1176 *Organometallics* **1996,** *15,* 1176−1187

Reactivity of Acetylenes toward the Titanocene Vinylidene Fragment [$Cp^*_2Ti{=}C{=}CH_2$]. Formation of Methylenetitanacyclobutenes and Vinyltitanium Acetylides. Crystal and Molecular Structures of $Cp^*_2TiCR'{=}CR''C{=}CH_2$ ($R' = R'' = CH_3$; $R' = SiMe_3$, $R'' = C_6H_5$) and $Cp^*_2Ti(CH{=}CH_2)(C{\equiv}CPh)$

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The titanocene vinylidene intermediate [$Cp^*_2Ti{=}C{=}CH_2$] (**4**) (Cp*, $C_5(CH_3)_5$), formed by ethylene or methane elimination from $Cp^*_2TiCH_2CH_2C{=}CH_2$ (**3**) and $Cp^*_2Ti(CH{=}CH_2)(CH_3)$ (**11**), respectively, reacts with symmetrical alkynes such as acetylene (**12a**), 2-butyne (**12b**), 1,2-diphenylacetylene (**12c**), 1,2-bis(trimethylsilyl)acetylene (**12d**), and 1,2-bis(tri-*n*-butylstannyl)acetylene (**12e**) by a [2 + 2] cycloaddition to give metallacyclobutenes $Cp^*_2TiCR{=}CRC{=}CH_2$ (**8a**−**e**). When unsymmetrical alkynes are used, such as 2-pentyne (**13g**), 2,4-hexadiyne (**13h**), 1,4-diphenyl-1,3-butadiyne (**13i**), 1-phenyl-1-propyne (**13j**), or 1-(trimethylsilyl)-2-phenylacetylene (**13k**), different regioisomers can be isolated. For the reaction products of **4** with **13g** and **13j**, kinetic and thermodynamic products can be distinguished. In reactions of 1-pentyne (**13f**) and **4**, a 1:1.5 mixture of the [2 + 2] cycloaddition product $Cp^*_2TiCH{=}C(n\text{Pr})C{=}CH_2$ (**17f**) and the alkyne C−H bond activation product, $Cp^*_2Ti(CH{=}CH_2)(C{\equiv}C\text{-}n\text{Pr})$ (**19f**), is formed. By using stronger acidic acetylenes, like phenylacetylene (**13l**), or terminal acetylenes with bulky substituents, such as 2,2-dimethyl-3-butyne (**13m**) or (trimethylsilyl)acetylene (**13n**), the vinyl acetylides $Cp^*_2Ti(CH{=}CH_2)(C{\equiv}CR)$ [R = Ph (**19l**), *t*-Bu (**19m**), $SiMe_3$ (**19n**)] are isolated in high yields. The structures of $Cp^*_2TiC(CH_3){=}C(CH_3)C{=}CH_2$ (**8b**) and $Cp^*_2TiC(SiMe_3){=}C(Ph)C{=}CH_2$ (**17k**) were determined. The pseudotetrahedral molecules contain planar cyclobutene rings. The X-ray structure of **19l** is presented. The regioselectivity of the formation of **17** and its regioisomer **16**, using unsymmetrically substituted acetylenes, is attributed to the polarity of the C≡C bond, on the basis of ^{13}C NMR data. The reactivity of the methylenetitanacyclobutenes depends on the substituents of the alkynes. The formation of *trans*-poly(acetylene) occurs via **8a** with an excess of acetylene. Analogous reactions of **8b**,**c** and substituted alkynes are not successful. The isomerization of the titanacyclobutenes **16** → **17** indicates a cycloreversion. Selective insertion reactions of **8b** and **8c** with $C_6H_{11}NC$ are observed in the TiC(R)=C(R) σ-bond opposite the *exo*-methylene group, forming five-membered rings $Cp^*_2TiC({=}NC_6H_{11})C(R){=}C(R)C{=}CH_2$ [R = Me (**25b**), Ph (**25c**)].

Introduction

While much work has been devoted to titanacyclobutanes **1**[1] as efficient starting molecules of a titanium methylene fragment **2**,[2] the homologous titana-[3] **4** or other metallaallene fragments of electron-poor metals[4,5] have attracted less attention. This is all the more surprising, considering that the titanium vinylidene species **4** (L_n = Cp^*_2) can easily be generated from a methylenetitanacyclobutane **3**[6] obtained via a $Cp^*_2Ti(CH{=}CH_2)_2$ intermediate in quantitative yield.[6c,7] α-H-elimination processes from alkyl derivatives, which are suitable for the formation of intermediates of type **2**,[8] are also suitable for alkenyl derivatives in a selective manner, leading to intermediates **4**.[9]

In comparing the subsequent products of **2** and **4**, respectively, in contrast to the behavior of **2**, by the reaction of **3** → **4**, a large scale yield of [2 + 2] cycloaddition products can be isolated by using functionalized substrates. First of all, cycloaddition products **5** and **6**, synthesized by trapping **4** with cumulenes,[6a,10] transition metal carbonyls,[9b,11] nitriles, and phosphaalkynes,[12] are of high thermal stability due to the stabilization effect of the α-*exo*-methylene group, the formation of stronger $C_{sp^2}{-}C_{sp^2}$ bonds in the four-membered ring, and the lowered electrophilicity of the

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[⊗] Abstract published in *Advance ACS Abstracts,* February 1, 1996.

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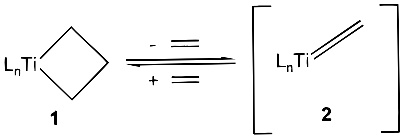
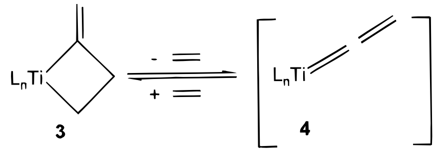
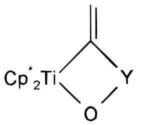


1 **2**



3 **4**

titanium center by the strongly basic Cp* ligands.[13] With cumulenes and heterocumulenes, monomeric metallaoxetanes exhibiting planar ring geometry are obtained for the first time.[6a,10,14] Acidic compounds such as alcohols, water, or ketones react with the strongly nucleophilic α-C-atom of the titanium vinylidene **4** in a selective manner, forming vinyl derivatives **7**.[15]



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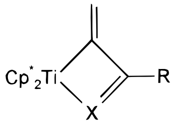
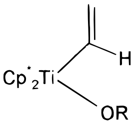
a) Y: C=O, C=NR, C=CR_2
b) Y: C=ML_n



6

a) X: N
b) X: P



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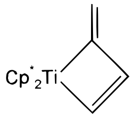

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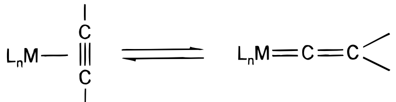
On the other hand, typical proton shift reactions of the vinylidene fragment are observed in bimetallic oxetanes **5b**, leading, by a surprising vinylidene−acetylene rearrangement (**10** → **9**), to oxatitanacyclopentene complexes,[9b] illustrating typical transformations of the vinylidene $C{=}CH_2$ molecule in the gas phase.[16] The interest in the acetylene−vinylidene rearrangement itself can be ascribed to the fact that the process (**9** → **10**) is discussed as the first step in the favorite mechanisms of the formation of poly(acetylene)s.[17] From this point of view in particular, we will report the behavior of the intermediate **4** toward terminal and internal acetylenes and will investigate the synthesis of complexes of type **8**. Metallacyclobutenes of the titanium group without the α-methylene group are known by reaction of cyclopropenes with low-valent metal complexes,[18] by reaction of carbenoid titanium derivatives, including the Tebbe reagent and derivatives thereof, with acetylenes,[2a,8e,8f,19] or as intermediates in organic synthesis.[20] Alternative mechanisms for the formation of poly(acetylene)s are also discussed via a carbene−metallacyclobutene−vinylcar-



9 **10**

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bene route[21] or via insertion reactions in transition metal σ-bonds.[22]

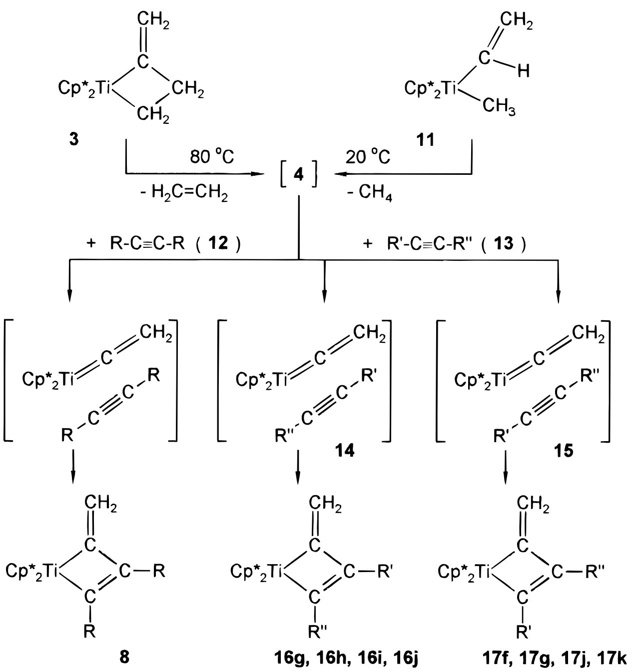
Results and Discussion

The metallacyclobutane **3** and the vinylmethyl derivative **11**, respectively, react with 1 equiv of the symmetrical acetylenes **12a**–**e** at 80 °C in a few minutes under liberation of ethylene (from **3**) or at room temperature by liberation of methane (from **11**) to give the metallacyclobutenes **8**. Complexes **8** are formed in nearly quantitative yields (NMR) and can be isolated as dark red crystals of high thermal stability [**8b**, mp 173 °C (dec); **8c**, mp 196 °C (dec)] or in the case of **8a**,**d**,**e** as waxy solids. These species are interesting in that each of the metallacyclobutene carbons is sp^2 hybridized. The mass spectra of **8** exhibit the expected molecular peaks. With the exception of **8d**, metatheses-like fragmentation behavior similar to that of metallacyclobutanes is not observed in the mass spectrometer.[6b]

To investigate the regiochemistry of the cycloaddition between **4** and **12**, asymmetrical substituted alkynes **13** were used in reactions of **3** as well as **11** (see Scheme 1). By using **13f**–**k**, mixtures of regioisomers as well as sterically pure compounds **16**/**17** are formed via **14** and **15**. By using butadiynes **13h** and **13i**, products with the acetylide substituent in the α-position (**16h**, **16i**) are formed without exception. In the reaction of **13k** with **4**, only the isomer **17** exhibiting the SiMe$_3$ group in the α-position is formed. Yields and product ratios are summarized in Table 1. ^{1}H and ^{13}C NMR data of the titanacyclobutenes **8**, **16**, and **17** are listed in Table 2.

The formation of **8a** and **17f** shows that terminal acetylenes are also able to form metallacyclobutenes. Types of products and ratios thereof depend on the nature of the alkyne used. By using the unsubstituted acetylene **12a** in a stoichiometric amount, the metallacyclobutene **8a** is the only isolable reaction product. The alternative possible formation of a vinyltitanium acetylide **19a** is not observed. However, by using **13f**, a 1:1.5 mixture of the metallacyclobutene **17f** (R″ = *n*-Pr in *β*-position) and the alkyne C–H bond activation product **19f** is obtained. Reactions of phenylacetylene **13l** or other terminal alkynes (**13m**, **13n**) with **4** lead to the vinyl acetylides **19l**–**n** without the formation of any other products.

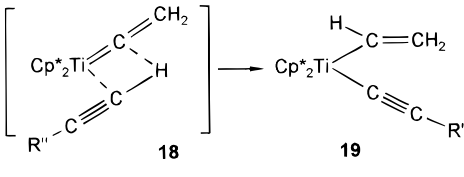
Scheme 1



R:	8
H	a
CH$_3$	b
Ph	c
SiMe$_3$	d
SnBu$_3$	e

R′:	R″:	16 / 17
H	n-Pr	f
Me	Et	g
Me	C≡CCH$_3$	h
Ph	C≡CPh	i
Me	Ph	j
SiMe$_3$	Ph	k

The reasons for the exclusive formation of **19l**–**n** in contrast to **19f** and **8a** can be explained by the high CH acidity of the acetylenes used;[23] moreover, it can be proposed that bulky substituents, like *tert*-butyl (**13m**) and trimethylsilyl (**13n**) lead to a geometry (**18**) that finally results in C–H bond activation. The use of PhC≡CD, which exclusively forms Cp*$_2$Ti(CD=CH$_2$)(C≡CPh) (**19l**–**D**), undoubtedly proves the alkyne to be the proton source. ^{1}H and ^{13}C NMR data of the vinyltitanium acetylides **19** are listed in Table 4.



