ORGANOMETALLICS

Steric Effects in Reactions of Decamethyltitanocene Hydride with Internal Alkynes, Conjugated Diynes, and Conjugated Dienes

Jiří Pinkas,[†] Róbert Gyepes,^{†,‡,§} Ivana Císařová,[§] Jiří Kubišta,[†] Michal Horáček,[†] and Karel Mach^{*,†}

[†]J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, v.v.i., Dolejškova 3, 182 23 Prague 8, Czech Republic

[‡]Faculty of Education, J. Selye University, Bratislavská cesta 3322, 945 01 Komárno, Slovak Republic

[§]Department of Inorganic Chemistry, Charles University, Hlavova 2030, 128 40 Prague 2, Czech Republic

Supporting Information

ABSTRACT: Titanocene hydride $[Cp*_2TiH]$ ($Cp* = \eta^{5}$ - C_3Me_5) (1) readily inserts simple internal alkynes $R^1C \equiv CR^2$ into its Ti-H bond, yielding titanocene alkenyl Ti(III) compounds of two structural types. The less sterically congested products $[Cp*_2Ti(R^1C=CHR^2)]$ (2a-e) contain a σ^1 -bonded alkenyl group, whereas the products bearing at least one trimethylsilyl substituent and other bulky substituents ($R^1 = SiMe_3$; $R^2 = SiMe_3$, 4a; CMe₃, 4b; and Ph, 4c) possess a remarkable Ti-H agostic bond of the σ^1 -bonded alkenyl group. This feature is consistent with solution EPR spectra of 4a-4c showing a doublet due to coupling of the



hydrogen nucleus with the Ti(III) d¹ electron. Compound 1 reacts with one molar equivalent of conjugated buta-1,3-diynes $(RC\equiv C)_2$ to give η^3 -butenyne complexes $(R = SiMe_3, Sa; CMe_3, Sb)$. The Ti(III) complexes 2a-2e and Sa and Sb were oxidatively chlorinated with PbCl₂ to give Ti(IV) chloro-alkenyl complexes $[Cp^*_2TiCl(R^1C=CHR^2)]$ 3a-3e and chloro-alkenynes 6a and 6b, respectively. ¹H and ¹³C NMR spectra of 3a-3e and 6a and 6b revealed that these compounds form equilibria of two atropisomers differing by the *anti*- and *syn*-position of the chlorine and the alkenyl hydrogen atoms. Such atropisomers are denoted by appended (a) and (b), respectively. Compound 1 reacted with 1,3-butadiene to give a thermally stable π -bonded 1-methylallyl complex (7) and with penta-1,3-diene to give a thermally labile 1,3-dimethylallyl complex (8). In toluene- d_8 solutions 7 dissociated at 80 °C and 8 at room temperature to give $[Cp^*Ti(C_5Me_4CH_2)]$ and corresponding alkenes. Other methyl-substituted dienes, isoprene, 4-methylpenta-1,3-diene, and 2,3-dimethylbuta-1,3-diene, did not yield observable π -bonded allyl products; the dienes were, however, hydrogenated to olefins with concomitant formation of $[Cp^*Ti(C_5Me_4CH_2)]$. Compound 1 was shown to catalyze the hydrogenation of the alkynes and dienes to olefins and ultimately to alkanes under lower than atmospheric hydrogen pressure at room temperature. Single-crystal structures were determined for 3d(a), 3e(a), 4a-4c, 5a, 6b, and 7.

INTRODUCTION

Titanocene hydrides have been postulated to be the catalysts for hydrogenations of olefins in systems composed of $[Cp_2TiCl_2]$ ($Cp = \eta^5-C_5H_5$) and various Li to Al alkyls, hydrides, or metals;¹ however, the only isolated $[Cp_2TiH]$ species were the marginally stable violet dimer assigned to $[(Cp_2TiH)_2]$,^{2a} a gray-green low-soluble polymer $[(Cp_2TiH)_n]$ of unknown structure,^{2b} and Pez's dimeric titanocene hydride $[Cp_2Ti(\mu-C_5H_4)Ti(H)Cp]$,³ a thermal precursor to "green dimeric titanocene".^{2a} A distressful way to recognize that all attempts to prepare the titanocene $[Cp_2Ti]$ resulted in the formation of hydride species and obtaining "green dimeric titanocene" $[(\mu-\eta^5:\eta^5-C_5H_4C_5H_4)(\mu-H)_2(CpTi)_2]$ has been thoroughly reviewed by Chirik.⁴ This compound was shown to be a poor hydrogenation catalyst compared to Pez's dimer;^{3a} however, it turned out to be a superior isomerization catalyst, bringing hydrocarbon double-bond systems to thermodynamic equilibria at temperatures above 150 °C.⁵ Dissociation of its

bridging Ti–H bonds was anticipated from the occurrence of an EPR signal at g = 1.993 arising coincidently with the isomerization activity. The signal was tentatively assigned to an allyltitanocene moiety, and the isomerization activity to rapid exchanges of Ti–C bonds.⁶ In no case could detailed insight into the mechanism of interaction of a titanocene hydride with an unsaturated substrate be achieved.

A recent improvement in the synthesis of decamethyltitanocene hydride $[Cp^{\ast}{}_{2}TiH]$ (1)⁷ by addition of hydrogen to singly tucked-in titanocene $[Cp^{\ast}Ti(C_{5}Me_{4}CH_{2})]^{8}$ and the subsequent application of 1 in synthesis of the sterically congested $[(Cp^{\ast}{}_{2}Ti)_{2}O]^{9}$ brought us to investigate reactions of 1 with internal alkynes, conjugated butadiynes, and conjugated butadienes as an authentic primary step in their catalytic hydrogenation.

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RESULTS AND DISCUSSION

Synthesis of Titanocene Alkenyls 2a-2e. Compound 1 in hexane reacted with equimolar amounts of internal alkynes at ambient temperature to give σ -bonded titanocene alkenyls (Scheme 1). The composition of crystalline products was determined by EI-MS spectra, which showed molecular ions of moderate to low abundance. Elimination of alkenyl groups was the main fragmentation reaction, yielding an m/z 318 of $[Cp_{2}^{*}Ti]^{+}$ as the base peak. The presence of titanium(III) in 2a-2e was revealed by EPR spectra in solution showing a single line, whose g-factor and half-line width ΔH varied with the nature of the alkenyl substituents. In toluene glass, the orthorhombic g-tensor had g_1 and g_2 components virtually identical with the values common to trigonal titanocene derivatives with an electronegative ligand (halide,¹⁰ alkox-ide,^{10,11} hydroxide,¹² sulfide¹³), whereas the g_3 components differed to give g_{av} close to g_{iso} values. The paramagnetism of 2a-2e was also demonstrated by ¹H NMR spectra displaying broad signals over a wide range of chemical shifts. A dominating broad resonance in the range δ 15.5–18.4 ppm $(\Delta \nu_{1/2} \approx 2100 - 8100 \text{ Hz})$ common to all compounds is assigned to Cp* ligands by analogy with the spectra of alkyl derivatives $[Cp_{2}^{*}TiR]$ (R = Me or $CH_{2}CMe_{3}$),¹⁴ whereas resonances of the alkenyl groups could be assigned only tentatively (Table S2 in the Supporting Information). Electronic absorption spectra of 2a-2e are characterized mostly by poorly resolved absorption bands $1a_1 \rightarrow 2a_1$ and $1a_1 \rightarrow b_1$ observed close to those of alkyltitanocene compounds.^{10a} Infrared spectra (KBr) displayed common absorption bands of the Cp*2Ti moiety and characteristic bands of alkyne substituents (Ph, SiMe₃, and *t*-Bu). The alkenyl ν (C=C) and ν (=C-H) vibrations were, however, of very low intensity and could not be determined in most cases.

Compounds of this class, except **2b**, could be purified by crystallization; however, they did not afford crystals suitable for X-ray single-crystal diffraction analysis.¹⁵ The mode of insertion of asymmetric alkynes into the Ti–H bond as presented in Scheme 1 was established after oxidative chlorination of 2c-2e with PbCl₂ in tetrahydrofuran¹⁶ by ¹H and ¹³C NMR spectra analysis of 3c-3e. Regioselectivity of the alkyne insertion into the Ti–H bond is apparently controlled by the different bulkiness of the R¹ and R² alkyne substituents, the less bulky Me group residing on the C_{α} atom in 2d and 2e. For 2c the opposite regioisomer was established in nearly equal amount as

a result of a less striking difference in bulkiness of the Me and Ph substituents (see below).

Structures of Chlorotitanocene Alkenyls 3a–3e. Compounds of this type display in solution two sets of ¹H and ¹³C NMR signals, which can be assigned to two atropisomers, differing by orientation of the *cis*-alkenyl group with respect to the chlorine atom. Atropisomers possessing the chlorine atom in *anti*-position to the hydrogen of the HC= group are denoted by appending (a) to the above denotation, and those with these moieties in *syn*-position by appending (b) (see Scheme 1). The two atropisomers differ remarkably in their chemical shift for the =CH proton: $\delta_{\rm H}$ (=CH) for the (a) (*anti*) atropisomer is about 2 ppm high-field shifted compared to atropisomer (b) (*syn*) (Table 1).

Table 1. Selected ¹H and ¹³C NMR Chemical Shifts (in ppm) of the Alkenyl Moiety in 3a-3e, 6a, and 6b

	(b)/(a) ^{<i>a</i>}	$\delta_{\mathrm{H}} (= CH)^{b}$ (b)/(a)	$\delta_{\mathrm{C}}(=C\mathrm{H})\ (\mathbf{b})/(\mathbf{a})$	$\delta_{ m C}({ m Ti}C)\ ({f b})/({f a})$
3a	40/60	5.33/3.68	123.35/119.92	206.50/200.31
3b	0/100	-/4.64	-/127.08	-/204.75
$3c^{c}$	18/38	6.57/4.84	130.65/128.2	212.08/207.83
3d	50/50	5.32/3.48	138.17/129.21	204.58/200.56
3e	25/75	5.51/3.97	130.73/127.17	237.15/232.15
6a	100/0	6.28/-	154.49/-	206.58/-
6b	65/35	5.72/4.01	152.72/147.12	177.19/172.82
$a \land \land \land$	<i>(</i> ,) <i>(</i>	. (1) (b	1

^{*a*}(a) (*anti*-) atropisomer, (b) (*syn*-) atropisomer. ^{*b*}Average values are given for multiplets. ^{*c*}Crude 3c contained 44% of the opposite regioisomer 3c(c).

For compounds 3c-3e obtained from asymmetrical alkynes the sterically more demanding group was found exclusively on the β -carbon atom of the *cis*-alkenyl group except 3c. The presence of a methyl group on the α -carbon atom in 3c-3eexhibited a characteristic allylic coupling between the methyl group protons and an olefinic proton (${}^{4}J_{\rm HH} = 1.1-1.7$ Hz) (see Supporting Information). For crude 3c the presence of a regioisomer containing the methyl group on the C_{β} atom and the phenyl group on the C_{α} atom (3c(c)) was deduced from a much stronger interaction (${}^{3}J_{\rm HH} = 6.6$ Hz) between the vicinal methyl and olefinic protons; the corresponding second atropisomer was not recognized by the 1 H and 13 C NMR spectra. Crystallization of 3c for obtaining single crystals afforded a crystalline solid of the composition 3c(a) 70%, 3c(b) 30%, whereas regioisomer 3c(c) remained in the mother liquor. The correctness of the NMR analyses above was corroborated by crystal structures of 3d(a) (Figure 1) and 3e(a) (Figure 2), both having the alkenyl plane roughly perpendicular to the plane of the bent titanocene. Important molecular parameters are gathered in Table 2.



Figure 1. PLATON drawing of 3d(a) at the 30% probability level with atom-labeling scheme. Hydrogen atoms are omitted for clarity.



Figure 2. PLATON drawing of 3e(a) at the 30% probability level with atom-labeling scheme. Hydrogen atoms are omitted for clarity.

Both compounds crystallized out from their hexane solutions; however, when dissolved in toluene- d_8 , they slowly isomerized to give an equilibrium composition of 3d(a)/3d(b) and 3e(a)/3e(b), respectively, on the time scale of months. The slow isomerization to an equilibrium is apparently the reason that Teuben et al.¹⁷ did not recognize the presence of atropisomers in their analogous synthesis of 3a, 3b, and 3c using [Cp*₂TiEt], which after dissociation of ethene reacted as 1. Their ¹H and ¹³C NMR data agree with the presence of 3a(a) and 3c(a), which indicates that fresh solutions of crystalline products were analyzed. For 3b their and the present

Table 2. Selected	Bond	Lengths	and	Bond	Angles	for	3d(a))
and 3e(a)								

	3d(a)	3e(a)
Bond Lengths (Å)		
$Ti-Cg(1)^a$	2.1432(10)	2.1330(7)
$Ti-Cg(2)^a$	2.1349(10)	2.1318(7)
Ti-C(21)	2.204(2)	2.1944(15)
C(21)-C(22)	1.331(3)	1.340(2)
Ti-Cl	1.3539(6)	2.3640(5)
Bond Angles (deg)		
Cg(1)-Ti- $Cg(2)$	138.21(4)	138.52(3)
Ti-C(21)-C(22)	122.75(16)	124.24(11)
C(21)-C(22)-C(27)	132.7(2)	$135.79(12)^{b}$
C(22) - C(21) - C(23)	122.3(2)	121.29(14)
Cl-Ti-C(21)	96.43(6)	96.02(4)
Dihedral Angles (deg)		
φ^{c}	44.03(11)	42.98(4)
ψ^d	1.61(18)	2.07(1)

^{*a*}Cg(1) and Cg(2) are centroids of cyclopentadienyl rings with lower and higher C-numbers, respectively. ^{*b*}Si instead of C(27). ^{*c*}Dihedral angle between the least-squares planes of cyclopentadienyl rings. ^{*d*}Dihedral angle between the planes defined by Ti, Cl, and C(21) and Ti, C(21), and C(22).

data indicate the presence of only one isomer, 3b(a). The kinetics of (a) to (b) isomerizations to equilibria were not investigated due to photosensitivity of all these chloro derivatives. For instance, compound 3b(a) in toluene completely decomposed, eliminating (Z)-stilbene after exposure to summer sunlight for 4 h.

