LINEAR DIMERIZATION OF TERMINAL ALKYNES BY BIS(TETRAMETHYLPHENYLCYCLOPENTADIENYL)TITANIUM–MAGNESIUM HYDRIDE AND ACETYLIDE COMPLEXES

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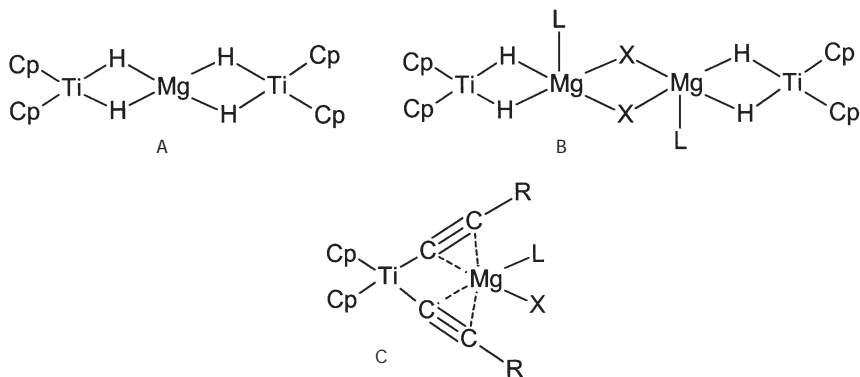
New tetramethylphenylcyclopentadienyl trinuclear titanocene hydride–magnesium hydride complexes [{Ti(η^5-C$_5$Me$_4$R)$_2$(μ-H)$_2$}$_2$Mg], where R = Ph (**1**) or 4-fluorophenyl (FPh; **2**), the dinuclear [Ti(η^5-C$_5$Me$_4$Ph)[η^5:η^1{Ti:Mg}-C$_5$Me$_4$(*o*-C$_6$H$_4$)](μ-H)$_2$Mg(THF)$_2$] (**3**) and [Ti(η^5-C$_5$Me$_4$Ph)$_2$-(μ-H)$_2$MgC(Me)=CHMe] (**4**) complexes, and the [{Ti(η^5-C$_5$Me$_4$Ph)$_2$(η^1-C≡CSiMe$_3$)$_2$}$^-$-{MgCl(THF)}$^+$] (**5**) tweezer complex initiated the dimerization of (trimethylsilyl)ethyne (TMSE) or 1-hexyne (HXYN) to exclusively head-to-tail (HTT) dimers at 60 °C with the turnover number ranging from 300 to 500 mol alkyne per mol of the Ti complex. In contrast, all of them were inactive in the dimerization of *tert*-butylethyne (TBUE). Monitoring of reactions of the **1**–**5** complexes with the alkynes by electron spin resonance (ESR) method revealed a decay of the initial complexes **1**–**5** in the dimerizing systems with TMSE and HXYN or a conversion of complexes **3**, **4**, and **5** into the Ti(III) acetylide [Ti(η^5-C$_5$Me$_4$Ph)$_2$-(η^1-C≡CCMe$_3$)] (**6**) in systems with TBUE. The acetylide **6** also initiated the dimerization of TMSE and HXYN to HTT dimers only. This fact together with the absence of ESR signals of tweezer complexes and acetylides in the reacting hydride systems allow us to assume that the rate of conversion of complexes **1**–**4** to tweezer complexes is slower than the rate of dissociation of the tweezer complexes to give the acetylides which are apparently the ultimate catalytic species. Most of the evidence on the catalytic complexes has been obtained from ESR spectra which are reliably characteristic of each type of the complexes. Crystal structures of **4** and **6** were determined.

Keywords: Titanium; Alkynes; Dimerization; Hydrides; Magnesium; Titanocene acetylide; Crystal structure; ESR spectroscopy; Homogeneous catalysis; Metallocenes.

Terminal alkynes RC≡CH not containing an electron donor atom in their substituent are known to be catalytically dimerized with high turnover numbers by early transition metals[1], rare-earth metals and lanthanide

permethylmetallocene catalysts[2]. Among them permethyltitanocene catalysts show a fascinating regioselectivity forming exclusively head-to-tail (HTT) dimers $RC{\equiv}C{-}CR{=}CH_2$ from all terminal alkynes except *t*-butylethyne (TBUE) with turnover numbers (TON) ranging from 500 to 700 mol alkyne per mol of a titanium complex[3]. *t*-Butylethyne did not dimerize at all with these catalysts; however, analogous catalysts containing tetramethylcyclopentadienyl ligands appeared to dimerize just and only this alkyne to HTT dimer with TON as high as 8000 (ref.[4]). These catalysts are based on titanocene hydride–magnesium hydride complexes of trinuclear type A (ref.[5]) or dimeric binuclear type B (refs[4,6]) (Scheme 1) which are easily formed in various titanocene dichloride–magnesium or alkyl magnesium systems. Investigations of such catalysts in the presence of terminal alkynes revealed that the hydrides of both types were first converted to tweezer complexes of type C (Scheme 1) which then decayed during the alk-1-yne dimerization. The dimerization reaction has been proposed to run on simple titanocene acetylides that should be generated by dissociation of the tweezer complexes in the excess of alk-1-ynes[3,4]. This hypothesis could not be verified because the steady state concentration of the generated acetylides was very low. Moreover, the only ESR spectrum reported for titanocene acetylides, that of $[Ti(\eta^5\text{-}C_5Me_5)_2(\eta^1\text{-}C{\equiv}CMe)]$ was characterized by a very broad signal linewidth $\Delta H = 49$ G at $g = 1.941$ (ref.[7]) implying a low sensitivity of the ESR method in detection of the acetylide complexes. The nature of the catalytical center became even more obscured when it has been shown that also the titanium(II) complexes, $[Ti(\eta^5\text{-}C_5Me_4R)_2(\eta^2\text{-}Me_3SiC{\equiv}CSiMe_3)]$ (R = Me or H), catalyze the dimerization of terminal alkynes with the same, nearly absolute regioselectivity and high activity as the above Ti(III) catalysts[8].

Cp = $C_5H_{5-n}Me_n$; n = 0–5; X = Cl, Br; L = THF, OEt$_2$; R = alkyl, aryl

SCHEME 1

Here we report syntheses of new bis(tetramethylphenylcyclopentadienyl)-titanium magnesium hydride and acetylide complexes (Chart 1), their catalytic activity in dimerization of selected terminal alkynes, and a support for an opinion that simple titanocene(Ti^{III}) acetylides are true catalytic species.
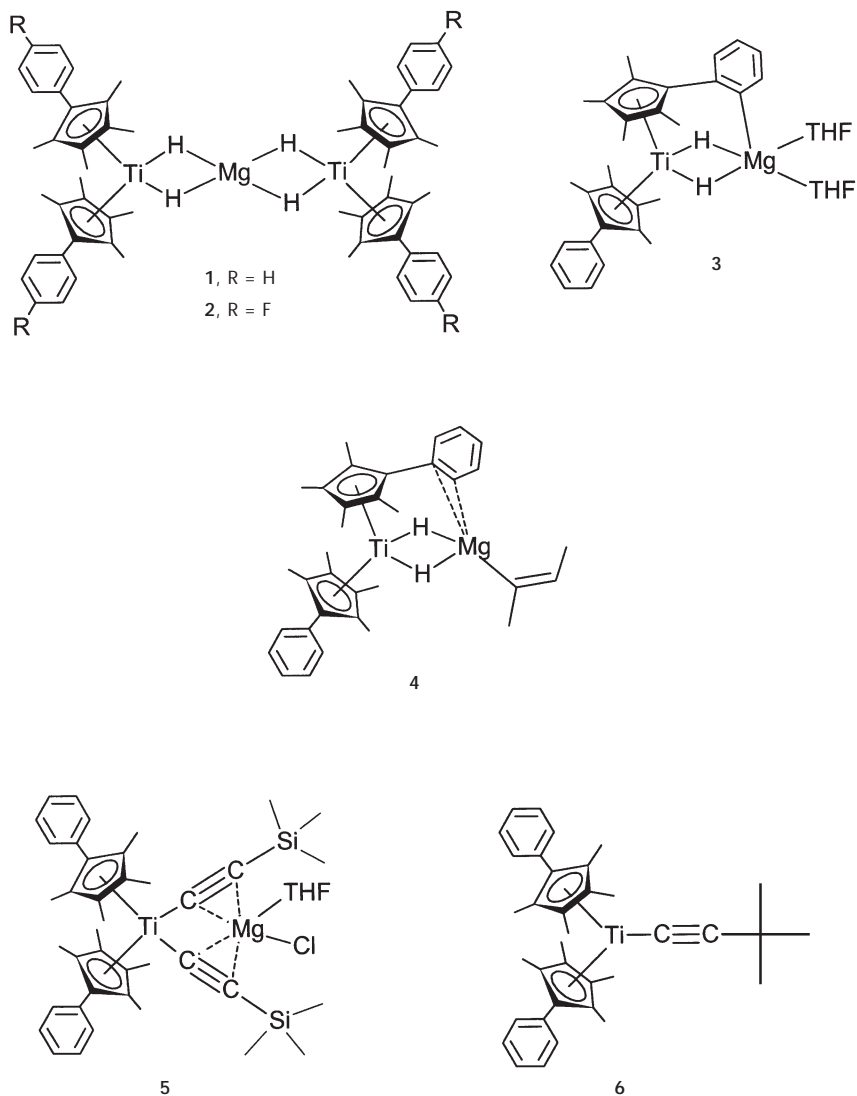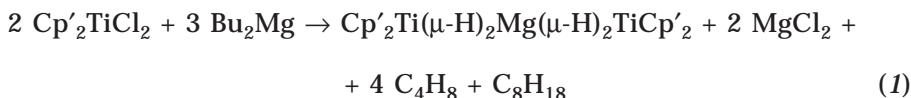