R″:	
n-Pr	f
Ph	l
t-Bu	m
SiMe$_3$	n

The two different chemical shifts for the protons of the *exo*-methylene group of **8**, **16**, and **17** in the ^{1}H NMR spectra appear to be a characteristic feature of the new complexes and similar metallacyclic structures.[6b,9,12] The chemical shifts were assigned through NOE experiments. In all cases, the high-field signal is assigned to the *endo*-position H1 and the low-field signal to the *exo*-position H2. Moreover, the chemical shifts of the ring carbon atoms in the ^{13}C NMR spectra are in accordance with two titanium σ-bonded sp^2 carbon atoms. The low-

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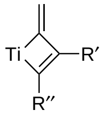
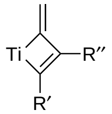
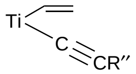
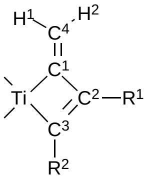
Table 1. Product Ratios in Reactions of 4 with Acetylenes

Acetylene			product ratios (%)		
R′C≡CR″	R′	R″	 **16**	 **17**	 **19**
12a	H		100[a]		0
12b	CH_3		100[a]		0
12c	Ph		100[a]		0
12d	$SiMe_3$		100[a]		0
12e	$SnBu_3$		100[a]		0
13f	H	*n*-Pr	0	40	60
13g	Me	Et[b]	25	75	
	ratio after 12 h, 80 °C		5	95	
13h	Me	C≡CMe	100	0	
13i	Ph	C≡CPh	100	0	
13j	Me	Ph[b]	43	57	
	ratio after 42 h, 80 °C		31	69	
13k	$SiMe_3$	Ph	0	100	
13l	H	Ph	0	0	100
13m	H	*t*-Bu	0	0	100
13n	H	$SiMe_3$	0	0	100

[a] Products **8a**−**e**. [b] Measured at room temperature after 1 h.

Table 2. NMR Data for the $\overline{\text{TiCR=CRC}}$=$CH_2$ Ring in Metallacyclobutene Complexes[a]

	^1H NMR data (ppm) (J_{HH} (Hz))					^{13}C NMR data				
	Cp*	H1 (endo)	H2 (exo)	R^1	R^2	Cp*	C1	C2	C3	C4
8a	1.65 (s)	4.79 (dd, 4.58; 2.24)	5.66 (m)	6.68 (ddd, 12.1, 2.52, 1.75)	7.81 (ddd, 12.1, 2.22, 1.15)	12.0 118.0	214.3	100.4	207.0	109.3
8b	1.67 (s)	4.57 (br s)	5.65 (dm, 0.62)	1.76 (d, 0.91)	2.01 (d, 0.61)	11.9 118.9	213.6	99.4	210.6	101.3
8c	1.73 (s)	4.61 (d, 1.22)	5.69 (d, 1.22)	6.78−7.42[b]		12.4 120.8	211.4	113.3	205.3	106.7
8d	1.63 (s)	5.12 (s)	6.14 (s)	0.47 (s)	0.53 (s)					
8e	1.67 (s)	5.13 (s)	5.85 (s)	0.93−1.68[b]		12.4 115.8	214.5	115.1	212.9	116.3
17f	1.66 (s)	4.57 (m)	5.73 (m)	1.07; 2.08; 2.23[b]	7.39 (m)	11.9 118.9	210.4	111.1	199.3	102.4
16g	1.67 (s)	4.56 (s)	5.68 (s)	1.73 (s)	2.51 (q, 7.43) 1.13 (t, 7.48)					
17g	1.67 (s)	4.54 (s)	5.66 (s)	2.31 (q, 7.63) 1.15 (t, 7.63)	1.99 (s)	11.9 118.8	212.0	105.1	210.2	100.8
16h	1.75 (s)	4.55 (d, 1.53)	5.71 (d, 1.53)	2.10 (s)	2.03 (s)	11.9 120.2	210.5	104.2	185.9	104.8
16i	1.78 (s)	4.57 (d, 1.53)	5.98 (d, 1.22)	6.83−7.81[b]		12.0 121.3	205.4	126.7	182.7	108.4
16j	1.66 (s)	4.62 (d, 0.91)	5.78 (d, 1.22)	2.10 (s)	6.96−7.46[b]	12.3 120.1	215.2	105.0	204.7	103.8
17j	1.72 (s)	4.54 (d, 0.61)	5.55 (d, 0.61)	7.12−7.38[b]	2.02 (s)	12.0 119.6	211.8	110.2	210.7	104.3
17k	1.75 (s)	4.71 (d, 1.53)	5.37 (d, 1.22)	7.11; 7.24; 7.36[b]	0.14 (s)	12.6 119.9	218.0	129.8	215.2	108.6

[a] Listed in ppm vs TMS; solvent was C_6D_6 and temperature = 25 °C. [b] For details see the Experimental Section.

field signals are consistent with the C1-atom (205−218 ppm), whereas C3 is shifted to higher fields δC1−δC3: **8**, 4−7; **16**, 10−25; **17**, 2−11 ppm). The largest shift is observed for the cycloaddition products with butadiynes exhibiting the C3 signal at 185.9 (**16h**) and 182.7 (**16i**) ppm.

The structures of **8b** and **17k** were confirmed by X-ray structure determination. Ortep plots are shown in Figures 1 and 2, and relevant bond distances and angles are given in Table 3. The geometries of **8b** and **17k** show a planar titanacyclobutene ring. The greatest deviations from the mean plane are 0.010(3) Å for **8b** and 0.019(5) Å for **17k**. The solid state structural data for complex **8b** are consistent with a metallacycle formalism. Partial ring opening, suggesting a fragmentation toward titanium vinylidene alkyne structures (**14**, **15**), comparable to trimethylsilyl-substituted titanacyclobutenes,[19b] can be denied for **8b**. The Ti−C1 bonds in **8b** and **17k** are identical in the range of standard deviation, but they are longer as in the titanacyclobutane **3** (2.068(6) Å)[6b] and shorter as in aza- and phosphatitanacyclobutenes (**6a**, 2.134(2); **6b**, 2.161(5) Å).[12]

Alternating bond lengths in the sequence C4−C1−C2−C3, comparable to a conjugated π-bond system and similar to free butadiene, are especially observed in **8b**. For the exocyclic C1−C4 distance (1.377(4) Å), the

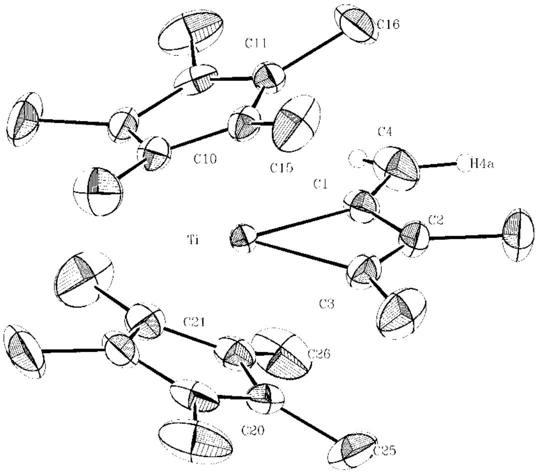


Figure 1. Ortep drawing of $\mathrm{Cp^*_2TiC(CH_3){=}C(CH_3)C{=}CH_2}$ (**8b**) (30% ellipsoids).[41]

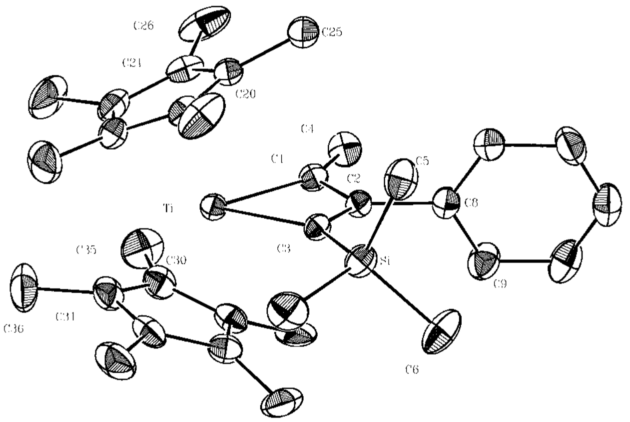


Figure 2. Ortep drawing of $\mathrm{Cp^*_2TiC(SiMe_3){=}C(Ph)C{=}CH_2}$ (**17k**) (30% ellipsoids).[41]

Table 3. Selected Bond Distances (Å) and Angles (deg) in $\mathrm{Cp^*_2TiC(CH_3){=}C(CH_3)C{=}CH_2}$ (8b) and in $\mathrm{Cp^*_2TiC(SiMe_3){=}C(Ph)C{=}CH_2}$ (17k)

	8b	17k		8b	17k
Ti−C1	2.104(3)	2.102(6)	C3−Ti−C1	68.0(1)	69.3(2)
Ti−C3	2.109(3)	2.173(6)	Cp−Ti−Cp	139.8	137.9
Ti−Cp$_1$[a]	2.125	2.135	Ti−C1−C2	87.8(2)	86.5(3)
Ti−Cp$_2$[a]	2.120	2.124	Ti−C1−C4	146.6(3)	149.0(5)
Ti···C2	2.500	2.507(6)	C1−C2−C3	114.8(2)	116.7(5)
C1−C4	1.377(4)	1.322(8)	C2−C3−Ti	89.4(2)	87.4(4)
C1−C2	1.434(4)	1.502(7)	C6−C3−Ti	145.2(2)	
C2−C3	1.365(4)	1.352(8)	Si−C3−Ti		148.2(3)
C2−C5	1.528(4)		C1−C2−C8		117.4(5)
C2−C8		1.511(8)			
C3−C6	1.474(4)				
C3−Si		1.870(6)			

[a] Cp$_{1/2}$, centroids of the cyclopentadienyl ligands.

longest value for all type **5** and **6** complexes is found [**6a**, 1.337(3); **6b**, 1.326(8);[12] **5a** (Y, C=NC$_6$H$_{11}$), 1.325(4);[10] **5a** (Y, C=C(C$_6$H$_5$)$_2$), 1.318(8);[24] **3**, 1.321(10) Å[6b]] in the case of **8b**. This observation is in agreement with the short C1−C2 bond, illustrating a conjugative effect in the carbocyclic part of the metallacyclobutene ring. The C1−C2 bond is shorter than expected for the distance of two C$_{sp^2}$ centers.[25] These structural data confirm the high thermal stability of **8b** and can be attributed to a discrimination of metathesis-like ring opening of the metallacyclobutene (vide infra). The angles are in the expected range for a planar metallacycle exhibiting C$_{sp^2}$-atoms [C1−Ti−C3 angles: **8b**, 68.0(1)°; **17k**, 69.3(2)°; **6a**, 67.85(8)°; **6b**, 68.2(1)°;[12] **5a** (Y, C=NC$_6$H$_{11}$), 67.6(1)°;[10] **5a** (Y, C=C(C$_6$H$_5$)$_2$), 67.5(2)° [24]]. A larger value is found in the titanacyclobutane **3** (83.1(4)°).[6b]

However, there are differences in the solid state structures of **8b** and **17k** to take into consideration. While for **8b**, characteristic alternating C−C bond distances in the sequence C4−C1−C2−C3 are discussed (vide supra), in the case of **17k** an elongation of the C1−C2 bond of 1.502(7) Å is found, which is comparable to the C$_{sp^2}$−C$_{sp^3}$ in **3** (1.521(10) Å).[6b] The significantly longer Ti−C3 distance in the solid state of **17k** (2.173(6) Å) is in agreement with our observation of a metathesis-like ring opening (**16**/**17** → **14**/**15**) for the substituted titanacyclobutenes compared with less substituted derivatives **8a** or **8b**.

The NMR data of the vinyltitanium acetylides (see Table 4) are in the expected range of σ-bonded vinyl[15a] and σ-bonded acetylide[26] ligands. The constitution of **19l** was confirmed by X-ray structure determination. The high thermal parameters of the Cp* carbon atoms indicate a serious rotational disorder around the C_5-axis. Due to the low diffraction intensity of the crystals, the data set did not allow for the resolution of this disorder. Therefore, all bond distances and angles show high estimated standard deviations and will not be discussed in this paper. However, the constitution of **19l** is undoubtedly proved by the results of the X-ray structure determination. A Schakal plot is shown in Figure 3. The vinyl group is exactly located in the main plane of the metallocene fragment, exhibiting a orientation of the α-C−H bond in the direction toward the lateral side of the molecule.[27] For intramolecular α-H-transformations, as observed by Teuben in a high-temperature reaction (170 °C) of a single vinyltitanium acetylide,[9c] a rotation of the vinyl group is proposed to be the first step.

