

Fermethyltitanocene(III) diacetylides – magnesium tweezer complexes, intermediates in the catalysis of linear head-to-tail dimerization of terminal acetylenes

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Abstract

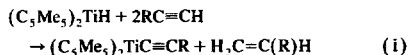
The $(C_5Me_5)_2TiCl_2/i-PrMgCl/Et_2O$ (Mg:Ti = 4–10) catalytic systems selectively catalyze the dimerization of terminal acetylenes $RC\equiv CH$ to 2,4-disubstituted 1-buten-3-yne for R = Me, Et, n-Pr, n-Bu, cyclohexyl, Ph, and $SiMe_3$ with a turnover number 500–700 after 5 days. The ESR investigation of these systems has revealed that permethyltitanocene tweezer complexes with embedded Mg ion between the acetylides arms $[(C_5Me_5)_2Ti(\eta^1-C\equiv CR)_2][Mg(OEt_2)_X]^+$ (X = Cl or C≡CR) (1A–1G for R = Me, Et, n-Pr, n-Bu, cyclohexyl, Ph, and $SiMe_3$) are intermediates in the formation of a dimerization catalytic center. Their ESR spectra are characterized by *g*-values in the range 1.990–1.993, coupling constant to the proton at α -carbon atom of the acetylene substituent 2.0–2.5 G and by coupling constants to ^{47}Ti and ^{49}Ti isotopes in the range 7.6–8.7 G. The tweezer complex $[(C_5Me_5)_2Ti(\eta^1-C\equiv CSiMe_3)_2][Mg(THF)Cl]^+$ (2G) has been synthesized. It catalyzes the head-to-tail dimerizations with the same selectivity and similar turnover numbers as the above systems.

Keywords: Permethyltitanocene; Tweezer complex; 1-alkynes; Titanium(III); ESR; Dimerization

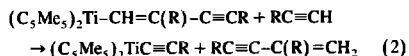
1. Introduction

The linear head-to-tail dimerization of terminal acetylenes induced by the $(C_5Me_5)_2TiCl_2/i-PrMgBr/Et_2O$ system [1] has been an outstanding example of a transition metal catalyzed highly selective reaction. The selectivity close to 99% was believed to be controlled by the restriction of coordination space around the titanium atom due to the Me substituents at the cyclopentadienyl ligands. A low activity of the $(C_5H_5)_2TiCl_2/i-PrMgBr$ system yielding a mixture of products with prevailing cyclotrimers supported this view. All other titanium-based Ziegler–Natta systems also afforded mostly cyclotrimers, with 1,2,4-trisubstituted benzene derivatives being more abundant than 1,3,5-isomers [2]. The catalytic complex for the head-to-tail dimerization was assumed to be permethyltitanocene acetylides formed from a hypothetical $(C_5Me_5)_2TiH$ by

reactions with two molecules of the acetylenes according to Eq. (1).



The catalytic cycle was proposed to consist of the regioselective insertion of the acetylene into the Ti–C_{ac} bond followed by the replacement of the formed enyne by another acetylene molecule with a hydrogen transfer (Eq. (2)).



The catalytic activity has been thus attributed to a Ti(III) center [1]. Guided by the above conclusions, permethylmetallocene carbyls of several trivalent lanthanide elements (Sc [3], Y [4], and Y, La, and Ce [5]) were used as catalysts for the dimerization of terminal acetylenes. The observation that the selectivity of the formation of head-to-tail dimers decreased with the metal atom size supported the opinion that the dimerization is sterically controlled. The participation of elec-

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tronic factors has been, however, inferred from an unexpected formation of the head-to-tail dimers of $\text{HC}\equiv\text{CPh}$ and $\text{HC}\equiv\text{CSiMe}_3$ on the La and Ce compounds [5].

We have recently studied the $(\text{C}_5\text{H}_{5-n}\text{Me}_n)_2\text{TiX}_2/i\text{-PrMgX}/\text{Et}_2\text{O}$ ($n = 0-4$; X = Cl, Br; Mg/Ti ≥ 4) systems in the absence of terminal acetylenes and have found that dimeric binuclear hydride complexes $[(\text{C}_5\text{H}_{5-n}\text{Me}_n)_2\text{Ti}(\mu\text{-H})_2\text{Mg}(\text{Et}_2\text{O})(\mu\text{-X})_2]$ (X = Cl or Br) were nearly quantitatively formed [6]. The structure evidence was obtained from the X-ray crystal analysis of the complexes for $n = 4$ and from ESR spectra of the whole series of the complexes showing a triplet splitting $a_H \sim 6.6-7.5$ G at $g = 1.991-1.993$ due to two equivalent bridging hydrogen atoms. The C_5Me_5 -containing systems ($n = 5$; X = Cl and Br) yielded mainly the trinuclear complex $[(\text{C}_5\text{Me}_5)_2\text{Ti}(\mu\text{-H})_2]_2\text{Mg}$ which was characterized by the X-ray crystal structure and by the electronic triplet state ESR spectrum [7].