CHART 1

RESULTS AND DISCUSSION

Preparation of Titanocene Hydride–Magnesium Hydride Complexes

The reduction of $[TiCl_2(\eta^5\text{-}C_5Me_4Ph)_2]$ (ref.[9]) or $[TiCl_2(\eta^5\text{-}C_5Me_4FPh)_2]$ (FPh, 4-fluorophenyl)[10] with 3 molar equivalents of dibutyl magnesium in a toluene/heptane mixture afforded nearly quantitatively the trinuclear hydride complexes of type A $[\{Ti(\eta^5\text{-}C_5Me_4Ph)_2(\mu\text{-}H)_2\}_2Mg]$ (**1**) and $[\{Ti(\eta^5\text{-}C_5Me_4FPh)_2(\mu\text{-}H)_2\}_2Mg]$ (**2**), respectively. This method was previously used for obtaining methyl substituted complexes $[\{(\eta^5\text{-}C_5Me_nH_{5-n})_2\text{-}Ti(\mu\text{-}H)_2\}_2Mg]$ (n = 3–5) with yields increasing with the number of Me groups[5b]. A three-fold molar excess of Bu_2Mg with respect to titanocene dichloride was used to ascertain the formation of trinuclear complexes of type A although the stoichiometry of Eq. (*1*) would require the Mg:Ti ratio of 1.5:1 only.

$$2\ Cp'_2TiCl_2 + 3\ Bu_2Mg \rightarrow Cp'_2Ti(\mu\text{-}H)_2Mg(\mu\text{-}H)_2TiCp'_2 + 2\ MgCl_2 +$$

$$+\ 4\ C_4H_8 + C_8H_{18} \tag{1}$$

At lower Mg:Ti ratio (2:1), however, a binuclear complex was also formed (see below). The molecular structure of **1** and **2** was determined from ESR spectra of the compounds in frozen toluene solutions, and their composition was confirmed by IR and EI-MS spectra. The ESR spectra display the features attributable to electronic triplet states of axial symmetry generated by two d^1 electrons with unpaired electron spins residing on Ti(III) ions. The outer features of the spectra (Fig. 1a) determine the values of zero-field splitting (**1**, D = 0.01240 cm^{-1}; **2**, D = 0.01230 cm^{-1}, E = 0), which are inversely proportional to the distance between the two Ti(III) ions[11]. The obtained values are very close to the D-values found for complexes $[\{(\eta^5\text{-}C_5Me_nH_{5-n})_2Ti(\mu\text{-}H)_2\}_2Mg]$ (n = 3–5) whose molecular structures were determined by X-ray diffraction analysis, and distances found in crystal structures did not differ much from those derived from ESR data for frozen toluene solutions[5b]. As the g-values of all the mentioned compounds fall into the range 1.989–1.990 the differences in D-values indicate that the Ti–Ti distance in **1** is shorter by *ca* 0.035 Å and in **2** by *ca* 0.020 Å than in $[\{Ti(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}H)_2\}_2Mg]$ where the crystallographic Ti–Ti distance was found to be 5.717(4) Å (ref.[5a]). The presence of the tetramethylphenyl-cyclopentadienyl ligands (Cp') in **1** and (4-fluorophenyl)tetramethyl-

cyclopentadienyl ligands (Cp″) in **2** was clearly observed in IR spectra, the positions of their absorption bands differing only marginally from those in $[TiCl_2(\eta^5\text{-}C_5Me_4Ph)_2)]$ (ref.[9]) and in $[TiCl_2(\eta^5\text{-}C_5Me_4FPh)_2]$ (see Experimental). It has to be stressed that no fluorine abstraction by the titanocene hydride moiety was noticed as the very strong bands of the C_5Me_4Ph ligand at 758–760 and 703–705 cm^{-1} were not observed in infrared spectra of **2**. The bridging Ti–H–Mg bonds gave rise to a broad absorption band underlying sharp absorption bands of the ligands; the absorption band is situated at *ca* 1230 cm^{-1} and its half-band width amounts to *ca* 70 cm^{-1} in both **1** and **2**. The position and the shape of the band agrees with the data obtained for the $[\{Ti(\eta^5\text{-}C_5Me_nH_{5-n})_2(\mu\text{-}H)_2\}_2Mg]$ (n = 3–5) complexes[5]. On the other hand, the monomeric hydrides $[TiH(\eta^5\text{-}C_5Me_4Ph)_2]$ (ref.[12]) and $[TiH(\eta^5\text{-}C_5Me5)_2]$ (ref.[13]) show the Ti–H vibration at 1505 and 1489 cm^{-1}, respectively. The EI-MS spectra of **1** and **2** did not display the molecular ions but mainly the fragment ions derived from Cp'_2Ti^+ or Cp''_2Ti^+ ions by a subsequent loss of hydrogen atoms. The mass spectra of **2** showed that the fluorine atom takes part in fragmentation as in addition to ions derived from Cp''_2Ti species the species derived from Cp'_2Ti ions are also observed although less abundant. The ESR spectra in solutions displayed besides the signal of the trinuclear complex (g = 1.990, ΔH = 1.4 mT) a sharp signal due to the presence of titanocene(Ti^{III}) alkoxy compounds at $g \approx 1.977$ (*cf*.

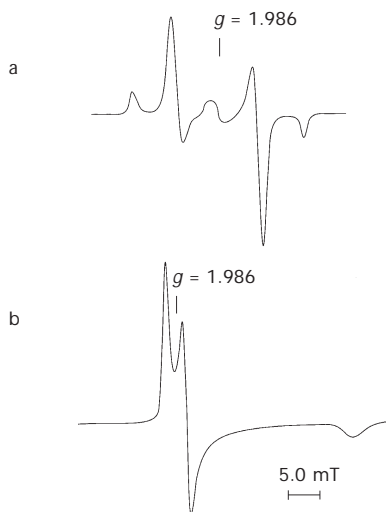FIG. 1
ESR spectra spectra of compounds **1** (a) and **6** (b) in toluene glass at –140 °C. ΔM_S = 2 transition in the spectrum of **1** is not reproduced

refs[4,14]) in the amount of less than 5%. These unpleasant impurities arising from the reaction of low valent titanocene derivatives with water, hydroxyl groups or oxygen are characterized by a sharp signal ($\Delta H \approx 5$ G) close to the above *g*-value. Unfortunately, reluctance of compounds **1** and **2** to crystallize precluded their purification.