Reactivity of Titanacyclobutenes. Generally the reactivity of metallacyclobutenes can be explained by different mechanisms starting from structure B. Cycloreversion processes are discussed by the reaction B → A;[19c,d,20a] the participation of a free vinylidene during the formation of type **8** metallacyclobutenes was proved by Grubbs in a kinetic study,[2b] whereas the formation of vinylcarbenes C and D are proved for tantalum,[21a] tungsten,[28] or metal complexes of the titanium group.[18,29]

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[24] Beckhaus, R. Unpublished results.

[25] C$_{sp^2}$−C$_{sp^2}$ distance expected for =C−C=: 1.474 Å, from the covalent radii. Bastiansen, O.; Traetteberg, M. *Tetrahedron* **1962**, *17*, 147−154.

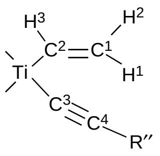
[26] Lang, H.; Seyferth, D. *Z. Naturforsch.* **1990**, *45b*, 212−220.

[27] Different rotamers of the vinyl group are discussed by Gleiter and Erker: (a) Erker, G.; Zwettler, R.; Krüger, C.; Hyla-Kryspin, I.; Gleiter, R. *Organometallics* **1990**, *9*, 524−530. (b) Hyla-Kryspin, I.; Gleiter, R.; Krüger, C.; Zwettler, R.; Erker, G. *Organometallics* **1990**, *9*, 517−523. (c) Gleiter, R.; Hyla-Kryspin, I.; Niu, S.; Erker, G. *Angew. Chem.* **1993**, *105*, 753−755.

[28] Macomber, D. W. *Organometallics* **1984**, *3*, 1589−1591.

[29] Binger, P.; Müller, P.; Benn, R.; Mynott, R. *Angew. Chem.* **1989**, *101*, 647−648.

Table 4. NMR Data for the Vinyltitanium Acetylides 19[a]



	^{1}H NMR data (ppm) (J_{HH} (Hz))				^{13}C NMR data				
	Cp*	H1	H2	H3	Cp*	C1	C2	C3	C4
19f	1.85	4.95 (trm, 11.3)	5.66 (m)		12.8 121.5	117.1	213.9	151.3	117.6
19l	1.85	5.03 (dd, 17.2; 4.7)	5.67 (dd, 14.0; 4.6)	5.61 (dd, 17.4; 14.0)	12.7[b] 122.4	116.8	214.9	162.0	118.3
19l-D	1.84	5.01 (d, 3.7)	5.66 (d, 3.9)						
19m	1.85[b]	4.47 (dd, 18.0; 4.6)	5.13 (dd, 14.0; 4.6)	5.43 (dd, 18.0; 14.7)	12.9 121.4	117.3	213.9	149.1	125.1
19n	1.81	4.97 (dd, 17.9; 4.4)	5.63 (dd, 14.0; 4.3)	5.49 (dd, 18.0; 14.0)	12.8 121.9	117.5	214.7	183.4	119.7

[a] Listed in ppm vs TMS; solvent was C_6D_6 and temperature = 25 °C. [b] Solvent was THF-d_8.

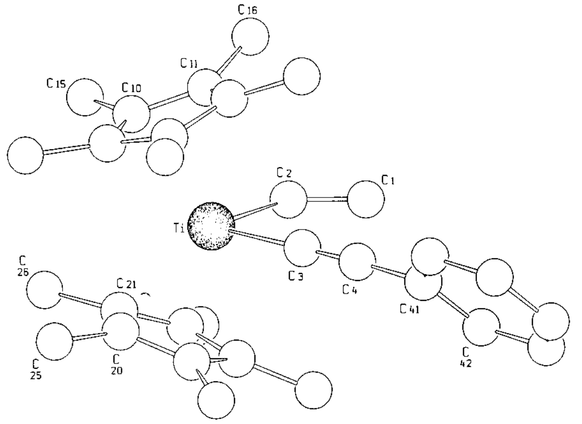
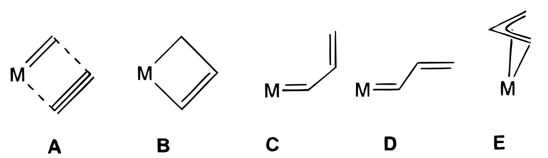


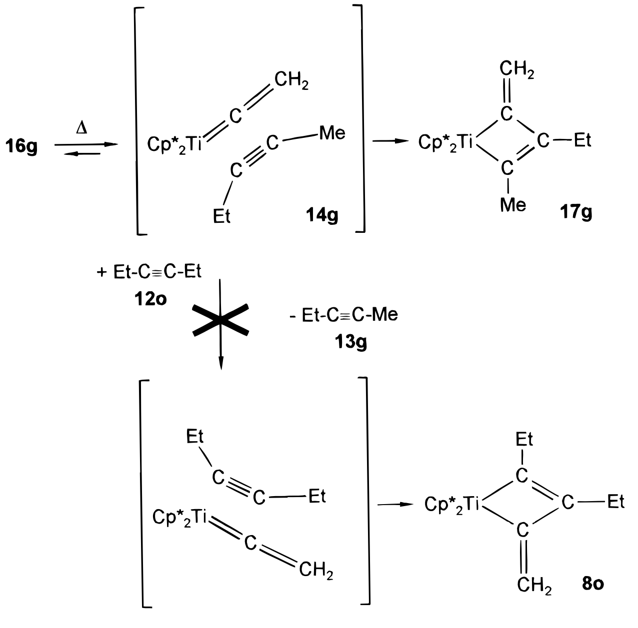
Figure 3. Schakal drawing of Cp*$_2$Ti(CH=CH$_2$)(C≡CPh) (**19l**).[42]

However, η^3-vinylcarbenes E, as discussed during the reaction course of the Doetz reaction,[30] can be ruled out for metallocene complexes of electron-poor metals due to steric reasons.



For the titanacyclobutene complexes **8**, exhibiting an α-methylene group, different reaction types are found. Slow rearrangement at 80 °C of **16g** and **16j**, forming the thermodynamic products **17g** and **17j**, can be attributed to a ring-opening reaction of the metathesis type. Attempts to exchange the alkyne during these rearrangements failed. By heating a mixture of 25% **16g** and 75% **17g** in the presence of excess 3-hexyne (**12o**), only a lowering of the content of **16g** and an increasing of **17g** to a 15%:85% ratio occurs, without the exchange of 2-pentyne by 3-hexyne and additioinal formation of **8o**.

In contrast to the behavior of the titanacyclobutene $Cp_2TiCH_2C(SiMe_3)=CSiMe_3$, which undergoes a fast exchange of bis(trimethylsilyl)acetylene by diphenylacetylene,[19c] in the case of **8d**, liberation of the alkyne **12d** occurs in solution followed by intramolecular C−H bond activation of the Cp* ligand to form the dark green vinylfulvenetitanium complex, Cp*(Fv)TiCH=CH$_2$,[15a] which does not react with additional alkynes either by cycloaddition or by insertion in the titanium−fulvene bond. The orientation of the substituents in the cyclobutenes can be attributed to the polarity of the alkyne molecule and the strongly nucleophilic α-C-atom in the vinylidene **4** [$Ti^{\delta+}=C^{\delta-}=CH_2$].[6b] The polarities of the alkynes can be deduced from the ^{13}C NMR chemical shift of the carbon atoms, due to the correlation of σ_p terms and the orbital expansion.[31] The more electron-rich carbon atoms are shifted to higher fields and the more electron-poor carbon atoms to lower fields. Due to the polarity of the titanium vinylidene fragment **4**, the alkyne usually coordinates as expected in **14**/**15** ($Ti^{\delta+}\cdots C^{\delta-}{}_{alkyne}$). The chemical shifts of the alkynes used are listed in Table 5. If the differences Δ are higher than 7 ppm, only one regioisomer is found at room temperature (**16f**, **16h**, **16i**, **17k**) exhibiting the carbon atom with higher electron density in the α-position.[32] If the Δ value is in the range below 7 ppm, the formation of mixtures of regioisomers is observed (**16**/**17g**, **16**/**17j**). Only for alkynes exhibiting small differ-



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(30) (a) Hofmann, P.; Hämmerle, M. *Angew. Chem.* **1989**, *101*, 94−942; *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 908−910. (b) Hofmann, P.; Hämmerle, M.; Unfried, G. *New J. Chem.* **1991**, *15*, 769−789.

(31) Günther, H. *NMR-Spektroskopie,* 3rd ed.; Georg Thieme Verlag: Stuttgart, New York, 1992.

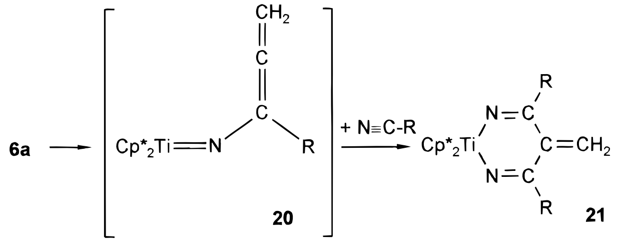
Table 5. Selected ^{13}C NMR Data of Alkynes Used in Cycloaddition with the Titanium Vinylidene Intermediate 4

	R′C′≡C″R″		^{13}C data			
	R′	R″	δC′	δC″	Δ[a]	ref
13f	H	*n*-Pr	66.7	81.8	15.1	37
13g	Me	Et	74.2	80.3	6.1	37
13h	Me	C≡CMe	72.0	64.7	7.3	38
13i	Ph	C≡CPh	83.0	75.7	7.3	39
13j	Me	Ph	86.1	80.5	5.6	37
13k	SiMe$_3$	Ph	94.2	105.8	11.6	37

[a] $\Delta = |\delta C' - \delta C''|$.

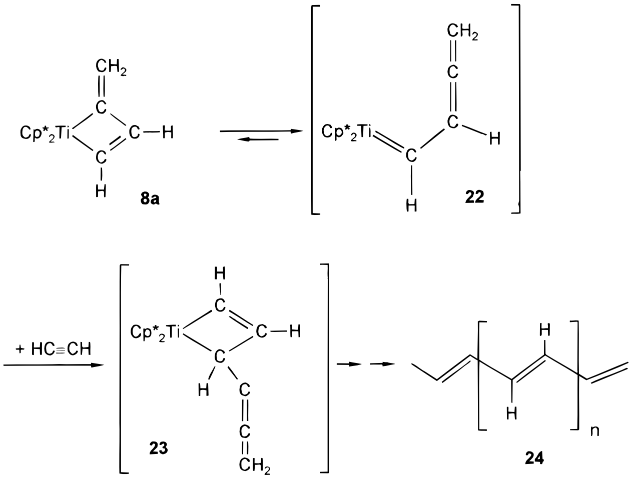
ences in the polarity of the C≡C triple bond are isomerization reactions observed. The ratio of these isomers depends on the temperature. At higher temperatures, isomers with the more bulky substituent in the β-position are preferred. Similar behavior is observed by using the heteroalkyne *t*-BuC≡P, forming a mixture of two regioisomers, $Cp^*_2TiC(tBu){=}PC{=}CH_2$ and **6b**, as the main product.[12]

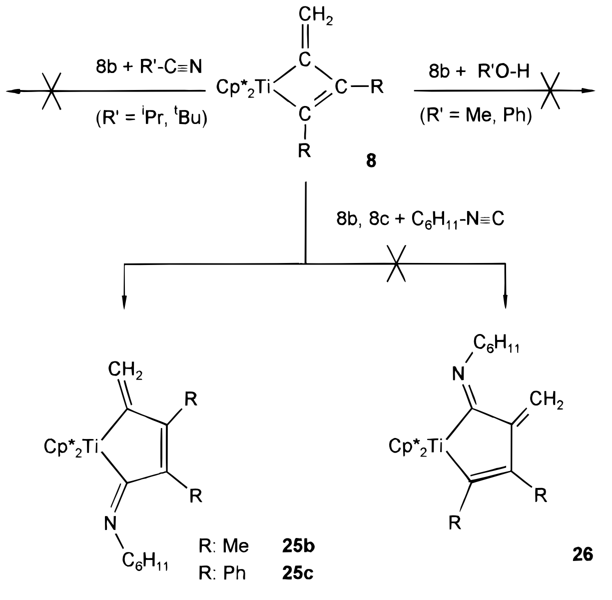
For metallacyclobutenes, the reactivity B → C is also observed in some cases.[19b] Heterocyclobutenes like **6a** in particular are able to undergo this type of ring opening under the formation of allenylideneimido intermediates **20**, due to the symmetry conform interaction between the lone pair of the nitrogen atom and the acceptor orbitals of the titanium center, followed by the formation of **21**.[12]



In general, the titanacyclobutene complexes **8** do not react with an excess of the alkynes,[33] the exception being the reaction between acetylene **12a** and **4** via **4** → **8a** forming a low quantity of *trans*-poly(acetylene) as a black insoluble solid. In the IR spectra of the poly(acetylene), the only band observed at 1014 cm^{-1} indicates the formation of pure *trans*-configured poly(acetylene) **24**. Alt postulated an intermediate similar to **8a** (Cp instead of Cp*) during the polymerization of acetylene.[17c] According to the proposed mechanism via **22**/**23**, our isolation of **8a** seems to confirm that $TiCH{=}CHC{=}CH_2$ derivatives are the main intermediates in poly(acetylene) formation. Attempts to stabilize subsequent products from **8a**, like **22** or derivatives thereof, have failed up to now.