Titanocene Alkenyls with Agostic Hydrogen 4a–4c. Compound 1 inserts alkynes bearing at least one trimethylsilyl substituent and other bulky substituents to give compounds 4a-4c ($R^1 = SiMe_3$, $R^2 = SiMe_3$, 4a; $R^2 = CMe_3$, 4b; and $R^2 =$ Ph, 4c) (Scheme 2). These compounds differ from 2a-2e by a remarkable Ti–H agostic bond of a σ^1 -bonded alkenyl group in the solid state as well as in solution.

The X-ray crystal structures of 4a, 4b (Figure 3), and 4c (Figure 4) show that the alkenyl ligand plane is approximately perpendicular to the plane of the bent titanocene moiety and nearly bisects the Cg(1)-Ti-Cg(2) angle.

In all cases the alkenyl hydrogen atom was localized on the difference Fourier electron density map and refined isotropically without any restraints. Selected geometric parameters pertinent to bonding of the alkenyl group to titanocene are gathered in Table 3. These data provide evidence that the requirements defining metal-hydrogen agostic bond forma-



Figure 3. PLATON drawing of 4a and 4b at the 30% probability level, with atom-labeling scheme. Hydrogen atoms except the agostic one are omitted for clarity.

Scheme 2



Figure 4. PLATON drawing of 4c at the 30% probability level, with atom-labeling scheme. Hydrogen atoms except the agostic one are omitted for clarity.

Table 3. Selected Bond Lengths and Bond Angles for 4a, 4b, and 4c

	4a	4b	4c
Bond Lengths (Å)			
$Ti-Cg(1)^a$	2.1019(10)	2.088(4)	2.0893(9)
$Ti-Cg(2)^a$	2.0942(10)	2.117(4)	2.0967(8)
$Ti-C_{\alpha}^{b}$	2.261(2)	2.206(2)	2.199(2)
$Ti-C_{\beta}^{b}$	2.308(2)	2.434(2)	2.403(2)
$C_{\alpha} - C_{\beta}^{\ b}$	1.306(3)	1.308(3)	1.321(3)
C_{β} -H	0.890(19)	1.08(3)	1.03(3)
Ti-H	1.91(2)	1.97(3)	1.99(3)
Bond Angles (deg)			
Cg(1)-Ti- $Cg(2)$	139.51(4)	137.85(19)	140.99(4)
$C_{\alpha}-C_{\beta}-H$	124.7(15)	116.3(13)	119.4(18)
$Ti-C_{\beta}-H$	53.3(15)	52.2(13)	54.4(18)
C_{α} -Ti-H	55.1(6)	58.0(8)	57.8(10)
$Ti-H-C_{\beta}$	104.7(16)	102.1(16)	101(2)
Dihedral Angles (deg)			
φ^{c}	39.73(8)	40.92(23)	38.85(8)
$\psi_1{}^d$	19.78(6)	19.70(28)	19.12(16)
$\psi_1^{\ e}$	19.94(9)	21.47(27)	19.80(12)

 ${}^{a}Cg(1)$ and Cg(2) are centroids of cyclopentadienyl rings with lower and higher C-numbers, respectively. ${}^{b}Alkenyl$ group sp² carbon atoms: C_{α} binds to Ti, C_{β} bears the hydrogen atom. ${}^{c}Dihedral$ angle between the least-squares planes of cyclopentadienyl rings. ${}^{d}Dihedral$ angle between the plane defined by Ti, C_{α} and C_{β} and the cyclopentadienyl least-squares plane containing Cg(1). ${}^{c}Dihedral$ angle between the plane defined by Ti, C_{α} , and C_{β} and the cyclopentadienyl least-squares plane containing Cg(2).

tion,¹⁸ namely, a comparable distance of Ti– C_{β} and Ti–H and a Ti– C_{β} –H angle smaller than 100°, are all fulfilled. The Ti–H

distance below 2.0 Å and the Ti–C_{β}–H angle close to 55° indicate the presence of a strong agostic Ti–H bond in comparison with the known Ti(III) compounds.¹⁹

Compounds 4a-4c are thermally stable, with melting points above 100 °C. EI-MS spectra of 4b and 4c showed low abundant molecular ions and the $[Cp*_{2}Ti]^{+}$ fragment as a base peak; however, 4a was dissociating during evaporation into bis(trimethylsilyl)ethyne and titanocene. Infrared spectra (KBr) gave evidence for the presence of a Cp*₂Ti moiety and alkenyl substituents. However, they provided no clear support for the presence of the alkenyl group double bond; only very weak absorption bands were observed in the region of the ν (C=C) vibration 1500-1700 cm⁻¹ except for the phenyl group vibrations at 1589 (m) and 1571 (w) cm⁻¹ for 4c. Similarly, no absorption band could be attributed to ν (C-H) of the agostic C=C-H moiety. ¹H NMR spectra of paramagnetic toluene- d_8 solutions allowed us to assign the most low-fieldshifted and broad resonance to Cp* ligands and narrower resonances at higher field to alkenyl substituents; however, they did not supply any evidence for an agostic hydrogen.

Support for agostic bonding in 4a-4c was obtained from their solution EPR spectra, which showed a doublet splitting due to coupling of the hydrogen nucleus to the Ti(III) d¹ electron. This assignment was justified by the EPR spectrum of the product obtained from the reaction of *tert*-butyl-(trimethylsilyl)ethyne with deuterated 1 (D \geq 80%). The doublet $a_{\rm H} = 3.5$ G ($\Delta H = 1.5$ G) observed at $g_{\rm iso} = 1.984$ for 4b was strongly attenuated with respect to a new central single line due to the unresolved coupling of ==C-D with the Ti(III) d¹ electron ($a_{\rm H}/a_{\rm D} = 6.5$). The agostic compounds 4a-4c differ from the nonagostic 2a-2e by a considerably smaller line width of their EPR signals, which occur at higher *g*-values. The electronic absorption spectra of 4a-4c display a distinct absorption band at 540 nm that gives rise to a characteristic purple color of these compounds.

For a better understanding of the formation of and the bonding in these compounds, DFT studies have been carried out. As a representative of the complexes lacking an agostic interaction, **2a** has been examined; as a representative of agostic complexes, **4b** has been chosen. Prior to examining the orbitals of the complexes, geometry optimization has been done on both geometries. The optimization was necessary mostly for **2a**, whose solid-state structure suffered from a severe disorder of all its ligands around the central atom.¹⁵ For **4b**, a geometry nearly identical to the one obtained from diffraction experiments was obtained.

To get some insight into the thermodynamics of formation, together with molecule 2a, its analogue, having its olefinic hydrogen in an agostic interaction, has also been investigated. After both isomers reached proper ground states via geometry optimization, the comparison of total energies has revealed a slight preference for the nonagostic σ -complex by 3.23 kJ/mol. Comparing both the agostic and nonagostic isomers of 2a (Figure 5), it has become evident that steric effects play a key role in determining the geometry of the final complex. The nonagostic arrangement for 2a yielded a lower nuclear repulsion energy (2979.7 h compared with 2998.1 h for the agostic counterpart), although its $R_1(Me)$ group in the plane of the butenyl ligand was simultaneously directed more to the side of the bent titanocene shell than in the agostic isomer. This arrangement becomes sterically hindered when the R₁ group becomes bulkier; increased repulsion with the titanocene moiety forces R₁ to seek the position closer to the central



Figure 5. Comparison of the agostic (left) and nonagostic (right) isomers of **2a** (distances in Å; for atom coordinates see the Supporting Information).

part of the titanocene shell. As a result, the whole alkenyl ligand is inclined by the other olefinic carbon atom to the metal atom and initiates the agostic interaction of the C–H bond.

The agostic interaction is readily examined by comparing the NBO results of both isomers of **2a**. Whereas for the nonagostic isomer the sum of delocalization energies to the metal amounted only to 5.86 kJ/mol, the agostic molecule yielded the analogous sum 82.37 kJ/mol. For the agostic molecule, the largest contribution occurred to a metallic acceptor orbital having a mixed p and d character (84% p; 15% d).

Attempts to carry out analogous studies for **4b** were only partially successful. Although computational studies of **4b** itself did not pose a problem, no stationary point could be found for its nonagostic counterpart, where geometry optimization converged smoothly back to the agostic arrangement. Inspection of displacement forces on individual atoms after computing the gradient and the Hessian for the initial nonagostic geometry has revealed the largest displacement force on the noncoordinated olefinic carbon, pushing it in the direction of the metal. It can thus be concluded that the failure of reaching a ground state with the nonagostic molecule is an inherent physical property and not the consequence of a poor starting geometry. The classification of relevant orbitals leads to a description of **4b** as a σ -complex. One olefinic carbon atom is σ -coordinated to the metal, whereas the C–H bond undergoes a concurrent agostic interaction with the metallic center. As observed also for other bent sandwich Ti complexes,²⁰ the σ -coordination of the olefinic carbon occurs to the doubly occupied b₂ frontier orbital of the bent titanocene. The singly occupied 1a₁ bent Cp*₂Ti frontier orbital becomes the molecular SOMO. This SOMO, due to the favorable orientation of the proximal olefinic C–H σ -bond, has a small overlap with the C–H σ -orbital (Figure 6).

Natural bond analysis reported a double bond between the two olefinic carbon atoms and some additional delocalization of the C–H bond to the metal. NBO thus supported the description of the complex as a Ti–C σ -bonded olefinic molecule, incorporating a C–H agostic interaction with the central atom. The presence of an agostic interaction was observable also by the decreased occupancy (0.93) of the C–H bond. For a quick overview of the olefinic ligand bonding, Mayer bond orders and computed bond lengths are depicted in Figure 7.



Figure 7. Mayer bond orders (left) and optimalized bond lengths (in Å, right) for the agostically bonded alkenyl moiety in 4b.

Reaction of 1 with Conjugated Diynes. Insertion of 1,4bis(trimethylsilyl)buta-1,3-diyne into the Ti-H bond of 1 afforded compound **5a** (Scheme 3), whose X-ray crystal structure has proven that a η^3 -butenyne ligand is coordinated to titanocene (Figure 8).

The geometry of the 1,4-bis(trimethylsilyl)but-1-ene-3-yne-2-yl ligand and its coordination to titanium is very similar to an analogous complex, 5 (Chart 1), generated by formal insertion



Figure 6. Perspective view of canonical orbital 130 (SOMO, 2% probability, alpha spin, $\varepsilon = -0.14364$ h) on the left and its contour diagram on the right. The plane of the contour diagram is defined by the metallic center and the two olefinic carbon atoms.

Scheme 3





Figure 8. PLATON drawing of 5a at the 30% probability level with atom-labeling scheme. Hydrogen atoms except H1 are omitted for clarity.

Chart 1. Schematic Formula of Compound 5



 Table 4. Selected Bond Lengths and Bond Angles for 5a

of 1,4-bis(trimethylsilyl)buta-1,3-diyne into the Ti–C bond of $[Cp*_2Ti(C\equiv CSiMe_3)]^{21}$ Compound 5 was formed in a complex system where $Cp*_2TiCl_2$ was reduced with magnesium in the presence of excess 1,4-bis(trimethylsilyl)-buta-1,3-diyne; the tweezer complex $[\{Cp*_2Ti(\eta^{1-}C\equiv CSiMe_3)_2\}\{MgCl(THF)\}]^{22}$ and the back-bonded acetylene complex $[Cp*_2Ti(\eta^2-Me_3SiC\equiv CC_2SiMe_3)]^{23}$ were considered to be intermediates.