Here we report the results of investigation of the catalytic activity and selectivity of the whole series of the $(\text{C}_5\text{H}_{5-n}\text{Me}_n)_2\text{TiCl}_2/i\text{-PrMgCl}/\text{Et}_2\text{O}/\text{RC}\equiv\text{CH}$ ($n = 0-5$) systems as depending on the number of Me substituents at the cyclopentadienyl rings and on the Mg:Ti ratio for the acetylenes containing Me, Et, *n*-Pr, *n*-Bu, *t*-Bu, cyclohexyl, Ph and SiMe_3 substituent. The ESR investigation of the catalytic systems as well as the catalytic and ESR investigations of the tweezer complex $[(\text{C}_5\text{Me}_5)_2\text{Ti}(\eta^1\text{-C}\equiv\text{CSiMe}_3)_2]^- [\text{Mg}(\text{THF})\text{Cl}]^+$ (**2G**) allowed us to draw conclusions about the structure of the catalytic intermediates.

2. Experimental

2.1. General data and methods

A vacuum technique using all sealed glass devices equipped with breakable seals, sealed quartz cuvettes and ESR tubes was used throughout the dimerization experiments and the synthesis of **2G**. A high vacuum/argon line without greased stopcocks was operated by means of glass-to-metal sealed valves (Hoke). ESR spectra were measured on an ERS-220 spectrometer (Centre for Production of Scientific Instruments, Academy of Sciences, Berlin, Germany) in the X-band. g -Values were determined using an Mn^{2+} standard ($M_I = -1/2$ line) at $g = 1.9860$ and a proton magnetometer MJ-110 R (Radiopan, Poznan, Poland). Concentrations of paramagnetic compounds were estimated from integrated first derivation spectra. A variable temperature unit STT-3 was used for the measurement in the range -140 to $+23^\circ\text{C}$. ^1H and ^{13}C NMR spectra of the dimers were measured on a Varian VXR-400 spectrometer (400 and 100 MHz respectively) in CDCl_3 at 25°C . Infrared spectra of the dimers (neat) were recorded

on a UR-75 (Ziess, Jena, Germany) spectrometer. GC analysis of terminal acetylenes and products of their catalytic oligomerization were performed on a CHROM 5 gas chromatograph (Laboratory Instruments, Prague, Czech Republic) using 10% SE-30 on a Chromatom N-AW-DMCS column. GC-MS analyses were carried out on a Hewlett Packard gas chromatograph (5890 series II) equipped with a mass spectrometric detector (5791 A) and a capillary column SPB-1 (Supelco). UV-vis, IR and MS spectra of **2G** were measured as described elsewhere [8].

2.2. Chemicals

Solvents hexane, toluene, diethyl ether, tetrahydrofuran (THF), 2-methyltetrahydrofuran (MTHF) were dried by refluxing over LiAlH_4 under argon, degassed and stored as solutions of green dimeric titanocene $(\mu\text{-C}_{10}\text{H}_8)(\text{C}_5\text{H}_5)_2\text{Ti}(\mu\text{-H})_2$ on a vacuum line. 1-Butyne, 1-pentyne, 1-hexyne, cyclohexylethyne, phenylethyne, trimethylsilylethyne and tert-butylethyne (all Aldrich) were degassed and distilled under vacuum on a small amount of solid dimeric titanocene. Impurities containing reactive hydrogen or oxygen were removed by the reaction with the hydride function of dimeric titanocene. A portion of the acetylene was also consumed by an induced polymerization. Then the acetylene was degassed, required volumes were distilled into ampoules and sealed off when cooled by liquid nitrogen. Propyne (Merck-Schuchardt, lecture bottle) was condensed under vacuum to give an approximate volume and then distilled to the catalyst without further purification. Titanocene dichlorides $(\text{C}_5\text{H}_{5-n}\text{Me}_n)_2\text{TiCl}_2$ ($n = 0-5$) were prepared as described earlier [9]. Isopropylmagnesium chloride and bromide were obtained from magnesium turnings (Fluka, for Grignard reactions) and isopropyl halides in diethyl ether either under argon or in a degassed sealed system. The concentration of the Grignard reagents was determined by the titration with 0.1 N HCl. The tweezer complex $[(\text{C}_5\text{HMe}_4)_2\text{Ti}(\eta^1\text{-C}\equiv\text{SiMe}_3)_2]^- [\text{Mg}(\text{THF})\text{Cl}]^+$ (**2**) was obtained as described elsewhere [10].

2.3. Preparation of $[(\text{C}_5\text{Me}_5)_2\text{Ti}(\eta^1\text{-C}\equiv\text{C-SiMe}_3)_2]^- [\text{Mg}(\text{THF})\text{Cl}]^+$ (**2G**)