Of the binuclear complexes of type B, the complex [Ti(η^5-C$_5$Me$_4$Ph)-[η^5:η^1{Ti:Mg}-C$_5$Me$_4$(*o*-C$_6$H$_4$)](μ-H)$_2$Mg(THF)$_2$] (**3**) was obtained as recently reported[15] and a similar compound [Ti(η^5-C$_5$Me$_4$Ph)$_2$(μ-H)$_2$Mg(CMe=CHMe)] (**4**) was accidentally obtained in low yield as a byproduct of **1**. In the experiment when the Ti:Bu$_2$Mg ratio 1:2 was used instead of 1:3, a small amount of yellow-brown rhombic plate crystals was obtained after cooling a hexane solution of the crude product to –18 °C. The structure of **4** was unequivocally determined by X-ray crystallography, and corroborated by ESR, EI-MS and IR spectra. The ESR spectrum in solution showed a triplet hyperfine splitting due to the interaction of d^1 electron with two equivalent bridging hydrogen atoms, the *g*-value of 1.990 and a_H = 0.7 mT (Fig. 2a) being very close to the values for **3** (ref.[15]) and generally for the whole class of B-type hydrides[4,6,16]. The EI-MS spectra did not display the molecular ions; the fragment ions attributable to [Cp'$_2$Ti–H]$^+$, [Cp'H]$^+$ and [Cp'–Me]$^+$ ions were the most abundant. The IR spectrum gave evidence of bridging
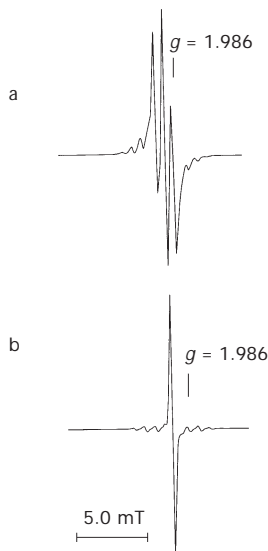

F$_{IG}$. 2
ESR spectra of compounds **4** (a) and **5** (b) in toluene solution at room temperature

Ti–H–Mg bonds by a strong absorption band at 1287 cm^{-1}, narrower than those in **1** or **2**. In coordinatively saturated **3** this band occurred at 1240 cm^{-1}. The absorption band of the double bond of but-2-en-2-yl group is probably overlapped by sharp absorption bands at 1504 and 1493 cm^{-1}; since the length of the double bond is considerably prolonged (1.418(7) Å, *vide infra*) the red shift of this presumably weak absorption band is to be anticipated. Although the stoichiometry of the reacting system is difficult to establish the structure of **4** implies a hydrogen transfer from n-butyl group into the titanium–magnesium bond and the formation of the magnesium but-2-en-2-yl moiety.

Preparations of Titanocene Acetylide Complexes

The tweezer complex [{Ti(η^5-C$_5$Me$_4$Ph)$_2$(η^1-C≡CSiMe$_3$)$_2$}$^-${MgCl(THF)}$^+$] (**5**) was prepared by the scission of 1,4-bis(trimethylsilyl)buta-1,3-diyne when reducing the titanocene dichloride with magnesium in THF, following the procedure used to obtain [{Ti(η^5-C$_5$Me$_4$H)$_2$(η^1-C≡CSiMe$_3$)$_2$}$^-${MgCl(THF)}$^+$] whose crystal structure is known[17]. The compound was obtained as a brownish yellow non-crystallizing material soluble in hexane. Its molecular structure was deduced from ESR, IR and EI-MS spectra. The ESR spectra of Ti(III) tweezer complexes show unique features quite characteristic of this type of complexes: a high g-value 1.992–1.993, a narrow linewidth of ESR signals and well-discernible a_{Ti} coupling to ^{47}Ti and ^{49}Ti isotopes possessing the nuclear spin of 5/2 and 7/2, respectively[18] (Fig. 2b). The infrared spectrum confirmed the presence of acetylide arms by a strong absorption band at 1937 cm^{-1} and the presence of a coordinated THF molecule by an absorption band at 1024 cm^{-1}. EI-MS spectra of **5** show the liberation of THF molecules at 50 °C and fragments commencing from [Cp′$_2$Ti(C≡CSiMe$_3$)$_2$]$^+$ at high temperature.

The simple acetylide [Ti(η^5-C$_5$Me$_4$Ph)$_2$(η^1-C≡CCMe$_3$)] (**6**) was obtained from compound **3** and a 12-fold molar excess of TBUE at 60 °C. The reaction required *ca* 20 h to run to completion. Compound **6** was separated from an alkoxy titanocene impurity ($g \approx 1.977$) by crystallization from hexane, and its composition and structure was determined by X-ray diffraction analysis (see below), ESR, UV-VIS, IR and EI-MS spectra. The ESR spectrum displays a very broad signal ($\Delta H = 3.8$ mT) at $g = 1.938$, similar to the data for [Ti(η^5-C$_5$Me$_5$)$_2$(η^1-C≡CMe)] (ref.[7]). In frozen toluene solution the signal of **6** is extremely broad, the g_3 component of its ***g***-tensor occurring at $g_3 = 1.837$ (Fig. 1b). It indicates a pure σ-bonding character of the Ti–C bond (see ref.[14b]). The electronic absorption spectrum resembles the spectra of

titanocene halides or alkyls[14b,19] showing the $1a_1 \rightarrow 2a_1$ transition at 490 nm and the $1a_1 \rightarrow b_1$ transition at 620 nm. Its IR spectrum shows the bands typical for the η^5-C_5Me_4Ph ligands and the $\nu(C\equiv C)$ vibration at 2068 cm^{-1} comparing well with the wavenumber for such a vibration in $[Ti(\eta^5$-$C_5Me_5)_2$-$(\eta^1$-$C\equiv CCMe_3)]$ (2071 cm^{-1})[20] and $[Ti(\eta^5$-$C_5Me_5)_2(\eta^1$-$C\equiv CMe)]$ (2080 cm^{-1})[7]. The EI-MS spectrum displayed a highly abundant molecular peak and a fragment ion due to the loss of the acetylene as a base peak, and the sample was completely evaporated displaying a constant fragmentation pattern.

Crystal Structure of Compound 4

The absence of an electron donor solvent in the synthesis of **4** resulted in some structural features (Fig. 3) differentiating the compound from all the so far known titanocene–magnesium hydride complexes[4,6,15,16c]. While the parameters for the hydride bridging bonds binding magnesium and titanium are esentially common to the whole class of B-type complexes, the magnesium atom bears for the first time an organyl substituent, and the coordinatively unsaturated magnesium atom then strongly attracts one phenyl ring through a bonding interaction with two carbon atoms of the phenyl ring. The X-ray data (Table I) proved that the substituent is the but-2-en-2-yl group. Its double bond is prolonged to 1.418(7) Å (*vs* 1.31(1) Å for average *trans* double bond[21]) due to its direct attachment to the magnesium atom. The valence angles at the double bond carbon atoms are somewhat smaller than for sp^2 carbon atoms apparently due to partial sp^3 hybridization, however, the double bond character is well preserved as fol-
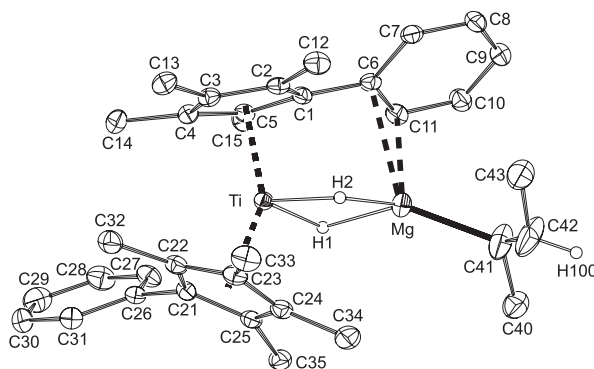

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PLATON drawing of compound **4** at the 30% probability level with atom labelling scheme

lows from the value of the torsion angle τ of its carbon chain amounting to 177.1(5)°. The Mg–C41 bond length of 2.123(4) Å is, on the other hand, shorter than in most organylmagnesium compounds[22]. The bent titanocene unit shows an extremely large Cg1–Ti–Cg2 (Cg, centroid of the cyclopentadienyl ring) angle (147.2(2)°) (see the discussion for **6**), which is caused by attraction of the phenyl substituent to a close vicinity of the magnesium