Both complexes display a very narrow EPR signal at high *g*-values (5: $g_{iso} = 1.991$, $\Delta H = 1.7$ G; **5a**: $g_{iso} = 1.993$, $\Delta H = 1.8$ G), which indicates a similar delocalization of the unpaired electron density over the η^3 -butenyne ligand. The triple bond of the η^3 -butenyne ligand (C(21)-C(22) 1.258(2) Å) is relatively weakly bonded to titanium by π -coordination, as follows from the long distances Ti-C(21) = 2.2883(16) Å and Ti-C(22) = 2.4086(17) Å. Correspondingly, the infrared $\nu(C \equiv C)$ valence vibration is shifted from 2109 cm⁻¹ for the free diyne to 1845 cm⁻¹, whereas the back-bonded triple bond in titanocene– alkyne complexes occurs close to 1600 cm^{-1.24}

The analogous reaction of 1 with 1,4-di-*tert*-butylbuta-1,3diyne yielded a brown, oily product, which could not be purified by crystallization. The solution EPR and paramagnetic ¹H NMR spectra of the product were similar to those of **5a** and did not reveal distinct impurities. The compound was assigned to be **5b** after its chlorination with PbCl₂, which yielded red crystalline **6b** (Scheme 3) in high yield. The crystal structure of

Bond Lengths (A)			
$Ti-Cg(1)^{a}$	2.1020(8)	$Ti-Cg(2)^a$	2.1047(8)
$Ti-Pl(1)^b$	2.1016(3)	$Ti-Pl(2)^{b}$	2.1042(3)
Ti-C(21)	2.2883(16)	C(21)-C(22)	1.258(2)
Ti-C(22)	2.4086(17)	C(21)-C(26)	1.375(2)
Ti-C(26)	2.2370(16)	C(26)-C(27)	1.339(2)
Si(1)-C(22)	1.8506(17)	Si(2)-C(27)	1.8661(18)
C(27)-H(1)	0.95(2)		
Bond Angles (deg)			
$Cg(1)$ -Ti- $Cg(2)^a$	140.50(3)	C(22) - Ti - C(26)	66.28(6)
Ti-C(26)-C(21)	74.36(9)	Ti-C(26)-C(27)	149.53(13)
Ti-C(21)-C(22)	79.83(10)	C(21)-C(22)-C(26)	150.09(16)
C(21)-C(26)-C(27)	136.10(16)	C(26)-C(27)-Si(2)	124.17(14)
C(21)-C(22)-Si(1)	136.52(14)	C(26)-C(27)-H(1)	117.5(12)
Dihedral Angles (deg)			
φ^c	40.12(7)	$\psi(1)^d$	20.00(6)
$\psi(2)^e$	20.13(9)		

 ${}^{a}Cg(1)$ and Cg(2) are centroids of the C(1–6) and C(11–15) cyclopentadienyl rings, respectively. ${}^{b}Pl(1)$ and Pl(2) are least-squares planes of the C(1–6) and C(11–15) cyclopentadienyl rings, respectively. ${}^{c}Dihedral$ angle between Pl(1) and Pl(2). ${}^{d}Dihedral$ angle between Pl(1) and the least-squares plane of Ti, C(21), C(22), and C(26) atoms. ${}^{c}Dihedral$ angle between Pl(2) and the least-squares plane of Ti, C(21), C(22), and C(26) atoms.

6b suffered from a considerable disorder, which, however, could be resolved into two atropisomers, 6b(b) (88.2(2)%) and 6b(a). The molecule of 6b(b) is depicted in Figure 9. The



Figure 9. PLATON drawing of 6b(b) at the 30% probability level with atom-labeling scheme. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Ti(1A)-Cl(1A) 2.3567(8), Ti(1A)-C(11A) 2.207(2), C(11A)-C(12A) 1.347(3), C(11A)-C(17A) 1.434(3), C(17A)-C(18A) 1.199(3), and bond angles (deg): Cg(1)-Ti-Cg(2) 137.90(6), Cl(1A)-Ti(1A)-C(11A) 93.64(6), C(11A)-C(12A)-C(13A) 129.1(2), C(12A)-C(11A)-C(17A) 119.20(19), C(11A)-C(17A)-C(18A) 179.4(2).

above composition of the atropisomers in the solid state agrees with a high abundance of 6b(b) (65%), as found by ¹H NMR for the product solution used for the crystallization.

Compound **5a** was chlorinated with $PbCl_2$ to give pure **6a(b)** according to the proton chemical shift, which occurred as high as at 6.28 ppm (see Table 1). Compared to titanocene chloro alkenyl compounds **3a**-**3e**, where atropisomers with chlorine and hydrogen atoms in *anti*-position prevailed, compounds **6a** and **6b** prefer the *syn*-position, apparently due to the presence of the rigid alkynyl group lying close to the double-bond plane.

Hydrogenation of the Titanocene Alkenyl Complexes and Catalytic Hydrogenation of the Alkynes. The above reactions of 1 with the alkynes should represent the first step in titanocene-induced hydrogenation of internal alkynes,²⁵ and hence, several exploratory experiments were carried out to shed light on perspectives of exploitation of 1 as a hydrogenation catalyst. As representatives, complexes 2a and 4c (0.5 mmol) in toluene- d_8 were left to react with excess gaseous hydrogen from an attached ampule (~3 mmol) overnight. After pumping off any unused hydrogen, organic volatiles were distilled into a trap under vacuum and then analyzed by ¹H and ¹³C NMR spectra to be pure butane for 2a and a mixture of (Z)-PhHC= $CH(SiMe_3)$, 56%, (E)-PhHC= $CH(SiMe_3)$, 8%, and PhCH₂CH₂(SiMe₃), 36%, for 4c. In both cases the solid residue was 1 with a minor amount of $[Cp*Ti(C_5Me_4CH_2)]$. In addition, amplified ¹H NMR spectra revealed the resonance of $[Cp_2^*Ti]$ (63.8 ppm, $\Delta v_{1/2} = 170$ Hz) with roughly 2 orders of magnitude lower intensity, forming an equilibrium concentration with the above two components.⁸

The analogous hydrogenation of hex-3-yne with 1 and hydrogen was interrupted when yielding (*Z*)-hex-3-ene (80%) and hexane (20%). An accomplished hydrogenation of 1-phenylprop-1-yne initiated with $[Cp*Ti(C_5Me_4CH_2)]$ afforded propylbenzene and 1. In this case hydrogen was admitted prior to the alkyne to avoid the reaction of the latter with $[Cp*Ti(C_5Me_4CH_2)]$, affording propenyl-tethered titanocene derivatives.²⁶ In the absence of hydrogen, compound 4c in toluene-*d*₈ cleanly dissociated to give pure (*Z*)-PhHC=

CH(SiMe₃) and $[Cp*Ti(C_5Me_4CH_2)]$ after heating to 110 °C for 8 h. The absence of the *cis/trans* isomerization to the thermodynamically more stable *trans*-isomer is in accordance with the previously established reluctance of $[Cp*Ti-(C_5Me_4CH_2)]$ to react with olefins except ethene.²⁶

These experiments showed that hydrogen at a lower than atmospheric pressure hydrogenates internal alkynes using **1** as a hydrogen transfer mediator or $[Cp*Ti(C_5Me_4CH_2)]$ as a precursor to **1**. The formation of (*Z*)-alkenes and their further hydrogenation to alkanes is outlined in Scheme 4.



Reaction intermediates 2 and 4 are thermally stable compounds (mp > 100 $^{\circ}$ C); however, addition of a hydrogen molecule brings about the elimination of (Z)-alkene at room temperature only. Different alkene/alkane ratios found in comparable experiments indicate that the bulkiness of substituents R¹ and R² strongly influences the pseudoequilibria, leading to sec-alkyltitanocene intermediates. These sterically congested compounds should rapidly decompose (cf. nhexyltitanocene has a half-lifetime $t_{1/2} = 4.8$ h at 20 °C)^{7b} to give $[Cp*Ti(C_5Me_4CH_2)]$ and an alkane in the absence of hydrogen. In the presence of hydrogen the concurrent hydrogenolysis of the Ti-C bond in either sec-alkyltitanocene or $[Cp*Ti(C_5Me_4CH_2)]$ closes the cycle. A high or exclusive selectivity for the formation of (Z)-alkenes should be achieved after consumption of one molar equivalent of hydrogen with respect to the alkyne. The formation of alkanes is controlled by the ratio of reaction rates of 1 with alkynes and alkenes. Other homogeneous catalysts for hydrogenation of internal alkynes to (Z)-alkenes are based on transition metals²⁷ and, recently, on frustrated Lewis pairs.²⁸

The use of 1 as a hydrogenation transfer agent allows stopping the reaction with concomitant formation of $[Cp^*Ti-(C_5Me_4CH_2)]$ and restarting it by restoring the hydrogen feed. So far no inherent deactivation process is foreseeable for these systems (except catalytic poisoning from outside). Application of 1 for hydrogenation of tri- and tetrasubstituted olefins may have limits due to steric hindrance; this topic has been so far beyond the scope of this research.

Reaction of 1 with Butadiene and Its Methyl Homologues. These conjugated dienes are known to react with a transient titanocene hydride, which was suggested to be formed, for example, in the Cp₂TiCl₂/*i*-PrMgBr system by elimination of propene. Stable titanocene(Ti^{III}) π -allyl derivatives were formed by diene insertion into the Ti–H bond.²⁹ As expected, compound **1** reacts with the dienes in an analogous way; however, the stability of the π -allyl products is strongly limited by the steric hindrance between the Cp*₂Ti shell and the diene methyl substituents. The thermally stable crystalline product [Cp*₂Ti(η^3 -C₄H₇)] (7) was obtained only from the reaction of 1 with butadiene in hexane. A mixture of green and purple crystals crystallized from a purple hexane solution, both dissolving to give reversibly the purple solution ($\lambda_{max} = 517$ nm). The solution showed a pseudosinglet EPR spectrum whose shape was identical with that obtained from the reaction of Cp*₂Ti(AlH₄) with butadiene.³⁰ The X-ray diffraction analysis of a green single crystal of 7 showed that its unit cell contains six crystallographically independent molecules that differ slightly in the placement of the Cp* and 1-methylallyl ligands. All the molecules (7A–7E) with the exception of the considerably disordered one (7F) proved that permethyltitanocene binds the 1-methylallyl group via a π -donation (Figure 10).



Figure 10. PLATON drawing of molecule 7 (B) at the 30% probability level with the atom-labeling scheme. Hydrogen atoms except those of the allyl group are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): Ti-C(21) 2.311(6), Ti-C(22) 2.358(5), Ti-C(23) 2.516 (6), C(21)-C(22) 1.388(8), C(22)-C(23) 1.370(8), C(23)-C(24) 1.508(8), Cg(1)-Ti-Cg(2) 138.38(11), C(21)-Ti-C(23) 61.5(2), C(21)-C(22)-C(23) 127.6(6).

The allyl plane is nearly perpendicular to the Cg1, Ti, and Cg2 plane, and the interconnection of the centroid of the η^3 -allyl group with the titanium atom approximately bisects the Cg1–Ti–Cg2 angle. Dihedral angles between the allyl plane (C(21), C(22), and C(23)) and the Ti, C(21), and C(23) plane amount to 64.5(7)–70.4(5)°, falling close to the upper range of values for the known titanocene allyl compounds (59–68°).³¹

The paramagnetic ¹H NMR spectrum of 7 shows a broad signal at 18.4 ppm ($\nu_{1/2}$ = 4500 Hz). This signal can be attributed to the Cp* ligands on the basis of experimental data for a number of permethyltitanocene(Ti^{III}) derivatives.^{9,14} Resonances for the 1-methylallyl ligand were not observed. Solid 7 and its toluene-*d*₈ solution were proved to be stable at room temperature for at least 9 months; heating its toluene solution to 80 °C for 3 h resulted in the complex decomposition yielding [Cp*Ti(C₅Me₄CH₂)] and a mixture of (*E*)-2-butene and (*Z*)-2-butene in roughly 2:1 ratio (Scheme 5).

Among butadiene methyl homologues isoprene, penta-1,3diene, 4-methylpenta-1,3-dieme, and 2,3-dimethylbuta-1,3-





diene only penta-1,3-diene reacted with 1 to give a welldiscernible π -allyltitanocene product. A sky-blue solution of the reaction product displayed an EPR spectrum (g = 1.9912, $\Delta H =$ 4.3 G) very similar to that of 7 and a distinct absorption band at 565 nm in its electronic absorption spectrum. The bathochromic shift of this absorption band with respect to the absorption band at 517 nm for 7 is in agreement with the analogous shift for the titanocene compounds Cp₂Ti(η^3 -1methylallyl) (538 nm) and Cp₂Ti(η^3 -1,3-dimethylallyl) (577 nm).^{29b,c} Hence, it is plausible to assign this product to $Cp*_{2}Ti(\eta^{3}-1,3-dimethylallyl)$ (8), although its appropriate characterization was precluded by its low thermal stability. The blue solution of 8 in toluene- d_8 turned purple within 3 h at room temperature, and its paramagnetic ^IH NMR spectrum showed the overwhelming presence of $[Cp*Ti(C_5Me_4CH_2)]$. A volatile organic product was identified by combination of GC-MS and ¹H and ¹³C NMR spectra to be pent-2-ene.

The other dienes reacted with 1 analogously to give $[Cp*Ti(C_5Me_4CH_2)]$ and an olefin; however, the reaction conditions depended strongly on steric hindrance of their double bonds (Scheme 6). Addition of excess isoprene to 1

Scheme 6



resulted in a transient green coloration, which could be ascribed to an η^3 -1,2-dimethylallyl complex. It changed within a minute to brown in agreement with observations that the 2-methyl substituent at the η^3 -allyl ligand decreases the thermal stability of its titanocene complex.^{29,30} The brown color of the apparently σ -allyl complex then slowly turned to a purple color of [Cp*Ti(C₅Me₄CH₂)].

The analogous reaction of 4-methylpenta-1,3-diene with 1 ran sluggishly at room temperature; however, warming to 60 $^{\circ}$ C for 3 h led to the full conversion. In both cases the olefinic products indicate that a more easily accessible vinyl group took part in the reaction with 1. The least reactive 2,3-dimethylbuta-1,3-diene dissolved 1 without any reaction, and heating to 80 $^{\circ}$ C for 40 h was necessary to convert 1 to [Cp*Ti-

Organometallics

 $(C_5 Me_4 CH_2)]$ and the stoichiometric part of the diene to tetramethylethene.