In the procedure following the synthesis of **2**, an ampoule containing $(\text{C}_5\text{Me}_5)_2\text{TiCl}_2$ (3 mmol, 1.167 g) and magnesium turnings (50 mmol, 1.2 g) was evacuated and THF (30 ml) was distilled on a vacuum line. The ampoule was sealed off when cooled by liquid nitrogen and $\text{Me}_3\text{SiC}\equiv\text{CC}\equiv\text{CSiMe}_3$ (3 mmol, 0.582 g) was added from an attached ampoule. The mixture was then stirred at 60°C . After 30 min the solution turned blue and after 1 h orange-red. Further warming for 5 h did not lead to another color change. The orange solu-

tion was separated from unreacted magnesium and THF was evaporated in vacuum. The residue was washed with hexane and then dissolved in toluene to a dirty yellow–green solution. A brown–green crystalline material was obtained by cooling of the saturated toluene solution. The conversion to **2G** was apparently complete as no other paramagnetic product was revealed in the hexane washings and no product of different color was recognized during the isolation procedure. The yield of crystalline **2G** was 1.74 g (2.7 mmol, 81%). Anal. Found: C, 63.5; H, 8.8. $C_{31}H_{56}ClOSi_2MgTi$ Calc.: C, 63.39; H, 8.76%. IR (toluene) (cm^{-1}): 1930 (s), 1924 (s) (both $\nu(C\equiv C)$), 1245 (s), 1063 (w), 1020 (m) ($\nu(C-O)$ THF), 855 (vs), 842 (vs), 760 (m), 670 (m), 450 (w); (KBr) the same spectrum, positions of the bands within $\pm 5 cm^{-1}$. ESR (toluene, 20°C): $g = 1.9932$, $\Delta H = 1.5 G$, $a_{Ti} = 7.3 G$; (toluene, $-130^\circ C$): $g_1 = 2.0018$, $g_2 = 1.9937$, $g_3 = 1.9870$, $g_{av} = 1.9942$; (MTHF, 20°C): $g = 1.9933$, $\Delta H = 1.8 G$, $a_{Ti} = 7.3 G$; (MTHF, $-140^\circ C$): $g_1 = 1.9987$, $g_2 = 1.9933$, $g_3 = 1.9889$, $g_{av} = 1.9936$. UV–vis (toluene) (λ_{max} , nm): 365 (s), 405 (vs), 450 (w, sh), 540 (vw, sh, extending to 800nm). MS (direct inlet, 70eV): decomposition at 220°C. The spectroscopic data of **2G** closely resemble those of the tetramethylated analogue **2** which was obtained by the same procedure and whose X-ray crystal structure is known [10]. Attempted X-ray single crystal analysis of **2G** (Philips PW 1100 four circle diffractometer using graphite monochromated Mo K α radiation ($\lambda = 0.71069 \text{ \AA}$)) has failed since all 19 crystals examined gave reflections which could not be centered.

2.4. Dimerization of 1-alkynes by the $(C_5Me_5)_2TiCl_2/i-PrMgCl$ system at the Mg:Ti = 10 molar ratio

$(C_5Me_5)_2TiCl_2$ (0.0097 g, 0.025 mmol) was charged into an ampoule attached to a vacuum line and equipped with a magnetic stirrer. This was evacuated, diethyl ether (5 ml) was condensed in, and a solution of *i*-PrMgCl in diethyl ether (0.05 M, 5 ml) was added from an attached ampoule. After stirring for 15 min (blue solution) acetylenes propyne, 1-butyne, 1-pentyne, 1-hexyne, cyclohexylethyne, phenylethyne, trimethylsilylethyne or tert-butylethyne (25 mmol, acetylene:Ti = 1000) were added from another ampoule and the mixture was kept at 25°C for 5 days. After this reaction time the light green color of the catalytic solution turned to yellow. The reaction was terminated by opening the ampoule to air. The sample for GC analysis (1 ml) was syringed into a small rubber-capped probe and a standard hydrocarbon with a retention time close to that of the dimer was added. The amount of dimer was determined using a calibration plot drawn from the measurement of mixtures of the pure dimer and the standard (e.g. dodecane was used for the dimer of 1-hexyne,

n-octane for the dimer of trimethylsilylethyne, etc.). The GC yields corresponded to the turnover numbers [acetylene (mmol)/titanium (1 mmol)] (TN) in the range 500–700 for all the acetylenes except tert-butylethyne which was unreactive. The yields strongly depended on the purity of the acetylene. If TN lower than 500 was obtained the acetylene was once more purified by dimeric titanocene. The isolation of pure dimers for their identification by GC-MS, NMR and IR methods was carried out by washing of the reaction solution with water and by fractional distillation of the organic layer.

Analogous experiments were carried out at the molar ratio Mg:Ti = 4 (using *i*-PrMgCl in diethyl ether (0.05 M, 2 ml) and 8 ml of diethyl ether) with 1-hexyne, trimethylsilylethyne and cyclohexylethyne. The yields corresponded to TN of at least 500.

2.5. Dimerization of 1-alkynes by the $(C_5Me_5)_2TiCl_2/i-PrMgCl$ and $(C_5Me_5)_2TiCl_2/i-PrMgBr$ systems at the Mg:Ti = 2 molar ratio

$(C_5Me_5)_2TiCl_2$ (0.12 g, 0.3 mmol), solutions of *i*-PrMgCl or *i*-PrMgBr in diethyl ether (0.05 M, 12 ml) and 27 mmol of the acetylenes (acetylene:Ti = 90 molar ratio) were used in the experiments which were performed in the same manner as described above for the Mg:Ti = 10 molar ratio. These experiments were terminated after 5 h since the conversion did not increase at longer reaction time. The GC yields for all the acetylenes corresponded to TN equal to 50–60 except for tert-butylethyne which did not react.