To distinguish between the titanacyclobutene reactivities cycloreversion (B → A) and ring opening (B → C), respectively, initial reactions were carried out. Ring-opening reactions with protic agents, similar to zirconacyclobutenes[18] or titanacyclobutanes,[15a] failed for **8**, **16**, or **17**. When nitriles or ketones are used, no insertion reactions can be observed.[8e,34] Whereas titanacyclobutenes are of low reactivity toward the substrates discussed before, fast insertion reactions occur by using cyclohexane isonitrile, forming the monoinsertion products **25b** and **25c** in the form of metallic green and light green solids. The alternative possible insertion into the TiC(=CH$_2$) σ-bond, forming **26**, is not observed. In this direction the behavior of **8b** and **8c** is similar to that of the titanacyclobutane **3**.[35] From **25**, no subsequent products are observed.[36]





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[32] Ab Initio calculations (3-21G(*)) of **13k** show a higher electron density of the Me$_3$Si*C* carbon (−0.57, {−0.37}) compared with the Ph*C* atom (0.02, {−0.15}). For comparison, [values (natural, {mulliken})]: **13f** CH$_2$*C*≡ (−0.02, {±0}), ≡*C*H (−0.27, {−0.43}); **13g**: Et*C*≡ (−0.04, {−0.11}), ≡*C*Me (−0.04, {−0.16}).

[33] An alternative reaction is found by using cobaltacyclobutene complexes, forming η^4-cyclopentadiene products: O'Connor, J. M.; Fong, B. S.; Ji, H.-L.; Iliibner, K. *J. Am. Chem. Soc.* **1995**, *117*, 8029−8030.

[34] (a) Doxsee, K. M.; Mouser, J. K. M. *Tetrahedron Lett.* **1991**, *32*, 1687−1690. (b) Doxsee, K. M.; Mouser, J. K. M. *Organometallics* **1990**, *9*, 3012−3014.

[35] Beckhaus, R.; Zimmermann, C.; Wagner, T.; Herdtweck, E. *J. Organomet. Chem.* **1993**, *460*, 181−189.

[36] Grubbs described the formation of vinylketene complexes from titanacyclobutenes and CO by preferred insertion in the Ti−Csp^3 bond: Meinhart, J. D.; Santarsiero, B. D.; Grubbs, R. H. Grubbs, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 3318−3323.

[37] Happ, B.; Bartik, T.; Zucchi, C.; Rossi, M. C.; Ghelfi, F.; Palyi, G.; Varadi, G.; Szalontai, G.; Horvath, I. T.; Chiesi-Villa, A.; Guastini, C. *Organometallics* **1995**, *14*, 809−819.

[38] Hesse, M.; Meier, H.; Zeeh, B. *Spektroskopische Methoden in der organischen Chemie*, 3rd ed.; Georg Thieme Verlag: Stuttgart, New York, 1987.

[39] Rosenthal, U.; Pulst, S.; Arndt, P.; Baumann, W.; Tillack, A.; Kempe, R. *Z. Naturforsch.* **1995**, *50b*, 368−376.

Further investigations concerning the reactivity problems of methylenetitanacyclobutenes are currently in progress.

Conclusions

We have demonstrated that the reaction of the titanocene vinylidene intermediate $[Cp^*{}_2Ti{=}C{=}CH_2]$ (**4**) with alkynes yields titanacyclobutene complexes (**8**, **16**, **17**) and, alternatively, vinyltitanium acetylides (**19**), depending on the nature of the alkynes used. By using unsymmetrical alkynes, different regioisomers can be isolated, whereas mixtures of different (**16g**/**17g**, **16j**/**17j**, **17f**/**19f**) could not be separated. The regiochemistry can be explained in accordance with the polarities of the alkynes. High differences in the partial charge of the alkyne C≡C atoms, determined by ^{13}C NMR measurements, lead to stereochemically pure compounds, with the more negative carbon bonded to titanium. α,*β*-Regioisomers are obtained by using alkynes with small differences. These can be isomerized by heating over a prolonged period of time, giving products with the bulky substituent in the *β*-position. The methylenetitanacyclobutene rings are of high thermal stability. Insertion reactions occur only in the Ti−C bond opposite the *exo*-methylene group. Ring opening of the methylenetitanocene cyclobutene to a titanium allenylidene alkylidene complex is not observed, but is proposed during the reaction course of the formation of *trans*-poly(acetylene) when using C_2H_2.

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 or VXR-300 spectrometer. Chemical shifts are reported in ppm and referenced to residual protons in deuterated solvents (benzene-d_6, $\delta = 7.15$ ppm; THF-d_8, $\delta = 1.78$ and 3.58 ppm for ^1H NMR spectroscopy; benzene-d_6 $\delta = 126.96$ 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 $Cp^*{}_2Ti(CH{=}CH_2)(CH_3)$ (**11**)^{9b} and $Cp^*{}_2\overline{TiCH_2CH_2C}{=}CH_2$ (**3**)^7 were prepared by literature procedures. The reagents HC≡CH (9.96% in He), $Me_3SiC{\equiv}CSiMe_3$, $Bu_3SnC{\equiv}CSnBu_3$, MeC≡CPh, $Me_3SiC{\equiv}CPh$, PhC≡CH, *t*-BuC≡CH, $Me_3SiC{\equiv}CH$, and PhC≡CC≡CPh were purchased from Aldrich. PhC≡CPh, MeC≡CEt, 2-pentyne, and 3-hexyne were from Merck, MeC≡CMe and 1-pentyne were from Fluka, and MeC≡CC≡CMe was from ABCR.

Preparation of Bis(η^5-pentamethylcyclopentadienyl)-2-methylenetitanacyclobutene (8a). A solution of **11** (392.5 mg, 1.089 mmol) in 30 mL of toluene was frozen, and 274 mL (1.226 mmol) of an acetylene/helium mixture (9.96% acetylene in helium) was added. The mixture was allowed to warm to room temperature. The red solution was stirred overnight, and the solvent was evaporated under reduced pressure, yielding **8a** as a reddish paste (0.38 g, 94%): ^1H NMR (C_6D_6, 500 MHz) δ 1.65 (s, 30H, $C_5(CH_3)_5$), 4.79 (d/d, $J = 4.58/2.24$ Hz, 1H, $=C\mathit{H}H$), 5.66 (m, 1H, $=CH\mathit{H}$), 6.68 (d/d/d, $J = 12.1/2.52/1.75$ Hz, CH), 7.81 (d/d/d, $J = 12.1/2.22/1.15$ Hz, 1H, Ti−CH) (the chemical shifts were assigned through an NOE experiment); $^{13}C\{^1H\}$ NMR (C_6D_6, 125 MHz) δ 12.0 ($C_5(\mathit{C}H_3)_5$), 100.4 (CH), 109.3 ($=CH_2$), 118.0 ($\mathit{C}_5(CH_3)_5$), 207.0 (Ti−CH), 214.3 (TiC=); EI-MS (85 °C) *m*/*e* (I_{rel}) 370 (5) (M^+), 353 (3), 337 (1), 318 (5) $(Cp^*{}_2Ti)^+$, 290 (1), 270 (1), 218 (1), 200 (5), 188 (9), 173 (16), 162 (18), 152 (79), 137 (94), 121 (62), 105 (37), 91 (43), 86 (30), 77 (21), 67 (11), 57 (100), 43 (71); exact mass *m*/*e* 370.2140 ($C_{24}H_{34}Ti$), calculated *m*/*e* 370.2143; IR (KBr) 2970 vs, 2905 vs, 1713 m, 1632 m, 1572 s, 1493 vs, 1436 vs, 1376 w, 1262 m, 1212 s, 1083 vs, 1019 s, 950 m, 895 m, 853 m, 805 vs, 692 s, 619 s, 590 m, 459 m, 407 w cm^{-1}.

Reaction of Bis(η^5-pentamethylcyclopentadienyl)-methylvinyltitanium (11) with Excess Acetylene 12a. A solution of **11** (280.2 mg, 0.777 mmol) in 30 mL of toluene was treated at room temperature with an excess of thoroughly dried acetylene. After 2 h, the solution color changed from yellow into dark red with a black precipitation. The solvent was evaporated under reduced pressure, yielding **8a** as a red oil (0.28 g, 97%) and 20 mg of solid, black poly(acetylene). The poly(acetylene) was identified as *trans*-poly(acetylene) by its IR spectrum, which exhibited only one absorption band at 1014 cm^{-1}.

Preparation of Bis(η^5-pentamethylcyclopentadienyl)-3,4-dimethyl-2-methylenetitanacyclobutene (8b). To a solution of **11** (298.2 mg, 0.827 mmol) in 30 mL of hexane was added 2-butyne (71.4 μL, 0.91 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 **8b** as red crystals after decantation that were suitable for X-ray structure determination (0.31 g, 93%): mp 173 °C (dec); ^1H NMR (C_6D_6, 500 MHz) δ 1.67 (s, 30H, $C_5(CH_3)_5$), 1.76 (d, $J = 0.91$ Hz, 3H, 3-CH_3), 2.01 (d, $J = 0.61$ Hz, 3H, 4-CH_3), 4.57 (br s, 1H, $=C\mathit{H}H$), 5.65 (d/m, $J = 0.62$ Hz, 1H, $=CH\mathit{H}$) (the chemical shifts were assigned through an NOE experiment); $^{13}C\{^1H\}$ NMR (C_6D_6, 125 MHz) δ 6.1 (3-CH_3), 11.9 ($C_5(\mathit{C}H_3)_5$), 20.3 (4-CH_3), 99.4 (C-CH_3), 101.3 ($=CH_2$), 118.9 ($\mathit{C}_5(CH_3)_5$), 210.6 ($Ti\mathit{C}CH_3$), 213.6 (TiC=); EI-MS (69 °C) *m*/*e* (I_{rel}) 398 (88) (M^+), 381 (21), 368 (11), 353 (2), 333 (6), 318 (93) $(Cp^*{}_2Ti)^+$, 299 (4), 262 (13), 216 (8), 199 (16), 181 (25), 159 (11), 136 (17), 121 (12), 119 (21), 105 (13), 101 (31), 91 (15), 86 (28), 83 (16), 71 (11), 57 (100); exact mass *m*/*e* 398.2453 ($C_{26}H_{38}Ti$), calculated *m*/*e* 398.2447; IR (KBr) 2899 vs, 2719 w, 1632 m, 1568 m, 1533 w, 1494 m, 1434 s, 1375 s, 1262 w, 1098 w, 1064 m, 1022 s, 844 s, 807 m, 745 w, 597 m, 548 w, 530 m, 451 w, 408 s cm^{-1}. Anal. Calcd for $C_{26}H_{38}Ti$: C, 78.37; H, 9.61. Found: C, 78.10; H, 9.67.