It can be concluded that dienes react by formal insertion of the more easily accessible terminal double bond into the Ti-H bond forming the π -allyl or σ -allyl Cp*₂Ti complexes. The π allyl complexes show a lower thermal stability than corresponding $Cp_2Ti(\pi$ -allyl) complexes due to a larger hindrance between the Cp^{*}₂Ti shell and the π -allyl ligand. In both titanocene series the compound stability depends on the number and position of the diene methyl substituents. The hydrogenation of the dienes with 1 is apparently preceded by the π -to- σ - isomerization and is accomplished by the hydrogen transfer from one Cp* C-H bond to the leaving alkenyl ligand. The latter step minics the formation of $[Cp*Ti(C_5Me_4CH_2)]$ by thermolysis of permethyltitanocene alkyl compounds.^{7b,c,8} The ability of titanocene alkyl or hydride species to optimize the thermodynamic stability of systems with double bonds via the succession of Ti-C bond formation and elimination⁵ likely is evident in the thermolysis of 7, yielding (E)/(Z)-but-2-enes, and in exclusive formation of tetramethylethene, which both proceeded at 80 °C.

An experiment on the hydrogenation of isoprene with one equivalent of dihydrogen catalyzed by $[Cp*Ti(C_5Me_4CH_2)]$ yielding 2-methylbut-1-ene and 1 proved that the catalytic cycle for hydrogenation of alkynes (Scheme 4) can be applied for dienes provided the alkenyl intermediates 2 and 4 are replaced by σ -allyl complexes.

CONCLUSIONS

Compound 1 rapidly reacts with internal alkynes to give paramagnetic decamethyltitanocene alkenyls 2a-2e. Although these products are largely crystalline, none of them afforded crystals suitable for X-ray diffraction analysis. Insight into their structure was obtained after their conversion to alkenylchlorotitanium(IV) derivatives 3a-3e. ¹H and ¹³C NMR spectra of 3a-3e revealed that they consist of atropisomers with the chlorine atom and the alkenyl C–H bond in *anti* (a) and syn (b) conformation, and X-ray structures of crystalline atropisomers 3d(a) and 3e(a) corroborated the NMR assignment. On this basis it was also shown that the bulkiness of alkyne substituents controls the regioselectivity of the asymmetric alkyne insertion in 2c-2e. In distinction from 2a-2e, very bulky substituents (t-Bu, SiMe₃, Ph) induce the formation of alkenyl compounds 4a-4c, containing a significant agostic bond of the alkenyl C-H bond to the titanium atom observable in their X-ray crystal structures. These compounds are distinguishable from the nonagostic 2a-2e by sharp EPR signals showing coupling to the alkenyl agostic hydrogen atom. DFT calculations on 2a and 4b revealed only a slight energy preference for the nonagostic isomer of 2a, whereas no stationary point could be found for the nonagostic 4b; its geometry optimization converged to the agostic arrangement with the alkenyl moiety bonded to titanium by σ -Ti-C and agostic Ti-H bonds. Exploratory experiments proved that compounds of type 2 and 4 are intermediates in the hydrogenation of internal alkynes producing (Z)-alkenes and/ or alkanes. Conjugated diynes RC=CC=CR (R = SiMe₃, t-Bu) insert into the Ti-H bond of 1 by one triple bond, whereas the other triple bond coordinates to the titanium atom to form the η^3 -butenyne ligand in compounds 5a and 5b. Among simple buta-1,3-diene methyl derivatives only the parent buta-1,3-diene reacted with 1 to give thermally stable π allyl complex 7. Other dienes were hydrogenated with 1 at the

sterically less hindered double bond, while 1 was converted to $[Cp*Ti(C_5Me_4CH_2)].$

EXPERIMENTAL SECTION

General Considerations. Synthesis of [Cp*₂TiH] (1) and its handling and reactions in solution were carried out under high vacuum in sealed all-glass devices equipped with breakable seals. 1H (300 MHz), ^{13}C (75 MHz), and ^{29}Si (59.6 MHz) NMR spectra were recorded on a Varian Mercury 300 spectrometer in toluene- d_8 at 25 °C. Chemical shifts (δ /ppm) are given relative to the residual solvent signals ($\delta_{\rm H}$ 2.08 or 7.09 ppm) and to the solvent resonance ($\delta_{\rm C}$ 137.48 ppm). The δ_{Si} values are related to tetramethylsilane. EI-MS spectra were obtained on a VG-7070E mass spectrometer at 70 eV. Crystalline samples in sealed capillaries were opened and inserted into the direct inlet under argon. The spectra are represented by the peaks of relative abundance higher than 7% and by important peaks of lower intensity. Crystalline samples for EI-MS measurements and melting point determinations were placed into glass capillaries in a Labmaster 130 glovebox (mBraun) under purified nitrogen (concentrations of oxygen and water were lower than 2.0 ppm) and were sealed with flame. KBr pellets of complexes were prepared in the glovebox and were measured in an air-protecting cuvette on a Nicolet Avatar FT IR spectrometer in the range 400-4000 cm⁻¹. UV-vis spectra in the range 300-800 nm were measured on a Varian Cary 17D spectrometer in all-sealed quartz cells (Hellma). Elemental analyses were carried out on a FLASH EA1112 CHN/O automatic elemental analyzer (Thermo Scientific). Melting points were measured on a Koffler block in sealed glass capillaries under nitrogen and are uncorrected.

Chemicals. The solvents hexane, toluene, and tetrahydrofuran (THF) were dried by refluxing over LiAlH_4 and stored as solutions of green dimeric titanocene $[(\mu-\eta^5:\eta^5-C_5H_4C_5H_4)(\mu-H)_2{Ti(\eta^5-\eta^5-C_5H_4C_5H_4)(\mu-H)_2}$ $(C_{5}H_{5})_{2}$].³² Toluene- d_{8} (99.5% D) (Aldrich) was degassed, distilled under vacuum on singly tucked-in permethyltitanocene [Cp*Ti- $(C_5Me_4CH_2)$],^{7b,c,8,33} and stored as its solution on a vacuum line. The titanocene hydride $[Cp^*_2TiH]$ (1) was prepared from $[Cp^*Ti-18]$ $(C_{5}Me_{4}CH_{2})$] by adding gaseous hydrogen as recently reported.⁸ The titanocene deuteride containing a total of at least 80% deuterium was obtained analogously to 1; the gaseous deuterium (99.8%, Sigma-Aldrich) was admitted to a stirred toluene solution of [Cp*Ti- $(C_5Me_4CH_2)]$, and after 5 h it was replaced with pure deuterium. This treatment was repeated three times; then all volatiles were evaporated under vacuum and the residue was crystallized from hexane. The EI-MS spectrum showed the base peak m/z 345. Internal alkynes but-2yne, 1,2-diphenylethyne, 1-phenylprop-1-yne, 1-tert-butylprop-1-yne, 1-(trimethylsilyl)prop-1-yne, 1-(trimethylsilyl)-2-phenylethyne, 1-tertbutyl-2-(trimethylsilyl)ethyne, and bis(trimethylsilyl)ethyne and conjugated diynes 1,4-bis(trimethylsilyl)buta-1,3-diyne and 2,2,7,7-tetramethylocta-3,5-diyne (all Aldrich) were degassed and handled in a vacuum. Buta-1,3-diene, isoprene, penta-1,3-diene, 4-methylpenta-1,3diene, and 2,3-dimethylbuta-1,3-diene (all Aldrich) were degassed on a vacuum line and distributed into breakable-seal ampules. Weighed amounts of PbCl₂ (Aldrich) were degassed on a vacuum line and used for oxidative chlorination of titanocene alkenyls. Hydrogen (anal. 3.0) was filled into an evacuated three-necked ampule (60 mL) equipped with two magnetically breakable glass seals via a Teflon valve at a slightly more than atmospheric pressure. This ampule, charged with ca. 3 mmol of H₂, was attached to an ampule containing the reagent solution (0.5 mmol) by magnetically breakable seals, which were broken under high vacuum.

Preparation of 2a. A solution of 1 in hexane (1.0 mmol in 4.0 mL) was mixed with 2-butyne (\sim 0.1 mL, 1.3 mmol), immediately changing the reddish-ocher color of 1 to greenish-brown. All volatiles were evaporated under vacuum, and a dry residue was dissolved in 2.0 mL of hexane. A green crystalline product was obtained by slow distillation of the solvent to an ampule arm placed in a space with slightly lower temperature in a refrigerator. The mother liquor (\sim 0.3 mL) was decanted into the distilled solvent, and the crystalline product was dissolved in a minimum of hexane and recrystallized in the same way. Green crystals¹⁵ were dried in a vacuum. Yield: 0.31 g (83%).

Data for **2a** are as follows. Mp: 140 °C. EI-MS (direct inlet, 70 eV, 130 °C): m/z (relative abundance) 373 (M⁺⁺; 16), 320 (20), 319 (50), 318 ([M – HC₂Me₂]⁺; 100), 317 (40), 316 (54), 315 (47), 313 (17), 182 (22), 181 ([Cp*Ti – 2 H]⁺; 32), 180 (33), 179 (17), 178 (26), 177 (15), 135 ([Cp*]⁺; 9), 119 (23), 105 (11), 91 (22), 79 (8), 77 (9), 55 (18), 53 (13). IR (KBr, cm⁻¹): 2976 (s, sh), 2952 (s), 2901 (vs), 2858 (s), 2720 (vw), 1583 (vw), 1489 (m), 1434 (s, b), 1377 (vs), 1164 (vw), 1064 (w), 1023 (s), 803 (vw), 615 (w), 483 (w), 423 (s). EPR (toluene- d_{sv} 23 °C): g_{iso} = 1.962, ΔH = 19 G; (toluene- d_{sv} , -140 °C): g_1 = 1.999, g_2 = 1.982, g_3 = 1.890, g_{av} = 1.957. UV–vis (toluene- d_{sv} nm): 340(sh) \gg 465(sh) > 620. ¹H NMR (toluene- d_{s}): -12.4 ($\nu_{1/2}$ = 1200 Hz, 3H); 12.3 ($\nu_{1/2}$ = 800 Hz, 3H); 17.7 ($\nu_{1/2}$ = 3000 Hz, 30H, $C_5M\varepsilon_5$). Anal. Calcd for $C_{24}H_{37}$ Ti (373.44): C, 77.19; H, 9.99. Found: C, 77.15; H, 9.96.

Preparation of 2b. A solution of 1 in hexane (1.0 mmol in 4.0 mL) was poured onto degassed tolan (0.18 g, 1.01 mmol) to give a brown solution. Attempts to crystallize the product were unsuccessful; hence, the solution was evaporated in a vacuum, and a brown solid residue was dissolved in toluene- d_8 for investigation by spectral methods. Yield of 2b higher than 74% is derived from the yield of its chlorinated product 3b (see below).

Data for **2b** are as follows. ¹H NMR (toluene- d_8): 3.7 ($\nu_{1/2} = 280$ Hz, 4H); 7.4 ($\nu_{1/2} = 11$ Hz, 1H); 7.6 ($\nu_{1/2} = 60$ Hz, 2H); 8.0 ($\nu_{1/2} = 40$ Hz, 2H); 10.1 ($\nu_{1/2} = 210$ Hz, 1H); 16.4 ($\nu_{1/2} = 4400$ Hz, 30H, C₅Me₅). EPR (toluene- d_8 , 23 °C): $g_{iso} = 1.972$, $\Delta H = 7.0$ G; (toluene- $d_{8^{-}} - 140$ °C): $g_1 = 2.001$, $g_2 = 1.985$, $g_3 = 1.964$, $g_{av} = 1.983$. UV-vis (toluene- $d_{8^{-}}$ nm): 360(sh) \gg 500(sh) > 695.

Preparation of 2c. Mixing of **1** in hexane (1.0 mmol in 4.0 mL) with degassed phenylpropyne (0.116 g, 1.0 mmol) afforded a greenishbrown solution. Crystallization by slow solvent distillation in a refrigerator yielded aggregates of thin-plate pale brown crystals. These were washed with condensing hexane vapor and dried in a vacuum. Yield: 0.24 g (56%).

Data for **2c** are as follows. Mp: 82 °C. EI-MS (direct inlet, 70 eV, 110 °C): m/z (relative abundance) 436 (9), 435 (M⁺⁺; 18), 320 (17), 319 (48), 318 ([M - HC₂MePh]⁺; 100), 317 (87), 316 (30), 315 (17), 182 (12), 181 ([Cp*Ti - 2 H]⁺; 14), 180 (13), 179 (11), 178 (18), 177 (10), 135 ([Cp*]⁺; 7), 119 (13), 117 (18), 115 (14), 105 (10). IR (KBr, cm⁻¹): 3075 (vw), 3052 (w), 2947 (s), 2930 (s, sh), 2900 (vs), 2855 (s), 2720 (vw), 1590 (m), 1567 (w), 1486 (s), 1437 (s, b), 1376 (s), 1076 (w), 1023 (m), 844 (w), 794 (m), 742 (m), 700 (s), 671 (w), 576 (w), 435 (m). EPR (toluene- d_8 , 23 °C): g_{iso} = 1.972, ΔH = 7.0 G; (toluene- d_8 , -140 °C): g_1 = 2.000, g_2 = 1.984, g_3 = 1.962, g_{av} = 1.982. UV-vis (toluene- d_8 , nm): 310(sh) \gg 495(sh) > 660(sh). ¹H NMR (toluene- d_8): -20.6 ($\nu_{1/2}$ = 2100 Hz); 7.5 ($\nu_{1/2}$ = 60 Hz); 8.1 ($\nu_{1/2}$ = 50 Hz); 9.7 ($\nu_{1/2}$ = 100 Hz); 17.3 ($\nu_{1/2}$ = 2500 Hz, 30H, C₅Me₅). Anal. Calcd for C₂₉H₃₉Ti (435.51): C, 79.98; H, 9.03. Found: C, 80.03; H, 9.06.

