Different C–C Coupling Reactions of Permethyltitanocene and Permethylzirconocene with Disubstituted 1,3-Butadiynes

Paul-Michael Pellny, Frank G. Kirchbauer, Vladimir V. Burlakov, Wolfgang Baumann, Anke Spannenberg, and Uwe Rosenthal*[a]

Dedicated to Professor Dirk Walther on the occasion of his 60th birthday

Abstract: Herein we describe different C–C coupling reactions of permethyltitanocene and -zirconocene with disubstituted 1,3-butadiynes. The outcomes of these reactions vary depending on the metals and the diyne substituents. The reduction of $[\mathrm{Cp}^*_2\mathrm{MCl}_2]$ ($\mathrm{Cp}^* = \mathrm{C_5Me_5}$; M = Ti, Zr) with Mg in the presence of disubstituted butadiynes $\mathrm{RC{\equiv}C{-}C{\equiv}CR'}$ is suitable for the synthesis of different C–C coupling products of the diyne and the permethylmetallocenes, and provides a new method for the generation of functionalized pentamethyl-cyclopentadienyl derivatives. For M = Zr and R = R′ = *t*Bu, the reaction gives, by a twofold activation of one pentamethylcyclopentadienyl ligand, the complex $[\mathrm{Cp^*Zr\{{-}C({=}C{=}CH\mathit{t}Bu){-}CH\mathit{t}Bu{-}CH_2{-}\eta^5\text{-}C_5Me_3{-}CH_2{-}\}}]$ (**3**), containing a fulvene ligand that is coupled to the modified substrate (allenic subunit). When using the analogous permethyltitanocene fragment "$\mathrm{Cp}^*_2\mathrm{Ti}$", the reaction depends strongly on the substituents R and R′. The coupling product of the butadiyne with two methyl groups of one of the pentamethylcyclopentadienyl ring systems, $[\mathrm{Cp^*Ti\{\eta^5\text{-}C_5Me_3(CH_2{-}CHR{-}\eta^2\text{-}C_2\text{-}CHR'{-}CH_2)\}}]$, is obtained with R = R′ = *t*Bu (**4**) and R = *t*Bu, R′ = $\mathrm{SiMe_3}$ (**5**). In these complexes one pentamethylcyclopentadienyl ligand is annellated to an eight-membered ring with a C–C triple bond, which is coordinated to the titanium center. A different activation of both pentamethylcyclopentadienyl ligands is observed for R = R′ = Me, resulting in the complex $[\{\eta^5\text{-}\mathrm{C_5Me_4(CH_2)}{-}\}\mathrm{Ti\{{-}C({=}CHMe){-}C({=}CHMe){-}CH_2{-}\eta^5\text{-}C_5Me_4\}}]$ (**6**), which displays a fulvene as well as a butadienyl-substituted pentamethylcyclopentadienyl ligand. The influence exerted by the size of the metal is illustrated in the reaction of $[\mathrm{Cp}^*_2\mathrm{ZrCl_2}]$ with $\mathrm{MeC{\equiv}C{-}C{\equiv}CMe}$. Here the five-membered metallacyclocumulene complex $[\mathrm{Cp}^*_2\mathrm{Zr}(\eta^4\text{-}1,2,3,4\text{-}\mathrm{MeC_4Me})]$ (**7**) is obtained. The reaction paths found for R = R′ = Me are identical to those formerly described for R = R′ = Ph.

Keywords: C–C coupling · C–H activation · diynes · titanocene · zirconocene

Introduction

Conjugated as well as nonconjugated diynes have been demonstrated to react with titanocene and zirconocene.[1] We investigated such reactions with 1,3-butadiynes by using the alkyne complexes $[\mathrm{Cp_2M(L)(\eta^2\text{-}Me_3SiC_2SiMe_3)}]$[11] (M = Ti, L = -; M = Zr, L = THF, pyridine) as metallocene sources. Different complexations, C–C single bond cleavage, and coupling reactions were unexpected results of these studies. The products obtained were found to be strongly dependent on the substituents R, the metals, and the stoichiometry employed in the conversions.[11]

The most interesting products of these reactions of the metallocenes "$\mathrm{Cp_2M}$" ($\mathrm{Cp = C_5H_5}$; M = Ti, Zr)[11] with $\mathrm{\mathit{t}BuC{\equiv}C{-}C{\equiv}C\mathit{t}Bu}$ were stable five-membered metallacyclocumulenes $[\mathrm{Cp_2M}(\eta^4\text{-}1,2,3,4\text{-}\mathit{t}\mathrm{BuC_4}\mathit{t}\mathrm{Bu})]$ (M = Zr, Ti).[2,3] It was established by X-ray diffraction studies that these contain a planar ring system with three C–C double bonds, of which the central bond is internally coordinated to the metal center. Some reactions of this novel type of compound were subsequently investigated.

Very recently we described different interactions of permethyltitanocene and -zirconocene complexes with 1,3-butadiynes $\mathrm{RC{\equiv}C{-}C{\equiv}CR}$. For zirconium, five-membered zirconacyclocumulenes (η^4 complexes, zirconacyclopenta-2,3,4-trienes), such as $[\mathrm{Cp}^*_2\mathrm{M}(\eta^4\text{-}1,2,3,4\text{-}\mathrm{RC_4R})]$(M = Zr, R = Ph, $\mathrm{SiMe_3}$), predominate as products.[4] For titanium, no metallacyclocumulenes were obtained, and formation of titanacyclopropenes (η^2 complexes), as well as different C–C coupling reactions of the permethyltitanocene systems were found to be typical.[4]

The replacement of Cp by the Cp* ligand in permethyltitanocene and -zirconocene complexes changes the steric and

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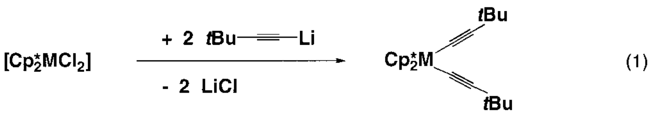
electronic influence of the ligands.[5] The increased steric bulk, solubility, and electron-donor characteristics lead to different reactivities and spectral properties in the Cp* complexes, compared with their Cp counterparts. Because of the enhanced oxidative, reductive, and thermal stability, permethylmetallocene compounds are often easier to isolate and to study.[6] Nevertheless, because of the short lengths of the C–H bonds and the existence of basic centers such as carbanionic groups, H-transfer reactions (formal "σ-bond metatheses") are often described. Pentamethylcyclopentadienyl cannot be regarded as an innocent spectator ligand, a fact that is demonstrated by a large number of unexpected (side) reactions involving the ligand system. In those reactions not only one but sometimes even two of the methyl groups of the pentamethylcyclopentadienyl moieties are involved. The pioneering results in this area came from Brintzinger et al.[7] and Bercaw et al.[8] Subsequent excellent studies by Teuben et al.[9] showed that a tetramethylfulvene Ti^{III} product, [Cp*Ti{$C_5Me_4(CH_2)$}],[10] is the crucial intermediate for the subsequent C–C coupling reactions of permethyltitanocenes with ketones[11] and isonitriles,[12, 13] for example. A second deprotonation, leading to [Cp*Ti{$C_5Me_3(CH_2)_2$}], was investigated by Beckhaus et al.[14] and Mach et al.[15] In this context no alkyne or diyne has been examined so far, with the exception of an intermediate [$Cp^*_2Zr{=}O$], generated by heating of [$Cp^*_2ZrPh(OH)$], which reacted with PhC≡C–C≡CPh to form, after a C–H activation of Cp* and a C–C coupling with the butadiyne, a Cp*-substituted, coordinated enolate.[16]