TABLE I
Selected bond lengths (in Å) and angles (in °) for complex **4**

Bond distances			
Ti–Cg1[a]	2.072(2)	Ti–Cg2[a]	2.064(2)
Ti–C(Cp)	2.362(4)–2.421(3)	C–C(Cp)	1.401(5)–1.445(5)
C(Cp)–C(Me)	1.501(5)–1.520(5)	C1–C6	1.487(5)
C21–C26	1.483(5)	C–C(Ph)	1.378(6)–1.413(6)
Ti–H1	1.87(3)	Ti–H2	1.77(3)
Mg–H1	1.85(3)	Mg–H2	1.85(3)
Mg–C41	2.123(4)	C40–C41	1.504(6)
C41–C42	1.418(7)	C42–C43	1.494(7)
Mg–C6[b]	2.657(4)	Mg–C11[b]	2.644(4)
Ti–Mg[b]	2.807(2)		
Bond angles			
Cg1–Ti–Cg2[a]	147.2(2)	H1–Ti–H2	79.8(1)
H1–Mg–H2	77.8(14)	Mg–H1–Ti	98.1(14)
Mg–H2–Ti	101.9(16)	Mg–C41–C42	113.3(4)
Mg–C41–C40	117.2(3)	C40–C41–C42	116.2(4)
C41–C42–C43	120.2(5)	C41–C42–H100	108(3)
C43–C42–H100	115(2)	Ti–Mg–C41[b]	157.6(3)
ε^c	7(3)	ϕ^d	31.8(2)
$\chi 1^e$	29.3(2)	$\chi 2^f$	49.5(2)
τ^g	177.1(5)		

[a] Cg1 and Cg2 denote the centroids of the C(1–5) and C(21–25) cyclopentadienyl rings, respectively. [b] Nonbonding distances and angles. [c] Dihedral angle between the H1,Ti,H2 and H1,Mg,H2 planes. [d] Dihedral angle subtended by the cyclopentadienyl least-squares planes. [e] Dihedral angle between the least-squares planes of the C(1–5) cyclopentadienyl ring and the C(6–11) phenyl ring. [f] Dihedral angle between the least-squares planes of the C(21–25) cyclopentadienyl ring and the C(26–31) phenyl ring. [g] Torsion angle C40–C41–C42–C43.

atom. Distances found between the magnesium atom and *ipso*-C6 2.657(4) Å and *ortho*-C11 atoms imply an intramolecular bonding interaction resembling π-bonding character (*cf.* refs[17,18,23]). To achieve these contact distances the concerned cyclopentadienyl ligand is turned from usual position with the phenyl group at the side position[9] so that the phenyl group is directed to the open side of a titanocene wedge (Fig. 4). The coordinated phenyl group is rotated with respect to the cyclopentadienyl ligand much less (χ1 29.3(2)°) than the other one which shows a dihedral angle known for other derivatives (see below discussion for **6**). This additional coordination of the magnesium atom resulted in distortion of the hydride bridge (different lengths of Ti–H bonds, the Mg atom lies away from the Cg1,Ti,Cg2 plane) which is more planar than in all other B-type complexes[4,6,15,16c] (ε ≈ 7(3)°). The coordinated phenyl group also apparently declines the but-2-en-2-yl group away (Ti–Mg–C41 157.6(3)°). This molecular arrangement is, however, stable only in the solid state since the bridging hydrogen atoms are equivalent in the ESR spectrum of **4** in solution (*vide supra*).

Crystal Structure of Compound 6

The unsymmetrical molecule of **6** contains a trigonally coordinated titanium atom π-bonding two cyclopentadienyl ligands and σ-bonding the *t*-butylethynyl group. The bent titanocene moiety with the phenyl substituents placed in opposite side positions (Fig. 5) lacks most of the steric hindrance which is common in persubstituted titanocene derivatives. The
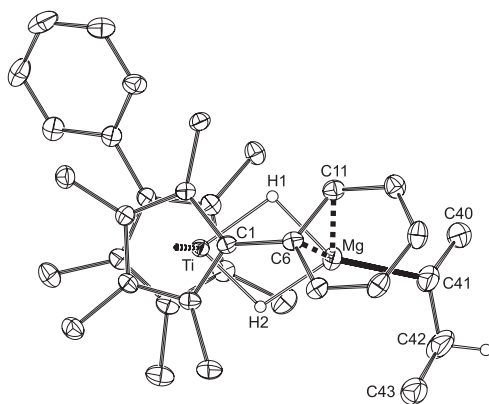

FIG. 4
View of the molecule **4** in the Cg1–Cg2 direction

Cg–Ti–Cg angle of 145.68(5)° in **6** (Table II) is larger than in [TiCl(η^5-C$_5$Me$_4$Ph)$_2$] (143.4(1)°) or [TiCl$_2$(η^5-C$_5$Me$_4$Ph)$_2$] (137.6(2)°)[9], and it is even slightly larger than that in [TiF(η^5-C$_5$Me$_5$)$_2$] (average 144.9°)[14b]. Correspondingly, declinations of methyl groups in hinge positions from the cyclopentadienyl ring planes in outward direction are smaller (maximum 0.325(5) Å for C(12)) than in the mentioned compounds. However, the benzene rings are rotated from the cyclopentadienyl rings similarly to all the compared compounds. The acetylide group is close to linear showing the Ti–C(31) and C(31)–C(32) and C(31)–C(32)–C(33) angles equal to 176.5(3) and 178.8(3)°, respectively. The Ti–C(31) distance of 2.113(3) Å does not practically differ from the Ti–C bond length in the only other titanocene acetylide structure of [Ti(η^5-C$_5$Me$_5$)$_2$(η^1-C≡CCMe$_3$)] (2.108(6) Å)[20] and the acetylenic bond lengths in these compounds are also similarly prolonged to 1.211(4) and 1.204(6) Å, respectively, with respect to the disubstituted acetylene value of about 1.18 Å (ref.[21]).

Reactivity of the Hydride and Acetylide Complexes to Terminal Alkynes – Dimerization

Trinuclear complexes **1** and **2** did not react with TBUE even after a long heating to 90 °C. On the other hand, dinuclear compounds **3** and **4** reacted with TBUE slowly at room temperature to give the acetylide **6**. The reaction was speeded up by heating to 60 °C at which temperature the conversion of
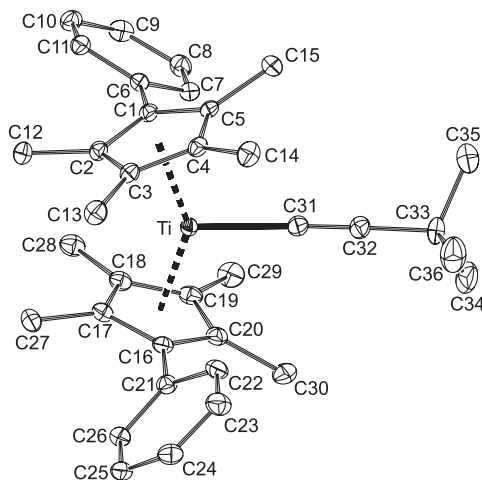

Fig. 5
PLATON drawing of compound **6** at the 30% probability level with atom labelling scheme

3 or **4** to **6** was completed within 5 h. The acetylide **6** was isolated and characterized (*vide supra*) from the reaction of **3**, and further used as a catalyst.

In contrast to TBUE, (trimethylsilyl)ethyne (TMSE) and 1-hexyne (HXYN) dimerized under catalysis by all the compounds **1**–**6** with total TON ranging 300–500 mol alk-1-yne per mol of the Ti complex. The TON data are very inaccurate because they depend on the purity of alk-1-yne and the vacuum system in which the catalyst solutions and alk-1-ynes were transferred. Moreover, the catalyst concentrations were determined by double integration of first derivative ESR spectra, whose precision was estimated to give figures with as high error as ±20%. The used devices with attached quartz cuvettes and quartz ESR tubes for the measurement of catalyst conversions and alk-1-yne consumption could not be thermostatted, and so the study confined to a qualitative description of the dimerization process.