Preparation of 2d. A solution of 1 in hexane (1.0 mmol in 4.0 mL) was added to degassed *t*-BuC \equiv CMe (0.15 mL, 1.1 mmol) to give a yellow-brown solution. Volatiles including an excessive alkyne were evaporated under dynamic vacuum at 40 °C overnight. The residue was repeatedly crystallized from hexane to give aggregates of brown needle crystals. Yield: 0.35 g (85%).

Data for **2d** are as follows. Mp: 110 °C. EI-MS (direct inlet, 70 eV, 110 °C): m/z (relative abundance) scan 12 416 (7), 415 (M^{+•}; 16), 414 (11), 320 (33), 319 (87), 318 ([M - HC₂MeBu]⁺; 100), 317 (95), 316 (60), 315 (42), 314 (13), 313 (18), 312 (8), 311 (9), 182 (19), 181 ([Cp*Ti - 2 H]⁺; 26), 180 (27), 179 (16), 178 (33), 177 (20), 176 (13), 135 ([Cp*]⁺; 6), 119 (14), 105 (13), 91 (13). IR (KBr, cm⁻¹): 2980 (m), 2949 (s), 2899 (vs), 2858 (s), 2720 (vw), 1490 (w), 1454 (m), 1434 (m), 1377 (s), 1356 (m), 1227 (w), 1201 (w), 1165 (vw), 1064 (w), 1021 (m), 801 (w), 752 (w), 719 (w), 648 (vw), 437 (m). ¹H NMR (toluene- d_8): 18.4 ($\nu_{1/2}$ = 2100 Hz, 30H, C₅Me₅); 1.7 ($\nu_{1/2}$ = 30 Hz, 9H, CMe₃). EPR (toluene- d_8 , 22 °C): g = 1.968, ΔH = 9.0 G; (-140 °C): g_1 = 2.000, g_2 = 1.983, g_3 = 1.964, g_{av} = 1.982. UV-vis (toluene- d_8 , nm): 345(sh) \gg 465 > 650. Anal. Calcd for C₂₇H₄₃Ti (415.52): C, 78.05; H, 10.43. Found: C, 78.10; H, 10.49.

Preparation of 2e. A brown reaction mixture of **1** in hexane (1.0 mmol in 4.0 mL) and degassed (trimethylsilyl)propyne (0.20 mL, 1.3

mmol) was evaporated in a vacuum overnight, and the residue was dissolved in hexane. Crystallization by slow solvent distillation in a refrigerator yielded ocher thin needle aggregates. Yield: 0.29 g, 67%.

Data for **2e** are as follows. Mp: 125 °C. EI-MS (direct inlet, 70 eV, 120 °C): m/z (relative abundance) 432 (10), 431 (M^{+•}; 20), 430 (9), 429 (13), 320 (15), 319 (60), 318 ([M - HC₂MeSiMe₃]⁺; 100), 317 (89), 316 (31), 315 (19), 182 (15), 181 ([Cp*Ti - 2 H]⁺; 19), 180 (16), 179 (11), 178 (19), 177 (10), 135 ([Cp*]⁺; 7), 119 (8), 112 ([C₂MeSiMe₃]⁺; 4), 105 (6), 97 ([C₂MeSiMe₃ - Me]⁺; 17), 91 (8), 73 ([SiMe₃]⁺; 80). IR (KBr, cm⁻¹): 2952 (s), 2904 (vs), 2858 (m), 2718 (vw), 1613 (w), 1552 (w), 1491 (w), 1436 (m,b), 1376 (s), 1245 (s), 1063 (w), 1022 (m), 849 (vs), 836 (vs), 766 (m), 730 (w), 684 (m), 614 (w), 571 (w), 546 (w), 499 (vw), 455 (w), 436 (m). EPR (toluene- d_8 , 23 °C): g_{iso} = 1.984, ΔH = 4.0 G; (toluene- d_8 , -140 °C): g_1 = 2.000, g_2 = 1.984, g_3 = 1.974, g_{av} = 1.986. UV-vis (toluene- d_8 , nm): 505 \gg 685(sh). ¹H NMR (toluene- d_8): -0.4 ($\nu_{1/2}$ = 40 Hz, 9H, SiMe₃); 15.5 ($\nu_{1/2}$ = 8100 Hz, 30H, C_5Me_5). Anal. Calcd for $C_{26}H_{43}$ SiTi (431.60): C, 72.36; H, 10.04. Found: C, 72.41; H, 10.09.

Preparation of 3a. Compound **2a** (0.16 g, 0.43 mmol) was dissolved in THF (4 mL), and the solution was added to degassed PbCl₂ (0.060 g, 0.215 mmol). After stirring for 30 min a red solution was decanted from a black powder of lead, and THF was evaporated. The residue was dissolved in a minimum of hexane and crystallized by slow solvent distillation in a refrigerator. A brownish-yellow mother liquor was separated, and a bright red crystalline solid was rinsed with condensing hexane vapor and dried in a vacuum. Yield: 0.14 g (79%). *Warning:* compounds **3a**–**3e** undergo photodecomposition when exposed to sunlight; storing their solutions in the dark is recommended.

Data for **3a** are as follows. Mp: 158 °C. EI-MS (direct inlet, 70 eV, 150 °C): m/z (relative abundance) 410 (9), 408 (M⁺⁺; 13), 355 (12), 354 ([M - C₂Me₂]⁺; 10), 318 ([M - C₂Me₂ - HCl]⁺; 10), 220 (37), 219 (51), 218 ([M - C₂Me₂ - Cp*H]⁺; 100), 217 (86), 216 (30), 215 (20), 213 (27), 181 ([Cp*Ti - 2 H]⁺; 8), 135 ([Cp*]⁺; 36), 119 (40), 105 (26), 91 (21), 79 (12), 77 (16). IR (KBr, cm⁻¹): 2985 (m), 2953 (m), 2898 (vs), 2845 (s), 2717 (vw), 1621 (vw), 1491 (m), 1449 (m), 1433 (s), 1375 (vs), 1165 (vw), 1102 (w), 1065 (w), 1022 (s), 957 (vw), 809 (w), 614 (vw), 596 (w), 477 (vw), 439 (vw), 403 (m). Anal. Calcd for C₂₄H₃₇CITi (408.89): C, 70.50; H, 9.12. Found: C, 70.53; H, 9.16. ¹H and ¹³C{¹H} NMR spectra resolved the presence of two atropisomers, **3a**(**a**) (60%) and **3a**(**b**) (40%).

Data for 3a(a): ¹H NMR (toluene- d_8): 1.62–1.69 (m, 3H, = CHMe); 1.74–1.78 partially overlapped (m, 3H, TiC(Me)=); 1.78 (s, 30H, C₅ Me_5); 3.62–3.73 (m, 1H, =CHMe). ¹³C{¹H} NMR (toluene- d_8): 12.97 (C₅ Me_5); 16.49 (=CHMe); 29.48 (TiC(Me)=); 119.92 (=CHMe), 124.72 (C₅ Me_5); 200.31 (TiC(Me)=).

Data for 3a(b): ¹H NMR (toluene- d_8): 1.50–1.57 (m, 3H, = CHMe); 1.81 (s, 30H, C_5Me_5); 5.28–5.38 (m, 1H, =CHMe). ¹³C{¹H} NMR (toluene- d_8): 12.97 (C_5Me_5); 16.51 (=CHMe); 21.34 (TiC(Me)=); 123.35 (=CHMe), 124.67 (C_5Me_5); 206.50 (TiC(Me)=).

Preparation of 3b. Solutions of crude compound **2b** in hexane and toluene- d_8 (see above) were combined and evaporated in a vacuum. The brown residue was dissolved in THF (4 mL), and the solution was poured onto degassed PbCl₂ (0.14 g, 0.5 mmol), turning red within 20 min. The red solution was evaporated, and the residue was repeatedly extracted with 15 mL of hexane. The combined extracts were reduced to 5 mL, and the brown mother liquor was separated from a finely crystalline red powder of **3b**. This was rinsed with condensing hexane vapor and dried. Yield: 0.39 g (74%).

Data for **3b** are as follows. Mp: 155 °C. ¹H NMR (toluene- d_8): 1.86 (s, 30H, C₅ Me_5); 4.64 (s, 1H, =CHPh); 6.79–7.18 (m, 10H, Ph). ¹³C{¹H} NMR (toluene- d_8): 13.30 (C₅ Me_5); 124.64, 124.97 (CH, Ph); 126.33 (C₅ Me_5); 127.08 (=CHPh); 128.19, 128.33, 128.62, 128.77 (CH, Ph); 204.75 (TiC=). EI-MS (direct inlet, 70 eV, 150 °C): m/z (relative abundance) 533 (9), 532 (M⁺⁺; 20), 497 ([M – Cl]⁺; 7), 396 ([M – Cp⁺H]⁺; 10), 354 ([M – C₂Ph₂]⁺; 19), 320 (15), 319 (40), 318 ([M – C₂Ph₂ – HCl]⁺; 100), 317 (67), 316 (20), 315 (10), 182 (8), 181 ([Cp⁺Ti – 2 H]⁺; 11), 180 (15), 179 (15), 178 ([C₂Ph₂]⁺; 28), 135 ([Cp⁺]⁺; 10), 119 (15), 105 (13), 91 (13). IR (KBr, cm⁻¹):

3095 (vw), 3076 (w), 3061 (w), 3012 (m), 2980 (m), 2956 (m), 2900 (s), 2855 (m), 2716 (vw), 1592 (s), 1577 (w), 1567 (vw), 1546 (w), 1488 (s), 1479 (s), 1434 (s), 1378 (s), 1154 (w), 1073 (w), 1020 (m), 922 (m), 883 (w), 837 (vw), 810 (vw), 779 (m), 765 (m), 752 (s), 700 (vs), 596 (w), 546 (vw), 523 (w), 484 (vw), 459 (w). Anal. Calcd for $C_{34}H_{41}$ CITi (533.03): C, 76.61; H, 7.75. Found: C, 76.58; H, 7.78.

Exposure of the NMR sample tube with **3b** to sunlight for 4 h turned its red color to greenish-brown, and (*Z*)-stilbene was identified by ¹H and ¹³C NMR spectra as the main diamagnetic product.

Preparation of 3c. The reaction mixture obtained from 1 in hexane (1.0 mmol in 4.0 mL) and phenylpropyne (0.116 g, 1.0 mmol) was evaporated in a vacuum and dissolved in THF (4 mL), and the solution was added to degassed PbCl₂ (140 mg, 0.50 mmol). After turning red, THF was replaced with hexane (10 mL), and the red product crystallized by slow solvent distillation in a refrigerator. The last 0.5 mL of a brownish-yellow mother liquor was removed from a red crystalline solid. This was dissolved, and the crystallization was repeated. The mother liquor (0.2 mL) was separated, and a finely crystalline solid was rinsed with condensing hexane vapor and dried in a vacuum. Yield: 0.40 g (86%).

Data for 3c are as follows. EI-MS (direct inlet, 70 eV, 150 °C): m/z(relative abundance) 472 (20), 471 (15), 470 (M^{+•}; 38), 469 (14), 435 ([M – Cl]⁺; 24), 356 (20), 355 (70), 354 ([M – C₂PhMe]⁺; 80), 353 ([M – HC₂PhMe]⁺; 75), 352 (27), 335 (13), 334 ([M – Cp^{*}H]⁺; 22), 320 (20), 319 (72), 318 ([M – C₂PhMe – HCl]⁺; 100), 317 (90), 316 (59), 315 (31), 220 (39), 219 (56), 218 ([M – C₂PhMe – Cp^{*}H]⁺; 74), 217 (54), 216 (38), 183 (10), 182 (37), 181 ([Cp^{*}Ti – 2 H]⁺; 50), 180 (45), 179 (24), 178 (34), 136 (24), 135 (85), 119 (62), 116 ([C₂PhMe]⁺; 30), 115 (70), 106 (23), 105 (43), 91 (34), 78 (22), 77 (40). IR (KBr, cm⁻¹): 3078 (w), 3040 (w), 2982 (m), 2956 (m), 2901 (vs), 2856 (s), 2839 (m), 2716 (vw), 1591 (m), 1576 (w), 1554 (m), 1487 (s), 1434 (s), 1377 (s), 1180 (vw), 1060 (w), 1020 (m), 909 (m), 869 (w), 811 (w), 752 (m), 700 (s), 654 (vw), 596 (w), 537 (w), 507 (w), 406 (m). Anal. Calcd for C₂₉H₃₉CITi (470.96): C, 73.96; H, 8.35. Found: C, 73.93; H, 8.36.

¹H and ¹³C{¹H} NMR spectra assessed the presence of two atropisomers, 3c(a) (38%) and 3c(b) (18%), and regioisomer 3c(c) (44%) (see ¹H NMR spectrum in the Supporting Information).

