Regioselective Reactions of 1,3-Diynes with the Titanocene Vinylidene Fragment [Cp*$_2$Ti=C=CH$_2$]. Crystal and Molecular Structure of Cp*$_2$TiC(C≡CSiMe$_3$)=C(SiMe$_3$)C=CH$_2$

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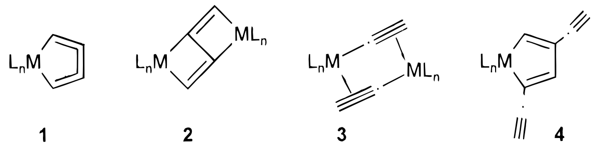
The titanocene vinylidene intermediate [Cp*$_2$Ti=C=CH$_2$] (**6**) (Cp*: C$_5$(CH$_3$)$_5$), formed by ethene or methane elimination from Cp*$_2$TiCH$_2$CH$_2$C=CH$_2$ (**5**) and Cp*$_2$Ti(CH=CH$_2$)(CH$_3$) (**7**), respectively, reacts with 1,3-diynes RC≡C-C≡CR (R = Me (**13a**), Ph (**13b**), SiMe$_3$ (**13c**), CMe$_3$ (**13d**)) by a [2 + 2]-cycloaddition, giving metallacyclobutenes Cp*$_2$TiC(C≡CR)=CRC=CH$_2$ (**9a**−**d**). Using the unsymmetrical 1,3-diyne RC≡CC≡CR^1 (R = CMe$_3$, R^1 = SiMe$_3$ (**13e**)), a 9:1 mixture of the metallacyclobutenes Cp*$_2$TiC(C≡CR)=CR^{1}C=CH$_2$ (**9e**) and Cp*$_2$TiC-(C≡CR^1)=CRC=CH$_2$ (**9e′**) is formed. In all cases, exclusive formation of one regioisomer exhibiting the C≡CR substituent in the α-position of the metallacycle is observed. The regioselectivity of the formation of **9** is attributed to the polarity of the C≡C bond as well as the stereochemical conditions, proven by *ab initio* calculations at the Hartree−Fock (HF) level of theory with the 3-21G(*) standard basis set and molecular modeling. The X-ray structure of **9c** is presented. Subsequent reactions of **9** with an excess of the titanocene intermediate **6**, to form binuclear metallacycles, are not observed.

Introduction

1,3-Diynes are versatile building blocks in organometallic synthesis.[1] They can react to form mononuclear compounds which exhibit the cyclocumulene structure **1,** when titanocene and zirconocene are used as generating complexes.[2] Additionally, formation of binuclear complexes of type **2**[3] and **3**,[4] with and without cleavage of the internal C−C σ-bond, has been observed.[5] The reaction course strongly depends on the stoichiometry used, the metals, the substituents, and additional ligands. Using an excess of 1,3-diyne, metal-centered cycloaddition products **4** and derivatives thereof are also formed.[2b−d]



1 **2** **3** **4**

L$_n$M: Cp$_2$Ti, Cp$_2$Zr

When diynes other than 1,3-diynes are used, e.g., α,ω-diynes, metallacyclopentadienes[6] are isolable. Furthermore, diynes have attracted attention in oligomerization reactions that form unsaturated macrocycles[7] or organosilicon polymers,[8] compounds which are of interest in material science or in the formation of new types of carbon networks.[9] Studies of the activation of diynes

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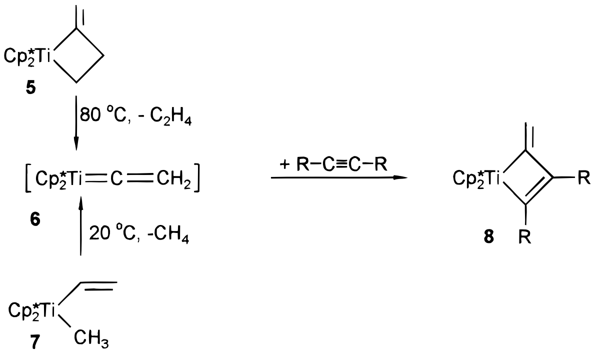
Table 1. Products from Reactions of 7 with 1,3-Diynes

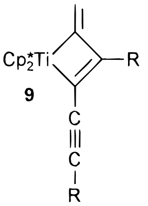
1,3-Diyne		products **9a**−**e**			
RC≡CC≡CR	R	yield (%)	color	mp (°C)	IR ν(C≡C) (cm^{-1})
13a	Me	68	red	153 (dec)	2169 m
13b	Ph	86	red	132−134 (dec)	2139 vs
13c	SiMe$_3$	79	purple	167 (dec)	2093 w
13d	CMe$_3$	83	dark red	143 (dec)	2162 m
13e	CMe$_3$/SiMe$_3$	76 (90/10)[a]	purple	152−153 (dec)	2067 m

[a] Ratio **9e**:**9e′**.

by ruthenium complexes suggested the formation of metallacumulenes.[10] We have demonstrated that the reaction of the titanocene vinylidene intermediate [Cp*$_2$-Ti=C=CH$_2$] (**6**)[11] with alkynes yields titanacyclobutene complexes (**8**) and alternatively vinyltitanium acetylides, depending on the nature of the alkyne used.[12] With unsymmetrical alkynes, different regioisomers can be isolated. The regiochemistry is in accordance with the polarities of the alkynes. Large differences in the partial charge of the alkyne C≡C atoms lead to stereochemically pure compounds with the more negative carbon bonded to titanium. α-,β-Regioisomers are obtained by using alkynes with small charge differences.