Abstract in German: *Diese Arbeit beschreibt unterschiedliche C-C-Kupplungs-Reaktionen von Permethyltitanocen und -zirconocen mit disubstituierten 1,3-Butadiinen, die abhängig von den Metallen und Diin-Substituenten verlaufen. Die Reduktion von [$Cp^*_2MCl_2$], M = Ti, Zr, mit Magnesium in Gegenwart der disubstituierten Butadiyne RC≡C–C≡CR′ ist geeignet, unterschiedliche C-C-Kupplungsprodukte von Permethylmetallocenen mit Diinen herzustellen, was eine neue Methode zur Synthese funktionalisierter Pentamethyl-cyclopentadienyl-Derivate darstellt. Für M = Zr und R = R′ = tBu gibt die Reaktion durch eine zweifache Aktivierung eines Pentamethylcyclopentadienyl-Liganden den Komplex [Cp*Zr{-C(=C=CHtBu)-CHtBu-CH_2-η^5-C_5Me_3-CH_2-}]* (**3**), *der einen Fulven-Liganden enthält, welcher mit dem modifizierten Substrat (Allen-Untereinheit) gekoppelt ist. Bei Verwendung des analogen Permethyltitanocen-Fragments „Cp^*_2Ti" hängt die Reaktion stark von den Substituenten R/R′ ab. Das Kupplungs-Produkt eines Butadiins mit zwei Methylgruppen eines Pentamethylcyclopentadienyl-Ringes Cp*Ti[η^5-C_5Me_3{CH_2-CHR-η^2-C_2-CHR′-CH_2}] erhält man für R = R′ = tBu* (**4**) *und R = tBu, R′ = $SiMe_3$* (**5**). *In diesem Komplex ist ein Pentamethylcyclopentadienyl-Ligand mit einem achtgliedrigen Ring anelliert, der eine C-C-Dreifachbindung enthält, welche am Titan koordiniert. Unterschiedliche Aktivierungen beider Pentamethylcyclopentadienyl-Liganden beobachtet man für R = R′ = Me, wobei der Komplex [{η^5-$C_5Me_4(CH_2)$-}Ti{-C(=CHMe)-C(=CHMe)-CH_2-η^5-C_5Me_4}]* (**6**) *resultiert, welcher einen Fulven- und einen Butadienyl-substituierten Pentamethylcyclopentadienyl-Liganden bindet. Der Einfluß der Größe des Zentralatoms wird durch die vergleichbare Reaktion des [$Cp^*_2ZrCl_2$] mit MeC≡C–C≡CMe illustriert. Hier bildet sich das fünfgliedrige Metallacyclocumulen [$Cp^*_2Zr(\eta^4$-1,2,3,4-$MeC_4Me)$]* (**7**). *Die gefundene Reaktion für Titan und R = R′ = Me zu Komplex* **6** *ist weitgehend identisch zu der vordem beschriebenen für R = R′ = Ph.*

Herein we report the interactions of permethyltitanocene and -zirconocene complexes with 1,3-butadiynes, which result in different C–H activations of one or of both of the pentamethylcyclopentadienyl ligands, with subsequent C–C coupling reactions.

Results and Discussion

Complex syntheses: The permethylmetallocene bis-acetylides [$Cp^*_2M(C{\equiv}CtBu)_2$] (M = Ti (**1**), Zr (**2**)) were prepared by a salt elimination reaction starting from the [$Cp^*_2MCl_2$] complexes and two equivalents of tBuC≡CLi [Eq. (1)].



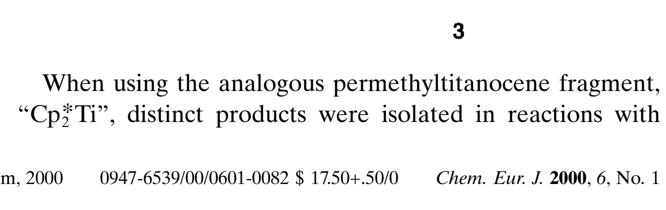
M = Ti, Zr

1: M = Ti
2: M = Zr

The rearrangement of these complexes in sunlight did not afford any defined products as found, for example, for M = Zr, R = Ph, $SiMe_3$,[4] when five-membered zirconacyclocumulenes, [$Cp^*_2Zr(\eta^4$-1,2,3,4-$RC_4R)$], were generated in high yields. Apparently the reaction does not work with R = tBu, an observation that illustrates again what has repeatedly been found: the tBu and the $SiMe_3$ groups show, despite their seeming analogy, distinctively different reaction behavior.[11]

The reduction of [$Cp^*_2MCl_2$] (M = Ti, Zr) with Mg in the presence of disubstituted butadiynes RC≡C–C≡CR′ led to metallacyclocumulenes only for M = Zr, R = Ph, $SiMe_3$, and Me. In this work different C–C coupling products of the diynes and the permethylmetallocenes are described. These were observed for M = Zr, R = R′ = tBu, M = Ti, R = R′ = tBu, Me, Ph, and R = tBu, R′ = $SiMe_3$.

For M = Zr and R = R′ = tBu, the reaction gives the complex [(η^5-C_5Me_5)Zr(–C(=C=CHtBu)–CHtBu–CH_2–η^5-C_5Me_3–CH_2–)] (**3**), by a twofold but diverse activation of one of the pentamethylcyclopentadienyl ligands [Eq. (2)].



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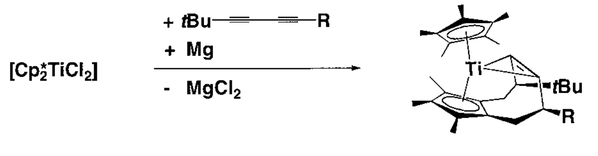
When using the analogous permethyltitanocene fragment, "Cp^*_2Ti", distinct products were isolated in reactions with various disubstituted butadiynes. A marked dependence on the substituents R and R′ was observed.

For R = R′ = *t*Bu, a coupling of the butadiyne with two methyl groups of one of the pentamethylcyclopentadienyl ring systems generates the complex $[Cp^*_2Ti\{\eta^5\text{-}C_5Me_3(CH_2{-}CHR{-}\eta^2\text{-}C_2{-}CHR'{-}CH_2)\}]$ (**4**) [Eq. (3)].



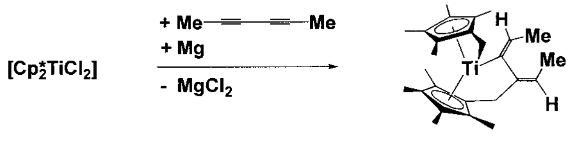
(3)

R = *t*Bu, SiMe$_3$

4: R = *t*Bu
5: R = SiMe$_3$

An analogous complex is obtained for R = *t*Bu, R′ = SiMe$_3$ (**5**). In both cases the resulting functionalized pentamethylcyclopentadienyl ligand contains a triple bond that is coordinated to the titanium center, forming a metallacyclopropene unit.

A different activation, involving both of the pentamethylcyclopentadienyl ligands, is observed for R = R′ = Me, resulting in the complex $[\{\eta^5\text{-}C_5Me_4(CH_2){-}\}Ti\{{-}C({=}CHMe){-}C({=}CHMe){-}CH_2{-}\eta^5\text{-}C_5Me_4\}]$ (**6**) [Eq. (4)].



(4)

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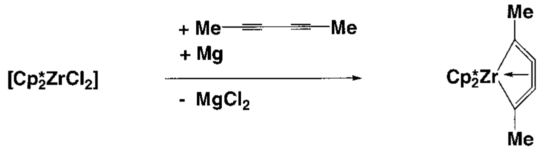
When using the larger metal, zirconium, in the corresponding reduction reaction, the five-membered zirconacyclocumulene $[Cp^*_2Zr(\eta^4\text{-}1,2,3,4\text{-}MeC_4Me)]$ (**7**) is afforded [Eq. (5)].