Data for 3c(a): ¹H NMR (toluene- d_8): 1.80 (s, 30H, C₅ Me_5); 1.95 (d, ⁴ J_{HH} = 1.7 Hz, 3H, TiC(Me)==); 4.84 (q, 1H, ⁴ J_{HH} = 1.7 Hz, 1H, =CHPh); 6.99–7.26 (partially overlapped by solvent signal, m, 5H, *Ph*). ¹³C{¹H} NMR (toluene- d_8): 12.98 (C₅ Me_5); 31.98 (TiC-(Me)=); 125.02 (C₅ Me_5); 128.2 overlapped by solvent signal (= CHPh); 128.41; the others are hidden under solvent signals (CH, *Ph*); 140.87 (C_{ipso}, *Ph*); 207.83 (TiC(Me)=).

Data for **3c(b)**: ¹H NMR (toluene- d_8): 1.41 (d, ⁴ J_{HH} = 1.5 Hz, 3H, TiC(Me)==); 1.81 (s, 30H, C_5Me_5); 6.57 (q, 1H, ⁴ J_{HH} = 1.5 Hz, 1H, =CHPh); 6.99–7.26 (partially overlapped by solvent signal, m, 5H, Ph). ¹³C{¹H} NMR (toluene- d_8): 12.89 (C_5Me_5); 23.96 (TiC-(Me)==); 124.82 (C_5Me_5); 128.10, 128.91 the last one is hidden under solvent signal (CH, Ph); 130.65 (=CHPh); 141.78 (C_{ipso} , Ph); 212.08 (TiC(Me)==).

Data for 3c(c) [Cp*₂TiCl(η^{1} -C(Ph)=CHMe)]: ¹H NMR (toluene- d_{8}): 1.62 (d, ${}^{3}J_{HH} = 6.6$ Hz, 3H, =CHMe); 1.82 (s, 30H, C₅Me₅); 3.68 (q, 1H, ${}^{3}J_{HH} = 6.6$ Hz, 1H, =CHMe); 6.88–7.15 (partially overlapped by solvent signal, m, 5H, Ph). ¹³C{¹H} NMR (toluene- d_{8}): 13.27 (C₅Me₅); 19.22 (=CHMe); 121.84 (=CHMe); 125.95 (C₅Me₅); 123.97, 126.38, 129.10 (CH, Ph); 153.90 (C_{ipso}, Ph); 198.80 (TiC(Ph)=).

A further crystallization of the above mixture in an effort to prepare single crystals yielded a red fine crystalline product consisting of 3c(a) (70%) and 3c(b) (30%), whereas 3c(c) was absent.

Preparation of 3d. A solution of 2d (0.17 g, 0.4 mmol) in THF (4 mL) was reacted with degassed PbCl₂ (0.14 g, 0.5 mmol). After stirring for 10 min, a red solution was separated from a black sediment, THF was replaced with hexane, and the product was crystallized by slow solvent distillation in a refrigerator. A yellow-brown mother liquor (0.4 mL) was separated, and a red solid was rinsed with condensing hexane vapor. Then, the solid was recrystallized from hexane to give a finely crystalline red solid. Its ¹H and ¹³C NMR

spectra revealed that it consists of 3d(a) (50%) and 3d(b) (50%). Yield: 0.15 g (81%).

Data for 3d(a)/3d(b) are as follows. Mp: 158 °C. EI-MS (direct inlet, 70 eV, 120 °C): m/z (relative abundance) 452 (9), 450 (M⁺⁺; 11), 355 (28), 354 ([M - C₂BuMe]⁺; 26), 353 ([M - HC₂BuMe]⁺; 19), 318 ([M - C₂BuMe - HCl]⁺; 9), 219 (42), 218 ([M - C₂BuMe - Cp*H]⁺; 100), 217 (93), 216 (30), 181 (9), 135 ([Cp*]⁺; 22), 119 (23), 105 (15), 91 (14), 57 (23), 55 (22). IR (KBr, cm⁻¹): 2976 (m), 2950 (s), 2896 (vs), 2858 (s), 2715 (vw), 1571 (vw), 1490 (m), 1457 (m), 1435 (s), 1375 (vs), 1358 (s), 1227 (m), 1199 (w), 1060 (m), 1018 (s), 949 (w), 918 (vw), 841 (w), 811 (vw), 648 (vw), 595 (w), 540 (vw), 434 (m). Anal. Calcd for C₂₇H₄₃CITi (450.97): C, 71.91; H, 9.61. Found: C, 71.83; H, 9.56.

Data for 3d(a) are as follows. ¹H NMR (toluene- d_8): 1.19 (s, 9H, CMe₃); 1.73 (d, ⁴ J_{HH} = 1.5 Hz, 3H, C(Me)=); 1.81 (s, 30H, C₅Me₅); 3.48 (q, 1H, ⁴ J_{HH} = 1.5 Hz, 1H, =CHCMe₃). ¹³C{¹H} NMR (toluene- d_8): 12.98 (C₅Me₅); 31.73 (TiC(Me)=); 31.93 (CMe₃); 34.02 (CMe₃); 124.56 (C₅Me₅); 129.21 (=CHCMe₃); 200.56 (TiC=).

Data for 3d(b) are as follows. ¹H NMR (toluene- d_8): 1.16 (s, 9H, CMe₃); 1.22 (d, ⁴ J_{HH} = 1.5 Hz, 3H, C(Me)=); 1.83 (s, 30H, C₅Me₅); 5.32 (q, 1H, ⁴ J_{HH} = 1.5 Hz, 1H, =CHCMe₃). ¹³C{¹H} NMR (toluene- d_8): 13.13 (C₅Me₅); 22.05 (TiC(Me)=); 32.10 (CMe₃); 35.56 (CMe₃); 124.58 (C₅Me₅); 138.17 (=CHCMe₃); 204.58 (TiC=).

Single crystals grown from the hexane solution of 3d(a)/3d(b) contained according to X-ray diffraction analysis compound 3d(a). When dissolved in toluene- d_8 , it rearranged to give a 50% mixture with 3d(b) within 3 weeks.

Preparation of 3e. Reaction of 2e (0.19 g, 0.44 mmol) with $PbCl_2$ performed as for 2d afforded a finely crystalline red solid. Its ¹H and ¹³C NMR spectra revealed that it consists of 3e(a) (75%) and 3e(b) (25%). Yield: 0.15 g (73%).

Data for 3e(a)/3e(b) are as follows. Mp: 138 °C. EI-MS (direct inlet, 70 eV, 120 °C): m/z (relative abundance) 468 (8), 466 (M^{+•}; 9), 431 ([M – Cl]⁺; 7), 356 (21), 355 (74), 354 ([M – C₂MeSiMe₃]⁺; 66), 353 ([M – HC₂MeSiMe₃]⁺; 92), 352 (34), 351 (27), 331 ([M – Cp^{*}]⁺; 16), 319 (22), 318 ([M – C₂MeSiMe₃ – HCl]⁺; 72), 317 (68), 316 (20), 315 (20), 220 (34), 219 (49), 218 ([M – C₂MeSiMe₃ – Cp^{*}H]⁺; 100), 217 (72), 216 (35), 215 (24), 214 (14), 213 (30), 182 (7), 181 ([Cp^{*}Ti – 2 H]⁺; 12), 180 (14), 179 (9), 178 (20), 177 (12), 176 (12), 135 ([Cp^{*}]⁺; 23), 119 (40), 105 (27), 91 (31), 83 (21), 79 (11), 77 (22), 73 (90). IR (KBr, cm⁻¹): 2993 (w), 2945 (s), 2898 (vs), 2855 (m,sh), 2718 (vw), 1580 (vw), 1534 (m), 1489 (w), 1434 (m), 1378 (m), 1244 (m), 1064 (vw), 1043 (w), 1020 (m), 908 (w), 847 (vs), 831 (s), 764 (w), 741 (vw), 682 (w), 669 (m), 556 (vw), 439 (vw), 403 (w). Anal. Calcd for C₂₆H₄₃ClSiTi (467.05): C, 66.86; H, 9.28. Found: C, 66.79; H, 9.23.

Crystallization of 3e(a)/3e(b) from hexane afforded well-developed crystals whose X-ray diffraction analysis identified them as 3e(a). After one month in toluene- d_8 it rearranged to a mixture of 3e(a) (80%) and 3e(b) (20%).

Data for **3e**(**a**) are as follows. Mp: 154 °C. ¹H NMR (toluene- d_8): 0.22 (s, 9H, SiM e_3); 1.78 (s, 30H, C_5Me_5); 1.84 (d, ⁴ J_{HH} = 1.1 Hz, 3H, C(Me)==); 3.96 (q, 1H, ⁴ J_{HH} = 1.1 Hz, 1H, =CHSiM e_3). ¹³C{¹H} NMR (toluene- d_8): 1.15 (SiM e_3); 13.09 (C_5Me_5); 37.66 (TiC-(Me)==); 124.66 (C_5Me_5); 127.17 (=CHSiM e_3); 232.15 (TiC=). ²⁹Si{¹H} NMR (toluene- d_8): -15.7 (SiM e_3). IR (KBr, cm⁻¹): 2993 (w), 2945 (s), 2897 (vs), 2855 (m,sh), 2716 (vw), 1580 (vw), 1534 (m), 1489 (w), 1434 (m), 1378 (m), 1243 (m), 1065 (vw), 1043 (w), 1020 (m), 908 (w), 847 (vs), 831 (s), 764 (w), 741 (vw), 681 (w), 669 (m), 596 (vw), 556 (vw), 403 (w).

Data for **3e**(**b**) are as follows. ¹H NMR (toluene- d_8): 0.20 (s, 9H, SiMe₃); 1.38 (d, ⁴ J_{HH} = 1.1 Hz, 3H, C(Me)==); 1.80 (s, 30H, C₅ Me_5); 5.51 (q, 1H, ⁴ J_{HH} = 0.9 Hz, 1H, =CHSiMe₃). ¹³C{¹H} NMR (toluene- d_8): 1.20 (SiMe₃); 12.96 (C₅ Me_5); 27.61 (TiC(Me)==); 124.43 (C₅ Me_5); 130.73 (=CHSiMe₃); 237.17 (TiC=). ²⁹Si {¹H} (toluene- d_8): -15.1 (SiMe₃).

Preparation of 4a. A solution of 1 in hexane (1.0 mmol in 4.0 mL) was added to $Me_3SiC \equiv CSiMe_3$ (0.19 g, 1.1 mmol) to give

immediately an intense purple solution. It was put into a refrigerator with a thermal gradient to distill the solvent into an ampule arm. Then the ampule with a separated purple oil and solvent was put into a freezer (-28 °C), where the oil solidified. The ampule was returned to the refrigerator (-5 °C), where excess alkyne was left to dissolve in hexane vapor while leaving crystalline thin plate aggregates of 4a. These were dissolved in a minimum of hexane and crystallized in a refrigerator. Purple crystals were dried in a vacuum. Yield: 0.41 g (84%).

Data for 4a are as follows. Mp: 148 °C. EI-MS (direct inlet, 70 eV, 150 °C): m/z (relative abundance) 489 (M⁺⁺) was not observed; products of its dissociation 318 ([M - HC₂(SiMe₃)₂]⁺) and its fragment ions and 170 ([C₂(SiMe₃)₂]⁺) \ll 155 ([C₂(SiMe₃)₂ - Me]⁺) were observed in abundance depending on the temperature of evaporation. IR (KBr, cm⁻¹): 2973 (m, sh), 2953 (s), 2900 (vs), 2858 (m), 2719 (vw), 1583 (vw), 1493 (w), 1452 (w, sh), 1418 (m), 1377 (m), 1245 (s), 1061 (vw), 1022 (w), 851 (vs), 838 (vs), 785 (w), 756 (m), 685 (vw), 659 (m), 617 (vw), 469 (m), 457 (vw), 430 (vw). EPR (toluene- d_8 , 22 °C): g_{iso} = 1.988, ΔH = 1.5 G, doublet a_H = 3.7 G; (toluene- d_8 , -140 °C): g_1 = 2.001, g_2 = 1.985, g_3 = 1.980, g_{av} = 1.988. UV-vis (toluene- d_8 , nm): 542 \gg 715. ¹H NMR (toluene- d_8): -0.7 ($\nu_{1/2}$ = 140 Hz, 9H, SiMe_3); 1.0 ($\nu_{1/2}$ = 460 Hz, 9H, SiMe_3); 14.6 ($\nu_{1/2}$ = 10300 Hz, 30H, C₅Me₅). Anal. Calcd for C₂₈H₄₉Si₂Ti (489.75): C, 68.67; H, 10.08. Found: C, 68.70; H, 10.03.

Preparation of 4b. A solution of 1 in hexane (1.0 mmol in 4.0 mL) was added to t-BuC \equiv CSiMe₃ (0.16 g, 1.04 mmol) to give an intense purple solution. This was left to crystallize by slow solvent distillation into an ampule arm to give pale purple crystalline aggregates. These were washed with condensing hexane vapor and were recrystallized by the same procedure. Large purple crystals were dried in a vacuum. Yield: 0.43 g (91%).