Preparation of Bis(η^5-pentamethylcyclopentadienyl)-2-methylene-3,4-diphenyltitanacyclobutene (8c). To a solution of **11** (350 mg, 0.971 mmol) in 30 mL of hexane was added diphenylacetylene (190 mg, 1.066 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 **8c** after decantation as a red microcrystalline solid (0.12 mg, 24%): mp 196 °C (dec); ^1H NMR (C_6D_6, 500 MHz) δ 1.73 (s, 30H, $C_5(CH_3)_5$), 4.61 (d, $J = 1.22$ Hz, 1H, $=C\mathit{H}H$), 5.69 (d, $J = 1.22$ Hz, 1H, $=CH\mathit{H}$), 6.78 (d/m, $J = 8.40$ Hz, 2H, *o*-$H^{(4)}$), 6.85 (tr/m, $J = 7.33$ Hz, 1H, *p*-$H^{(4)}$), 7.00 (m, 2H, *m*-$H^{(4)}$), 7.12 (tr/m, $J = 7.33$ Hz, 1H, *p*-$H^{(3)}$), 7.25 (tr/m, $J = 7.78$ Hz, 2H, *m*-$H^{(3)}$), 7.42 (d/m, $J = 8.09$ Hz, 2H, *o*-$H^{(3)}$) (the chemical shifts were assigned through an NOE experiment); $^{13}C\{^1H\}$ NMR (C_6D_6, 125 MHz) δ 12.4 ($C_5(\mathit{C}H_3)_5$), 106.7 ($=CH_2$), 113.3 (CPh), 120.8 ($\mathit{C}_5(CH_3)_5$), 125.0 (*p*-$C^{(4)}$), 126.0 (*p*-$C^{(3)}$), 127.3 (*m*-$C^{(4)}$), 128.6 (*m*-$C^{(3)}$), 131.02 (*o*-$C^{(4)}$), 131.3 (*o*-$C^{(3)}$), 137.4 (ipso-$C^{(4)}$), 142.4 (ipso-$C^{(3)}$), 205.3 (TiCPh), 211.4 (TiC=); EI-MS (138 °C) *m*/*e* (I_{rel}) 522 (21) (M^+), 505 (2), 439 (2), 398 (28), 377 (5), 353 (58), 332 (9), 318 (85) $(Cp^*{}_2Ti)^+$, 317 (89), 267 (9), 242 (6), 218 (43), 178 (100), 162 (15), 147 (30), 136 (51), 121 (69), 119 (56), 105 (40), 91 (29), 84 (52), 77 (15), 65 (6); exact mass *m*/*e* 522.2766 ($C_{36}H_{42}Ti$), calculated *m*/*e* 522.2766; IR (KBr) 3063 m, 3048 m, 3004 m, 2985 s, 2950 s, 2908 s, 2718 w, 1938 w, 1880 w, 1799 w, 1716 w, 1631 w, 1589 s, 1560 m, 1486 m, 1471 w, 1436 s, 1375 s, 1261 m, 1178 w, 1151 w, 1070 m, 1026 s, 953 w, 905 w, 855 s, 841 w, 808 w, 779 s, 765 s, 721 s, 700 vs, 648 w, 623 w, 611 m, 591 w, 528 m, 502 w, 477 m, 445 m, 425 m, 408 m cm^{-1}. Anal. Calcd for $C_{36}H_{42}Ti$: C, 82.74; H, 8.10. Found: C, 82.85; H, 7.89.

Preparation of Bis(η^5-pentamethylcyclopentadienyl)-2-methylene-3,4-bis(trimethylsilyl)titanacyclobutene (8d). To a solution of **11** (480.8 mg, 1.334 mmol) in 40 mL of hexane was added bis(trimethylsilyl)acetylene (333 μL, 1.467 mmol) at −78 °C. The mixture was slowly warmed to room temperature and stirred overnight. The hexane was removed under reduced pressure, yielding **8d** as a dark red oil (95%): ^{1}H NMR (C_6D_6, 500 MHz) δ 0.47 (s, 9H, $SiMe_3$), 0.53 (s, 9H, $SiMe_3$), 1.63 (s, 30H, $C_5(CH_3)_5$), 5.12 (s, 1H, =C*H*H), 6.14 (s, 1H, =CH*H*); SIMS-MS (Cs$^+$, 20 kV, 3,4-dimethoxybenzyl alcohol) positive ions *m*/*e* (I_{rel}) 514 (4) (M$^+$), 423 (2), 380 (8), 362 (15), 345 (7), 335 (6), 318 (100) $(Cp^*{}_2Ti)^+$, 217 (6), 200 (15), 181 (8), 151 (37), 135 (3); negative ions *m*/*e* (I_{rel}) 514 (24) (M$^+$), 393 (7), 380 (19), 361 (100), 226 (39), 209 (13), 203 (21), 195 (12), 135 (14).

Preparation of Bis(η^5-pentamethylcyclopentadienyl)-3,4-bis(tri-*n*-butylstannyl)-2-methylenetitanacyclobutene (8e). To a solution of **11** (266.1 mg, 0.783 mmol) in 40 mL of hexane was added bis(tri-*n*-butylstannyl)acetylene (427.7 μL, 0.8121 mmol) at −78 °C. The mixture was slowly warmed to room temperature and stirred overnight. The hexane was removed under reduced pressure, yielding **8e** as a dark violet oil (94%): ^{1}H NMR (C_6D_6, 500 MHz) δ 0.93 (tr, *J* = 7.33 Hz, 18H, $Sn(CH_2)_3CH_3$), 0.99 (tr/m, *J* = 8.09 Hz, 6H, $Sn(CH_2)_2CH_2CH_3$), 1.04 (q/m, *J* = 6.31 Hz, 6H, $Sn(CH_2)_2CH_2CH_3$), 1.39 (q/m, *J* = 7.43 Hz, 12H, $SnCH_2CH_2CH_2CH_3$), 1.54 (tr/m, *J* = 6.41 Hz, 6H, $SnCH_2(CH_2)_2CH_3$), 1.68 (m, *J* = 7.18 Hz, 6H, $SnCH_2(CH_2)_2CH_3$), 1.67 (s, 30H, $C_5(CH_3)_5$), 5.13 (s, 1H, =C*H*H), 5.85 (s, 1H, =CH*H*); $^{13}C\{^1H\}$ NMR (C_6D_6, 125 MHz) δ 11.7 (CH_3), 12.4 ($C_5(CH_3)_5$), 12.6 (CH_2), 13.0 (CH_3), 15.0 (CH_2), 28.2 (CH_2), 28.3 (CH_2), 30.1 ($SnCH_2$), 30.2 ($SnCH_2$), 116.3 (=CH_2), 115.1 (CSn(*n*-Bu)$_3$), 115.8 ($C_5(CH_3)_5$), 212.9 (TiCSn(*n*Bu)$_3$), 214.5 (TiC=).

Preparation of Bis(η^5-pentamethylcyclopentadienyl)-2-methylene-3-methyl-4-(1-propynyl)titanacyclobutene (16h). To a solution of **11** (261.9 mg, 0.727 mmol) in 30 mL of hexane was added 2,4-hexadiyne (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 **16h** after decantation as red crystals (207.3 mg, 67.5%): mp 153 °C (dec); ^{1}H NMR (C_6D_6, 500 MHz) δ 1.75 (s, 30H, $C_5(CH_3)_5$), 2.03 (s, 3H, ≡CCH_3), 2.10 (s, 3H, =CCH_3), 4.55 (d, *J* = 1.53 Hz, 1H, =C*H*H), 5.71 (d, *J* = 1.53 Hz, 1H, =CH*H*) (the chemical shifts were assigned through an NOE experiment); $^{13}C\{^1H\}$ NMR (C_6D_6, 125 MHz) δ 5.7 (CCH_3), 11.5 (C≡CCH_3), 11.9 ($C_5(CH_3)_5$), 84.0 (C≡CCH_3), 104.2 (CCH_3), 104.8 (=CH_2), 114.7 (C≡CCH_3), 120.2 ($C_5(CH_3)_5$), 185.9 (TiC≡), 210.5 (TiC=); EI-MS (76 °C) *m*/*e* (I_{rel}) 422 (12) (M$^+$), 407 (5), 337 (5), 318 (47), $(Cp^*{}_2Ti)^+$, 270 (2), 239 (6), 200 (12), 181 (7), 162 (8), 152 (15), 147 (19), 135 (29), 119 (31), 105 (16), 86 (23), 57 (100); exact mass *m*/*e* 422.2453 ($C_{28}H_{38}Ti$), calculated *m*/*e* 422.2456; IR (KBr) 3018 w, 2981 s, 2904 vs, 2722 w, 2169 m, 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 Bis(η^5-pentamethylcyclopentadienyl)-2-methylene-3-phenyl-4-(2-phenyl-1-ethynyl)titanacyclobutene (16i). To a solution of **11** (268.8 mg, 0.746 mmol) in 30 mL of hexane was added 1,4-diphenylbutadiyne (150.8 mg, 0.746 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 **16i** after decantation as red crystals (350.5 mg, 86%): mp 134 °C (dec); ^{1}H NMR (C_6D_6, 500 MHz) δ 1.78 (s, 30H, $C_5(CH_3)_5$), 4.57 (d, *J* = 1.53 Hz, 1H, =C*H*H), 5.98 (d, *J* = 1.22 Hz, 1H, =CH*H*), 6.83−6.90 (m, 1H, *p*-H$^{(4)}$), 6.94−6.90 (tr/m, *J* = 7.48 Hz, 1H, *p*-H$^{(3)}$), 7.02 (tr/m, *J* = 7.63 Hz, 2H, *m*-H$^{(4)}$), 7.34 (tr/m, *J* = 7.63 Hz, 4H, *o*-H$^{(4)}$, *m*-H$^{(3)}$), 7.81 (d/d, *J* = 8.24/1.22 Hz, 2H, *o*-H$^{(3)}$) (the chemical shifts were assigned through an NOE experiment); $^{13}C\{^1H\}$ NMR (C_6D_6, 125 MHz) δ 12.0 ($C_5(CH_3)_5$), 94.6 (C≡CPh), 108.4 (=CH_2), 109.1 (C≡CPh), 121.3 ($C_5(CH_3)_5$), 124.7 (ipso-C$^{(4)}$), 126.4 (*p*-C$^{(4)}$), 126.7 (CPh), 126.8 (*p*-C$^{(3)}$), 128.3 (*m*-C$^{(4)}$), 128.4 (*m*-C$^{(3)}$), 130.2 (*o*-C$^{(4)}$), 131.1 (*o*-C$^{(3)}$), 135.6 (ipso-C$^{(3)}$), 182.7 (TiCC≡), 205.4 (TiC=); EI-MS (177 °C) *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), 121 (20), 119 (18), 105 (13), 91 (18); exact mass *m*/*e* 546.2766 ($C_{38}H_{42}Ti$), calculated *m*/*e* 546.2766; IR (KBr) 3075 m, 3052 m, 3010 s, 2983 s, 2956 s, 2901 vs, 2719 w, 2139 vs, 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}.

Preparation of Bis(η^5-pentamethylcyclopentadienyl)-3-ethyl-4-methyl-2-methylenetitanacyclobutene (17g). Thermodynamic product, 75%. To a solution of **11** (257.0 mg, 0.713 mmol) in 30 mL of hexane was added 2-pentyne (75 μL, 0.784 mmol) at −78 °C. The mixture was slowly warmed to room temperature and stirred overnight. The hexane was removed under reduced pressure, yielding **17g** and **16g** in a 3:1 ratio as red crystals: ^{1}H NMR (C_6D_6, 500 MHz) δ 1.15 (tr, *J* = 7.63 Hz, 3H, CH_2CH_3), 1.67 (s, 30H, $C_5(CH_3)_5$), 1.99 (s, 3H, 4-CH_3), 2.31 (q, *J* = 7.63 Hz, 2H, CH_2CH_3), 4.54 (s, 1H, =C*H*H), 5.66 (s, 1H, =CH*H*); $^{13}C\{^1H\}$ NMR (C_6D_6, 125 MHz) δ 11.9 ($C_5(CH_3)_5$), 15.1 (CCH_2CH_3), 19.8 (4-CH_3), 27.9 (CCH_2CH_3), 100.8 (=CH_2), 105.1 (CCH_2CH_3), 118.8 ($C_5(CH_3)_5$), 210.2 ($TiCCH_3$), 212.0 (TiC=); EI-MS (76 °C) *m*/*e* (I_{rel}) 412 (39) (M$^+$), 395 (5), 382 (4), 362 (4), 337 (5), 318 (43) $(Cp^*{}_2Ti)^+$, 291 (3), 270 (12), 262 (4), 228 (8), 213 (10), 200 (29), 181 (21), 162 (32), 152 (40), 147 (76), 135 (100), 119 (86), 105 (48), 91 (46), 77 (22), 57 (22); exact mass *m*/*e* 412.2610 ($C_{27}H_{40}Ti$), calculated *m*/*e* 412.2607.