(5)

7

The observed reaction paths for R = R′ = Me are analogous to the one recently described for R = R′ = Ph.[4]

Notably, the $[Cp^*_2TiCl_2]/Mg/Me_3SiC{\equiv}C{-}C{\equiv}CSiMe_3$ system has afforded three different products, depending on the stoichiometry and the reaction time. Mach and co-workers reported in a recent paper that a tweezer-like compound, $[Cp^*_2Ti(C{\equiv}CSiMe_3)_2][MgCl(thf)]$, is formed if an excess of magnesium is used.[17] We have found a η^2 complex[4] as well as the formation of a ligand with a C$_6$ backbone.[18] These results illustrate that the reduction of metallocene dichlorides with magnesium can in fact be very complicated.[17, 19]

Spectroscopic investigations: The NMR spectra of the bis-acetylides, **1** and **2**, and of the zirconacyclocumulene **7** show similar patterns. As a result of C_{2v} symmetry in both structural types, only one signal at low field for the metalated (α) carbon atom, and a second at higher field for the β carbon atom of the former butadiyne are observed, aside from the Cp* resonance. The distinction between the two structural types can be seen in their chemical shifts. The low field shift for C-α is more pronounced for the metallacyclocumulenes (typically δ = 170–190)[2, 3a, 3e, 4] which indicates a stronger polarization of the (C-α)–(C-β) bond. A $\Delta\delta$((C-α)–(C-β)) of 60.2 ppm for complex **7** shows that it is a zirconacyclocumulene, differentiated from the bis-acetylides **1** and **2**, where $\Delta\delta$ values of 21.2 and 13.8 ppm, respectively, are found. The bond polarization in **7** is also considerably stronger than in its cyclopentadienyl analog (39.2 ppm),[20] which fits the general trend observed upon replacement of Cp by Cp*. Further discrimination between the two structural types is possible by the cyclopentadienyl resonances. Characteristic shifts for permethylmetallocene bis-acetylides[4] are $\delta(^1H)$ values of 2.0–2.1 ppm and $\delta(^{13}C_{quart})$ values of 120—121 ppm, consistent with the findings for **1** and **2**. In contrast, the corresponding signals of the cumulene **7** are shifted to higher fields (δ = 1.63 and 111.7).

The NMR signals of the Cp* methyl groups are very useful for structure elucidation of complexes **3**–**6**. These complexes result from proton transfer reactions, and the molecular symmetries and sites of the C–H activation are revealed by those signals. In all cases, complete analyses could be performed by NOE and shift correlation methods.

The twofold methyl group activation within the same permethylcyclopentadienyl group of complex **3** is immediately evident from its ^{1}H NMR spectrum, for it exhibits six singlets, three for the inequivalent methyl groups, in addition to one of fivefold intensity (unactivated C$_5$Me$_5$) and two representing the two *tert*-butyl groups (Table 1). The different

Table 1. NMR data of complex **3** in [D$_6$]benzene at ambient temperature (labeling according to the numbering scheme used in the corresponding crystal structure (Figure 4).

	major isomer (Figure 1)		*minor* isomer	
Position	$\delta(^1H)$	$\delta(^{13}C)$	$\delta(^1H)$	$\delta(^{13}C)$
1		124.8		124.5
2		117.3		115.7
3		118.1		118.7
4		125.7		126.9
5		127.5		126.6
6	2.39 (dd, A) 2.46 (dd, B)	27.0	2.28[a]	25.7
7	1.35[b]	44.6	1.36[b]	45.8
8		35.3		35.7
9/22/23	1.02 (s)	28.1 (br)	1.06 (s)	28.6
10–14		118.4		118.1
15 etc.	1.92 (s)	11.4	1.96 (s)	11.9
16	1.81 (d, A) 2.13 (d, B)	66.6	1.85 (d, A) 2.19 (d, B)	65.5
17		188.0		181.7
18		131.8		136.8
19[c]	4.22 (d)	90.8	4.09 (d)	92.0
20		32.5		33.1
21/30/31	1.18 (s)	31.7	1.31 (s)	31.6
24	2.07 (s)	13.3	1.89 (s)	12.0
25	1.35 (s)	10.4	1.35 (s)	10.1
26	1.56 (s)	10.4	1.62 (s)	10.5

[a] AB part of an ABX spin system. [b] Obscured by other signals. [c] $^5J(H,H)$ = 4.2 Hz (major) and 1.9 Hz (minor).

character of the methylene groups 6 and 16 is clearly visible (for atom labels see Figure 1). C16 has an increased s character ($^1J_{C,H} = 145$ Hz, $^{22}J_{H,H} = 6.2$ Hz), and in connection with the low field shifted resonance (δ 66.6), it follows that the functionalized Cp* ligand has changed to a π-η^5:π-η^1-fulvene system (Fv ligand). C6 has the characteristics of an sp^3 carbon attached to an aromatic system (δ 27.0, $^{22}J_{H,H} = 13.0$ Hz), and provides the link to the former butadiyne system, as can be seen from the spin-spin couplings [^3J(6-H$_A$,7-H) = 7.3 Hz, ^3J(6-H$_B$, 7-H) = 12.0 Hz]. The 1,3-butadiyne system is converted to a 1,2-butadiene system through the dual activation and shows some peculiarities, especially the shift of the central (sp) carbon atom 18 ($\delta = 131.8$), which is not as low field as expected for allenes. Instead, a low field shift is found for C17 ($\delta = 188.0$), characteristic for metalated sp^2 carbon atoms. These data show that, despite the unsuspicious infrared absorption for the cumulenic stretching vibration (1891 cm^{-1}), this description may be taken as intuitive but simplifies the true bonding situation (see discussion of the molecular structure below). The CH groups (C7 and C19) exhibit unspectacular properties ($^1J_{C,H} = 123$ and 155 Hz, respectively).

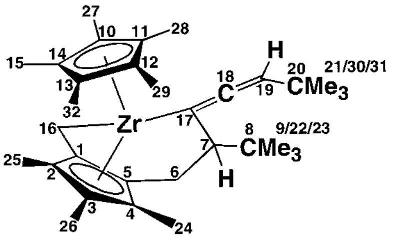


Figure 1. Molecular structure of **3**, labeled according to the numbering scheme of the corresponding crystal structure. The labels are used for the assignment of the NMR signals.

Solutions of complex **3** exhibit NMR spectra with two signal sets, representing two isomers, which must be very similar, in a 4:1 ratio (Table 1). The only difference is found for the neighborhood of the substituents at C19. From the observed NOE cross peaks, as shown in Figure 2, it becomes clear that the major isomer is that characterized by X-ray crystallography (see Figure 4).

In the minor isomer, the *tert*-butyl group and the hydrogen atom at C19 have changed places. Finally, a broadening of the resonance line for the *tert*-butyl group at C7 is noteworthy; its free rotation seems to be hindered by the close proximity to the second *tert*-butyl group, for this phenomenon occurs only with the major isomer.

The permethyltitanocene alkyne complexes **4** and **5** are isostructural and do not differ in their NMR spectroscopic properties, the detailed discussion will therefore be restricted to **5**. Four Cp* methyl singlets of ratio 5:1:1:1 appear in the proton spectrum (Table 2). Activation of two methyl groups in the same permethylcyclopentadienyl system, as observed in the zirconium complex **3**, must be concluded. But this does not result in the formation of a substituted fulvene ligand. Both methylene groups show properties ($\delta(^{13}C) = 26.4$ and 25.8, $^1J_{C,H} = 128$ Hz) characteristic of sp^3 hybridization. The linkage between the butadiyne and the permethylcyclopentadienyl produces a chiral bicyclic ligand system, an eight-membered cycloalkyne fused to the aromatic system (C15 and C18 are stereogenic centers), so that the complex becomes C_1-symmetric (for atom labels in complexes **4** and **5** see Figure 3). A diastereomer with inverted configuration at one of these

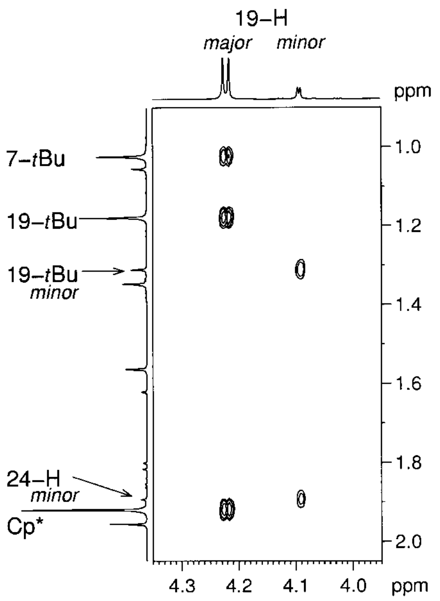


Figure 2. Part of the ^{1}H NOESY NMR spectrum of complex **3** in [D$_6$]benzene (mixing time 1.5 s): Two isomers with a different environment around C19.