2.6. Oligomerization of 1-hexyne by the $(C_5H_5-nMe_n)_2TiCl_2/i-PrMgCl/Et_2O$ ($n = 0, 3-5$) systems at the Mg/Ti = 10 ratio

Compounds $(C_5H_5-nMe_n)_2TiCl_2$ (0.025 mmol) were weighed into an ampoule, this was evacuated, diethyl ether (5 ml) was distilled in, and *i*-PrMgCl in diethyl ether (0.05 M, 5 ml) was added from an attached ampoule. After 15 min of stirring, 1-hexyne (2.9 ml, 25 mmol) was added from an attached ampoule. After 5 days at 25°C the reaction mixtures were opened to air and the yields of products were estimated by the GC analysis as described above. The tentative product composition was determined by GC-MS analysis. The results are given in Table 1.

2.7. Dimerization of 1-alkynes by **2G** and **2**

A solution of **2G** in toluene ($2 \times 10^{-3} M$, 5 ml) was mixed with 10 mmol of 1-alkyne in a sealed ampoule and this was kept at 25°C for 10 days. Then the ampoule was opened to air and the reaction mixture analyzed. The GC analysis revealed 50–70% conversions to the head-to-tail dimer which corresponded to

TN = 500–700. It has to be noticed that the results were much less reproducible than in the above experiments probably because the catalyst was irreversibly deactivated by impurities (see Section 2.8). Therefore, when TN lower than 500 was achieved the acetylenes were purified by partial dimerization induced by **2G** and then they were distilled off under vacuum. The highest conversions were obtained for 1-hexyne and trimethylsilylethyne, the lowest for propyne and phenylethyne. Tert-butylethyne remained unreacted. The trace amount of a mixed dimer of trimethylsilylethyne and 1-hexyne was detected by GC-MS analysis in the isolated dimer of 1-hexyne. Its MS spectrum [m/z (%): 180 (M^{+} , 12), 165 (70), 138 (44), 123 (100), 107 (14), 97 (15), 83 (18), 73 (41), 59 (45), 43 (27)] fits to 2-butyl-4-trimethylsilyl-1-buten-3-yne, the exclusive codimer of these acetylenes obtained with the $(C_3Me_5)_2TiCl_2$ -based catalyst [1].

Analogous experiments with trimethylsilylethyne and 1-hexyne using 10-times higher concentration of complex **2** did not show a remarkable conversion of the acetylenes.

2.8. ESR investigations

The catalytic experiments with the $(C_3Me_5)_2TiCl_2/i$ -PrMgCl systems as described above were carried out in an ampoule with an attached ESR tube in such a way that the solution in the ESR tube could be diluted by the distillation of the solvent from the ampoule. The systems were measured without addition of the acetylene, and then after its addition. Independently of the reaction time in the absence of acetylene, the ESR spectra listed in Table 2 were observed within 30 min after the acetylene was added. The maximum intensity of the ESR signal coincided with the light green coloration of the solution. Then, the ESR signal slowly decayed and the color was turning yellow. The $(C_3H_5-nMe_n)_2TiCl_2/i$ -

Table 1
Oligomerization of 1-hexyne by the $(C_3H_5-nMe_n)_2TiCl_2/i$ -PrMgCl/ Et_2O ($n = 0, 3-5$) systems^a

<i>n</i>	Con- version (%)	TN ^b	Composition of products (%) ^c		
			RC=C-CR=CH ₂	Other dimers	Cyclo- trimers
5	70	700	99.3	—	—
4	2	20	1.4	—	0.1
3	4	40	0.5	0.1	3.1
0	6	60	0.2	0.5	4.3

^a Conditions: $(C_3H_5-nMe_n)_2TiCl_2$ 0.025 mmol; *i*-PrMgCl 0.25 mmol; 1-hexyne 25 mmol; diethyl ether 10 ml; temperature 25 °C, 5 days.

^b Turnover number [1-hexyne (mmol)/Ti (1 mmol), 5 days].

^c The difference between the conversion and the contents of identified products is due to a number of unidentified very minor product components.

Table 2

EPR spectra of the $(C_3Me_5)_2TiCl_2/i$ -PrMgCl/RC=C/ Et_2O systems (**IA-IG**) and the tweezer complexes $[(C_3Me_5)_2Ti(\eta^1-C\equiv C-R)_2]^- [Mg(THFC)]^+$ (**2G**) and $[(C_3HMec)_2Ti(\eta^1-C\equiv CSiMe_3)]^- [Mg(THFC)]^+$ (**2**)

R	<i>g</i> ^a	multiplet	<i>a</i> _H (G)	<i>a</i> _{Ti} (G)	ΔH (G)
IA methyl	1.9905	7	2.5	8.6	1.5
IB ethyl	1.9904	5	2.3	8.7	1.5
IC propyl	1.9906	5	2.2	8.7	1.5
ID n-butyl	1.9904	5	2.2	8.7	1.5
IE cyclohexyl	1.9908	3	2.7	8.6	1.5
IF phenyl	1.9926	1	—	7.6	1.5
IG trimethylsilyl	1.9930	1	7.2	1.4	—
IH tert-butyl	1.9906	1	8.5	1.2	—
2G ^b	1.9933	1	7.3	1.8	—
2 ^c	1.9935	1	7.3	2.5	—

^a *g*-value determined with accuracy to 0.0003 using an Mn²⁺ standard ($M_s = -1/2$ line) at *g* = 1.9860.