The formation of tweezer complexes as intermediates in the pathway to a catalytic center was previously well evidenced by ESR spectroscopy for the

TABLE II
Selected bond lengths (in Å) and angles (in °) for complex **6**

Bond distances			
Ti–Cg1[a]	2.0627(15)	Ti–Cg2[a]	2.0623(15)
Ti–C(Cp)	2.356(3)–2.418(3)	C–C(Cp)	1.414(4)–1.430(4)
C(Cp)–C(Me)	1.503(4)–1.510(4)	C1–C6	1.486(4)
C16–C21	1.485(4)	Ti–C31	2.113(3)
C31–C32	1.211(4)	C32–C33	1.489(4)
C33–C(Me)	1.513(4)–1.551(4)	C–C(Ph)	1.375(4)–1.396(4)
Bond angles			
Cg1–Ti–Cg2[a]	145.68(5)	Ti–C31–C32	176.5(3)
C31–C32–C33	178.8(3)	C32–C33–C(Me)	108.8–110.3(3)
Cg1–Ti–C31[a]	106.3(1)	Cg2–Ti–C31[a]	108.0(1)
ϕ[b]	34.66(14)	$\chi 1$[c]	46.5(1)
$\chi 2$[d]	53.5(1)		

[a] Cg1 and Cg2 denote the centroids of the C(1–5) and C(16–20) cyclopentadienyl rings, respectively. [b] Dihedral angle subtended by the cyclopentadienyl least-squares planes. [c] Dihedral angle between the least-squares planes of the C(1–5) cyclopentadienyl ring and the C(6–11) phenyl ring. [d] Dihedral angle between the least-squares planes of the C(16–20) cyclopentadienyl ring and the C(21–26) phenyl ring.

dinuclear complexes of type B containing the η^5-C_5Me_5 or η^5-C_5HMe_4 ligands[4,6]. In contrast, analogous complexes **3** and **4** as well as **1** and **2** readily dimerized TMSE and HXYN while the presence of the corresponding tweezer complexes, which would be observable in very low concentrations due to narrow linewidths of their signals, were not detected. On the other hand, the tweezer complex **5** appeared to catalyze the HTT dimerization of TMSE and HXYN similarly to **1**–**4**. This may indicate that the conversion of **1**–**4** to corresponding tweezer complexes is slower than their dissociation into the suggested acetylides [$Ti(C_5Me_4Ph)_2(\eta^1$-C≡CSiMe$_3$)] and [$Ti(C_5Me_4Ph)_2$-(η^1-C≡CBu)] or their C_5Me_4FPh analogs for **2**. Somewhat suprisingly, acetylide **6** catalyzed the dimerization of TMSE and HXYN at rates not strikingly faster than observed for **1**–**5**. Unfortunately, no information on the expected exchange of acetylide groups can be obtained from ESR spectra of reacting systems as the broad line signal is not sensitive to the acetylide substituent (at variance with the narrow lines of tweezer complexes which are split by protons on α-carbon atoms of the acetylide substituent[3]). Nonetheless, it is unlikely that the exchange of the *t*-butylacetylide group for trimethylsilyl- or butylacetylide groups would hinder the rate of TMSE and HXYN dimerization. To get a deeper insight into the mechanism of alk-1-yne dimerization by Ti(III) acetylides, a more exact and quantitative study allowing kinetic measurements is to be carried out. A direct synthetic way to titanocene(Ti^{III}) acetylides has been disclosed recently[20]. The study of kinetics was outside the scope of this work; however, the present results allow to draw several conclusions:

1. The change of stereoelectronic factors introduced by the phenyl substituent in C_5Me_4Ph ligands does not change the catalyst regiospecificity known for the permethylated complexes. The present complexes are active in dimerization of terminal alkynes except TBUE.

2. The presence of fluorine in C_5Me_4FPh ligands of **2** does not observably change the catalyst property.

3. The tweezer complex **5** catalyzes the dimerization of TMSE and HXYN, and dissociates under the action of TBUE to give **6**. The absence of ESR signals of tweezer **5** when TMSE is dimerized under the action of **1** implies that the rate of dissociation of **5** is higher than the rate of its formation from **1**.

4. The simple acetylide **6** dimerizes TMSE and HXYN – it strongly supports the opinion[1a,3,4] that titanocene acetylides are the ultimate catalytic complexes.

EXPERIMENTAL

General Data and Methods

Preparation of hydride and acetylide complexes, their isolation, handling and spectroscopic measurements were performed *in vacuo*. An all-sealed glass device equipped with breakable seals, an EPR sample tube and a pair of quartz cuvettes (d = 1.0 and 10 mm; Hellma) were used for the measurement of ESR and UV-VIS spectra. The adjustment of single crystals of **4** and **6** into Lindemann glass capillaries for X-ray analysis and preparation of KBr pellets for IR measurements were performed in a glovebox (mBraun) under purified nitrogen. Mass spectra were measured on a VG 7070E spectrometer at 75 eV (only important mass peaks and peaks of intensity ≥5% are reported) using a direct inlet. Crystalline samples in capillaries were opened and inserted into the direct inlet under argon. ESR spectra were registered on an ERS-220 spectrometer (Centre for Production of Scientific Instruments, Academy of Sciences of GDR, Berlin, Germany) equipped with a magnet controlling and data acquisition CU1 unit (Magnettech, Berlin, Germany) in the X-band. g-Values were determined using an Mn^{2+} (M_I = –1/2 line) standard at g = 1.9860. Concentrations of paramagnetic compounds were estimated from integrated first-derivative spectra related to a standard sample ([Ti(η^5-C_5H_5)$_2$(μ-Cl)$_2$Al(Cl)Et], 5.275×10^{-3} M in benzene)[24]. An STT-3 variable temperature unit was used for the measurement in the range from –130 to +20 °C. UV-near IR spectra were measured in the range 270–2000 nm on a Varian Cary 17D spectrometer using all-sealed quartz cuvettes (Hellma). Infrared spectra of KBr pellets were measured in an air-protecting cuvette on a Nicolet Avatar FTIR spectrometer in the range 400–4000 cm^{-1}.

Chemicals

Hexane and toluene were purified by conventional methods, dried by refluxing over LiAlH$_4$ and stored as solutions of dimeric titanocene [{Ti(μ-H)(C_5H_5)}$_2$(μ-η^5:η^5-$C_{10}H_8$)] (ref.[25]). *t*-Butylethyne (Aldrich) was degassed, distilled on solid doubly tucked-in titanocene [Ti(η^5-C_5Me_5){η^3:η^4-$C_5Me_3(CH_2)_2$}] (ref.[26]), and the formed solution was heated to 80 °C in a sealed ampoule for 2 h. This procedure was repeated with the fresh titanium complex until the solution remained blue. Then, the ampoule was attached to a vacuum line with a metal valve, and the alkyne was distributed by vacuum distillation into ampoules for catalytic experiments. (Trimethylsilyl)ethyne (Aldrich) was degassed and distilled onto the solid complex [{(η^5-C_5HMe_4)$_2$Ti(μ-H)$_2$}$_2$Mg] (ref.[5b]). After the evolution of hydrogen ceased, the whole purification procedure was repeated with a fresh titanium complex until *ca* 2 mole % of the latter, relative to TMSE, was consumed. Finally, the solution was degassed on a vacuum line, and the alkyne distributed into ampoules by vacuum distillation. Analogous purification procedure was carried out with hex-1-yne (Aldrich). Dibutylmagnesium (1 M in heptane; Aldrich) was degassed and distributed into ampoules which were then sealed off. [TiCl$_2$(C_5Me_4Ph)$_2$] (ref.[9]) and [TiCl$_2$(C_5Me_4FPh)$_2$] (FPh, 4-fluorophenyl)[10] were prepared by literature methods, and used after recrystallization from toluene. Solid complex [(η^5-C_5Me_4Ph)[η^5:η^1{Ti:Mg}-C_5Me_4(o-C_6H_4)]Ti(μ-H)$_2$Mg(THF)$_2$](toluene) (ref.[15]) (0.38 g, 0.48 mmol) was dissolved in toluene and used as 0.1 M toluene solution.