In a series of such studies we were interested in the behavior of 1,3-diynes toward the vinylidene intermediate **6** in order to obtain metallacyclobutenes of type **9** and **11**, as potential candidates for the formation of cross-conjugated dimers **10** as well as **12**.



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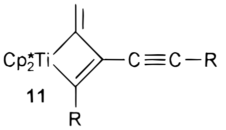

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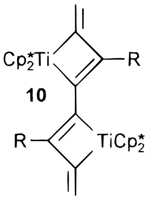

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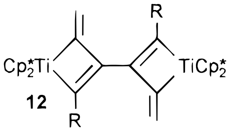

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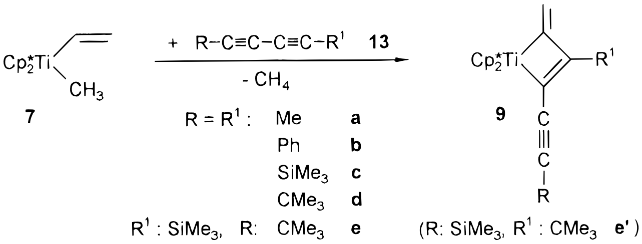
Preliminary studies using 1,3-diynes showed the formation of metallacyclobutenes **9** (R: CH$_3$, Ph).[12] We report here full details of the reaction of the intermediate **6** with 1,3-diynes.

Results and Discussion

The vinylmethyl derivative **7** reacts with 1 molar equiv of the 1,3-diynes **13a**−**d** at room temperature with evolution of methane to give the metallacyclobutenes **9**. These are formed in nearly quantitative yield (NMR) and can be isolated (67−86%) as red or purple crystals of high thermal stability (Table 1). The mass spectra of **9** exhibit the expected molecular peaks. A metathesis-like fragmentation behavior similar to that of metallacyclobutanes is not observed in the mass spectrometer.



Products with the acetylide substituent in the α-position are formed exclusively. Using the unsymmetrical 1,3-diyne **13e**, the cycloaddition leads to a mixture of **9e** (90%) and **9e′** (10%), whose separation is not possible. ^{1}H and ^{13}C NMR data of the titanacyclobutenes **9a**−**e** are listed in Table 2.

From the ν(C≡C) values in the IR spectra of **9a**−**e** (2066−2169 cm^{-1}), the formation of a C≡C triple bond which is not coordinated to titanium in the α-position of the metallacycle can be deduced. Comparable values of a noncoordinated C≡C triple bond are also found in η^2-1,3-diyne complexes of nickel (2077−2188 cm^{-1}).[13] This behavior is confirmed by a nonbonding distance of Ti−C4 (3.3 Å) in the molecular structure of **9c**.

The two different chemical shifts for the protons of the *exo*-methylene group in **9** in the ^{1}H NMR spectra in particular appear to be a characteristic feature of the new complexes and similar metallacyclic structures.[12] The chemical shifts were assigned through NOE experiments. Moreover, the chemical shifts of the ring carbon atoms in the ^{13}C NMR spectra are in accordance with two σ titanium-bonded sp^2 carbon atoms. The low-field signals are consistent with the C^1 atom (205−218 ppm), whereas C^3 is shifted to higher fields ($\Delta = \delta$(C1) − δ(C3) = 6−25 ppm), compared to cyclobutenes without acetylide substituents **8**.[12]

The PLATON plot of **9c** is shown in Figure 1, and relevant bond distances and angles are given in Table

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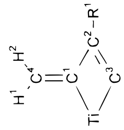
Table 2. NMR Data for the $\overline{\mathrm{TiC(C{\equiv}CR){=}CRC}}{=}\mathrm{CH_2}$ Ring in the Metallacyclobutene Complexes 9[a]

	R	^{1}H-NMR data (ppm) (J_{HH} (Hz))					^{13}C-NMR data								
		Cp*	H^1 (*endo*)	H_2 (*exo*)	R^1	R^2	Cp*	C^1	C^2	C^3	C^4	C^5	C^6	R^1	R^2
9a	Me	1.75	4.55 (d, 1.5)	5.71 (d, 1.5)	2.10	2.03	11.9, 120.2	210.5	104.2	185.9	104.8	114.7	84.0	11.5	5.7
9b	Ph	1.78 (s)	4.57 (d, 1.3)	5.98 (d, 1.3)	6.83–7.81		12.0, 121.3	205.4	126.7	182.7	108.4	109.1	94.6	126.8, 128.4, 131.1, 135.6	124.7, 126.4, 128.3, 130.2
9c	$SiMe_3$	1.70 (s)	4.86 (d, 0.9)	6.00 (d, 0.9)	0.58 (s)	0.30 (s)	11.9, 118.5	217.5	123.3	211.6	110.9	112.6	109.8		0.3, 3.2
9d	CMe_3	1.78 (s)	4.19 (d, 0.8)	5.90 (d, 0.7)	1.58 (s)	1.23 (s)	12.1, 121.0	203.5	120.0	182.9	104.7	129.5	83.8	32.4, 39.0	29.4, 31.2
9e	$R^1 = SiMe_3$	1.72 (s)	4.86 (s)	5.99 (s)	0.58 (s)	1.29 (s)	11.9, 118.0	218.3	121.4	214.9	109.3	105.4	83.8	3.3	29.5, 31.2
9e´	$R^1 = CMe_3$	1.77 (s)	4.20 (s)	5.92 (s)	1.57 (s)	0.25 (s)									