Data for 4b are as follows. Mp: 158 °C. EI-MS (direct inlet, 70 eV, 150 °C): m/z (relative abundance) 473 (M^{+•}; 5), 320 (35), 319 (88), 318 ($[M - HC_2BuSiMe_3]^+$; 100), 317 (75), 316 (46), 315 (35), 314 (28), 313 (41), 182 (24), 181 ([Cp*Ti - 2 H]+; 30), 180 (23), 179 (19), 178 (32), 177 (17), 154 ([C₂BuSiMe₃]⁺; 20), 139 ([C₂BuSiMe₃ - Me]⁺; 81), 97 ([C₂BuSiMe₃ - Bu]⁺; 43), 73 ([SiMe₃]⁺; 24). IR (KBr, cm⁻¹): 2985 (m, sh), 2963 (s), 2902 (vs), 2858 (s), 2719 (vw), 1624 (vw), 1487 (w, sh), 1473 (m), 1456 (m, b), 1377 (s), 1360 (m), 1254 (w), 1241 (s), 1204 (w), 1063 (vw), 1023 (w), 932 (vw), 906 (w), 844 (vs), 832 (s, sh), 750 (w), 669 (m), 614 (vw), 450 (vw), 422 (m). EPR (toluene- d_8 , 23 °C): $g_{iso} = 1.984$, $\Delta H = 1.5$ G, doublet $a_H =$ 3.5 G; (toluene- d_8 , -140 °C): $g_1 = 2.001$, $g_2 = 1.9827$, $g_3 = 1.976$, $g_{av} =$ 1.986. UV-vis (toluene- d_8 , nm): 542 \gg 720. ¹H NMR (toluene- d_8): $-0.7 (\nu_{1/2} = 320 \text{ Hz}, 9\text{H}); 1.4 (\nu_{1/2} = 340 \text{ Hz}, 9\text{H}); 16.7 (\nu_{1/2} = 16400 \text{ Hz}); 16.7 (\nu_{1/2} = 1640$ Hz, 30H, C₅Me₅). Anal. Calcd for C₂₉H₄₉SiTi (473.68): C, 73.53; H, 10.43. Found: C, 73.57; H, 10.49.

Preparation of 4c. Purple crystalline 4c was obtained analogously to 4b from the solution of 1 in hexane (1.0 mmol in 4.0 mL) and $PhC\equiv CSiMe_3$ (0.18 g, 1.03 mmol). Yield: 0.46 g (93%).

Data for 4c are as follows. Mp: 125 °C. EI-MS (direct inlet, 70 eV, 140 °C): *m*/*z* (relative abundance) 493 (M^{+•}; 11), 320 (14), 319 (45), 318 ($[M - HC_2PhSiMe_3]^+$; 100), 317 (75), 316 (25), 315 (13), 182 (10), 181 ($[Cp^*Ti - 2H]^+$; 19), 180 (15), 179 (10), 178 (17), 177 (10), 174 ($[C_2PhSiMe_3]^+$; 17), 159 ($[C_2PhSiMe_3 - Me]^+$; 61), 135 $([Cp^*]^+; 11), 105 (11), 91 (15), 77 ([Ph]^+; 13), 73 ([SiMe_3]^+; 92).$ IR (KBr, cm⁻¹): 3078 (vw), 3060 (vw), 3042 (w), 2952 (s), 2942 (s), 2899 (vs), 2856 (s), 2720 (vw), 1589 (m), 1571 (w), 1553 (vw), 1520 (vw), 1490 (m,sh), 1480 (m), 1451 (m), 1436 (m), 1376 (m), 1244 (s), 1067 (w), 1023 (m), 863 (s), 837 (vs), 786 (m), 760 (m), 734 (m), 725 (m), 691 (s), 621 (w), 593 (vw), 566 (w), 515 (w), 504 (w), 441 (w), 428 (w), 406 (m). ¹H NMR (toluene- d_8): -0.6 ($\nu_{1/2}$ = 70 Hz, 9H, SiMe₃); 5.4 ($\nu_{1/2}$ = 140 Hz, 1H, Ph); 8.3 ($\nu_{1/2}$ = 80 Hz, 2H, *Ph*); 9.4 ($\nu_{1/2}$ = 190 Hz, 2H, *Ph*); 15.9 ($\nu_{1/2}$ = 7400 Hz, 30H, C₅Me₅). UV-vis (toluene- d_{8} , nm): 515 \gg 710. EPR (toluene- d_{8} , 23 °C): $g_{iso} =$ 1.985, $\Delta H = 1.7$ G, triplet $a_{\rm H} = 3.2$ G; (toluene- d_{8} , -140 °C): $g_1 =$ 2.001, $g_2 = 1.985$, $g_3 = 1.979$, $g_{av} = 1.988$. Anal. Calcd for $C_{31}H_{45}SiTi$ (493.67): C, 75.42; H, 9.19. Found: C, 75.48; H, 9.24.

Preparation of 5a. A solution of 1 in hexane (1.0 mmol in 4.0 mL) was added to degassed crystalline $(Me_3SiC\equiv C)_2$ (0.194 g, 1.0

mmol). After warming to 60 °C for 10 min a brownish-yellow solution was put into a refrigerator for the product crystallization during a slow solvent distillation. A crystalline solid was twice recrystallized from hexane to give brown crystals. Yield: 0.40 g (79%).

Data for **Sa** are as follows. Mp: 110 °C. EI-MS (direct inlet, 70 eV, 100 °C): m/z (relative abundance) 514 (9), 513 (M^{+•}; 20), 320 (20), 319 (44), 318 ([M - HC₄(SiMe₃)₂]⁺; 100), 317 (91), 316 (31), 315 (15), 182 (12), 181 ([Cp*Ti - 2 H]⁺; 15), 180 (12), 179 (9), 178 (10), 135 ([Cp*]⁺; 7), 119 (13), 105 (9), 91 (9), 73 ([SiMe₃]⁺; 98). IR (KBr, cm⁻¹): 2955 (s), 2901 (s), 2855 (m), 2718 (vw), 1845 (s), 1591 (m), 1490 (w), 1452 (m), 1432 (m), 1411 (w), 1374 (m), 1245 (s), 1230 (m), 1144 (vw), 1064 (vw), 1020 (m), 962 (s), 837 (vs, b), 756 (m), 740 (w), 703 (m), 687 (w), 626 (w), 493 (vw), 460 (vw), 403 (m). EPR (toluene- d_8 , 23 °C): g_{iso} = 1.993, ΔH = 1.8 G; (toluene- d_8 , -140 °C): g_{\parallel} = 2.002, g_{\perp} = 1.991, g_{av} = 1.995. UV-vis (toluene- d_8): 1.8 ($\nu_{1/2}$ = 150 Hz, 9H, SiMe_3); 4.9 ($\nu_{1/2}$ = 800 Hz, 9H, SiMe_3); 16.1 ($\nu_{1/2}$ = 10 800 Hz, 30H, C_5Me_5). Anal. Calcd for $C_{30}H_{49}Si_2Ti$ (513.77): C, 70.13; H, 9.61. Found: C, 70.20; H, 9.66.

Preparation of 5b. A solution of 1 in hexane (1.0 mmol in 4.0 mL) was added to degassed crystalline $(t\text{-BuC})_2$ (0.162 g, 1.0 mmol), forming a brown solution. This was warmed to 60 °C for 20 min. Attempts to crystallize the product by slow solvent distillation afforded a brown oil. A small part of it was dissolved in toluene- d_8 in order to assess the product purity by spectroscopic methods. Both EPR and ¹H NMR spectra did not reveal impurities. The structure of **5b** was derived from the crystal structure of its chlorinated product **6b**, and yield of **5b** is higher than that for the chlorinated product **6b** (84%) (see below).

Data for **Sb** are as follows. ¹H NMR (toluene- d_8): 2.9 ($\nu_{1/2} = 100$ Hz, 9H, CM e_3); 6.1 ($\nu_{1/2} = 270$ Hz, 9H, CM e_3); 15.1 ($\nu_{1/2} = 1700$ Hz, 30H, C₅M e_5). EPR (toluene- d_8 , 22 °C): $g_{iso} = 1.993$, $\Delta H = 4.0$ G; (-140 °C): $g_{\parallel} = 2.002$, $g_{\perp} = 1.992$, $g_{av} = 1.995$. UV-vis (toluene- d_8 , nm): 405(sh) \gg 485 > 690(sh).

Preparation of 6a(b). Compound **Sa** (0.27 g, 0.53 mmol) in THF (4 mL) was added to $PbCl_2$ (75 mg, 0.27 mmol). After stirring for 20 min a red solution was separated from lead, and THF was replaced with hexane. Crystallization in a refrigerator afforded a red crystalline powder. Yield: 0.24 g (83%).

Data for **6a(b)** are as follows. Mp: 175 °C dec. ¹H and ¹³C NMR spectra are consistent with a *syn*-isomer. ¹H NMR (toluene- d_8): 0.20 (s, 9H, C=CSiMe₃); 0.29 (s, 9H, =CHSiMe₃); 1.90 (s, 30H, C₅Me₅); 6.28 (s, 1H, =CHSiMe₃). ¹³C{¹H} NMR (toluene- d_8): 0.01, 0.10 (SiMe₃); 13.16 (C₅Me₅); 105.27 (C=CSiMe₃); 113.40 (C=CSiMe₃); 125.76 (C₅Me₅); 154.49 (=CH); 206.58 (TiC=). ²⁹Si{¹H} NMR (toluene- d_8): -21.2 (=CSiMe₃); -14.1 (=CHSiMe₃). IR (KBr, cm⁻¹): 2987 (w, sh), 2954 (s), 2897 (vs), 2856 (m), 2719 (vw), 2098 (m), 1577 (vw), 1490 (m), 1445 (m, sh), 1434 (m), 1376 (s), 1247 (s), 1143 (vw), 1065 (vw), 1012 (m), 838 (vs, b), 757 (m), 704 (w), 679 (w), 628 (w), 480 (vw), 415 (w). Anal. Calcd for C₃₀H₄₉ClSi₂Ti (549.23): C, 65.57; H, 8.99. Found: C, 65.62; H, 9.06.

Preparation of 6b. A brown, oily product from the synthesis of **5b** was combined with its toluene- d_8 solution (see above). This solution was evaporated in a vacuum, the oily residue was dissolved in THF (4 mL), and the solution was added to PbCl₂ (0.14 g, 0.5 mmol). After stirring for 20 min a red solution was separated from lead, and THF was replaced with 10 mL of hexane. Crystallization of the product afforded an orange-red solid. Its recrystallization afforded a finely crystalline red solid. Yield: 0.43 g (84% on 1). According to ¹H and ¹³C NMR spectra this product contained **6b**(a) (35%) and **6b**(b) (65%). This material was further crystallized from hexane to give suitable crystals for X-ray diffraction analysis. It revealed that the structure was disordered, consisting of **6b**(b) (88.2(2)%) and **6b**(a).

Data for a mixture of **6b(b)** (88.2%) and **6b(a)** (11.8%) are as follows. Mp: 171 °C. EI-MS (direct inlet, 70 eV, 150 °C): m/z(relative abundance) 518 (11), 516 (M^{+•}; 14), 381 ([M – Cp^{*}]⁺; 12), 357 (10), 356 (28), 355 (67), 354 (76), 353 ([M – HC₄Bu₂]⁺; 82), 352 (31), 351 (27), 318 ([M – C₄Bu₂ – HCl]⁺; 17), 220 (33), 219 (50), 218 ([M – C₄Bu₂ – Cp^{*}H]⁺; 100), 217 (55), 216 (30), 215 (24), 213 (34), 182 (10), 181 (8), 178 (12), 135 ([Cp^{*}]⁺; 49), 119 (46), 105 (36), 93 (17), 91 (38), 79 (17), 77 (31). IR (KBr, cm⁻¹): 2959 (s), 2899 (vs), 2859 (s), 2718 (vw), 2172 (vw), 2037 (b, vw), 1668 (vw), 1491 (m), 1475 (w), 1455 (s), 1434 (s), 1375 (vs), 1354 (s), 1259 (s), 1232 (w), 1203 (m), 1065 (vw), 1020 (m), 903 (vw), 837 (w), 810 (vw), 775 (vw), 615 (vw), 595 (vw), 531 (w), 436 (w). Anal. Calcd for $C_{32}H_{49}$ ClTi (517.08): C, 74.33; H, 9.55. Found: C, 74.92; H, 9.52.

Data for **6b**(**b**) are as follows. ¹H NMR (toluene- d_8): 1.22 (s, 9H, C=CCM e_3); 1.31 (2 × s, 2 × 9H, =CHCM e_3); 1.93 (s, 30H, C₅M e_5); 5.72 (s, 1H, =CHCM e_3). ¹³C{¹H} NMR (toluene- d_8): 13.22 (C₅M e_5); 29.02 (C=CCM e_3); 31.00, 31.14 (CM e_3); 36.14 (= CHCM e_3); 86.43 (C=CCM e_3); 108.53 (C=CCM e_3); 125.55 (C₅M e_5); 152.72 (=CH); 177.19 (TiC=).

Data for **6b**(a) are as follows. ¹H NMR (toluene- d_8): 1.24 (s, 9H, C=CCM e_3); 1.35 (s, 9H, =CHCM e_3); 1.86 (s, 30H, C₅M e_5); 4.01 (s, 1H, =CHCM e_3). ¹³C{¹H} NMR (toluene- d_8): 13.31 (C₅M e_5); 30.03 (C=CCM e_3); 30.71, 30.73 (CM e_3); 35.78 (=CHCM e_3); 89.85 (C=CCM e_3); 111.70 (C=CCM e_3); 125.25 (C₅M e_5); 147.12 (= CH); 172.82 (TiC=).