Table 2. NMR data of the complexes **4** (E = C) and **5** (E = Si) in [D$_6$]benzene at ambient temperature.

	E = C (**4**)		E = Si (**5**)	
Position	$\delta(^1H)$	$\delta(^{13}C)$	$\delta(^1H)$	$\delta(^{13}C)$
1–5		120.5		120.5
6 etc.	1.74 (s)	12.3	1.74 (s)	12.3
7		109.7		110.1
8		120.2		119.4
9		143.8		140.2
10		141.2		141.6
11		118.5		118.7
12	0.99 (s)	9.6	1.01 (s)	9.5
13		205.5		210.4
14		214.7		215.6
15	1.66 (dd)	79.9	1.78 (dd)	80.4
16		34.7		34.5
17/30/31	0.95 (s)	29.6	0.93 (s)	29.6
18	4.31 (dd)	85.1	3.96 (t)	61.5
19	2.37 (dd, A) $^2J = 13.7$ Hz $^3J = 5.9$ Hz 2.93 (dd, B) $^3J = 7.9$ Hz	27.7[a]	2.48 (dd, A) $^2J = 13.7$ Hz $^3J = 7.8$ Hz 3.09 (dd, B) $^3J = 8.0$ Hz	26.4
20/21/22	0.46 (s)	28.1	−0.22 (s)	−2.3
24	1.60 (s)	11.0	1.62 (s)	11.1
26	2.66 (dd, A) $^2J = 11.8$ Hz $^3J = 7.5$ Hz 2.34 (dd, B) $^3J = 10.1$ Hz	26.4[a]	2.64 (dd, A) $^2J = 11.9$ Hz $^3J = 7.4$ Hz 2.44 (dd, B) $^3J = 10.4$ Hz	25.8
27	1.11 (s)	9.8	1.10 (s)	9.6
E		33.3		

[a] Assignment interchangeable.

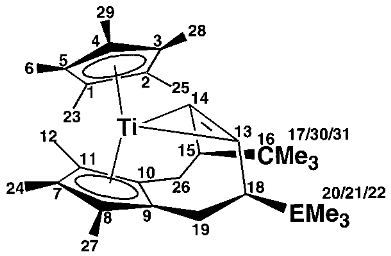


Figure 3. Molecular structure of **4** (E = C) and **5** (E = Si), labeled according to the numbering scheme of the crystal structure of **5**. The labels are used for the assignment of the NMR signals.

atoms was not detected (such an isomer of **4**, with two *tert*-butyl substituents, would possess a mirror plane and therefore be a *meso* form). For the diastereomer obtained, the silyl group at C18 occupies an *endo* position and the *tert*-butyl group at C15 is *exo* oriented. It is found for both **4** and **5** that the signals of the protons and of the butyl and silyl groups appear high field shifted if they occupy the *endo* position, probably due to the magnetic anisotropy of the π-electron systems (e.g. 15-H, *endo*, $\delta = 1.78$; 18-H, *exo*, $\delta = 3.96$). The values for the titanacyclopropene are as expected, and in spite of the nonideal coordination of the triple bond to the titanium center (see structural discussion below) low-field shifts of almost the same extent as for other titanocene-alkyne complexes are found: $\delta(C13) = 210.4$, $\delta(C14) = 215.6$ (compare with $[Cp^*_2Ti(\eta^2\text{-}Me_3SiC_2\text{–}C{\equiv}CSiMe_3)]$ $\delta = 205.3$ and 227.5).[4] Nevertheless, the strained bonding situation might be the reason for the unconventionally large shifts found for the methine carbon atoms C15 and C18 ($\delta = 80.4$ and 61.5, ${}^1J_{C,H} = 137$ and 117 Hz, respectively). The latter shows a ${}^1J_{C,Si}$ of 59 Hz (indicating a slight tendency toward sp^2 hybridization), but the adjacent silicon atom exhibits $\delta(^{29}Si) = -0.8$, as expected for a tetraalkylsilane.

Complex **6** results from a twofold C–H activation, as do compounds **3**–**5**, but its Cp* methyl proton spectrum looks completely different. Six singlets, two of them with double intensity, are found, leading to the conclusion that the two protons transferred onto the 2,4-hexadiyne came from different Cp* ligands. One of these is converted to a tetramethylfulvene ligand, as illustrated by the data of that methylene group: $\delta(^{13}C) = 78.6$, ${}^1J_{C,H} = 150$ Hz, ${}^2J_{H,H} = 4.4$ Hz. This type of reaction and an analogous product were already found with diphenylbutadiyne,[4] and as **6** has the same structure and spectroscopic behavior as the previously described analogue, a further discussion is not presented here.

Structural investigations: The coupling products **3**–**6**, as well as the metallacyclocumulene **7** were investigated by X-ray crystal structure analysis. The crystallographic data of these complexes are collected in Table 3. Additionally, ORTEP plots of **3**, **5**, **6**, and **7** are shown in Figures 4, 5, 6, and 7, respectively.

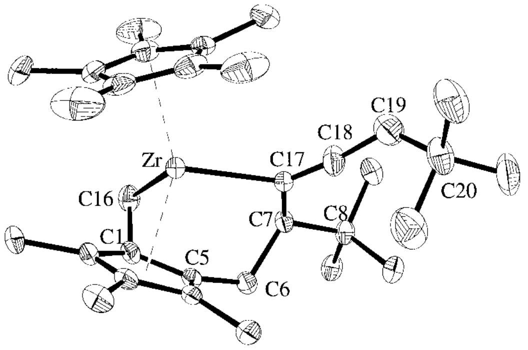


Figure 4. Molecular structure of **3** (ORTEP plot, 30% probability). Selected bond lengths [Å] and angles [°]: Zr–C16 2.389(5), Zr–C17 2.332(5), C17–C18 1.268(7), C18–C19 1.366(8), C19–C20 1.499(10), C7–C17 1.536(8), C7–C8 1.551(8), C7–C6 1.552(7), C6–C5 1.510(8); C16-Zr-C17 100.2(2), Zr-C17-C18 124.7(4), C17-C18-C19 172.3(7), C18-C19-C20 128.2(6), C7-C17-C18 126.1(5), C6-C7-C17 108.6(4), C5-C6-C7 113.9(4).

Table 3. Crystallographic data of complexes **3**, **4**, **5**, **6**, and **7**.

	3	**4**	**5**	**6**	**7**
cryst. color, habit	red, prism	yellow, prism	brown, prism	green, prism	yellow, prism
cryst. system	triclinic	triclinic	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$P2_1/n$
lattice constants					
a [Å]	10.190(2)	9.226(2)	9.249(2)	8.902(2)	16.751(3)
b [Å]	10.563(2)	11.883(2)	12.201(2)	19.710(4)	16.722(3)
c [Å]	14.601(3)	13.588(3)	14.057(3)	12.880(3)	18.211(4)
α [°]	99.04(3)	87.99(3)	88.91(3)		
β [°]	90.62(3)	82.31(3)	82.28(3)	92.69(3)	116.72(3)
γ [°]	110.55(3)	72.36(3)	71.49(3)		
Z	2	2	2	4	8
cell volume	1449.6(5)	1412.9(5)	1490.1(5)	2257.4(9)	4556.4(15)
ρ [g cm^{-3}]	1.200	1.130	1.107	1.166	1.282
temp. [K]	200(2)	293(2)	293(2)	293(2)	200(2)
$\mu(Mo_{K\alpha})$ [mm^{-1}]	0.396	0.320	0.343	0.387	0.490
θrange [°]	1.42–21.07	1.80–24.25	2.34–24.32	1.89–24.22	1.75–24.22
no. of rflns. (measd)	2942	4205	4446	6588	12772
no. of rflns. (indep.)	2942	4205	4446	3559	6769
no. of rflns. (obsd.)	2657	2930	3103	2691	4657
no. of parameters	302	322	303	352	487
$R1$ ($I > 2\sigma(I)$)	0.047	0.046	0.054	0.045	0.044
$wR2$ (all data)	0.140	0.118	0.151	0.135	0.121