Bis(η^5-pentamethylcyclopentadienyl)-4-ethyl-3-methyl-2-methylenetitanacyclobutene (16g): 25%, kinetic product; ^{1}H NMR (C_6D_6, 500 MHz) δ 1.13 (tr, *J* = 7.48 Hz, 3H, CH_2CH_3), 1.67 (s, 30H, $C_5(CH_3)_5$), 1.73 (s, 3H, 3-CH_3), 2.51 (q, *J* = 7.43 Hz, 2H, CH_2CH_3), 4.56 (s, 1H, =C*H*H), 5.68 (s, 1H, =CH*H*).

Preparation of Bis(η^5-pentamethylcyclopentadienyl)-4-methyl-2-methylene-3-phenyltitanacyclobutene (17j) (57%). To a solution of **11** (233.6 mg, 0.648 mmol) in 30 mL of hexane was added methylphenylacetylene (89.2 μL, 0.713 mmol) at −78 °C. The mixture was slowly warmed to room temperature and stirred overnight. The hexane was removed under reduced pressure, yielding **17j** and **16j** as a dark red oil: ^{1}H NMR (C_6D_6, 500 MHz) δ 1.72 (s, 30H, $C_5(CH_3)_5$), 2.02 (s, 3H, 4-CH_3), 4.54 (d, *J* = 0.61 Hz, 1H, =C*H*H), 5.55 (d, *J* = 0.61 Hz, 1H, =CH*H*), 7.12 (m, 1H, *p*-H), 7.32 (tr/m, 2H, *m*-H), 7.38 (d/m, 2H, *o*-H); $^{13}C\{^1H\}$ NMR (C_6D_6, 125 MHz) δ 12.0 ($C_5(CH_3)_5$), 21.1 (4-CH_3), 104.3 (=CH_2), 110.2 (CPh), 119.6 ($C_5(CH_3)_5$), 125.5 (*p*-, *m*-C), 131.3 (*o*-C), 144.1 (ipso-C), 210.7 ($TiCCH_3$), 211.8 (Ti-C=).

Bis(η^5-pentamethylcyclopentadienyl)-3-methyl-2-methylene-4-phenyl)titanacyclobutene (16j): 43%; ^{1}H NMR (C_6D_6, 500 MHz) δ 1.66 (s, 30H, $C_5(CH_3)_5$), 2.10 (s, 3H, 3-CH_3), 4.62 (d, *J* = 0.91 Hz, 1H, =C*H*H), 5.78 (d, *J* = 1.22 Hz, 1H, =CH*H*), 6.96 (m, 1H, *p*-H), 7.24 (tr/m, 2H, *m*-H), 7.46 (d/m, 2H, *o*-H); $^{13}C\{^1H\}$ NMR (C_6D_6, 125 MHz) δ 10.5 (3-CH_3), 12.3 ($C_5(CH_3)_5$), 103.8 (=CH_2), 105.0 (CCH_3), 120.1 ($C_5(CH_3)_5$), 124.4 (*p*-, *m*-C), 130.3 (*o*-C), 136.1 (ipso-C), 204.7 (TiCPh), 215.2 (TiC=).

Preparation of Bis(η^5-pentamethylcyclopentadienyl)-2-methylene-3-propyltitanacyclobutene (17f). Cycloaddition product, 40%. To a solution of **11** (273.7 mg, 0.759 mmol) in 30 mL of hexane was added 1-pentyne (82 μL, 0.835

mmol) at −78 °C. The mixture was slowly warmed to room temperature and stirred overnight. The hexane was removed under reduced pressure, yielding **17f** and **19f** in a 1:1.5 ratio as a red microcrystalline solid: ^{1}H NMR ($\mathrm{C_6D_6}$, 500 MHz δ 1.07 (tr, $J = 7.33$ Hz, 3H, $\mathrm{CH_2CH_2C}H_\mathrm{3}$), 1.66 (s, 30H, $\mathrm{C_5(CH_3)_5}$), 2.08 (m, 2H, $\mathrm{CH_2C}H_\mathrm{2}\mathrm{CH_3}$), 2.23 (tr/d, $J = 1.53$ Hz, 2H, $\mathrm{C}H_\mathrm{2}\mathrm{CH_2CH_3}$), 4.57 (m, 1H, $=\mathrm{C}H\mathrm{H}$), 5.73 (m, 1H, $=\mathrm{CH}H$), 7.39 (m, 1H, TiCH); ^{13}C{^{1}H} NMR ($\mathrm{C_6D_6}$, 125 MHz) δ 11.9 ($\mathrm{C_5(}C\mathrm{H_3)_5}$), 15.2 ($\mathrm{CH_2CH_2}C\mathrm{H_3}$), 21.7 ($\mathrm{CH_2}C\mathrm{H_2CH_3}$), 23.7 ($C\mathrm{H_2CH_2CH_3}$), 102.4 ($=\mathrm{CH_2}$), 111.1 ($=\mathrm{C{-}CH_2}$), 118.9 ($C_\mathrm{5}\mathrm{(CH_3)_5}$), 199.3 (TiCH), 210.4 ($\mathrm{TiC}{=}$).

Bis(η^5-pentamethylcyclopentadienyl)-1-pentynylvinyltitanium (19f): 60%, C−H activation product; ^{1}H NMR ($\mathrm{C_6D_6}$, 500 MHz) δ 0.95 (tr, $J = 7.33$ Hz, 3H, $\mathrm{CH_2CH_2C}H_\mathrm{3}$), 1.50 (q, $J = 7.22$ Hz, 2H, $\mathrm{CH_2C}H_\mathrm{2}\mathrm{CH_3}$), 1.85 (s, 30H, $\mathrm{C_5(CH_3)_5}$), 2.25 (tr, $J = 7.02$ Hz, 2H, $\mathrm{C}H_\mathrm{2}\mathrm{CH_2CH_3}$), 4.95 (tr/m, $J = 11.3$ Hz, 1H, $=\mathrm{C}H\mathrm{H}$), 5.66 (d/d, $J = 11.1/1.68$ Hz, 2H, $=\mathrm{CH}H$/α-H); ^{13}C{^{1}H} NMR ($\mathrm{C_6D_6}$, 125 MHz) δ 12.8 ($\mathrm{C_5(}C\mathrm{H_3)_5}$), 14.1 ($\mathrm{CH_2CH_2}C\mathrm{H_3}$), 23.5 ($\mathrm{CH_2}C\mathrm{H_2CH_3}$), 30.0 ($C\mathrm{H_2CH_2CH_3}$), 117.1 ($=\mathrm{CH_2}$), 117.6 ($\equiv C\mathrm{CH_2CH_2CH_3}$), 121.5 ($C_\mathrm{5}\mathrm{(CH_3)_5}$), 151.3 ($\mathrm{TiC}{\equiv}$), 213.9 ($\mathrm{TiC}{=}$).

Preparation of Bis(η^5-pentamethylcyclopentadienyl)-2-methylene-4-(trimethylsilyl)-3-phenyltitanacyclobutene (17k). To a solution of **11** (416.7 mg, 1.156 mmol) in 40 mL of hexane was added 1-(trimethylsilyl)-2-phenylacetylene (0.25 mL, 1.271 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 (−25 °C), yielding **17k** after decantation as small red crystals suitable for X-ray structure determination (485.0 mg, 51%, mp 175 °C (dec)): ^{1}H NMR ($\mathrm{C_6D_6}$, 500 MHz) δ 0.14 (s, 9H, $\mathrm{SiMe_3}$), 1.75 (s, 30H, $\mathrm{C_5(CH_3)_5}$), 4.71 (d, $J = 1.53$ Hz, 1H, $=\mathrm{C}H\mathrm{H}$), 5.37 (d, $J = 1.22$ Hz, 1H, $=\mathrm{CH}H$), 7.11 (tr/m, $J = 7.48$ Hz, 1H, *p*-H), 7.24 (tr/m, $J = 7.63$ Hz, 2H, *m*-H), 7.36 (d/m, $J = 6.41$ Hz, 2H, *o*-H) (the chemical shifts were assigned through an NOE experiment); ^{13}C{^{1}H} NMR ($\mathrm{C_6D_6}$, 125 MHz) δ 4.8 ($\mathrm{SiMe_3}$), 12.6 ($\mathrm{C_5(}C\mathrm{H_3)_5}$), 108.6 ($=\mathrm{CH_2}$), 119.9 ($C_\mathrm{5}\mathrm{(CH_3)_5}$), 126.0 (*p*-C), 127.7 (*m*-C), 129.8 (CPh), 131.1 (*o*-C), 141.0 (ipso-C), 215.2 ($\mathrm{TiCSiMe_3}$), 218.0 ($\mathrm{TiC}{=}$); EI-MS (112 °C) *m*/*e* (I_rel) 518 (3) (M$^+$), 382 (7), 362 (26), 344 (10), 335 (13), 317 (52) $(\mathrm{Cp^*_2TiH})^+$, 268 (8), 211 (3), 200 (100), 181 (12), 159 (26), 136 (45), 121 (57), 105 (30), 91 (18), 77 (8), 65 (3); exact mass *m*/*e* 518.2845 ($\mathrm{C_{30}H_{38}Ti}$), calculated *m*/*e* 518.2848; IR (KBr) 3079 m, 3055 m, 2958 s, 2893 s, 2717 w, 1937 w, 1734 w, 1629 w, 1592 m, 1559 w, 1490 s, 1455 s, 1436 s, 1375 s, 1259 m, 1240 s, 1196 w, 1175 w, 1100 w, 1071 m, 1020 m, 964 w, 907 w, 860 vs, 831 s, 772 s, 755 m, 701 vs, 675 m, 625 w, 601 w, 472 m, 451 w, 424 s, 403 s cm^{-1}. Anal. Calcd for $\mathrm{C_{30}H_{38}Ti}$: C, 76.42; H, 8.94. Found: C, 75.87; H, 8.98.

Preparation of Bis(η^5-pentamethylcyclopentadienyl)-(2-phenyl-1-ethynyl)vinyltitanium (19l). To a solution of **11** (330 mg, 0.916 mmol) in 30 mL of hexane was added phenylacetylene (111 μL, 1.01 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 **19l** after decantation as light red crystals suitable for X-ray structure determination (365.0 mg, 89%, mp 144 °C (dec)): ^{1}H NMR ($\mathrm{C_6D_6}$, 500 Mhz) δ 1.85 (s, 30H, $\mathrm{C_5(CH_3)_5}$), 5.03 (d/d, $J = 17.2/4.73$ Hz, 1H, $=\mathrm{C}H\mathrm{H}$), 5.61 (d/d, $J = 17.4/14.0$ Hz, 1H, α-H), 5.67 (d/d, $J = 14.0/4.58$ Hz, 1H, $=\mathrm{CH}H$), 6.97 (tr/m, $J = 7.48$ Hz, 1H, *p*-H), 7.08 (tr/m, $J = 7.79$ Hz, 2H, *m*-H), 7.46 (d/m, $J = 7.02$ Hz, 2H, *o*-H); ^{13}C{^{1}H} NMR (THF-d_8, 125 MHz) δ 12.7 ($\mathrm{C_5(}C\mathrm{H_3)_5}$), 116.8 ($=\mathrm{CH_2}$), 118.3 ($\equiv C\mathrm{Ph}$), 122.4 ($C_\mathrm{5}\mathrm{(CH_3)_5}$), 126.3 (*p*-C), 127.8 (ipso-C), 128.5 (*m*-C), 130.8 (*o*-C), 162.0 ($\mathrm{TiC}{\equiv}$), 214.9 ($\mathrm{TiC}{=}$); EI-MS (121 °C) *m*/*e* (I_rel) 446 (13) (M$^+$), 438 (2), 419 (2), 380 (7), 362 (3), 353 (31), 344 (6), 337 (24), 318 (100) $(\mathrm{Cp^*_2Ti})^+$, 284 (25), 264 (3), 249 (5), 218 (37), 200 (21), 181 (16), 162 (8), 147 (19), 136 (29), 129 (47), 119 (37), 105 (22), 91 (23), 77 (14); exact mass *m*/*e* 446.2453 ($\mathrm{C_{30}H_{38}Ti}$), calculated *m*/*e* 446.2453; IR (KBr) 3072 m, 3047 w, 3007 m, 2982 m, 2901 vs, 2861 s, 2721 w, 2067 w, 1940 w, 1780 w, 1636 w, 1592 m, 1567 s, 1540 m, 1483 vs, 1436 s, 1377 s, 1291 w, 1219 m, 1201 s, 1171 w, 1067 m, 1021 s, 959 w, 907 w, 889 s, 810 w, 783 m, 755 vs, 691 vs, 597 w, 546 m, 533 m, 509 m, 448 m, 424 m, 409 m cm^{-1}. Anal. Calcd for $\mathrm{C_{30}H_{38}Ti}$: C, 80.70; H, 8.58. Found: C, 80.18; H, 8.88.