Hydrogenation of 2a. Crystalline **2a** obtained from **1** (0.5 mmol) as above was dissolved in 1.2 mL of toluene- d_{sv} and hydrogen (~3 mmol) was admitted. After stirring for 2 days the solution was cooled with liquid nitrogen, and residual hydrogen was pumped off. After a thaw–freeze cycle under high vacuum all volatiles were distilled to an ampule cooled with liquid nitrogen. ¹H and ¹³C NMR spectra of the distillate found butane in toluene- d_{sv} and its presence was confirmed by GC-MS analysis (Supporting Information contains GC-MS and ¹H and ¹³C NMR data for organic products in this and following experiments). The distillation residue was dissolved in toluene- d_{sv} and its paramagnetic ¹H NMR spectrum consisted of signals for **1** and a trace of [Cp*Ti(C_sMe₄CH₃)].

Hydrogenation of 4c. Crystalline 4c (0.15 g, 0.3 mmol) was dissolved in 1.2 mL of toluene- d_{8} , and hydrogen (~3 mmol) was admitted. After stirring for 2 days the solution was cooled with liquid nitrogen, and residual hydrogen was pumped off. After a thaw–freeze cycle under high vacuum the toluene- d_8 and all other volatiles were distilled at maximum 80 °C to the empty hydrogen-supplying ampule cooled with liquid nitrogen. According to ¹H NMR analysis, the volatiles contained (Z)-PhHC=CH(SiMe₃), 56%, (E)-PhHC=CH-(SiMe₃), 8%, and PhCH₂CH₂(SiMe₃), 36%, in toluene- d_8 . GC-MS analysis confirmed the presence of the two olefin isomers (m/z 176) and the saturated product (m/z 178). The distillation residue was dissolved in toluene- d_8 , and its paramagnetic ¹H NMR spectrum consisted of signals for 1 and a trace of [Cp*Ti(C₅Me₄CH₂)].

Thermolysis of 4c. A solution of 4c in toluene- d_8 (0.1 M, 1.0 mL) was heated stepwise in a flame-sealed NMR sample tube, and EPR spectra were measured at room temperature with magnetic field modulation of 0.1 G. The sharp EPR signal of 4c ($g_{iso} = 1.985$, $\Delta H = 1.7$ G) changed into the broad signal of [Cp*Ti(C₅Me₄CH₂)] after heating to 110 °C for 8 h. This compound was also confirmed by paramagnetic ¹H NMR spectra. The volatile products were analyzed by ¹H and ¹³C NMR spectra to be nearly pure (Z)-1-phenyl-2-(trimethylsilyl)ethene.

Catalytic Hydrogenation of 1-Phenylprop-1-yne in the Presence of $[Cp*Ti(C_5Me_4CH_2)]$. A solution of $[Cp*Ti(C_5Me_4CH_2)]$ (0.2 mmol) in toluene- d_8 , gaseous hydrogen (~3 mmol), and 1-phenylprop-1-yne (0.12 mL, 1.0 mmol) were in this order introduced into a reactor, and the mixture was stirred for 2 days. After degassing by freeze—thaw cycles volatiles were distilled under vacuum into a cooled trap. ¹H and ¹³C NMR spectra established the presence of only propylbenzene. The distillation residue contained according to paramagnetic ¹H NMR 1 with a trace of $[Cp*Ti(C_5Me_4CH_2)]$.

Catalytic Hydrogenation of Hex-3-yne in the Presence of 1. Compound 1 (0.25 mmol) in hexane was mixed with excess hex-3-yne (0.2 mL). After 15 min a brown solution was evaporated in high vacuum, and the residue was dissolved in toluene- d_8 (1.2 mL). The paramagnetic ¹H NMR spectrum revealed the resonance of the titanocene Cp* ligands at δ 17.4 ppm ($\nu_{1/2}$ = 2800 Hz, 30H, C₅Me₅), whereas the narrow signals at 1.0 ($\nu_{1/2}$ = 20 Hz, 6H) and -1.1 ppm $(\nu_{1/2} = 80 \text{ Hz}, 4\text{H})$ could be assigned tentatively to the methyl and methylene groups of the hex-3-en-3-yl ligand. To this solution was added hex-3-yne (0.22 mL, 2.0 mmol), and gaseous hydrogen (~3.0 mmol) was admitted. After stirring overnight the reaction mixture was degassed by freeze—thaw cycles, and volatiles were distilled into a cooled trap. ¹H and ¹³C NMR spectra established the presence of (*Z*)hex-3-ene (80%) and hexane (20%). The residue after the product distillation contained according to paramagnetic ¹H NMR spectra $\mathbf{1} \gg$ [Cp*Ti(C₅Me₄CH₂)].

Reaction of 1 with Butadiene to Give 7. A solution of 1 in hexane (1.0 mmol in 4.0 mL) was added to an excess of degassed butadiene (0.5 mL, \sim 6 mmol). A yellow, amorphous solid instantly precipitated on the ampule walls; however, within 20 min at room temperature it dissolved to give a purple solution. All volatiles were evaporated in a vacuum, and the residue was dissolved in hexane (4 mL). Crystallization driven by slow solvent distillation in a refrigerator afforded a mixture of green and purple crystalline solids that both were dissolved by hexane vapor at room temperature to a purple solution. The last 0.2 mL of the purple mother liquor was removed in an effort to purify the product. Recrystallization from hexane produced a mixture of green and red crystals, which did not differ in their spectroscopic properties. A green crystal was used for the single-crystal X-ray diffraction analysis. The yield of dried crystalline solid was 0.35 g (94%).

Data for 7 are as follows. Mp: 125 °C dec. EI-MS (70 °C): m/z (relative abundance) 373 (M^{+•}; 6), 320 (11), 319 (37), 318 ([M – C₄H₇]⁺; 100), 317 (57), 316 (21), 315 (9), 182 (6), 181 (8), 180 (7), 179 (6), 178 (9), 177 (7), 56 (6), 41 (7). IR (KBr, cm⁻¹): 3079 (w), 2967 (s), 2904 (vs), 2855 (s), 2719 (w), 1542 (w), 1489 (m), 1435 (s,b), 1379 (vs), 1275 (w), 1191 (m), 1061 (vw), 1022 (s), 993 (m), 811 (s), 742 (s), 654 (w), 565 (vw), 517 (vw), 432 (m). The absorption bands printed in italic are due to the η^3 -1-methylallyl ligand. EPR (toluene- d_{sv} 22 °C): g_{iso} = 1.990, poorly resolved triplet, outer features ΔH = 7.0 G; (-140 °C): g_1 = 2.000, g_2 = 1.990, g_3 = 1.984, g_{av} = 1.991. UV–vis (toluene- d_{sv} nm): 517. ¹H NMR (toluene- d_{sl}): 18.4 ($\nu_{1/2}$ = 4500 Hz, 30H, C_5Me_5). Anal. Calcd for $C_{24}H_{37}$ Ti (373.44): C, 77.19; H, 9.99. Found: C, 77.13; H, 9.94.

Thermal Decomposition of 7. Heating of 7 in toluene- d_8 in a flame-sealed NMR tube to 80 °C for 3 h resulted in complex decomposition yielding [Cp*Ti(C₅Me₄CH₂)], identified by its paramagnetic ¹H NMR spectrum. The volatiles were distilled under vacuum into another NMR tube and assessed to be a mixture of (*E*)-but-2-ene and (*Z*)-but-2-ene in roughly 2:1 ratio (GC-MS and ¹H and ¹³C NMR data for organic products of this and following experiments are in the Supporting Information).

Reaction of 1 with Penta-1,3-diene. A solution of 1 (0.5 mmol in 3.0 mL of hexane) was mixed with degassed penta-1,3-diene (0.2 mL, 2.0 mmol), turning its color to sky blue. After 10 min all volatiles were evaporated in a vacuum, and a blue solid was dissolved in toluene- d_8 (1.2 mL). Both EPR and electronic absorption spectra measured within 30 min after the synthesis were consistent with structure 8. Compound 8 appeared to be unstable at room temperature, turning from a blue color to purple. The ¹H NMR spectrum of the solution taken after 3 h revealed the overwhelming presence of paramagnetic [Cp*Ti(C₅Me₄CH₂)] and pent-2-ene. Geometry at the double bond could not be determined from the ¹H and ¹³C NMR data.

Data for 8 are as follows. EPR (toluene- d_8 , 22 °C): g = 1.9912, $\Delta H = 4.3$ G. UV-vis (toluene- d_8 , nm): 565.

Reaction of 1 with Isoprene. A solution of 1 in hexane (0.5 mmol in 3.0 mL) was mixed with degassed isoprene (0.2 mL, 2.0 mmol), turning color rapidly from greenish-yellow to brown. After 20 min all volatiles were evaporated in a vacuum, and the residue was dissolved in 1.0 mL of toluene- d_8 . After standing overnight the solution turned purple, and the complete conversion of 1 to $[Cp*Ti(C_5Me_4CH_2)]$ was confirmed by the paramagnetic ¹H NMR spectrum. The contents of the NMR sample tube were transferred under vacuum to an ampule, where the volatiles were distilled from $[Cp*Ti(C_5Me_4CH_2)]$. GC-MS analysis of the volatiles found, besides

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toluene- d_8 , the hydrogenated isoprene (m/z 68). The olefin was identified by ¹H and ¹³C NMR spectra to be 2-methylbut-1-ene.

Reaction of 1 with 4-Methylpenta-1,3-diene. A solution of 1 (0.5 mmol in 1.0 mL of toluene- d_8) was mixed with the degassed diene (0.2 mL, 1.7 mmol), turning only slowly to brown. After warming to 60 °C for 3 h the solution turned purple, and the complete conversion of 1 to [Cp*Ti(C₅Me₄CH₂)] was proved by the paramagnetic ¹H NMR spectrum. GC-MS analysis showed that the volatiles contained, besides toluene- d_8 and the initial diene, its hydrogenated product (m/z 84). The olefin was determined by ¹H and ¹³C NMR spectra to be 2-methylpent-2-ene.

Reaction of 1 with 2,3-Dimethylbuta-1,3-diene. A solution of 1 (0.5 mmol in 1.0 mL of toluene- d_8) was mixed with the degassed diene (0.2 mL, ~1.7 mmol) and flame-sealed in an NMR tube. ¹H NMR spectra proved that the hydrogen transfer reaction required heating to 80 °C to proceed and was accomplished after 40 h. The products were [Cp*Ti(C₅Me₄CH₂)] and tetramethylethene in a mixture with the initial diene.

Catalytic Hydrogenation of Isoprene in the Presence of $[Cp*Ti(C_5Me_4CH_2)]$. The product from the above reaction of 1 with isoprene (0.5 mmol in 1.2 mL of toluene- d_8) was mixed with isoprene (0.2 mL, 2.0 mmol), and hydrogen (~3.0 mmol) was admitted. After stirring overnight, the reaction mixture was degassed by freeze—thaw cycles, and volatiles were distilled under vacuum into a cooled trap. They contained 2-methylbut-1-ene (95%) according to ¹H and ¹³C NMR spectra. The distillation residue was overwhelming 1 according to the paramagnetic ¹H NMR spectrum.

X-ray Crystallography. Single crystals or crystal fragments of 3d(a), 3e(a), 4a, 4b, 4c, 5a, 6b, and 7 were mounted into Lindemann glass capillaries in a Labmaster 130 glovebox (mBraun) under purified nitrogen. Diffraction data were collected on a Nonius Kappa diffractometer with a Bruker ApexII detector (Mo K_a radiation, λ = 0.71073 Å) and processed by the Apex2 program package.³⁴ The phase problem was solved by direct methods (SHELXS), followed by consecutive Fourier syntheses, and refined by full-matrix least-squares on F^2 (SHELXL-97).³⁵ Relevant crystallographic data are gathered in the Supporting Information. All non-hydrogen atoms were refined anisotropically. The C-H hydrogen atoms were placed into idealized positions and refined isotropically using the riding model except for the C=C-H hydrogen atoms in 4a-4c and 5a. These were refined isotropically without any restraints. The disorder in 4a and 4b due to placement of the alkenyl group in opposite direction and the presence of a minor atropisomer in 6b was resolved; however, the data precision was slightly lowered. Among the six symmetrically nonequivalent molecules in the unit cell of 7 one molecule (F) suffered from heavy disorder. Molecular graphics were carried out with the PLATON program.³⁶

Computational Details. DFT calculations have been carried out at the Fermi cluster at the J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of Czech Republic, v.v.i., using Gaussian 09, Revision C.01.³⁷ Geometry optimizations and NBO analyses were done using the M06 functional, and the 6-31G(d,p) basis set was used for all atoms. The differences of total energy between nonagostic and agostic **2a** were determined using the M06 functional and an ultrafine integration grid, and the 6-31++G(d,p) basis set was used for all atoms

ASSOCIATED CONTENT

Supporting Information

CIF file for the structures 3d(a), 3e(a), 4a, 4b, 4c, 5a, 6b, and 7. Table of crystallographic data and data collection and structure refinement details for 3d(a), 3e(a), 4a, 4b, 4c, 5a, 6b, and 7. Table of ¹H NMR and EPR data for paramagnetic compounds 2a-2d, 4a-4c, 5a, and 5b. ¹H NMR spectrum of a mixture of 3c isomers. Atom coordinates for optimized agostic and nonagostic isomers of 2a. NMR and GC-MS data on organic hydrogenated products from 2a, 2c, 4c, and hex-3-yne and thermolysis of 4c. NMR and GC-MS data on organic hydrogenated products from 7, 8, and methyl-substituted buta-1,3-dienes. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

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