[a] Listed in ppm vs TMS; solvent was C_6D_6 and temperature = 25 °C.

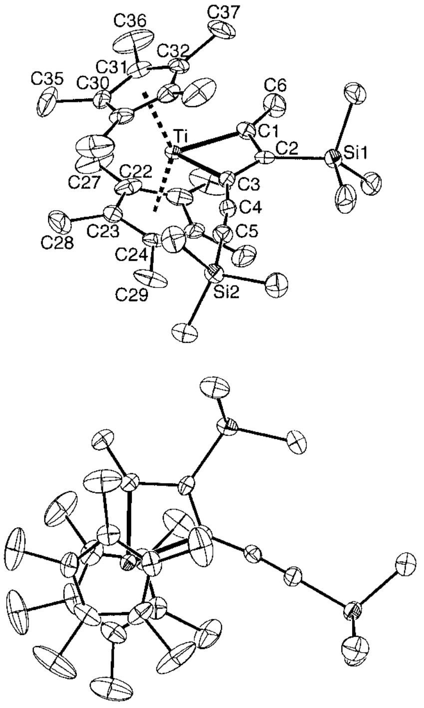


Figure 1. PLATON drawing of $\mathrm{Cp^*{}_2\overline{TiC(C{\equiv}CSiMe_3){=}C(SiMe_3)C}{=}CH_2}$ (**9c**) (30% ellipsoids).[16]

Table 3. Selected Bond Distances (Å) and Angles (deg) in $Cp^*{}_2TiC(C{\equiv}CSiMe_3){=}C(SiMe_3)C{=}CH_2$ (9c)

Distances			
Ti–C1	2.110(3)	C2–C3	1.367(4)
Ti–C3	2.111(3)	C3–C4	1.406(5)
Ti–Cp$_1$[a]	2.117	C4–C5	1.214(5)
Ti–Cp$_2$[a]	2.107	C2–Si1	1.891(3)
C1–C6	1.342(5)	C5–Si2	1.810(4)
C1–C2	1.495(5)		
Angles			
C1–Ti–C3	68.5(1)	C2–C3–Ti	91.4(2)
Cp–Ti–Cp	141.4	C4–C3–Ti	137.7(2)
Ti–C1–C2	88.0(2)	C3–C4–C5	172.4(4)
Ti–C1–C6	146.7(3)	C4–C5–Si2	179.2(3)
C1–C2–C3	112.1(3)		

[a] Centroids of the Cp* ligands: Cp$_1$, C20–C24; Cp$_2$, C30–C34.

3. The geometry of **9c** shows the typical bent metallocene structure as well as a planar titanacyclobutene ring (side view). The solid-state structural data for complex **9c** are consistent with a metallacycle formalism. Partial ring opening, suggesting a fragmentation toward the titanocene vinylidene–alkyne structure, comparable to trimethylsilyl-substituted titanacyclobutenes,[12,14] can be discounted for **9c**. The Ti–C1 bond in **9c** (2.110(3) Å) is longer than in the titanacyclobutane **5** (2.068(6) Å [15]) and also longer than in other titanacyclobutenes (**8**: 2.104(3) Å (R = Me); 2.102(6) Å (R = $SiMe_3$, Ph)[12]).

The observed alternating bond lengths in the sequence C6–C1–C2–C3 of **9c** are comparable to a conjugated π-bond system and similar to that in free butadiene. This observation is in agreement with the

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Table 4. Selected ^{13}C-NMR Data and Electron Densities of 1,3-Diynes Used in Cycloaddition with the Titanium Vinylidene Intermediate 6

	RC≡C′R′		^{13}C-data				electron densities[a]		
	R	R′	δ(C)	δ(C′)	Δ[b]	ref	C	C′	Δ[c]
13a	Me	C≡CMe	72.0	64.7	7.3	17a	0.38	−0.67	1.05
13b	Me	C≡CPh	83.0	75.7	7.3	17b	0.34	−0.71	1.05
13c	Me_3Si	$C≡CSiMe_3$	86.8	90.1	3.3	17c	−0.08	−0.40	0.32
13d	Bu^t	$C≡CBu^t$	86.3	65.4	20.9	17c	0.61	−0.72	1.33
13e[d]	Bu^t	$C≡CSiMe_3$	87.6	65.4	22.2	3a	0.54	−0.78	1.32
	Me_3Si	$C≡CBu^t$	84.2	89.8	5.6		−0.03	−0.29	0.26