Preparation of Phenylacetylene-*d*. Phenylacetylene (2 mL) was dissolved in 10 mL of hexane, cooled to −78 °C, and treated with butyllithium. The suspension was warmed to room temperature and hydrolyzed with $\mathrm{D_2O}$. The organic phase was dried over $\mathrm{Na_2SO_4}$ and distilled. According to the NMR spectrum, the phenylacetylene was deuterated to at least 96%.

Preparation of Bis(η^5-pentamethylcyclopentadienyl)-(2-phenyl-1-ethynyl)vinyltitanium-*vinyl-d* (19l-D). To a solution of **11** (152.9 mg, 0.424 mmol) in 20 mL of hexane was added phenylacetylene-*d* (0.048 mg, 0.466 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 **19l-D** after decantation as light red crystals (mp 136 °C (dec)): ^{1}H NMR ($\mathrm{C_6D_6}$, 500 MHz) δ 1.84 (s, 30H, $\mathrm{C_5(CH_3)_5}$), 5.01 (d, $J = 3.66$ Hz, 1H, $=\mathrm{C}H\mathrm{H}$), 5.66 (d, $J = 3.96$ Hz, 1H, $=\mathrm{CH}H$), 6.97 (tr/m, $J = 7.48$ Hz, 1H, *p*-H), 7.09 (tr/m, $J = 7.63$ Hz, 2H, *m*-H), 7.45 (d/m, $J = 8.24$ Hz, 2H, *o*-H); IR (KBr) 3072 m, 3048 w, 3005 s, 2982 s, 2901 vs, 2720 w, 2119 m [ν-(C−D)], 2067 m, 1956 w, 1940 m, 1884 w, 1813 w, 1786 m, 1746 w, 1663 w, 1592 s, 1566 m, 1530 m, 1483 vs, 1436 vs, 1389 w, 1376 vs, 1290 w, 1201 vs, 1171 m, 1109 s, 1066 s, 1023 vs, 958 w, 907 w, 893 vs, 810 m, 782 s, 755 vs, 691 vs, 597 m, 546 s, 533 s, 519 w, 497 s, 409 s cm^{-1}.

Preparation of Bis(η^5-pentamethylcyclopentadienyl)-(3,3-dimethyl-1-butynyl)vinyltitanium (19m). To a solution of **11** (301.1 mg, 0.835 mmol) in 30 mL of hexane was added 3,3-dimethyl-1-butyne (113 μL, 0.919 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 **19m** after decantation as orange crystals (0.34 g, 95.4%, mp 70 °C (dec >140 °C)): ^{1}H NMR (THF-d_8, 500 MHz) δ 1.12 (s, 9H, $\mathrm{C(CH_3)_3}$), 1.85 (s, 30H, $\mathrm{C_5(CH_3)_5}$), 4.47 (d/d, $J = 18.0/4.58$ Hz, 1H, $=\mathrm{C}H\mathrm{H}$), 5.13 (d/d, $J = 14.0/4.58$ Hz, 1H, $=\mathrm{CH}H$), 5.43 (d/d, $J = 18.0/14.0$ Hz, 1H, α-H); ^{13}C{^{1}H} NMR ($\mathrm{C_6D_6}$, 125 MHz) δ 12.9 ($\mathrm{C_5(}C\mathrm{H_3)_5}$), 28.2 ($C\mathrm{(CH_3)_3}$), 31.8 ($\mathrm{C(}C\mathrm{H_3)_3}$), 117.3 ($=\mathrm{CH}_\infty$), 121.4 ($C_\mathrm{5}\mathrm{(CH_3)_5}$), 125.1 ($\equiv C\mathrm{C(CH_3)}_)$, 149.1 ($\mathrm{TiC}{\equiv}$), 213.9 ($\mathrm{TiC}{=}$); EI-MS (72 °C) *m*/*e* (I_rel) 426 (9) (M$^+$), 344 (7), 318 (59) $(\mathrm{CP^*_2Ti})^+$, 291 (5), 270 (17), 248 (11), 181 (10), 164 (4), 159 (9), 152 (12), 147 (22), 136 (100), 119 (42), 105 (28), 91 (23), 77 (16), 67 (12), 57 (30); exact mass *m*/*e* 426.2769 ($\mathrm{C_{28}H_{42}Ti}$), calculated *m*/*e* 426.2766; IR (KBr) 3077 w, 2959 vs, 2938 s, 2898 vs, 2861 s, 2719 w, 2071 s, 1784 w, 1634 br m, 1541 m, 1492 m, 1451 s, 1435 s, 1377 s, 1356 m, 1261 w, 1241 s, 1217 w, 1200 w, 1066 m, 1020 s, 891 m, 793 s, 727 m, 678 w, 615 w, 596 w, 549 w, 540 w, 506 m, 462 m, 419 m cm^{-1}. Anal. Calcd for $\mathrm{C_{28}H_{42}Ti}$: C, 78.85, H, 9.93. Found: C, 78.94; H, 9.30.

Preparation of Bis(η^5-cyclopentadienyl)[2-(trimethylsilyl)-1-ethynyl]vinyltitanium (19n). To a solution of **11** (263.7 mg, 0.732 mmol) in 30 mL of hexane was added (trimethylsilyl)acetylene (114 μL, 0.805 mmol) at −78 °C. The mixture was slowly warmed to room temperature and stirred overnight. The hexane was removed under reduced pressure, yielding **19n** as an orange powder (291 mg, 89.9%, mp 68 °C (dec >120 °C)): ^{1}H NMR ($\mathrm{C_6D_6}$, 500 MHz) δ 0.27 (s, 9H, $\mathrm{SiMe_3}$), 1.81 (s, 30H, $\mathrm{C_5(CH_3)_5}$), 4.97 (d/d, $J = 17.9/4.43$ Hz, 1H, $=\mathrm{C}H\mathrm{H}$), 5.49 (d/d, $J = 18.0/14.0$ Hz, 1H, α-H), 5.63 (d/d, $J = 14.0/4.28$ Hz, 1H, $=\mathrm{CH}H$); ^{13}C{^{1}H} NMR ($\mathrm{C_6D_6}$, 125 MHz) δ 0.74 ($\mathrm{SiMe_3}$), 12.8 ($\mathrm{C_5(}C\mathrm{H_3)_5}$), 117.5 ($=\mathrm{CH_2}$), 119.7 ($\equiv \mathrm{CSiMe_3}$), 121.9 ($C_\mathrm{5}\mathrm{(CH_3)_5}$), 183.4 ($\mathrm{TiC}{\equiv}$), 214.7 ($\mathrm{TiC}{=}$); EI-MS (101 °C) *m*/*e* (I_rel) 442 (17) (M$^+$), 247 (3), 415 (3), 318 (100) $(\mathrm{Cp^*_2Ti})^+$, 280 (25), 204 (5), 182 (17), 159 (7), 136 (6), 119 (6), 83 (6), 73 (7); exact mass *m*/*e* 442.2535 ($\mathrm{C_{27}H_{42}TiSi}$), calculated *m*/*e* 442.2535; IR (KBr) 3014 w, 2983 m, 2951 s, 2899 s, 2719 w,

Table 6. Crystal Data and Parameters of Structure Refinement for 8b, 17k, and 19l

	8b	**17k**	**19l**
formula	$C_{26}H_{38}Ti$	$C_{33}H_{46}SiTi$	$C_{30}H_{38}Ti$
fw	398.49	518.72	446.54
space group (no.)	$P2_1/n$ (14)	$P2_1/n$ (14)	$P2_1/c$ (14)
crystal data			
a (Å)	8.680(2)	9.671(2)	9.222(2)
b (Å)	17.702(5)	19.239(2)	10.495(2)
c (Å)	14.997(4)	15.849(1)	26.73(2)
β (deg)	90.85(2)	91.77(1)	101.54(4)
V (Å^3)	2304(2)	2947(1)	2535(3)
Z	4	4	4
d_{calc} (g cm^{-3})	1.149	1.169	1.170
μ (cm^{-1})	3.73	29.79	3.46
temperature (°C)	25	25	−20
radiation	Mo Kα	Cu Kα	Mo Kα
λ (Å)	0.7107	1.5418	0.7107
crystal dimensions (mm^{-3})	0.40 × 0.30 × 0.50	0.70 × 0.50 × 0.40	0.35 × 0.50 × 0.55
measured reflections	8973	10684	4860
scan range (deg)	$3 \le \theta \le 30$	$5 \le \theta \le 65$	$3 \le \theta \le 25$
Ewald spere	(h, k, ±l)	(h, k, ±l)	(h, k, ±l)
sec. ext coeff	not refined	$E = 1.96 \times 10^{-7}$	not refined
observed indep reflns	4250	2667	2004
$I >$	$1\sigma(I)$	$1\sigma(I)$	$0.5\sigma(I)$
parameters refined	252	317	214
agreement factors			
R	0.091	0.061	0.134
R_w	0.067	0.064	0.100
GOF	1.483	1.113	1.884
res el density (e Å^{-3})	0.58	0.67	0.64

Table 7. Positional Parameters and Estimated Standard Deviations for 8b[a]

atom	x	y	z	B (Å^2)
Ti	0.16821(6)	0.86619(3)	0.24208(3)	2.490(8)
C1	0.0435(4)	0.8791(2)	0.3603(2)	3.77(7)
C2	0.1839(4)	0.9038(2)	0.4027(2)	4.25(7)
C3	0.3079(4)	0.9068(2)	0.3479(2)	3.99(7)
C4	−0.0958(4)	0.8700(2)	0.4019(2)	5.98(9)
C5	0.1914(6)	0.9235(3)	0.5018(2)	7.5(1)
C6	0.4626(5)	0.9342(3)	0.3738(3)	7.3(1)
C10	0.3300(4)	0.7576(2)	0.2738(2)	3.52(6)
C11	0.1864(4)	0.7400(2)	0.3076(2)	3.60(6)
C12	0.0801(4)	0.7353(2)	0.2371(2)	3.88(7)
C13	0.1613(4)	0.7476(2)	0.1577(2)	3.89(7)
C14	0.3147(4)	0.7630(2)	0.1806(2)	3.49(6)
C15	0.4813(4)	0.7546(2)	0.3238(3)	7.3(1)
C16	0.1577(5)	0.7192(2)	0.4035(2)	7.1(1)
C17	−0.0859(5)	0.7122(2)	0.2430(3)	8.0(1)
C18	0.1007(5)	0.7265(2)	0.0658(2)	7.7(1)
C19	0.4515(4)	0.7679(2)	0.1193(3)	7.0(1)
C20	0.1491(4)	1.0026(2)	0.2207(2)	4.21(7)
C21	0.0037(4)	0.9732(2)	0.2025(2)	4.27(7)
C22	0.0133(4)	0.9260(2)	0.1263(2)	5.20(8)
C23	0.1664(5)	0.9283(2)	0.0972(2)	5.39(9)
C24	0.2501(4)	0.9746(2)	0.1559(2)	5.12(8)
C25	0.1829(6)	1.0612(2)	0.2902(3)	7.8(1)
C26	−0.1428(4)	0.9983(3)	0.2452(3)	7.9(1)
C27	−0.1240(5)	0.8913(3)	0.0784(3)	10.2(1)
C28	0.2226(7)	0.9031(3)	0.0067(3)	11.3(2)
C29	0.4185(5)	0.9954(3)	0.1464(4)	9.7(1)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter, defined as $(^4/_3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ac(\cos\beta)\beta_{13}]$.