^b In toluene solution.

^c In toluene solution, Ref. [10].

PrMgCl/ Et_2O /1-hexyne ($n = 3, 4$) systems at the Mg:Ti = 10 ratio were also investigated in the same manner. The ESR spectra were dominated by single lines at *g* = 1.96, $\Delta H = 7.0$ G, however, very weak quintuplets at *g* = 1.9913, *a* = 2.3 G were also observed in both cases.

The reactions of **2G** in toluene with 1-hexyne as described in Section 2.7 were also followed by ESR spectroscopy. A rapid decay of the ESR signal of **2G** (see Table 2) accompanied by the occurrence of new less intense single lines, e.g. for 1-hexyne $\Delta H = 1.6$ G at *g* = 1.9896 and 1.9881 and a broader line $\Delta H = 4.0$ G at *g* = 1.977 indicated the reaction of **2G** with impurities contained in the acetylenes. The remaining signal of **2G** was then decreasing very slowly on the time scale of days and this decrease can be related to the deactivation of **2G** in the catalytic reaction. In such an experiment TN close to 100 was obtained. The role of impurities was proved in experiments with 1-hexyne which was finally purified by solid **2G** and distilled away from the solution still containing 5–20% of undecomposed **2G**. Addition of this 1-hexyne to the catalytic amount of **2G** largely turned the ESR signal of **2G** into a broad signal $\Delta H = 20$ G at *g* = 1.947 within 10 days and the above signals of impurities were not observed at all. The conversion of 1-hexyne corresponded to TN ca. 600.

3. Results and discussion

3.1. The head-to-tail dimerization of 1-alkynes induced by the $(C_3H_5-nMe_n)_2TiCl_2/i$ -PrMgCl/ Et_2O systems

Reinvestigation of the oligomerization of propyne, 1-butyne, 1-pentyne, 1-hexyne, cyclohexylethyne,

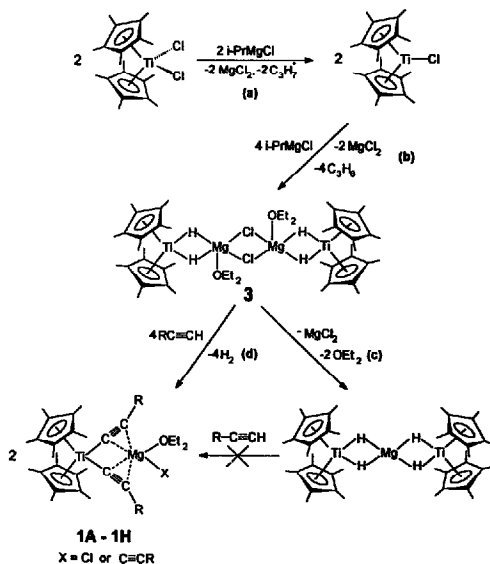
phenylethyne and trimethylsilylethyne catalyzed by the reported $(C_5Me_5)_2TiCl_2/i-PrMgBr/Et_2O$ system at the molar ratio $Mg:Ti = 2$ and at the molar ratio acetylene:Ti = 70 afforded 2,4-disubstituted 1-buten-3-yne with TN = 50–70 after 5 h at 25 °C. These results are comparable with those achieved by Nakamura and coworkers [1] who reported conversions 90–100% at the initial 1-alkyne:Ti molar ratio equal to 50 after 1–3 h at 30 °C. Practically the same results were also obtained for the $(C_5Me_5)_2TiCl_2/i-PrMgCl$ system and in both cases the systems appeared to be inactive after the reaction time of 5 h. Newly, we found that an increase in the Mg:Ti ratio to at least 4 led to a considerable increase in the catalytic activity of both systems at the retained nearly 100% selectivity. Using the initial molar ratio 1-alkyne:Ti = 1000 the $(C_5Me_5)_2TiCl_2/i-PrMgCl$ (Mg:Ti = 10) system reached TN in the range 500–700 after 5 days. Similar conversions were obtained also for 1-hexyne, trimethylsilylethyne and cyclohexylethyne at the Mg:Ti = 4 molar ratio. All of the catalytic systems were inactive towards tert-butylethyne in agreement with the previous report [1].

The influence of Me substituents at the cyclopentadienyl ligand on the activity and selectivity of the

$(C_5H_5-nMe_n)_2TiCl_2/i-PrMgCl/Et_2O/RC\equiv CH$ ($n = 0,3-5$; Mg:Ti = 10) systems was examined in detail for the oligomerization of 1-hexyne, and the representative results are listed in Table 1. They confirm that the C_5Me_5 -containing systems are unique in their high activity as well as high selectivity towards the formation of the head-to-tail linear dimers. Only the next less methylated system based on $(C_5HMe_4)_2TiCl_2$ produces the head-to-tail dimer, however, with a low selectivity, and the overall activity of the system is lower by nearly two orders. The systems containing less methylated cyclopentadienyl ligands exert only a low catalytic efficiency, producing mostly cyclotrimers (tributylbenzenes) and some dimers. Structures of these dimers are, according to GC-MS, different from the head-to-tail isomer, however, the dimers were not isolated and their structures remain unknown. All the other terminal acetylenes except unreactive tert-butylethyne gave very similar results.