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The complex [Cp*Zr{−C(=C=CH*t*Bu)−CH*t*Bu−CH$_2$−η^5-C$_5$Me$_3$−CH$_2$−}] (**3**) contains a fulvene ligand coupled to the substrate, which now displays an allenic subunit. The molecular structure reveals a characteristically bent metallocene arrangement of the ligands around zirconium. Distances from the zirconium to the ring centers are 2.154 Å for the functionalized Cp* moiety and 2.225 Å for the unaltered Cp* ring. The angle between the geometrical centers of both rings and the titanium center is 144.9°. These data are in good agreement with those of previously described zirconocenes. The bond lengths show a typical π-η^5:π-η^1-tetramethylfulvene ligand (Zr−C16 2.389(5), C1−C16 1.475(8) Å), which is substituted at the neighboring methyl group. The data are similar to those found in the titanium complex Cp*FvTi (2.281(14), 1.437(14) Å).[10] The allenic moiety is nearly linear (C17−C18−C19 172.3(7)°) and displays one extremely short and one normal double bond (C17−C18 1.268(7), C18−C19 1.366(8) Å). The allene carbon bonded to the metal center is planar (sum of angles around C17 = 359.9°), as expected for an sp^2 hybridized atom. The Zr−C17 bond length (2.332(5) Å) is about the same as that for the other Zr−C σ bond (Zr−C16 2.389(5) Å), both being typical for Zr−C single bonds.[21] The bending of the substituent on the allenic subunit (*t*Bu) is as expected (C18−C19−C20 128.2(6)°), as is its orientation (perpendicular to the plane stretched out by the atoms attached to C17). The C−C distances in the bridge between the allenic group and the Cp* ligand (C7−C17 1.536(8), C6−C7 1.552(7) Å) are typical for C−C single bonds. The seven-membered ring system, fused with the fulvene ring, is not planar, allowing the ring atoms to display bond angles appropriate for their hybridization (C5−C6−C7 113.9(4), C6−C7−C17 108.6(4)°), and thus mitigating the ring strain.

The molecular structures of complexes **4** and **5** closely resemble each other, therefore only the crystal structure of **5** is shown (Figure 5). They both demonstrate the characteristically bent metallocene arrangement of ligands around titanium.[22] Distances from the titanium center to the ring centers are 2.078 Å (**4**) and 2.075 Å (**5**) for the functionalized Cp* groups, and 2.082 Å (**4**) and 2.080 Å (**5**) for the unchanged Cp* ring systems. The angles between the geometrical centers of both rings and the titanium center are 147.0° (**4**) and 147.1° (**5**). Both complexes show coupling of the butadiyne unit with two methyl groups of one of the pentamethylcyclopentadienyl ring systems and a complexation of the resulting triple bond to the metal center in the newly formed chelating ligand, [η^5-C$_5$Me$_3$(CH$_2$−CHR−η^2-C$_2$−CHR'−CH$_2$)]. In contrast to complex **3**, which displays one normal Cp* and one functionalized Fv group, complexes **4** and **5** consist of one unchanged and one functionalized Cp* group. The η^2-complexation of the alkyne group is illustrated by the considerably lengthened C−C bonds (**4**: 1.297(4), **5**: 1.295(5) Å). However, a comparison with similar metallacyclopropene compounds, for example [Cp$^*_2$Ti(η^2-1,2-Me$_3$SiC$_2$−C≡CSiMe$_3$)][4] (1.311(4) Å), [Cp$^*_2$Ti(η^2-Me$_3$SiC$_2$SiMe$_3$)][23] (1.309(4) Å), and [Cp$^*_2$Ti(η^2-PhC$_2$SiMe$_3$)][23] (1.308(3) Å), indicates that the bonding in **4** and **5** should be considered weaker. This can be attributed to the fact that the plane of the metallacyclopropene is explicitly bent in the direction of the coupling Cp* ligand. Aside from the complexed triple bond, all other C−C distances in the eight-membered ring (fused with the Cp* ring) (**4**: C14−C15 1.520(4), C15−C26 1.569(4), C13−C18 1.513(4), C18−C19 1.567(4); **5**: C14−C15 1.497(5), C15−C26 1.571(5), C13−C18 1.510(5), C18−C19 1.575(5) Å) correspond to C−C single bonds.

An interesting aspect of this structure is the angle between the centroids of both cyclopentadienyl ligands in **4** (147.0°) and **5** (147.1°). It is larger than that found in the alkyne complex [(C$_5$Me$_5$)$_2$Ti(η^2-Me$_3$SiC$_2$SiMe$_3$)][23] (139°). This can be ascribed to the weaker complexation of the triple bond in **4** and **5**. In this context it is of note that the first linear titanocene complexes [(η^5-C$_5$Me$_4$(SiMe$_2$R))$_2$Ti], R = *t*Bu[24a] and R = Me[24b] [180°], which contain no further ligands, have been found very recently.

The molecular structure of complex **6** (Figure 6) is very similar to that of the formerly described compound [(η^5-C$_5$Me$_4$(CH$_2$)−)Ti(−C(=CHR)−C(=CHR)−CH$_2$−η^5-C$_5$Me$_4$)],

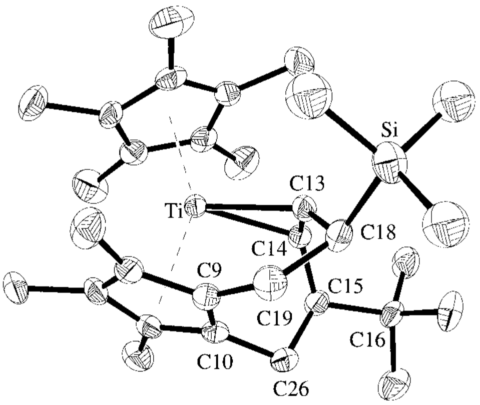


Figure 5. Molecular structure of **5** (ORTEP plot, 30 % probability). The disordered group (SiMe$_3$ substituent) has been omitted for clarity. Selected bond lengths [Å] and angles [°]: Ti−C13 2.121(3), Ti−C14 2.089(3), C13−C14 1.295(5), C13−C18 1.510(5), C18−Si 1.846(4), C18−C19 1.575(5), C19−C9 1.522(5), C10−C26 1.509(5), C26−C15 1.571(5), C15−C14 1.497(5), C15−C16 1.558(4); C13-Ti-C14 35.81(12), C14-C13-C18 133.2(3), C18-C19-C9 111.8(3), C19-C9-C10 126.7(3), C9-C10-C26 126.1(3), C10-C26-C15 110.1(3), C26-C15-C14 101.4(3), C26-C15-C16 117.7(3), C15-C14-C13 137.1(3).

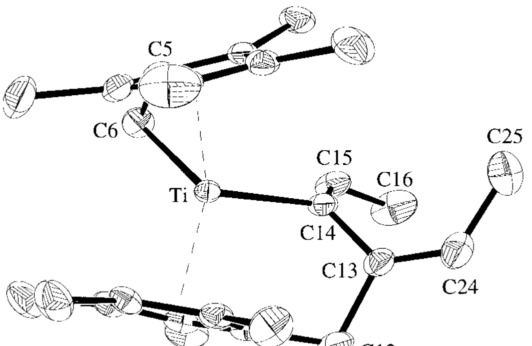


Figure 6. Molecular structure of **6** (ORTEP plot, 30 % probability). Selected bond lengths [Å] and angles [°]: Ti−C14 2.200(3), C14−C15 1.340(4), C15−C16 1.505(5), C14−C13 1.474(4), C13−C24 1.328(5), C24−C25 1.483(6), C13−C12 1.527(4), C12−C11 1.504(4), Ti−C6 2.262(3); C6-Ti-C14 102.17(12), C5-C6-Ti 66.6(2), Ti-C14-C15 126.2(3), Ti-C14-C13 111.6(2), C14-C15-C16 127.8(3), C13-C14-C15 119.8(3), C12-C13-C14 108.8(3), C12-C13-C24 122.5(3), C13-C24-C25 126.2(4), C11-C12-C13 108.4(2).