Table 8. Positional Parameters and Estimated Standard Deviations for 17k[a]

atom	x	y	z	B (Å^2)
Ti	0.1592(1)	0.18324(5)	−0.12605(5)	2.86(2)
Si	0.1594(2)	0.36211(8)	−0.01181(9)	3.87(4)
C1	−0.0314(5)	0.2173(3)	−0.1783(3)	3.1(1)
C2	−0.0069(5)	0.2833(3)	−0.1294(3)	3.0(1)
C3	0.1087(5)	0.2861(3)	−0.0794(3)	2.8(1)
C4	−0.1423(6)	0.2046(3)	−0.2267(3)	4.2(1)
C5	0.0548(7)	0.3702(3)	0.0852(3)	5.2(2)
C6	0.1423(8)	0.4469(3)	−0.0685(4)	6.2(2)
C7	0.3428(6)	0.3559(3)	0.0260(4)	5.7(2)
C8	−0.1123(6)	0.3408(3)	−0.1413(3)	3.4(1)
C9	−0.1116(7)	0.3820(3)	−0.2121(3)	4.9(2)
C10	−0.2065(7)	0.4369(3)	−0.2214(4)	5.7(2)
C11	−0.2989(7)	0.4503(3)	−0.1607(4)	5.4(2)
C12	−0.3026(7)	0.4097(3)	−0.0904(4)	5.5(2)
C13	−0.2084(6)	0.3545(3)	−0.0796(4)	4.4(1)
C20	0.0097(6)	0.1431(3)	−0.0140(3)	3.4(1)
C21	0.0114(6)	0.0897(3)	−0.0745(3)	4.0(1)
C22	0.1453(7)	0.0625(3)	−0.0758(3)	4.5(1)
C23	0.2285(6)	0.1000(3)	−0.0175(3)	3.9(1)
C24	0.1434(6)	0.1491(3)	0.0215(3)	3.7(1)
C25	−0.1130(6)	0.1809(3)	0.0168(4)	5.9(1)
C26	−0.1112(7)	0.0587(3)	−0.1207(4)	7.1(2)
C27	0.1743(8)	−0.0048(3)	−0.1201(4)	8.5(2)
C28	0.3712(7)	0.0819(4)	0.0163(4)	7.3(2)
C29	0.1834(8)	0.1910(3)	0.0978(3)	6.8(2)
C30	0.2430(6)	0.1482(3)	−0.2620(3)	4.2(1)
C31	0.3549(6)	0.1383(3)	−0.2054(3)	4.3(1)
C32	0.3917(6)	0.2039(3)	−0.1718(3)	4.3(1)
C33	0.3070(6)	0.2549(3)	−0.2135(3)	4.1(1)
C34	0.2161(5)	0.2206(3)	−0.2684(3)	3.8(1)
C35	0.1715(7)	0.0949(3)	−0.3179(3)	6.3(2)
C36	0.4416(7)	0.0763(3)	−0.2005(4)	7.3(2)
C37	0.5137(6)	0.2186(4)	−0.1141(4)	6.4(2)
C38	0.3310(7)	0.3318(3)	−0.2096(4)	5.8(2)
C39	0.1239(6)	0.2542(3)	−0.3348(3)	5.2(1)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter, defined as $(^4/_3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ac(\cos\beta)\beta_{13}]$.

2016 s, 1803 w, 1735 w, 1707 w, 1702 w, 1697 w, 1686 w, 1677 w, 1654 w, 1629 m, 1561 w, 1556 w, 1541 w, 1492 m, 1434 s, 1377 s, 1253 w, 1242 vs, 1216 w, 1065 w, 1016 m, 900 m, 854 vs, 836 vs, 755 m, 692 vs, 606 w, 597 w, 510 w, 448 w, 413 w cm^{-1}. Anal. Calcd for $C_{27}H_{42}Ti$: C, 73.27; H, 9.56. Found: C, 73.04; H, 9.48.

Preparation of Bis(η^5-pentamethylcyclopentadienyl)-2-(cyclohexylimino)-3,4-dimethyl-5-methylenetitanacyclopentene (25b). 8b (187.4 mg, 0.47 mmol) was dissolved in 20 mL of hexane, cooled to −30 °C, and treated with cyclohexaneisonitrile (58.5 μL, 0.47 mmol). The mixture was warmed to room temperature within 5 min, and after 2 h the solvent was removed under reduced pressure. After the remaining liquid was cooled to −78 °C, green metallic crystals were formed (205 mg, 86%, mp 146 °C (dec)): ^{1}H NMR (C_6D_6, 500 MHz) δ 1.07−1.18 (q/tr, J = 12.8/3.70 Hz, 1H), 1.20−1.31 (q/tr, J = 13.0/3.36 Hz, 3H), 1.42−1.51 (q/d, J = 12.3/2.98 Hz, 3H), 1.57−1.63 (m, 2H), 1.95−1.97 (m, 1H), all signals CH_2 ring protons 1.74 (s, 30H, $C_5(CH_3)_5$), 1.92 (d, J = 0.61 Hz, 3H, CH_3), 1.98 (s, 3H, CH_3), 3.40 (d, J = 0.92 Hz, 1H, $=CHH$), 3.72 (tr/tr, J = 11.0/3.66 Hz, 1H, NCH), 5.98 (d, J = 0.92 Hz, 1H, $=CHH$); $^{13}C\{^1H\}$ NMR (C_6D_6, 125 MHz) δ 13.0 ($C_5(CH_3)_5$), 15.0 (CH_3), 17.0 (CH_3), 26.2, 26.3, 36.8, all signals CH_2 ring carbons 61.8 (=NCH), 112.1 ($=CH_2$), 120.0 ($C_5(CH_3)_5$), 137.8 ($=C(CH_3)C=C$), 161.9 ($=C(CH_3)C=N$), 208.0 ($TiC=CH_2$), 225.1 (TiC=N); EI-MS (151 °C) m/e (I_{rel}) 507 (0.23) (M^+), 505 (0.31), 424 (6), 398 (14), 353 (8), 318 (100) $(Cp^*{}_2Ti)^+$, 181 (8), 119 (6), 107 (7), 55 (6); exact mass m/e 507.3345 ($C_{33}H_{49}NTi$), calculated m/e 507.3343; IR (KBr) 3017 m, 2988 s, 2932 vs, 2851 vs, 2715 w, 1592 s, 1560 s [ν(C=N)], 1494 m, 1450 s, 1433 s, 1373 s, 1341 m, 1282 m, 1229 m, 1180 w, 1159 w, 1142 w, 1086 w, 1063 m, 1021 s, 970 w, 923 w, 901 w, 880 m, 857 w, 842 w, 809 w, 664 w, 636 w, 617 w, 596 w, 545 w, 505 w, 463 m, 432 m, 421 m cm^{-1}. Anal. Calcd for $C_{33}H_{49}NTi$: C, 78.08; H, 9.73; N, 2.76. Found: C, 77.91; H, 9.58; N, 2.86.

Preparation of Bis(η^5-pentamethylcyclopentadienyl)-2-(cyclohexylimino)-5-methylene-3,4-diphenyltitanacyclopentene (25c). 8c (99.8 mg, 0.191 mmol) was dissolved in 20 mL of hexane, cooled to −30 °C, and treated with cyclohexaneisonitrile (23.8 μL, 0.191 mmol). The mixture was warmed to room temperature within 15 min, and after 1 h the solvent was removed under reduced pressure, yielding pale

Table 9. Positional Parameters and Estimated Standard Deviations for 19l[a]

atom	x	y	z	B (Å^2)
Ti	0.0904(2)	0.2306(2)	0.38972(7)	4.01(4)
C1	−0.165(1)	0.047(1)	0.4087(5)	7.5(4)
C2	−0.028(1)	0.092(1)	0.4242(4)	5.2(3)
C3	−0.0889(9)	0.2582(9)	0.3288(3)	4.1(2)
C4	−0.1944(9)	0.268(1)	0.2940(3)	4.6(2)
C10	0.176(1)	0.344(1)	0.4684(4)	6.9(3)
C11	0.025(1)	0.336(1)	0.4619(4)	7.4(3)
C12	−0.039(1)	0.405(1)	0.4218(5)	7.4(4)
C13	0.077(1)	0.4556(9)	0.4002(3)	5.8(3)
C14	0.210(1)	0.419(1)	0.4315(4)	6.1(3)
C15	0.277(2)	0.290(1)	0.5164(5)	18.4(7)
C16	−0.064(2)	0.284(1)	0.4992(5)	21.3(5)
C17	−0.196(1)	0.435(1)	0.4006(6)	20.1(5)
C18	0.064(2)	0.547(1)	0.3574(6)	17.5(8)
C19	0.358(1)	0.480(1)	0.4349(6)	15.3(5)
C20	0.308(1)	0.210(1)	0.3533(4)	6.0(3)
C21	0.327(1)	0.132(1)	0.3942(4)	6.2(3)
C22	0.232(1)	0.037(1)	0.3874(4)	6.8(3)
C23	0.136(1)	0.053(1)	0.3385(5)	7.3(3)
C24	0.193(1)	0.164(1)	0.3180(4)	6.5(3)
C25	0.411(1)	0.308(1)	0.3398(6)	15.6(6)
C26	0.466(1)	0.135(2)	0.4383(5)	13.6(5)
C27	0.237(2)	−0.082(1)	0.4211(6)	16.7(6)
C28	0.024(1)	−0.040(1)	0.3147(6)	19.5(5)
C29	0.142(2)	0.214(2)	0.2633(4)	16.0(6)
C41	−0.3187(9)	0.275(1)	0.2511(3)	4.9(3)
C42	−0.384(1)	0.165(1)	0.2305(4)	6.3(3)
C43	−0.505(1)	0.171(1)	0.1886(5)	8.4(4)
C44	−0.555(1)	0.282(1)	0.1699(4)	8.1(4)
C45	−0.493(1)	0.391(1)	0.1891(4)	7.6(4)
C46	−0.374(1)	0.390(1)	0.2302(4)	6.5(3)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter, defined as $(^4/_3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ac(\cos\beta)\beta_{13}]$.

green crystals (110 mg, 91%, mp 201 °C (dec)): ^{1}H NMR (C_6D_6, 300 MHz) δ 0.6−0.8 (q/m, 2H), 0.85−1.05 (m, 2H), 1.2−1.4 (m, 4H), 1.6−1.8 (m, 2H), all signals CH$_2$ ring protons 1.87 (s, 30H, $C_5(CH_3)_5$), 3.05 (tr/tr, J = 10.9/3.80 Hz, 1H, NCH), 3.51 (d, J = 2.02 Hz, 1H, =C*H*H), 5.44 (d, J = 2.01 Hz, 1H, =CH*H*), 6.85 (m, *p*-CH), 6.95 (tr/m, J = 7.39 Hz, *m*-CH), 7.03 (tr/m, J = 7.73 Hz, *m*-CH), 7.11 (d/m, J = 6.05 Hz, *o*-CH); $^{13}C\{^1H\}$ NMR (C_6D_6, 75 MHz) δ 13.3 ($C_5(\mathit{C}H_3)_5$), 26.0, 26.2, 36.1, all signals CH$_2$ ring carbons 61.8 (=NCH), 119.6 (=CH$_2$), 121.5 ($\mathit{C}_5(CH_3)_5$), 125.6, 125.7 (both *p*-C), 127.3, 127.4 (both *m*-C), 129.5, 129.7 (both *o*-C), 141.8 (ipso-C), 142.3 (=*C*(Ph)C=C), 143.9 (ipso-C), 166.1 (=*C*(Ph)C=N), 210.8 (Ti*C*=CH$_2$), 215.1 (TiC=N); EI-MS (27 °C) *m/e* (I_{rel}) 522 (100) (M − $C_6H_{11}NC)^+$, 518 (11), 505 (12), 440 (6), 386 (10), 377 (8), 353 (9), 340 (21), 318 (97) (Cp*$_2$Ti)$^+$, 242 (9), 230 (61), 203 (27), 181 (47), 178 (26), 134 (18), 119 (43), 105 (23), 91 (36), 77 (18), 67 (78), 57 (71); IR (KBr) 3041 w, 3012 w, 2923 vs, 2989 vs, 2849 s, 2717 w, 2602 w, 2358 w, 1942 w, 1636 m, 1598 m, 1572 w [ν(C=N)], 1535 m, 1484 m, 1440 s, 1375 s, 1340 m, 1294 m, 1261 w, 1233 w, 1176 w, 1069 m, 1023 m, 928 w, 892 w, 839 w, 807 m, 757 m, 740 s, 698 vs, 682 w, 620 w, 590 w, 520 w, 484 w, 464 w, 439 w cm^{-1}. Anal. Calcd for $C_{43}H_{53}NTi$: C, 81.75; H, 8.46; N, 2.22. Found: C, 81.36; H, 8.43; N, 2.14.

X-ray Structure Determination of 8b, 17k, and 19l. For all compounds geometry and intensity data were collected on Enraf-Nonius CAD4 diffractometers equipped with graphite monochromators. A summary of crystallographic data, data collection, and refinement parameters is given in Table 6. The structures of **8b** and **19l** were solved and refined with the SDP package[40a] and **17k** with MolEN.[40b] All non-hydrogen atoms were refined (full matrix) anisotropically, and all hydrogen atoms were treated as riding with idealized geometry [C−H = 0.98 Å, $B_{iso}(H) = 1.3B_{iso}(C)$]. For **8b** the hydrogen atoms at the *exo*-methylene group were refined isotropically. A statistical weighting scheme, $w^{-1} = \sigma^2(F_o)$, was used for all reflections. No absorption corrections were applied. 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-404519 (**8b**), -404520 (**17k**), and -404521 (**19l**).

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