[a] Mulliken values, 3-21G(*). [b] Δ = |δ(C) − δ(C′)|. [c] Δ = |electron density of C − electron density of C′|. [d] Means $Bu^tC≡C'C'≡CSiMe_3$.

short C1−C2 bond (1.495(5) Å), illustrating a conjugative effect in the carbocyclic part of the metallacyclobutene ring (top view). The C≡C distance of the exocyclic triple bond C5−C4 (1.214(5) Å) is in the expected range for noncoordinated acetylides, e.g., comparable to those in η^2-diyne complexes of nickel(0) ((η^2-$Me_3SiC≡CC≡CSiMe_3$)$Ni(PPh_3)_2$: η^2-C≡C, 1.288(4) Å; free C≡C, 1.213(4) Å [13]). Additionally, the large angles C3−C4−C5 (172.4(4)°) and C4−C5−Si2 (179.2(3)°) are in agreement with a free C≡C triple bond (top view). Generally, all angles are in the expected range for a planar metallacycle exhibiting C_{sp^2} atoms (C1−Ti−C3 angles in **9c**: 68.5(1)°). A larger value is found in the titanacyclobutane **5** (83.1(4)° [15]).

The orientation of the substituents in the cyclobutenes can be attributed to the polarity of the 1,3-diyne molecule and the strongly nucleophilic α-C atom in the vinylidene **6** [$Ti^{\delta+}{=}C^{\delta-}{=}CH_2$]. The polarities of the 1,3-diynes can be deduced from the ^{13}C-NMR chemical shifts of the carbon atoms, as discussed for alkynes also.[3a,12,17] Chemical shifts and electron densities of diynes used are listed in Table 4. Generally, 1,3-diynes are characterized by an increased electron density at the inner carbon atoms.

Due to the large differences of the chemical shifts and the electron densities, only one regioisomer is expected and found. The carbon atom with higher electron density is bonded to the titanium center. Using the bis(trimethylsilyl)-substituted diyne **13c**, the regioisomer **11c**, expected from the reverse polarity, is not formed. The differences in the chemical shifts of the acetylenic carbon atoms are compensated by the β-silicon effect,[18] leading simultaneously to smaller differences in the electron densities (Δ = 0.32). Therefore, the obtained regioselectivity must be attributed to steric hindrance due to the $SiMe_3$ group in the α-position (**11c**) compared to the $C≡CSiMe_3$ substituent in **9c**. Increasing the space requirement of the substituent in the α-position leads to a lowering of the Cp−Ti−Cp angle, as proven for **9c**: 141.4° ($Cp^*_2TiC(CH_3){=}C(CH_3)C{=}CH_2$, 139.8°;[12] $Cp^*_2TiC(SiMe_3){=}C(Ph)C{=}CH_2$, 137.9° [12]).

Table 5. MMX Energies of the Isomers 9 and 11

	energies		
	9 (kcal mol^{-1})	**11** (kcal mol^{-1})	Δ[a]
a	−72.9	−70.5	2.4
b	−45.1	−46.3	1.2
d	−69.7	−56.7	13.0
e	−79.2	−68.2	11.0

[a] Δ = difference of MMX energies |**9** − **11**|.

It is also possible to demonstrate this effect of steric hindrance by using molecular mechanics (MMX) calculations.[19] The results are listed in Table 5. The regioisomers **9d**,**e** are 13.0 and 11.0 kcal mol^{-1} more stable than **11d**,**e**, respectively. The higher energy of **11d**,**e** is due to steric hindrance between the bulky $-CMe_3$ or $-SiMe_3$ group and the wheels of the Cp* ligands. This effect cannot be found for the isomers **11a**,**b**. The $-CH_3$ group in **11a** and the phenyl group in **11b** fit well between the Cp* groups. Therefore, there are only very small differences in the MMX energies of **9a**/**11a** and **9b**/**11b**. The selective formation of **9a**,**b** must, therefore, be attributed to the high differences of the polarities of the C≡C triple bond in **13a**,**b**. With respect to the different substituents in the unsymmetrical substituted diyne **13e**, the preferred formation of **9e** vs **9e′** must be attributed to dominating steric influences when comparing the steric effects of the CMe_3 and $SiMe_3$ groups. Compared to CMe_3, the $SiMe_3$ group is more flexible and has a longer σ-bond distance to the alkyne carbon atom (CMe_3, 1.498 Å; $SiMe_3$, 1.825 Å [20]). That gives less interaction with the *exo*-methylene group and, what is more important, with the Cp* groups in **9e**.

In general, the titanacyclobutene complexes **9** do not react with an excess of the vinylidene precursor **7** to form binuclear complexes **10**. The excess of the vinylidene intermediate **6** reacts to form a dark green vinyl fulvene intermediate.[21] The reason for the low reactivity of the exocyclic acetylide group is also attributed to the steric hindrance caused by the Cp* ligands. There is also no reaction with $Co_2(CO)_8$ to form a binuclear Ti−Co complex involving the exocyclic triple bond. Ring enlargement reactions, as shown for metallacycles of type **4**,[1,2a,b,d] are not found.