R = Ph.[4] Both structures show coupling of the butadiyne with one permethylcyclopentadienyl ring under formation of one functionalized Cp* ligand. In the other Cp* moiety, one methyl group is activated, generating a tetramethylfulvene ligand.[15] Distances from the metal to the ring centers (2.034 and 2.076 Å) and the angle between the geometrical centers (143.3°) are in good agreement with those reported for permethyltitanocene complexes.[24a] The fulvene ligand shows lengths typical for a π-η^5:π-η^1-tetramethylfulvene ligand (**6**: Ti–C6 2.262(3), C5–C6 1.432(4); R = Ph: 2.271(5), 1.444(6) Å). These data are very close to those found in the complex Cp*FvTi (2.281(14), 1.437(14) Å). The metal–carbon distances for the functionalized Cp* ligand (**6**: Ti–C14 2.200(3), R = Ph: 2.246(4) Å) are within the expected range for Ti–C(alkyl) bonds.[21] The other bond lengths in this chelating group are typical of C–C single bonds (**6**: C14–C13 1.474(4), C13–C12 1.527(4), C12–C11 1.504(4); R = Ph: 1.467(6), 1.525(6), 1.513(6) Å). The exocyclic distances (**6**: C14–C15 1.340(4), C13–C24 1.328(5), R = Ph: 1.322(6), 1.357(6) Å) are typical for double bonds, making the substrate a disubstituted 2,4-hexadiene. The orientation of the methyl groups minimizes steric repulsion between the substituents.

The structure of complex **7** (Figure 7) is similar to that of the formerly described corresponding five-membered metallacyclocumulenes of [Cp^*_2M].[4] The four carbon atoms of the former butadiyne unit and the Zr atom are planar. The three C–C bond lengths (1.286(8), 1.311(9), 1.283(9) Å) indicate that these bonds are of roughly similar bond order, displaying double bond character. All four carbon atoms of the ring have p orbitals perpendicular to the plane of the cyclocumulene. The sp hybridized internal C atoms possess additional p orbitals in that plane. Employing these orbitals, the central C–C double bond is coordinated to the metal center, resulting in an elongated C–C bond. In accordance with this description the M–(C-β) distances (2.307(5), 2.308(5) Å) are shorter than the M–(C-α) bonds (2.325(5), 2.334(5) Å).

Mechanistic discussion: A variety of C–C coupling products of permethylzirconocene and -titanocene with butadiynes were obtained. The conversions could start from the following possible intermediates:

a) π-η^5:π-η^1-tetramethylfulvene complexes [Cp*{C_5Me_4-(CH_2)}MH] or similar bis-complexes [Cp*{C_5Me_3-(CH_2)$_2$}MH_2][11, 14, 15]

b) η^2 complexes (metallacyclopropenes) [Cp^*_2M(η^2-1,2-RC_2–C≡CR)][4]

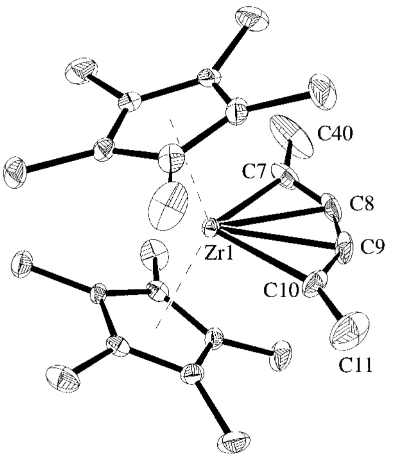
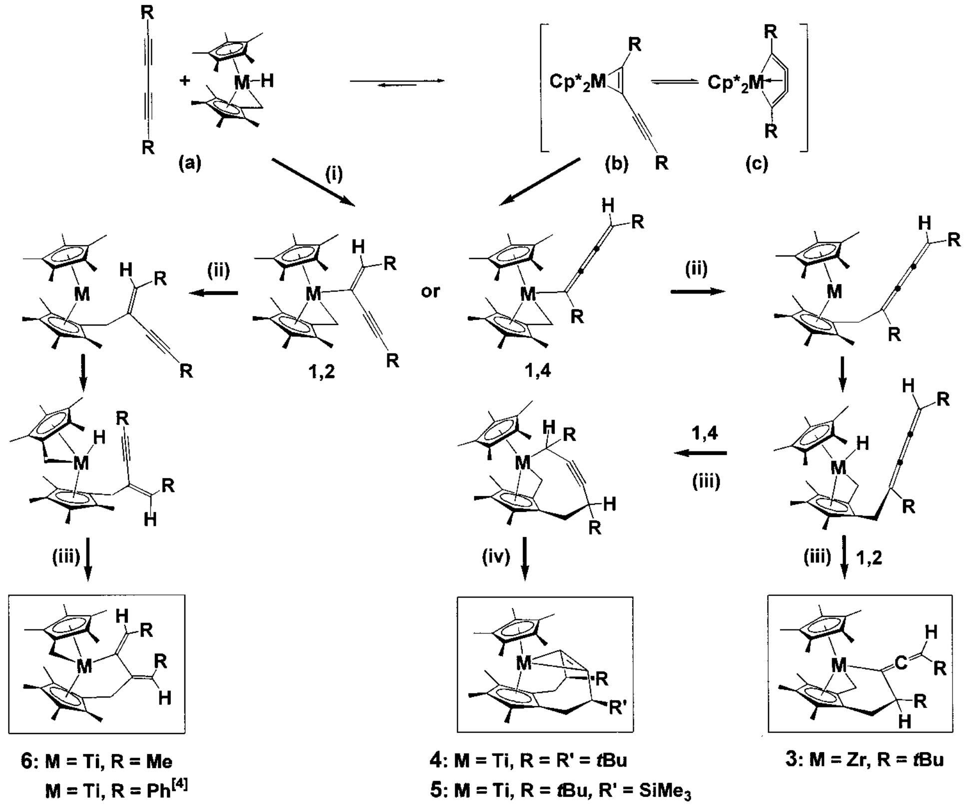


Figure 7. Molecular structure of one of symmetry independent molecules of complex **7** (ORTEP plot, 30% probability). Selected bond lengths [Å] and angles [°]: C7–C8 1.286(8), C8–C9 1.311(9), C9–C10 1.283(9), Zr1–C7 2.325(5), Zr1–C8 2.307(5), Zr1–C9 2.308(5), Zr1–C10 2.334(5); C7-Zr1-C10 97.3(2), C40-C7-C8 136.1(6), C7-C8-C9 148.2(5), C8-C9-C10 148.6(5), C9-C10-C11 135.8(6).

c) η^4 complexes (metallacyclocumulenes) [Cp^*_2M(η^4-1,2,3,4-RC_4R)][4]

The first (a) could insert the diyne to afford two different alkenyl complexes by either a 1,2- or a 1,4-hydrometalation. These can rearrange in such a way that the fulvene unit couples with the alkenyl unit to give the obtained products (Scheme1). Cp*-mediated cleavage of Group 4 metal–carbon bonds can also occur.[25, 26] If this process works with metal-



Scheme 1. Proposed reaction pathway for the formation of the complexes **3**–**6**. It should be mentioned that the listed molecules, and especially the hydride complexes, very probably do not represent real intermediates. A synchronous course of reaction is much more likely.

lacyclopropenes (b), one could assume a "σ-bond metathesis"[27] reaction to obtain identical products.