3.2. The ESR investigation of the $(C_5Me_5)_2TiCl_2/i-PrMgCl/Et_2O/RC\equiv CH$ systems

The reacting $(C_5Me_5)_2TiCl_2/i-PrMgCl/Et_2O$ systems at the Mg:Ti = 10 molar ratio gave at first a broad



Scheme 1.

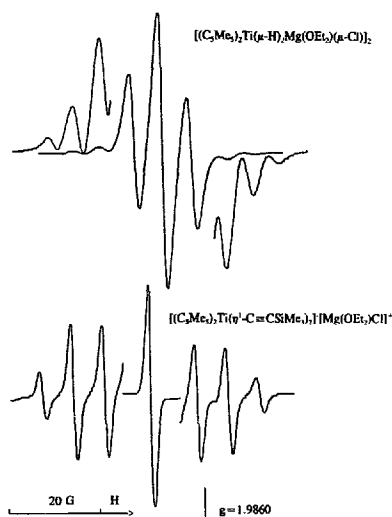


Fig. 1. The EPR spectra of the $(C_5Me_5)_2TiCl_2/i-PrMgCl/Et_2O$ ($Mg:Ti = 10$) system recorded 45 min after mixing the components (upper spectrum) and 30 min after subsequent addition of trimethylsilylthyne (1G) ($Me_3SiC\equiv CH:Ti = 1000$); wings of the spectra amplified by a factor of 24 (lower spectrum).

ESR signal at $g = 1.956$, $\Delta H = 38$ G and a blue color of the solution ($\lambda_{max} = 530$ and 640 (sh) nm) which are both indicative of the formation of $(C_5Me_5)_2TiCl_2$ [11,12] (Scheme 1, step (a)). Within the initial 15 min of the catalyst formation period in the absence of terminal acetylene, an additional ESR signal started to grow at $g = 1.9901$. This was characterized by the triplet splitting (1:2:1) $a_H = 6.7$ G and by coupling to the titanium isotopes $a_{Ti} = 5.4$ G which was observed in low intensity wings of the spectrum (Fig. 1, upper record). This spectrum can be assigned to the dimeric titanocene hydride magnesium(chloro)hydride complex $[(C_5Me_5)_2Ti(\mu-H)_2Mg(OEt_2)(\mu-Cl)]_2$ (3) (see Scheme 1, step (b)) on the basis of similar ESR parameters with $[(C_5HMe_4)_2Ti(\mu-H)_2Mg(OEt_2)(\mu-Cl)]_2$ [6]. The ESR spectrum of 3 differs from that of the latter mainly by the absence of the superhyperfine splitting due to the cyclopentadienyl ring hydrogen atoms. As judged from

¹ Isotopes ^{47}Ti ($I_N = 5/2$, natural abundance 7.75%, magnetic moment μ in multiples of nuclear magneton ($eh/4\pi Mc$) -0.7871), and ^{49}Ti ($I_N = 7/2$, 5.51%, $\mu = -1.102$), give practically the same coupling constant $a_{Ti} = \mu/I_N$.

the solution ESR spectra, the conversion of $(C_5Me_5)_2TiCl_2$ to 3 was accomplished within another 30 min reaction time, whereas the blue color of the solution persisted. Addition of terminal acetylene ($RC\equiv CH:Ti = 1000$) to this solution of 3 led to an immediate color change to light green and the ESR spectrum of 3 was replaced by narrow-line ($\Delta H \leq 1.5$ G) ESR spectra of odd multiplicity from singlet to septuplet at g -values in the range 1.9903–1.9930. The spectra were further characterized by well-discernible low-intensity wings where splittings due to titanium isotopes ($a_{Ti} = 7.2$ – 8.7 G) were overlaid by multiplets identical with those displayed in the central part of the spectra. The splitting between the outermost multiplets allowed us to determine a_{Ti} with an accuracy of ± 0.2 G. One of the simplest spectra, observed after adding $HC\equiv CSiMe_3$, is shown in Fig. 1, lower record. The spectra showing additional hyperfine multiplets are shown in Fig. 2. The parameters of ESR spectra result-

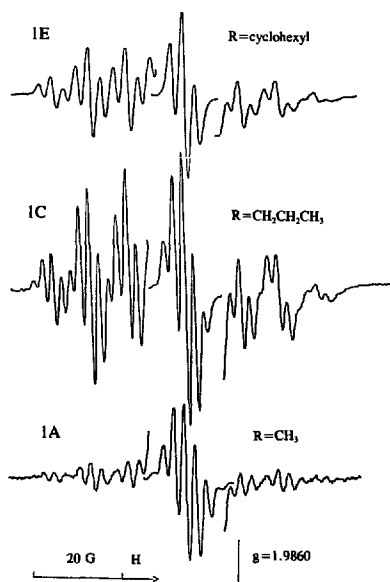


Fig. 2. EPR spectra of the $(C_5Me_5)_2TiCl_2/i-PrMgCl/Et_2O$ ($Mg:Ti = 10$) system reacting with $RC\equiv CH$ ($RC\equiv CH:Ti = 1000$) for 4 h (wings of the spectra amplified by a factor of 16 for 1A, 32 for 1C, and 24 for 1E).

ing from addition of all the studied terminal acetylenes are listed in Table 2. Addition of terminal acetylenes to the 15 min aged catalytic system speeded up the disappearance of $(C_5Me_5)_2TiCl$ and light green solutions exerting the above odd multiples spectra were obtained after about a 15 min period.