Conclusions

We have demonstrated that the reaction of the titanocene vinylidene intermediate [$Cp^*_2Ti{=}C{=}CH_2$] (**6**)

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with 1,3-diynes yields titanacyclobutene complexes (**9**). Only one regioisomer is formed, containing the acetylide group in the α-position of the metallacyclic ring. The regioselectivity can be explained in terms of the polarities of the diynes and stereochemical conditions in the cyclobutene ring. This behavior is in accordance with *ab initio* calculations and results of molecular modeling. 1,3-Diynes exhibiting nonbulky substituents react under electronic control forming **9**. Using an excess of **7**, no further cycloaddition reactions and no formation of binuclear complexes are observed.

Experimental Section

General Considerations. The preparation and handling of the described compounds were performed under rigorous exclusion of air and moisture under a nitrogen atmosphere, using standard vacuum line and Schlenk techniques. All solvents were dried with the appropriate drying agents and distilled under a nitrogen atmosphere. Deuterated solvents were degassed by freeze−pump−thaw cycles and dried over molecular sieves (3, 4 Å) prior to use. ^1H and ^{13}C NMR spectra were recorded on a Varian Unity 500 spectrometer. Chemical shifts are reported in ppm and referenced to residual protons in deuterated solvents (benzene-d_6, $\delta = 7.15$ ppm for ^1H NMR spectroscopy; benzene-d_6, $\delta = 127.96$ ppm for ^{13}C NMR spectroscopy). Mass spectroscopic analyses were performed on a Finnigan MAT 95 mass spectrometer. Infrared spectra were recorded as KBr pellets on a Perkin-Elmer 1720X FT-IR spectrometer. Elemental analyses were carried out at the Analytische Laboratorien in Lindlar, Germany.

The titanocene complexes $Cp^*_2Ti(CH{=}CH_2)(CH_3)$[22] and $Cp^*_2\overline{TiCH_2CH_2C}{=}CH_2$[23] were prepared by literature procedures. The reagents $H_3CC{\equiv}CC{\equiv}CCH_3$, $(H_3C)_3CC{\equiv}CC{\equiv}CC(CH_3)_3$, $(H_3C)_3SiC{\equiv}CC{\equiv}CSi(CH_3)_3$, and $PhC{\equiv}CC{\equiv}CPh$ were purchased from Aldrich.

Preparation of 1,1-Bis(η^5-pentamethylcyclopentadienyl)-3-methyl-2-methylene-4-(1-propynyl)titanacyclobutene (9a). To a solution of **7** (261.9 mg, 0.727 mmol) in 30 mL of hexane was added 2,4-hexadiyne (**13a**) (62.4 mg, 0.8 mmol) at −78 °C. The mixture was slowly warmed to room temperature and stirred overnight. The hexane was partially removed under reduced pressure until crystallization took place (0 °C), yielding **9a** after decantation as red crystals (207.3 mg, 67.5%): mp 153 °C (dec); ^1H-NMR (C_6D_6, 500 MHz) δ 1.75 (s, 30H, $C_5(CH_3)_5$), 2.03 (s, 3H, $\equiv CCH_3$), 2.10 (s, 3H, $=CCH_3$), 4.55 (d, $J = 1.5$ Hz, 1H, $=CHH$), 5.71 (d, 1.5 Hz, 1H, $=CHH$) (the chemical shifts were assigned through a NOE experiment); $^{13}C\{^1H\}$ NMR (C_6D_6, 125 MHz) δ 5.7 ($C{\equiv}CCH_3$), 11.5 (CCH_3), 11.9 ($C_5(CH_3)_5$), 84.0 ($C{\equiv}CCH_3$), 104.2 (CCH_3), 104.8 ($=CH_2$), 114.7 ($C{\equiv}CCH_3$), 120.2 ($C_5(CH_3)_5$), 185.9 ($TiCC{\equiv}$), 210.5 ($TiC{=}$); EI-MS (70 eV) *m/e* (I_{rel}) 422 (12) (M^+), 407 (5) $(M - CH_3)^+$, 337 (5), 318 (47) $(Cp^*_2Ti)^+$, 270 (2), 239 (6), 200 (12), 181 (7), 162 (8), 152 (15), 147 (19), 135 (29) $(Cp^*)^+$, 119 (31), 105 (16), 86 (23), 57 (100); exact mass *m/e* 422.2453 ($C_{28}H_{38}Ti$), calcd *m/e* 422.2456; IR (KBr) 3018 w, 2981 s, 2904 vs, 2722 w, 2169 m [$\nu(C{\equiv}C)$], 2037 w, 1714 m, 1627 w, 1565 m, 1492 s, 1433 vs, 1379 vs, 1261 w, 1165 w, 1065 m, 1023 s, 964 w, 853 s, 806 m, 597 m, 573 w, 548 w, 506 m, 480 w, 416 s cm^{-1}.