Both of the above possible reactions seem rather unlikely, because tetramethylfulvene complexes have never been shown to insert internal alkynes.[28] The same holds true for the reactions of permethyltitanocene and -zirconocene with internal[29, 30, 31] and terminal[32] alkynes, as well as acetylene[33], where no coupling with the Cp* ligand was observed.

The third possibility starts from the metallacyclocumulenes [$Cp^*_2M(\eta^4$-1,2,3,4-$RC_4R)$] (c), which were isolated only for M = Zr, R = Ph, $SiMe_3$,[4] Me (this paper). These complexes are possibly formed in the first step, but being rather unstable, they are subsequently protonated and cleaved by Cp* ligands[25, 26] for M = Zr, R = *t*Bu and M = Ti, R = Ph, *t*Bu, and so on, as shown in Scheme 1.

The intermediates can rearrange in such a way that the fulvene unit couples with the alkenyl unit to give the obtained products (Scheme 1, ii).

The details of the conversion to the final products **3**–**6** are not yet clear, but it is assumed to proceed similarly to what has been described for the first step. Rearrangements to different complexation modes and another hydrometalation (Scheme 1, iii) as well as a coupling reaction (Scheme 1, iv) can lead to the complexes **3**–**6**. Formally, the metal and the methyl group, or alternatively two methyl groups, can add to the butadiyne in a 1- and 2-position (to give **3**), 2- and 3-position (to form **6**) and in 1- and 4-position (to yield **4** and **5**). Which product is formed depends on the metals for R = *t*Bu (Zr: **3** or Ti: **4**), and on the substituents for titanium (*t*Bu: **3** or Me: **6**). Interestingly, an activation of two methyl groups is preferred in all cases. Activation of the CH_3 groups is found to take place in only one of the pentamethylcyclopentadienyl ligands, with the exception of **6**, where the activation effects both of the Cp* ligands. This observed preference is in agreement with the existence of bis-complexes, [$Cp^*\{C_5Me_3(CH_2)_2\}MH_2$],[11, 14, 15] which are formed instead of hypothetical bis(tetramethylfulvene) complexes, [$\{C_5Me_4(CH_2)\}_2MH_2$]. All products obtained represent examples of functionalization of the Cp* groups.

Conclusion

The reduction of [$Cp^*_2MCl_2$] (M = Ti, Zr) with Mg in the presence of disubstituted butadiynes $RC{\equiv}C{-}C{\equiv}CR$ is suitable for the synthesis of different C–C coupling products of the diyne and permethylmetallocenes. It presents a new method for obtaining pentamethylcyclopentadienyl derivatives. The products depend strongly on the metals used and the substituents attached to the diyne (M = Zr, R = *t*Bu (**3**): different twofold coupling of one Cp* ligand; M = Ti, R = R′ = *t*Bu (**4**) and R = *t*Bu, R′ = $SiMe_3$ (**5**): identical coupling with two methyl groups of one Cp* ligand, M = Ti, R = Me (**6**): different twofold coupling of both Cp* ligands).

Unstable five-membered metallacyclocumulenes seem to be the starting complexes for the twofold coupling reactions, in which the Cp* ligands cleave the metal–carbon bonds representing twofold "σ-metathesis" reactions.

Experimental Section

All operations were carried out under an argon atmosphere using standard Schlenk techniques. Prior to use, solvents were freshly distilled from sodium tetraethylaluminate under argon. Deuterated solvents were treated with sodium or sodium tetraethylaluminate, distilled, and stored under argon. NMR spectra were obtained on a Bruker ARX 400 spectrometer at 9.4 T (chemical shifts given in ppm relative to TMS, the benzene solvent signals were used as reference: $\delta(^1H) = 7.16$, $\delta(^{13}C) = 128.0$). Melting points were measured in sealed capillaries on a Büchi 535 apparatus. Elemental analyses were preformed on a Leco CHNS-932 elemental analyzer.

[$Cp^*_2M(C{\equiv}CtBu)_2$]: $HC{\equiv}CtBu$ (about 200 mg) was dissolved in THF (5 mL), cooled to −78 °C, and an equimolar amount of *n*-butyllithium (2.5 M solution in *n*-hexane) was added. After warming the mixture to room temperature, one equivalent of the complex [$Cp^*_2MCl_2$] was added, and the solution was stirred for 24 h. The solvents were removed under vacuum and the residue was suspended in *n*-hexane (10 mL). After filtration and crystallization at −78 °C, the mother liquor was decanted and the crystals were dried in vacuo.

M = Ti (1): [$Cp^*_2TiCl_2$] (360 mg, 0.92 mmol) and $tBuC{\equiv}CH$ (150 mg, 1.83 mmol) gave **1** (270 mg, 62 %). M.p. 150–155 °C (decomp under argon); ^1H NMR ([D_6]benzene): $\delta = 1.31$ (s, 18H, Me), 1.99 (s, 30H, C_5Me_5); ^{13}C NMR ([D_6]benzene): $\delta = 12.4$ ($C_5\mathit{Me}_5$), 27.5 ($\mathit{C}Me_3$), 30.9 ($C\mathit{Me}_3$), 121.3 (C_5Me_5), 125.7 (C-β), 147.0 (C-α); IR (Nujol): $\tilde{\nu} = 2075$, 1356, 1244, 1200, 1022, 903, 728, 464, 444 cm^{-1}; MS (70 eV): *m/z*: 398 [$M^+ - C_6H_9$]$^+$, 318 [Cp^*_2Ti]$^+$, 181 [Cp^*_2Ti]$^+$; $C_{32}H_{48}Ti$ (480.6): calcd C 79.97, H 10.07; found C 79.64, H 10.26.

M = Zr (2): [$Cp^*_2ZrCl_2$] (730 mg, 1.69 mmol) and $tBuC{\equiv}CH$ (280 mg, 3.41 mmol) gave **2** (461 mg, 52 %). M.p. 136–139 °C (decomp under argon); ^1H NMR ([D_6]benzene): $\delta = 1.27$ (s, 18H, CMe_3), 2.04 (s, 30H, C_5Me_5); ^{13}C NMR ([D_6]benzene): $\delta = 12.6$ ($C_5\mathit{Me}_5$), 28.4 ($\mathit{C}CH_3$), 31.8 ($C\mathit{Me}_3$), 119.6 (C_5Me_5); 124.9 (C-β); 138.7 (C-α); IR (Nujol): $\tilde{\nu} = 2072$, 1356, 1243, 1199, 1025, 725, 691, 448 cm^{-1}; MS (70 eV): *m/z*: 522 [M]$^+$, 440 [$M^+ - C_6H_9$]$^+$, 361 [Cp^*_2Zr]$^+$; $C_{32}H_{48}Zr$ (523.9): calcd C 73.36, H 9.23; found C 73.76, H 9.50.

[$Cp^*Zr\{{-}C({=}C{=}CHtBu){-}CHtBu{-}CH_2{-}\eta^5\text{-}C_5Me_3{-}CH_2{-}\}$] (3): [$Cp^*_2ZrCl_2$] (1160 mg, 2.68 mmol), Mg turnings (68 mg, 2.80 mmol), and 2,2,7,7-tetramethyl-octa-3,5-diyne (440 mg, 2.71 mmol) were stirred in THF (20 mL) at 55–60 °C for 8 h. The resulting yellow-red solution was evaporated to dryness. The residue was extracted with *n*-hexane (40 mL). Concentration of the hexane solution to about 15 mL and subsequent cooling to −78 °C afforded red crystals, which were separated, washed with cold *n*-hexane, and dried in vacuo to yield **3** (523 mg, 37 %). M.p. 163–165 °C (decomp under argon); NMR: see Table 1; IR (Nujol): $\tilde{\nu} = 1891$ cm^{-1} (C=C=C); MS (70 eV): *m/z*: 522 [M]$^+$; $C_{32}H_{48}Zr$ (524.0): calcd C 73.36, H 9.23; found C 72.99, H 9.08.