The comparative examination of the ESR spectra revealed that the multiplicity of the hyperfine splitting was related to the number of protons at the α -carbon atom of the acetylene substituent. The single line spectra occurred in the absence of such protons, i.e. for $HC\equiv CPh$, $HC\equiv CSiMe_3$, and $HC\equiv CMe_3$ (systems denoted 1F, 1G, and 1H). The triplet splitting was obtained for cyclohexylethyne (1E), the quintuplet splitting for 1-butyne (1B), 1-pentyne (1C), and 1-hexyne (1D), and the septuplet spectrum for propyne (1A). The occurrence of these multiplets on the transitions due to the coupling to titanium isotopes in spectral wings implies that the spectra arise from the interaction of the Ti(III) d^1 electron with the acetylenic protons. The approximate binomial intensities of the multiplets allow us to assume that the unpaired electron couples to the doubled number of protons at the α -carbon atom of the acetylene substituents which are magnetically equivalent. A similar appearance of the ESR spectrum of the first Ti(III) tweezer complex $[(C_5HMe_4)_2Ti(\eta^1-C\equiv CSiMe_3)_2]^- [Mg(THF)Cl]^+$ (**2**) (see Table 2), whose structure has been determined by the X-ray crystal diffraction analysis [10], and of the spectrum obtained from the $(C_5Me_5)_2TiCl_2/i-PrMgCl/Et_2O/HC\equiv CSiMe_3$ system (**1G**) brought us to suggest that the spectra observed in the 1A–1H systems are attributable to the same type of tweezer complexes. This assignment fully relates the observed multiplicities with the number of equivalent protons at the α -carbon atoms of substituents of the two acetylide arms. Some uncertainty remains about the nature of ligands bound to magnesium. In the diethyl ether solution, there is no doubt that the magnesium atom is coordinated by the ether solvent, like in **2** by one molecule of THF. The THF molecule is strongly coordinated in **2** as it is not released under high vacuum or by evaporation of toluene solutions under vacuum. The presence of the chloride ligand is, however, uncertain since the excessive isopropyl Grignard reagent has to be converted in the presence of terminal acetylenes into magnesium chloro-acetylides, and these can disproportionate with the tweezer complexes in the 1A–1H systems to give the magnesium acetylide cation. Hence, the ligand at the magnesium cation in tweezer complexes formed in step (d) of Scheme 1 is denoted X, where X is either Cl or $C\equiv CR$. Complex **3** has not been prepared in the solid state as it easily loses two molecules of ether and one molecule of $MgCl_2$ to give the trinuclear complex $[(C_5Me_5)_2Ti(\mu-H)_2Mg]_2$ [7] (Scheme 1, step (c)). It is of interest that this complex is unreactive towards termi-

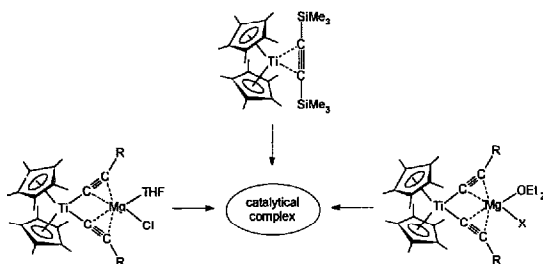
nal acetylenes on the time scale of days and crystallizes unchanged from the toluene/trimethylsilylethyne solution.

To confirm the suggested catalytic role of tweezer complexes in the dimerization of terminal acetylenes, the complex $[(C_5Me_5)_2Ti(\eta^1-C\equiv CSiMe_3)_2]^- [Mg(THF)Cl]^+$ (**2G**) was prepared by the scission of 1,4-bis(trimethylsilyl)buta-1,3-diyne (BSD) by a permethyltitanocene species in statu nascendi in the $(C_5Me_5)_2TiCl_2/Mg/THF/BSD$ system, the method previously used to obtain **2** [10], and its spectroscopic and catalytic properties have been investigated.