Preparation of 1,1-Bis(η^5-pentamethylcyclopentadienyl)-2-methylene-3-phenyl-4-(2-phenyl-1-ethynyl)titanacyclobutene (9b). A reaction of **7** (268.8 mg, 0.746 mmol) in 30 mL of hexane with 1,4-diphenylbutadiyne (**13b**) (150.8 mg, 0.746 mmol) was carried out using the same procedure as in the case of **9a**. Similar workup gave **9b** as small, red crystals (350.3 mg, 85.9%): mp 132−134 °C (dec); ^1H-NMR (C_6D_6, 500 MHz) δ 1.78 (s, 30H, $C_5(CH_3)_5$), 4.57 (d, $J = 1.3$ Hz, 1H, $=CHH$(cis)), 5.98 (d, $J = 1.3$ Hz, 1H, $=CHH$(trans)), 6.83−6.90 (m, 1H, para-$CH^{(4)}$), 6.94−6.90 (tr/m, $J = 7.5$ Hz, 1H, para-$CH^{(3)}$), 7.02 (tr/m, $J = 7.6$ Hz, 2H, meta-$CH^{(4)}$), 7.34 (tr/m, $J = 7.6$ Hz, 4H, ortho-$CH^{(4)}$, meta-$CH^{(3)}$), 7.81 (d/d, $J = 8.2/1.2$ Hz, 2H, ortho-$CH^{(3)}$) (the chemical shifts were assigned through a NOE experiment); $^{13}C\{^1H\}$-NMR (C_6D_6, 125 MHz) δ 12.0 ($C_5(CH_3)_5$), 94.6 ($C{\equiv}CPh$), 108.4 ($=CH_2$), 109.1 ($C{\equiv}CPh$), 121.3 ($C_5(CH_3)_5$), 124.7 (ipso-$C^{(4)}$), 126.4 (para-$C^{(4)}$), 126.7 (CPh), 126.8 (para-$C^{(3)}$), 128.3 (meta-$C^{(4)}$), 128.4 (meta-$C^{(3)}$), 130.2 (ortho-$C^{(4)}$), 131.1 (ortho-$C^{(3)}$), 135.6 (ipso-$C^{(3)}$), 182.7 ($TiCC{\equiv}$), 205.4 ($TiC{=}$); EI-MS (70 eV) *m/e* (I_{rel}) 546 (7) (M^+), 452 (8), 364 (100), 349 (25), 316 (83), 286 (8), 230 (13), 202 (14), 178 (10), 136 (12) $(Cp^*H)^+$, 121 (20), 119 (18), 105 (13), 91 (18); exact mass *m/e* 546.2766 ($C_{38}H_{42}Ti$), calcd *m/e* 546.2766; IR (KBr) 3075 m, 3052 m, 3010 s, 2983 s, 2956 s, 2901 vs, 2719 w, 2139 vs [$\nu(C{\equiv}C)$], 1939 w, 1870 w, 1735 w, 1636 w, 1593 s, 1567 m, 1559 m, 1488 vs, 1473 s, 1449 s, 1439 s, 1377 vs, 1261 w, 1213 w, 1155 w, 1100 w, 1069 m, 1021 s, 993 w, 907 w, 863 m, 838 w, 806 w, 776 m, 754 vs, 717 m, 698 vs, 690 vs, 620 w, 601 w, 550 w, 530 s, 507 w, 475 m, 434 s cm^{-1}. Anal. Calcd for $C_{38}H_{42}Ti$: C, 83.50; H, 7.74. Found: C, 83.69; H, 7.83.

Preparation of 1,1-Bis(η^5-pentamethylcyclopentadienyl)-2-methylene-3-(trimethylsilyl)-4-(2-(trimethylsilyl)-1-ethynyl)titanacyclobutene (9c). A reaction of **7** (290.0 mg, 0.805 mmol) in 30 mL of hexane with 1,4-bis(trimethylsilyl)butadiyne (**13c**) (172.1 mg, 0.885 mmol) was carried out using the same procedure as in the case of **9a**. Similar workup gave **9c** as purple crystals (343.1 mg, 79.1%) that were suitable for X-ray structure determination: mp 167 °C (dec); ^1H-NMR (C_6D_6, 500 MHz) $\delta = 0.30$ (s, 9H, $\equiv CSiMe_3$), 0.58 (s, 9H, $=CSiMe_3$), 1.70 (s, 30H, $C_5(CH_3)_5$), 4.86 (d, $J = 0.9$ Hz, 1H, $=CHH$), 6.00 (d, $J = 0.9$ Hz, 1H, $=CHH$) (the chemical shifts were assigned through a NOE experiment); $^{13}C\{^1H\}$-NMR (C_6D_6, 125 MHz) $\delta = 0.28$ ($SiMe_3$), 3.2 ($SiMe_3$), 11.9 ($C_5(CH_3)_5$), 109.8 ($C{\equiv}CSiMe_3$), 110.9 ($=CH_2$), 112.6 ($C{\equiv}CSiMe_3$), 118.5 ($C_5(CH_3)_5$), 123.3 ($CSiMe_3$), 211.6 ($TiCC{\equiv}$), 217.5 ($TiC{=}$); EI-MS (70 eV) *m/e* (I_{rel}) 538 (11) (M^+), 465 (2) $(M - Si(CH_3)_3)^+$, 356 (2), 337 (8), 333 (7), 318 (100) $(Cp^*_2Ti)^+$, 299 (3), 283 (1), 221 (1), 200 (7), 179 (20), 159 (7), 152 (6), 135 (13) $(Cp^*)^+$, 119 (21), 105 (10), 91 (10), 73 (11), 57 (12); exact mass *m/e* 538.2931 ($C_{32}H_{50}TiSi_2$), calcd *m/e* 538.2931; IR (KBr) 3007 w, 2953 s, 2898 s, 2093 m [$\nu(C{\equiv}C)$], 2066 s, 1725 w, 1636 br w, 1563 w, 1493 m, 1450 m, 1433 m, 1376 s, 1240 s, 1111 m, 1046 m, 1022 m, 959 s, 846 vs, 755 s, 678 s, 646 s, 620 w, 596 w, 509s, 448 m, 413 s cm^{-1}. Anal. Calcd for $C_{32}H_{50}TiSi_2$: C, 71.33; H, 9.35. Found: C, 70.69; H, 9.14.