[$Cp^*_2Ti\{\eta^5\text{-}C_5Me_3(CH_2{-}CHtBu{-}\eta^2\text{-}C_2{-}CHtBu{-}CH_2)\}$] (4): A suspension of [$Cp^*_2TiCl_2$] (689 mg, 1.77 mmol), Mg turnings (43 mg, 1.77 mmol), and 2,2,7,7-tetramethyl-octa-3,5-diyne (287 mg, 1.77 mmol) in THF (15 mL) was stirred for 8 h at 55–60 °C. The resulting yellow solution was evaporated to dryness and the residue was extracted with hot *n*-hexane (25 mL, 50 °C). After the solution was left to stand at −78 °C for two days, yellow crystals appeared, which were separated, washed with cold *n*-hexane (−75 °C), and dried in vacuo to give **4** (578 mg, 68 %). M.p. 195–196 °C (decomp under argon); NMR: see Table 2; IR (Nujol): $\tilde{\nu} = 1663$ cm^{-1} (coord. C≡C); MS (70 eV): *m/z*: 480.2 [M]$^+$, 57.0 [tBu]$^+$; $C_{32}H_{48}Ti$ (480.6): calcd C 79.97, H 10.07; found C 80.08, H 10.32.

[$Cp^*Ti\{\eta^5\text{-}C_5Me_3(CH_2{-}CHtBu{-}\eta^2\text{-}C_2{-}CHSiMe_3{-}CH_2)\}$] (5): A suspension of [$Cp^*_2TiCl_2$] (1469 mg, 3.77 mmol), Mg turnings (92 mg, 3.78 mmol), and 1-trimethylsilyl-4-*tert*-butyl-buta-1,3-diyne (673 mg, 3.77 mmol) in THF (15 mL) was stirred for 8 h at 55–60 °C. The resulting green solution was evaporated to dryness, and the residue was extracted with hot *n*-hexane (25 mL, 50 °C). The hexane solution was concentrated to 3 mL, and after standing at room temperature for one week, light brown crystals appeared, which were separated, washed with cold *n*-hexane (−75 °C), and dried in vacuo to give **5** (1160 mg, 62 %). M.p. 164–165 °C (decomp under argon); NMR: see Table 2; IR (Nujol): $\tilde{\nu} = 1645$ cm^{-1}(coord. C≡C); MS (70 eV): *m/z*: 495.7 [M]$^+$, 73.0 [$SiMe_3$]$^+$, 57.0 [tBu]$^+$; $C_{31}H_{48}SiTi$ (496.7): calcd C 74.96, H 9.74; found C 74.83, H 9.66.

[{η^5-C_5Me_4–(CH_2)–}Ti{–C(=CHMe)–C(=CHMe)–CH_2–η^5-C_5Me_4}] (6): A suspension of [$Cp^*_2TiCl_2$] (920 mg, 2.36 mmol), Mg turnings (59 mg, 2.43 mmol), and hexa-2,4-diyne (190 mg, 2.43 mmol) in THF (25 mL) was stirred for 24 h at 60 °C. The color changed gradually to dark green. The volatile material was removed under vacuum and the residue was extracted with *n*-hexane (30–40 mL) at 60 °C. The green extract was filtered and the solution was concentrated to about 10 mL. Subsequent cooling to –30 °C produced green crystals of **6** (663 mg, 71 %), which were separated from the mother liquor by decanting and dried in vacuo. M.p. 161–162 °C (decomp under argon); ^1H NMR ([D_6]benzene, 297 K, Figure 8): $\delta = 1.83$ (d, $J = 4.4$ Hz, 1 H, 6-H_A), 1.49 (d, $J = 4.4$ Hz, 1 H, 6-H_B), 3.07 (d, $J = 13.9$ Hz, 1 H, 12-H_A), 3.52 (d of quintets, $^2J = 13.9$ Hz, $^4J = {}^5J = 2.2$ Hz, 1 H, 12-H_B), 3.92 (q, $J = 6.2$ Hz, 1 H, 15-H), 1.54 (d, $J = 6.2$ Hz, 3 H, 16-H), 2.14 (s, 3 H, 17-H), 1.65 (s, 3 H, 18-H), 1.53 (s, 3 H, 19-H), 1.43 (s, 3 H, 20-H), 1.53 (s, 3 H, 21-H), 1.14 (s, 3 H, 22-H), 1.43 (s, 3 H, 23-H), 4.62 (dq, $^3J = 6.6$ Hz, $^4J = 2.2$ Hz, 1 H, 24-H), 1.39 (dd, $^3J = 6.6$ Hz, $^5J = 2.2$ Hz, 3 H, 25-H), 2.12 (s, 3 H, 26-H); ^{13}C NMR ([D_6]benzene, 297 K): $\delta = 129.0$ (C1), 126.4 (C2), 122.2 (C3), 125.2 (C4), 128.1 (C5), 78.6 ($^1J_{C,H} = 150$ Hz, C6), 113.3 (C7), 118.6 (C8), 113.7 (C9), 119.8 (C10), 133.0 (C11), 32.3 ($^1J_{C,H} = 128$ Hz, $^3J_{C,H} = 7$ Hz, C12), 148.7 (C13), 201.0 (C14), 116.9 ($^1J_{C,H} = 154$ Hz, C15), 15.1 ($^1J_{C,H} = 125$ Hz, $^2J_{C,H} = 7$ Hz, C16), 16.6 (C17), 9.3 (C18), 11.6 (C19), 10.5 (C20 or C23), 10.7 (C21 *and* C23 or C20), 10.2 (C22), 105.8 ($^1J_{C,H} = 151$ Hz, C24), 15.0 ($^1J_{C,H} = 128$ Hz, C25), 13.6 (C26); MS (70 eV): *m/z*: 396.3 [M]$^+$; $C_{26}H_{36}Ti$ (396.5): calcd C 78.77, H 9.15; found: C 78.64, H 9.02.

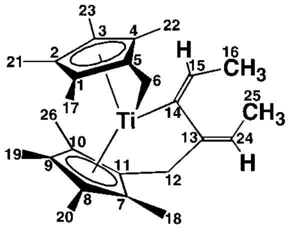


Figure 8. Molecular structure of **6**, labeled according to the numbering scheme of the respective crystal structure. The labels are used for the assignment of the NMR signals.

[Cp^*_2Zr(η^4-1,2,3,4-MeC_4Me)] (7): A suspension of [$Cp^*_2ZrCl_2$], (1033 mg, 2.39 mmol), Mg turnings (63 mg, 2.59 mmol), and hexa-2,4-diyne (200 mg, 2.56 mmol) in THF (15 mL) was stirred for 24 h at 55–60 °C. The resulting yellow solution was evaporated to dryness and the residue was dissolved in *n*-hexane (25 mL). The hexane solution was filtered and cooled to –30 °C, and in one day yellow crystals precipitated, which were separated, washed with cold *n*-hexane (–75 °C) and dried in vacuo to give **7** (735 mg, 70 %). M.p. 220–223 °C (decomp under argon); ^1H NMR ([D_6]benzene, 297 K): $\delta = 1.63$ (s, 30 H, C_5Me_5), 2.67 (s, 6 H, Me); ^{13}C NMR ([D_6]benzene, 297 K): $\delta = 11.2$ (C_5*Me*$_5$), 16.6 (*Me*), 111.5 (C-β), 111.7 (*C*$_5$Me$_5$), 171.7 (C-α); MS (70 eV): *m/z*: 438.2 [M]$^+$; $C_{26}H_{36}Zr$ (439.8): calcd C 71.01, H 8.25; found C 70.87, H 8.09.

X-ray crystallographic study of complexes 3–7: Data were collected with a STOE-IPDS-diffractometer using graphite-monochromated $Mo_{K\alpha}$ radiation. The structures were solved by direct methods (SHELXS-86)[34] and refined by full-matrix least squares techniques against F^2 (SHELXL-93).[35] The hydrogen atoms were included at calculated positions. All other nonhydrogen atoms, except atoms of disordered groups, were refined anisotropically. Cell constants and other experimental details were collected and recorded in Table 3. XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 125746–125750. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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