Preparation of Titanocene Hydride–Magnesium Hydride Complex **1** and Isolation of Byproduct **4**

Crystalline dichlorobis[η^5-tetramethyl(phenyl)cyclopentadienyl]titanium(IV)[9] (1.024 g, 2.0 mmol) was degassed, dissolved in 10 ml of toluene, and 1.0 M Bu$_2$Mg solution in heptane (4.0 ml) was added under shaking. The initial red solution rapidly turned green. After stirring at 60 °C for 1 h, the solution was evaporated *in vacuo*, and the residue was repeatedly extracted with hexane until the extract was nearly colorless. The intense khaki-green solution (20 ml) was cooled with dry ice for 2 days to give a small amount of khaki-green rhombic plates of **4** which were separated. Yield 0.055 g (5%). Their structure was identified by X-ray diffraction analysis, ESR, IR and MS spectra. On a vacuum line, 0.2 ml of TBUE was condensed to the mother liquor, and the sealed mixture was heated to 60 °C for 30 min. The solution was concentrated to *ca* 10 ml and cooled in a refrigerator overnight. A crystalline dark green solid was separated from pale brown solution. The latter displayed an EPR spectrum containing the signal of acetylide **6** formed by the reaction of the remaining **4** with TBUE ($g = 1.938$, $\Delta H = 3.8$ mT), the signal of residual **1**, and signals of impurities at $g = 1.977$ of some titanocene alkoxides. This solution was discarded. The solid was extracted with hexane to give a pale green solution which was separated. After numerous unsuccessful attempts to crystallize **1** from hexane or toluene a khaki-green solid separated from hexane was dried *in vacuo* and used for the characterization. Yield 0.75 g (82%). Compound **1** was also obtained by the procedure described for **2** using the Ti:Mg molar ratio 1:3 in a similar yield.

Compound **1**. EPR (hexane, 23 °C): $g = 1.989$, $\Delta H = 1.4$ mT; (toluene, –140 °C): electronic triplet state of axial symmetry $g = 1.990$, $D = 0.01240$ cm^{-1}, $E = 0$. UV-VIS (hexane, 22 °C): 390 >> 590 (extending to 900 nm). IR (KBr, cm^{-1}): 3083 (w), 3053 (m), 2945 (sh), 2905 (vs), 2858 (s), 1600 (s), 1573 (w), 1506 (s), 1483 (m), 1450 (s), 1377 (s), 1279 (vs, b), 1175 (vs), 1073 (w), 1023 (m), 1003 (w), 983 (m), 915 (w), 838 (vw), 758 (vs), 703 (vs), 665 (vw), 644 (w), 618 (vw), 588 (w), 497 (vw), 426 (m, sh). EI-MS (210 °C, m/z (rel. abundance)): M$^{•+}$ not observed; 443 (31), 442 (82), 441 ([Cp$'_2$Ti – H]$^+$; 100), 440 (80), 439 (63), 437 (23), 436 (7), 435 (10), 264 (10), 242 (11), 241 (18), 240 (14), 239 (11), 238 (10), 237 (17), 213 (11), 199 (9), 198 ([Cp$'$H]$^+$; 47), 197 (10), 196 (13), 183 (24), 181 (12), 165 (14).

Compound **4**. EPR: $g = 1.9915$, $\Delta H = 0.23$ mT, $a_H = 0.73$ mT, $a_{Ti} = 0.60$ mT; impurities <5%, $g = 1.982$, $\Delta H = 2.5$ G; $g = 1.978$, $\Delta H = 3.5$ G. UV-VIS (toluene, 23 °C): 390 >> 590 (extending to 900 nm). IR (KBr, cm^{-1}): 3082 (vw), 3053 (w), 2947 (s), 2908 (vs), 2853 (s), 2813 (m), 2789 (m), 1599 (s), 1573 (w), 1504 (m), 1493 (m), 1450 (s), 1391 (w), 1377 (m), 1287 (s, b), 1180 (vw), 1154 (vw), 1075 (vw), 1021 (w), 984 (vw), 953 (vw), 913 (w), 814 (m), 758 (vs), 705 (vs), 644 (vw), 588 (vw), 491 (vw). EI-MS (210 °C, m/z (rel. abundance)): M$^{•+}$ not observed; 443 (14), 442 (44), 441 ([Cp$'_2$Ti – H]$^+$; 100), 440 (52), 439 (30), 438 (10), 437 (10), 241 (10), 199 (17), 198 ([Cp$'$H]$^+$; 97), 197 (18), 196 (24), 183 (51), 181 (18), 168 (16), 167 (14), 166 (13), 165 (20), 105 (11), 91 (15), 57 (19).

Unfortunately, the ESR spectrum of frozen toluene solution made from the crystalline material remaining after selection of single crystals of **4** for X-ray analysis, IR and MS spectra revealed the presence of a non-negligible amount of compound **1**. Therefore, it had no sense to subject this material to elemental analysis.

Preparation of Titanocene Hydride–Magnesium Hydride Complex **2**

The synthesis of **2** from [TiCl$_2$(C$_5$Me$_4$FPh)$_2$] (ref.[10]) (0.548 g, 1.0 mmol) and 1.0 M Bu$_2$Mg (3 ml) was carried out in the same way as for **1**. In contrast to the above isolation of **1**, practically no product was obtained by extraction with hexane, and the extract in toluene contained only pure compound **2**. The presence of a dinuclear complex analogous to **4** was not observed in the EPR spectra of the toluene solution. Therefore, the use of TBUE for its removal was unnecessary. Attempts to crystallize out compound **2** led to separation of another portions of magnesium dichloride which was partially soluble in the solution. Finally, solid **2** separated from the solution as an amorphous dark solid, and this was used for the IR and EI-MS measurements. According to EPR spectra in toluene solution, compound **2** was the only paramagnetic product contained in the toluene extract; due to the difficulty with complete separation of MgCl$_2$ no attempt was made to isolate the solid product and to determine the yield.

Compound **2**. EPR (toluene, 23 °C): g = 1.989, ΔH = 16 G; (toluene, –140 °C): electronic triplet state of axial symmetry g = 1.989, D = 0.01230 cm^{-1}, E = 0. UV-VIS (hexane, 22 °C): 390 >> 590 (extending to 900 nm). EI-MS (250 °C, *m/z* (rel. abundance)): M$^{•+}$ not observed; 498 (6), 497 ([Cp″$_2$TiF]$^+$; 16), 495 (6), 479 (14), 478 (20), 477 ([Cp″$_2$Ti – H]$^+$; 41), 476 (38), 475 (15), 474 (7), 461 (8), 460 (13), 459 ([Cp″$_2$Ti – F]$^+$; 30), 458 ([Cp″$_2$Ti – HF]$^+$; 31), 457 (12), 441 ([Cp″$_2$Ti – H]$^+$; 11), 440 (10), 282 (19), 281 (17), 280 (11), 279 (15), 264 (9), 263 (10), 262 (8), 261 (10), 260 (13), 259 (12), 258 (8), 217 (23), 216 ([Cp″H]$^+$; 100), 215 (28), 214 (26), 213 (8), 202 (11), 201 ([Cp″H – Me]$^+$; 54), 200 (10), 199 (26), 198 ([Cp′H]$^+$; 41), 197 (14), 196 (13), 186 (14), 185 (17), 184 (20), 183 ([Cp′H – Me]$^+$; 41), 181 (11), 179 (11), 173 (10), 167 (10), 166 (18), 165 (26), 159 (13), 146 (10), 133 (12), 109 (21), 105 (16), 91 (18), 83 (10), 77 (14), 69 (11), 57 (18), 56 (10), 55 (30), 44 (19), 43 (25). IR (KBr, cm^{-1}): 3054 (w), 2960 (sh), 2906 (vs), 2854 (s), 1603 (m), 1591 (w), 1517 (vs), 1485 (s), 1442 (m), 1378 (m), 1275 (s, b), 1223 (vs), 1156 (s), 1094 (m), 1023 (m), 988 (w), 848 (s), 821 (s), 766 (w), 748 (w), 722 (vw), 587 (m), 563 (m), 513 (w), 461 (vw), 407 (m).

For comparison, IR spectrum of [TiCl$_2$(η^5-C$_5$Me$_4$FPh)$_2$] which was not published in ref.[10]: 3070 (w), 3055 (vw), 2958 (m), 2915 (vs), 2860 (s), 1603 (m), 1593 (sh), 1516 (vs), 1476 (s), 1452 (m), 1437 (m), 1376 (s), 1299 (w), 1227 (vs), 1160 (s), 1099 (m), 1015 (m), 990 (w), 853 (s), 835 (m), 820 (s), 769 (m), 752 (b), 725 (vw), 656 (w), 617 (w), 596 (m), 588 (m), 560 (m), 523 (m), 456 (w), 409 (m).