Preparation of 1,1-Bis(η^5-pentamethylcyclopentadienyl)-2-methylene-3-*tert*-butyl-4-(2-*tert*-butyl-1-ethynyl)titanacyclobutene (9d). A reaction of **7** (286.9 mg, 0.796 mmol) in 30 mL of hexane with 2,2,7,7-tetramethylocta-3,5-diyne (**13d**) (133.5 mg, 0.823 mmol) was carried out using the same procedure as in the case of **9a**. Similar workup gave **9d** as small dark red crystals (335.0 mg, 83.1%): mp 143 °C (dec); ^1H-NMR (C_6D_6, 500 MHz) δ 1.23 (s, 9H, $\equiv CC(CH_3)_3$), 1.58 (s, 9H, $=CC(CH_3)_3$), 1.78 (s, 30H, $C_5(CH_3)_5$), 4.19 (d, $J = 0.8$ Hz, 1H, $=CHH$), 5.90 (d, $J = 0.7$ Hz, 1H, $=CHH$); $^{13}C\{^1H\}$ NMR (C_6D_6, 125 MHz) δ 12.1 ($C_5(CH_3)_3$), 29.4 ($C{\equiv}CC(CH_3)_3$), 31.2 ($C{\equiv}CC(CH_3)_3$), 32.4 ($C(CH_3)_3$), 39.0 ($C(CH_3)_3$), 83.8 ($C{\equiv}CC(CH_3)_3$), 104.7 ($=CH_2$), 120.0 ($CC(CH_3)_3$), 121.0 ($C_5(CH_3)_5$), 129.5 ($C{\equiv}CC(CH_3)_3$), 182.9 ($TiCC{\equiv}$), 203.5 ($TiC{=}$); EI-MS (70 eV) *m/e* (I_{rel}) 506 (12) (M^+), 449 (3) $(M - C(CH_3)_3)^+$, 362 (6), 335 (3), 318 (55) $(Cp^*_2Ti)^+$, 270 (5), 267 (5), 200 (29), 178 (5), 162 (54), 152 (44), 147 (78), 137 (68), 119 (100), 105 (60), 91 (60), 77 (28), 67 (13), 57 (53); exact mass *m/e* 506.3393 ($C_{34}H_{50}Ti$), calcd *m/e* 506.3392; IR (KBr) 2971 vs, 2942 s, 2898 vs, 2861 s, 2725 w, 2162 m [$\nu(C{\equiv}C)$], 1715 w, 1637 br m, 1556 m, 1494 m, 1456 s, 1377 s, 1357 s, 1261 s, 1232 w, 1199 m, 1068 m, 1022 s, 853 s, 806 w, 694 w, 591 w, 525 w, 499 w, 453 s

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Table 6. Crystal Data and Parameters of Structure Refinement for 9c

formula	$C_{32}H_{50}TiSi_2$	temp (°C)	−40
fw	538.83	radiation	Mo Kα
space group (No.)	$P\bar{1}$ (2)	λ (Å)	0.7107
cryst data			
a (Å)	12.123(3)	cryst dimens (mm^{-3})	0.6 × 0.4 × 0.4
b (Å)	13.884(5)	measd reflcns	9017
c (Å)	10.299(3)	scan range (deg)	$3 \le \theta \le 27$
α (deg)	99.08(3)	unique obsd reflcns ($I > 1.0\sigma(I)$)	4445
β (deg)	110.71(2)		
γ (deg)	92.24(2)	params refined	316
V (Å^3)	1592.6(9)	agreement factors	$R = 0.084$
Z	2		$R_w = 0.078$
d_{calc} (g cm^{-3})	1.124		GOF = 2.145
μ (cm^{-1})	3.55	res el density (e Å^{-3})	0.89

cm^{-1}. Anal. Calcd for $C_{34}H_{50}Ti$: C, 80.60; H, 9.95. Found: C 80.80; H 10.14.

