_2 = 0.131$ (all data)[14].

Preparation of **7**: To a solution of 0.727 g (2.09 mmol) of $Cp_2Ti(Me_3SiC_2SiMe_3)$ in 3 ml of *n*-hexane was added 0.811 g (4.17 mmol) of 1,4-bis(trimethylsilyl)-1,3-butadiyne in *n*-hexane (7 ml). After filtration and standing of the filtrate at room temp. for 5 h, red-brown crystals (0.691 g) were obtained. The mother liquor was decanted and placed in a refrigerator. After 1 d additional 0.261 g of **7** crystallized. The crystals were washed with cold *n*-hexane and dried in vacuo. Yield: 0.952 g (80.5%) of **7**, m.p. 162–163 °C (dec.). – MS, *m/z*: 566 [M^+]. – IR (Nujol mull): 2052, 2081 and 2124 cm^{-1} [v(C≡C)]. – ^1H-NMR ([D_8]THF): $\delta = 0.04$ (s, 9H, $SiMe_3$), 0.11 (s, 9H, $SiMe_3$), 0.13 (s, 9H, $SiMe_3$), 0.24 (s, 9H, $SiMe_3$), 6.30 (s, 10H, Cp). – $^{13}C\{^1H\}$ NMR ([D_8]THF): $\delta = -0.2$, 0.2, 1.2, 2.2 ($SiMe_3$), 91.5, 122.1, 157.0, 245.6 ($C\mathit{C}SiMe_3$), 106.6, 109.9, 130.4, 198.4 ($\mathit{C}CSiMe_3$), 115.0 (Cp). – ^{29}Si NMR ([D_8]THF): $\delta = -20.7$, -20.1, -15.4, -8.6 ($SiMe_3$). – $C_{30}H_{46}Si_4Ti$ (568.9): calcd. C 63.56, H 8.18; found C 63.54, H 8.18.

Crystal data for **7**: $a = 11.155(1)$, $b = 19.905(29$, $c = 30.838(3)$ Å, $V = 6847.3(11)$ Å^3, space group *Pbca*, $Z = 8$, mol. mass = 566.93 for $C_{30}H_{46}Si_4Ti$, d(calcd) = 1.10 g/cm^3, $\lambda = 0.71069$ Å, measured reflections 6009, independent reflections 6009, observed reflections 2299, refined parameters 316, $R = 0.045$ [$I \geqslant 2\sigma(I)$] and $wR_2 = 0.191$ (all data)[14].

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[14] Further details of the crystal structure investigations are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository number CSD-59043.

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