Preparation of [Ti(η^5-C$_5$Me$_4$Ph)$_2$(η^1-C≡CSiMe$_3$)$_2$]$^-$[MgCl(THF)]$^+$ (**5**)

A mixture of crystalline [TiCl$_2$(η^5-C$_5$Me$_4$Ph)$_2$] (0.512 g, 1.0 mmol), Mg turnings (0.12 g, 5.0 mmol) and 1,4-bis(trimethylsilyl)buta-1,3-diyne (0.20 g, 1.03 mmol) was evacuated on a vacuum line and THF (20 ml) was added by vacuum distillation. After stirring at 60 °C for 2 h, when the color of the solution turned to brown-orange, all volatiles were evaporated *in vacuo* and the residue was extracted with hexane. All the attempts to crystallize the product from hexane failed but additional MgCl$_2$ was separated during these attempts. Finally, a part of the solution was evaporated to dryness *in vacuo*, and samples for MS and IR spectra were prepared from the amorphous yellow solid. The ESR spectra of toluene solutions displayed only signals typical of Ti(III) tweezer complexes[17,18a] and a weak signal at g = 1.954 attributable to [TiCl(C$_5$Me$_4$Ph)$_2$] (ref.[9]). The powdery compound reluctant to crystallize was not suitable for elemental analysis, however, the EI-MS spectra showed the liberation of THF molecules at low temperature. At temperatures above 200 °C, the titanocene diacetylide fragment was ob-

served with very low abundance of 2.0%, the titanocene monoacetylide fragment with 4% abundance, the $[Cp'_2Ti - H]^+$ ion with 59% abundance, while the $[SiMe_3]^+$ ion was the base peak. The presence of m/z 477 (6%) indicated contamination of the sample by $[TiCl(C_5Me_4Ph)_2]$ observed also in ESR spectra. Since it is a base peak in the spectrum of the pure compound[9] its content should be in the range of few per cents. The IR spectrum gives evidence for the presence of coordinated THF and (trimethylsilyl)acetylide arms.

Compound **5**. EPR (toluene, 23 °C): $g = 1.9926$, $\Delta H = 0.30$ mT, $a_{Ti} = 0.76$ mT; (toluene, –140 °C): $g_1 = 2.0014$, $g_2 = 1.9925$, $g_3 = 1.9860$, $g_{av} = 1.993$; $A_2(Ti) = 10.9$ G. UV-VIS (toluene, 23 °C): 386–400 >> 470 (sh) > 600 (sh) nm. IR (KBr, cm^{-1}): 3085 (vw), 3056 (w), 2954 (s), 2899 (s), 2859 (sh), 2013 (vw), 1937 (s; ν(C≡C)), 1601 (m), 1574 (w), 1506 (m), 1481 (m), 1446 (m, b), 1377 (m), 1246 (s; SiMe$_3$), 1180 (vw), 1155 (vw), 1076 (w), 1024 (m; THF), 984 (w), 917 (vw), 850 (vs, b; SiMe$_3$), 759 (s), 704 (s), 644 (vw), 589 (w), 502 (vw). EI-MS (210 °C, m/z (rel. abundance)): elimination of THF (m/z 72) at 50 °C; 636 ($[Cp'_2Ti(C≡CSiMe_3)_2]^+$; 2), 539 ($[Cp'_2Ti(C≡CSiMe_3)]^+$; 4), 477 ($[Cp'_2TiCl]^+$; 6), 443 (10), 442 (28), 441 ($[Cp'_2Ti - H]^+$; 59), 440 (12), 439 (10), 280 (10), 279 (8), 242 (13), 240 (9), 198 ($[Cp'H]^+$; 31), 197 (14), 196 (23), 183 (15), 181 (24), 179 (10), 167 (7), 166 (10), 165 (14), 155 (8), 115 (7), 91 (8), 83 (22), 75 (9), 74 (8), 73 ($[SiMe_3]^+$; 100), 41 (11).

Preparation of Bis(tetramethylphenyl-η⁵-cyclopentadienyl)(η¹-*t*-butylethynyl)titanium(III) (**6**)

Compound **3** (0.47 g, 0.66 mmol) was dissolved in 5 ml of toluene and TBUE (1.0 ml, 8 mmol) was added by vacuum distillation under cooling with liquid nitrogen. The reaction mixture (sealed in an ampule equipped with an EPR sample tube and a quartz cuvette ($d = 2.0$ mm) was heated to 60 °C and the conversion of **3** into **6** was followed by the measurement of ESR spectra and the consumption of TBUE by the decrease of the absorption band at 1534 nm. After 5 h of heating the ESR spectrum of **3** disappeared ($g = 1.9876$, $a_H = 0.80$ mT, 1:2:1 triplet, $a_{Ti} = 0.70$ mT), whereas a new, broad signal of **6** arose at $g = 1.938$ and TBUE was only marginally consumed. The solution was evaporated *in vacuo*, a brown residue was extracted with 10 ml of hexane, the solution was concentrated and cooled with dry ice overnight. A crop of brown crystals were separated, and used for characterization by X-ray diffraction analysis, ESR, IR and EI-MS spectra. Yield 0.22 g (64%).

Compound **6**. M.p. 110 °C. ESR (hexane, 23 °C): $g = 1.938$, $\Delta H = 3.8$ mT; (toluene, –140 °C): $g_1 = 1.998$, $g_2 = 1.978$, $g_3 = 1.837$, $g_{av} = 1.938$. UV-VIS (toluene, 22 °C): 490 (sh) > 620 nm. EI-MS (130 °C, m/z (rel. abundance)): 525 (9), 524 (25), 523 (M$^{•+}$; 53), 522 (11), 521 (6), 444 (7), 443 (32), 442 (81), 441 ($[M - HC≡CCMe_3]^+$; 100), 440 (39), 439 (42), 438 (9), 437 (13), 435 (6), 262 (6), 254 (6), 244 (7), 243 (11), 242 ($[Cp'Ti - 3 H]^+$; 30), 241 (20), 239 (8), 238 (7), 237 (6), 67 (14), 57 (8), 41 (12). IR (KBr; cm^{-1}): 3053 (w), 2966 (vs), 2910 (s, b), 2863 (s), 2068 (m), 1600 (s), 1574 (w), 1504 (m), 1479 (m), 1450 (s), 1376 (m), 1357 (m), 1243 (s), 1201 (w), 1180 (w), 1076 (w), 1028 (w), 984 (w), 919 (w), 852 (vw), 760 (vs), 727 (m), 705 (vs), 660 (vw), 645 (w), 588 (w), 445 (s), 433 (m), 401 (m).

Dimerization of Alk-1-ynes

Solutions of complexes **1**, **3–6** in hexane and **2** in toluene (5×10^{-3} to 1×10^{-2} M concentration, 2–5 ml) were dosed into an ampoule equipped with a quartz cuvette ($d = 2.0$ mm) and a quartz EPR sample tube, so that the total amounts of the compounds were 0.02–0.05 mmol and TMSE, HXYN or TBUE (0.5–3.0 ml) was added by distillation through a vacuum line. The presence of free alk-1-yne was indicated by an absorption band in near IR region: TBUE

and HXYN at 1534 nm, TMSE at 1545 nm. The conversions of the complexes were followed by EPR spectroscopy at room temperature. When all alk-1-yne was consumed while the active catalyst was still present, another portion of the alkyne was added using breakable seals attached to the vacuum line. The dimers were not collected quantitatively. All volatiles including the dimers were distilled off from the catalyst residue under vacuum, and then subjected to GC-MS and GC analysis[3]. The solvent was distilled off from the less volatile dimer at room temperature and the identity of HTT dimers was controlled by IR spectra of neat samples.