Reaction of 7 and 13e. A reaction of **7** (287.0 mg, 0.796 mmol) in 30 mL of hexane with **13e** (149.0 mg, 0.835 mmol) was carried out using the same procedure as in the case of **9a**. Similar workup gave a mixture of **9e** (90%) and **9e′** (10%) as purple crystals (314.4 mg, 75.6%): mp 152−153 °C (dec); **9e** ^{1}H-NMR (C_6D_6, 500 MHz) δ 1.72 (s, 30H, $C_5(C\mathit{H}_3)_5$), 1.29 (s, 6H, ≡$CC(C\mathit{H}_3)_3$), 0.58 (s, 6H, $Si(C\mathit{H}_3)_3$), 4.86 (s, 1H, =$C\mathit{H}H$), 5.99 (s,1H, =$CH\mathit{H}$); $^{13}C\{^1H\}$ NMR (C_6D_6, 125 MHz) δ 31.2 (C≡$CC(\mathit{C}H_3)_3$), 3.3 ($Si(\mathit{C}H_3)_3$), 11.9 ($C_5(\mathit{C}H_3)_5$), 29.5 ($\mathit{C}(CH_3)_3$), 83.8 (C≡$\mathit{C}C(CH_3)_3$), 109.3 (=$\mathit{C}H_2$), 105.4 (C≡$CC(CH_3)_3$), 118.0 ($\mathit{C}_5(CH_3)_5$), 121.4 (=$\mathit{C}Si(CH_3)_3$), 214.9 (TiCC≡), 218.3 (TiC=); **9e′** ^{1}H-NMR (C_6D_6, 500 MHz) δ 1.77 (s, 30H, $C_5(C\mathit{H}_3)_5$), 1.57 (s, 6H, =$CC(C\mathit{H}_3)_3$), 0.25 (s, 6H, $Si(C\mathit{H}_3)_3$), 4.20 (s, 1H, =$C\mathit{H}H$), 5.92 (s, 1H, =$CH\mathit{H}$); EI-MS (70 eV) m/e (I_{rel}) 522 (0.94) (M^+), 465 (0.04) $(M - CMe_3)^+$, 449 (0.02) $(M - SiMe_3)^+$, 338 (7), 318 (4) $(Cp^*{}_2Ti)^+$, 283 (2), 218 (4), 200 (4), 178 (20), 163 (100), 152 (10), 147 (52), 135 (18) $(Cp^*)^+$, 119 (30), 105 (16), 91 (16), 73 (9); exact mass m/e 522.3158 ($C_{33}H_{50}SiTi$), calcd m/e 522.3161; IR (KBr) 3004 w, 2970 vs, 2900 vs, 2067 m [ν(C≡C)], 1819 w, 1713, w, 1562 w, 1494 w, 1451 s, 1434 s, 1376 s, 1458 w, 1257 s, 1242 s, 1198 w, 1114 m, 1065 w, 1022 s, 959 s, 844 vs, 754 m, 687 m, 646 s, 511 m, 491 w, 479 m, 409 s cm^{-1}.

***Ab initio* and Modeling Calculations.** The electron densities were calculated from fully optimized structures of the diynes **13a**−**e**. The geometry optimizations have been carried out at the Hartree−Fock (HF) level of theory with the 3-21G(*) standard basis set. The symmetries were restricted to D_{3d} for **13c**,**d** and to C_3 for **13e**. The characterization of the minima was effected by evaluating the second energy derivative matrix. The calculations have been carried out using the program packages SPARTAN 3.1[24] on IBM RS6000-355 and GAMESS[25] on CONVEX-C3420. The relative energies of the titanacyclobutenes **9a**−**e** and **11a**−**e** were calculated with the MMX force field.[19] The ring carbon atoms of the cyclopentadienyl groups were defined as aromatic carbon atom type. The cyclopentadienyl ring was coordinated to the titanium using the COATM command, and the titanium was defined as a saturated 18-electron metal having zero charge. The optimized structures were checked for further minima by use of the dihedral driver of PCMODEL at the CMe_3 and the $SiMe_3$ groups. We were not able to calculate **9c** and **11c** with the MMX force field, since the SiC≡ bond is not parametrized in the program.

X-ray Structure Determination of 9c. Geometry and intensity data were collected on an Enraf-Nonius CAD4 diffractometer equipped with a graphite monochromator. A summary of crystallographic data, data collection, and refinement parameters is given in Table 6. Data were collected on the $+h,\pm k,\pm l$ diffraction hemisphere and, in part, on the $-h,\pm k,\pm l$ hemisphere and averaged after an empirical absorption correction by azimuthal scans. The structure was solved with direct methods (SHELXS 86) and refined with the SDP package.[26] All non-hydrogen atoms were refined (full matrix) anisotropically, and all hydrogen atoms were treated as riding with an idealized geometry (C−H = 0.98 Å, $B_{iso}(H) = 1.3B_{iso}(C)$). A statistical weighting scheme $w^{-1} = \sigma^2(F_o)$ was used. Pronounced anisotropic displacement parameters for the methyl C atoms of the Cp* rings indicate a certain degree of libration disorder for the ligands and are responsible for the relatively high R and GOF values encountered. Further details of the crystal structure investigations are available on request from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, FRG, on quoting the depository numbers CSD-405669 (**9c**).

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Supporting Information Available: Tables giving positional and thermal parameters and estimated standard deviations for all atoms and bond distances and angles for **9c** and NMR spectra of **9a** and **9e**/**9e′** (11 pages). Ordering information is given on any current masthead page.

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