3.3. Spectroscopic and catalytic properties of $[(C_5Me_5)_2Ti(\eta^1-C\equiv CSiMe_3)_2]^- [Mg(THF)Cl]^+$ (**2G**)

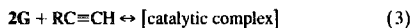
The identity of $[(C_5Me_5)_2Ti(\eta^1-C\equiv CSiMe_3)_2]^- [Mg(THF)Cl]^+$ (**2G**) stems from the EPR parameters (Table 2), the electronic absorption spectrum and infrared spectrum which all bear features common with the analogous spectra of **2**. The composition of **2G** is further corroborated by satisfactory elemental analysis data. The presence of two infrared absorption bands at 1930 and 1924 cm^{-1} belonging to $\nu(C\equiv C)$ valence vibration apparently arises from the coupling of acetylide arms via the embedded Mg atom. In the diacetylide $(C_5HMe_4)_2Ti(\eta^1-C\equiv CSiMe_3)_2$ such a splitting of the $\nu(C\equiv C)$ valence vibration (2017 cm^{-1}) was not observed while it was inherently present in tweezer complexes with embedded alkali metal cations $[(C_5HMe_4)_2Ti(\eta^1-C\equiv CSiMe_3)_2]^- [M]^+$ ($M = Li-Cs$) [13]. Compound **2** showed $\nu(C\equiv C)$ at 1930 cm^{-1} , however, a shoulder on the long wavelengths slope of the band was not reported [10]. The UV–vis spectra of both **2G** and **2** exhibit two intense bands near 400 and 370 nm which were tentatively ascribed to charge transfer transitions and a ca. 20-times weaker shoulder close to 600 nm apparently due to a d–d transition [10].

Complex **2G** in toluene solution behaved towards all the studied acetylenes like the $(C_5Me_5)_2TiCl_2/i-PrMgCl$ system, affording the head-to-tail dimers with close to 100% selectivity, except for the unreactive tert-butylethyne. The reactivity of **2G** was, however, lower, as $TN \sim 500$ was achieved after ca. 10 days reaction time, whereby the ESR spectra still indicated the presence of up to 20% of initial **2G**. In the systems with acetylenes bearing protons at α -carbon atoms of their substituents, no exchange of trimethylsilylethynyl groups in **2G** with the acetylide groups of the substrate was observed. Instead, the signal of **2G** was converted approximately quantitatively into the signals with low g -value, close to 1.947 and $\Delta H \sim 20G$. As no more data concerning this new species are available, its nature can only tentatively be suggested. Its ESR parameters do not differ much from those of $(C_5Me_5)_2Ti(C\equiv CMe)$ ($g = 1.941$, $\Delta H = 49G$) [14], and this al-



Scheme 2.

lows us to suggest that **2G** deactivates by forming $(C_5Me_5)_2Ti(C\equiv CR)$ complexes. This is at variance with the original proposal of the catalytic cycle where the $(C_5Me_5)_2Ti(C\equiv CR)$ complexes played a key role in the active species [1]. The direct ESR investigation into the **2G**-propyne system, whose ESR spectra should confirm the identity or diversity of the deactivation product with $(C_5Me_5)_2Ti(C\equiv CMe)$, was, however, precluded by the difficult purification of propyne in low-pressure glass devices. The low reactivity of **2G** towards terminal acetylenes, as indicated by the absence of acetylide group exchange, slow dimerization rate and slow conversion into another paramagnetic species, implies that the equilibrium (3) is strongly shifted to the side of the reagents and that the concentration of the catalytic complex is extremely low.



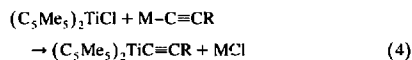
A somewhat slower reaction rate of **2G** compared to the **1A–1G** systems may be due to the stronger coordination of THF compared to diethyl ether and the different solvating power of toluene versus diethyl ether. The difference in reactivity can also arise from the presence of the Cl ligand at the Mg atom in **2G** and from the possible presence of the Mg-acetylide cations in **1A–1G** systems.

3.4. Implications for the structure of the catalytic complex

The present results bring evidence that the head-to-tail dimerization activity of titanocene-based systems is confined to permethyltitanocene derivatives and that the catalytic complex arises from the interaction of terminal acetylenes, except tert-butylethyne, with the permethyltitanocene(III) diacetylide tweezer complexes with embedded magnesium cation generated in **1A–1G** systems or synthesized by the titanocene-induced scission of BSD. Virtually the same catalytic properties as ex-

erted by the above systems have recently been reported for the permethyltitanocene(III)-bis(trimethylsilyl)acetylene complex $(C_5Me_5)_2Ti[\eta^2-C_2(SiMe_3)_2]$ [15]. Also in that case, the starting complex persisted in the presence of $RC\equiv CH$ for many days and the product of deactivation was not convincingly established. This common catalytic behaviour implies that a highly active particle is generated from these precursors (Scheme 2), very slowly and in a low concentration. The formation of the catalytic species from both Ti(II) and Ti(III) precursors shows that the valency of the Ti atom in the precursor is not a lead for the valency of the catalytic complex. It also allows us to presume that an access to the catalytic complex will have apparently more, so far unknown, entries.

In all the investigated systems, permethyltitanocene(III) acetylides presumably play an important role, either as the catalytic species or as products of deactivation, and the investigation of their properties would be mostly desirable. Unfortunately, the direct route to them according to reaction (4) is accompanied by the formation of Ti(III) tweezer complexes $[(C_5Me_5)_2Ti(C\equiv CR)_2]^-M^+$ [13] which may interfere with the acetylides in their action upon terminal acetylenes.



Methods avoiding the presence of Group I and II metal derivatives, for instance the reactions of various permethyltitanocene alkyl, allyl or hydride derivatives with terminal acetylenes, are therefore to be attempted.

Acknowledgements

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