TABLE III
Crystal and structure refinement data for 4 and **6**

Parameter	4	6
Empirical formula	$C_{34}H_{43}MgTi$	$C_{36}H_{43}Ti$
Formula weight	523.89	523.60
Crystal system	orthorhombic	monoclinic
Space group	*Pbca*	*P*2$_1$/*n*
a, Å	19.8380(4)	12.4450(6)
b, Å	14.3330(8)	15.1370(5)
c, Å	20.5710(8)	18.3790(8)
β, °	–	121.453(2)
V, Å^3	5849.1(4)	2636.0(5)
Z	8	4
Calculated density, g cm^{-3}	1.190	1.178
μ(MoKα), mm^{-1}	0.334	0.312
F(000), e	2248	1124
Crystal size, mm^3	$0.53 \times 0.30 \times 0.08$	$0.25 \times 0.23 \times 0.23$
θ_{min}, θ_{max}, °	3.18, 25.05	2.99, 25.03
Range of *hkl*	−23→23, −17→17, −24→24	−14→14, −18→16, −21→21
Reflections collected	37 723	23 754
Independent reflections	5151	5190
Data/restraints/parameters	5151/0/347	5190/0/345
Goodness-of-fit on F^2	1.040	1.038
*R*1, *wR*2 (all data)	0.1191, 0.1302	0.0848, 0.1191
*R*1, *wR*2 [$I > 2\sigma(I)$]	0.0577, 0.1092	0.0494, 0.1044
Maximal and minimal residual density e Å^{-3}	0.414, −0.322	0.466, −0.276

X-Ray Crystal Structure Determination

A khaki colored rhombic plate of **4** and a brown fragment of **6** were inserted into a Lindenmann glass capillaries under purified nitrogen in a glovebox (mBraun) and the capillaries were sealed with flame. Diffraction data were collected on a Nonius KappaCCD diffractometer and analyzed using the HKL program package[27]. The structures were solved by direct methods (SIR97)[28], followed by consecutive Fourier syntheses and refined by full-matrix least-squares on F^2 (SHELX97)[29]. Crystal and structure refinement data are given in Table III. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in ideal positions and refined as riding atoms except H1, H2 and H100 of **4** which were located on the difference Fourier map and refined isotropically.

CCDC-213963 and -213964 contain the supplementary crystallographic data for this paper (compounds **4** and **6**, respectively). These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

REFERENCES

1. a) For Ti: Akita H., Yasuda H., Nakamura A.: *Bull. Chem. Soc. Jpn.* **1984**, *57*, 480; b) for Zr: Horton A. D.: *J. Chem. Soc., Chem. Commun.* **1992**, 185; c) for Hf: Yoshida M., Jordan R. F.: *Organometallics* **1997**, *16*, 4508.
2. a) For Sc: Thompson M. E., Baxter S. M., Bulls A. R., Burger B. J., Nolan M. C., Santarsiero B. D., Schaefer W. P., Bercaw J. E.: *J. Am. Chem. Soc.* **1987**, *109*, 203; b) for Y: den Haan K. H., Wielstra Y., Teuben J. H.: *Organometallics* **1987**, *6*, 2053; c) for Y, La, Ce: Heeres H. J., Teuben J. H.: *Organometallics* **1991**, *10*, 1980.
3. Varga V., Petrusová L., Čejka J., Mach K.: *J. Organomet. Chem.* **1997**, *532*, 251.
4. Horáček M., Císařová I., Karban J., Petrusová L., Mach K.: *J. Organomet. Chem.* **1999**, *577*, 103.
5. a) Troyanov S. I., Varga V., Mach K.: *J. Chem. Soc., Chem. Commun.* **1993**, 1174; b) Gyepes R., Mach K., Císařová I., Loub J., Hiller J., Šindelář P.: *J. Organomet. Chem.* **1995**, *497*, 33.
6. Troyanov S. I., Varga V., Mach K.: *J. Organomet. Chem.* **1993**, *461*, 85.
7. Luinstra G. A., ten Cate L. C., Heeres H. J., Pattiasina J. W., Meetsma A., Teuben J. H.: *Organometallics* **1991**, *10*, 3227.
8. a) Varga V., Petrusová L., Čejka J., Hanuš V., Mach K.: *J. Organomet. Chem.* **1996**, *509*, 235; b) Štěpnička P., Gyepes R., Císařová I., Horáček M., Kubišta J., Mach K.: *Organometallics* **1999**, *18*, 4869; c) Gyepes R., Císařová I., Horáček M., Čejka J., Petrusová L., Mach K.: *Collect. Czech. Chem. Commun.* **2000**, *65*, 1248.
9. Horáček M., Polášek M., Kupfer V., Thewalt U., Mach K.: *Collect. Czech. Chem. Commun.* **1999**, *64*, 61.

10. Langmaier J., Samec Z., Varga V., Horáček M., Mach K.: *J. Organomet. Chem.* **1999**, *579*, 348.

11. a) Samuel E., Harrod J. F., Gourier D., Dromzee Y., Robert F., Jeannin Y.: *Inorg. Chem.* **1992**, *31*, 3252; b) Mach K., Varga V., Schmid G., Hiller J., Thewalt U.: *Collect. Czech. Chem. Commun.* **1996**, *61*, 1285.

12. de Wolf J. M., Meetsma A., Teuben J. H.: *Organometallics* **1995**, *14*, 5466.

13. Lukens W. W., Matsunaga P. T., Andersen R. A.: *Organometallics* **1998**, *17*, 5240.

14. a) Pattiasina J. W., Heeres H. J., van Bolhuis F., Meetsma A., Teuben J. H., Spek A. L.: *Organometallics* **1987**, *6*, 1004; b) Lukens W. W., Smith III, M. R., Andersen R. A.: *J. Am. Chem. Soc.* **1996**, *118*, 1719.

15. Kupfer V., Thewalt U., Horáček M., Petrusová L., Mach K.: *Inorg. Chem. Commun.* **1999**, *2*, 540.

16. a) Brintzinger H. H.: *J. Am. Chem. Soc.* **1967**, *89*, 6871; b) Kenworthy J. G., Myatt J., Symons M. C. R.: *J. Chem. Soc. A* **1971**, 1020; c) Horáček M., Hiller J., Thewalt U., Polášek M., Mach K.: *Organometallics* **1997**, *16*, 4185.

17. Troyanov S. I., Varga V., Mach K.: *Organometallics* **1993**, *12*, 2820.

18. a) Varga V., Hiller J., Polášek M., Thewalt U., Mach K.: *J. Organomet. Chem.* **1996**, *515*, 57; b) Hiller J., Varga V., Thewalt U., Mach K.: *Collect. Czech. Chem. Commun.* **1997**, *62*, 1446.

19. Mach K., Raynor J. B.: *J. Chem. Soc., Dalton Trans.* **1992**, 683.

20. Kirchbauer F. G., Pellny P.-M., Sun H., Burlakov V. V., Arndt P., Baumann W., Spannenberg A., Rosenthal U.: *Organometallics* **2001**, *20*, 5289.

21. Allen F. H., Kennard O., Watson D. G., Brammer L., Orpen A. G., Taylor R.: *J. Chem. Soc., Perkin Trans. 2* **1987**, S1.

22. Markies P. R., Akkerman O. S., Bickelhaupt F., Smeets W. J. J., Spek A. L.: *Adv. Organomet. Chem.* **1991**, *32*, 147; and references therein.

23. Varga V., Mach K., Schmid G., Thewalt U.: *J. Organomet. Chem.* **1994**, *475*, 127.

24. Mach K., Antropiusová H., Polášek J.: *J. Organomet. Chem.* **1990**, *385*, 335.

25. Antropiusová H., Dosedlová A., Hanuš V., Mach K.: *Transition Met. Chem. (London)* **1981**, *6*, 90.

26. Varga V., Mach K., Polášek M., Sedmera P., Hiller J., Thewalt U., Troyanov S. I.: *J. Organomet. Chem.* **1996**, *506*, 241.

27. Otwinowski Z., Minor W.: *HKL Denzo and Scalepack Program Package*. Nonius BV, Delft 1997. For a reference, see: Otwinowski Z., Minor W.: *Methods Enzymol.* **1997**, *276*, 307.

28. Altomare A., Burla M. C., Camalli M., Cascarano G., Giacovazzo C., Guagliardi A., Polidori G.: *J. Appl. Crystallogr.* **1994**, *27*, 435.

29. Sheldrick G. M.: *SHELXL97. Program for Crystal Structure Refinement from Diffraction Data*. University of Göttingen, Göttingen 1997.