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Permethyltitanocene–bis(trimethylsilyl) acetylene, an efficient catalyst for the head-to-tail dimerization of 1-alkynes

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Abstract

In the series of the $(C_5H_{5-n}Me_n)_2Ti[\eta^2\text{-}C_2(SiMe_3)_2]$ ($n = 0-5$) (1A–1F) complexes only $(C_5Me_5)_2Ti[\eta^2\text{-}C_2(SiMe_3)_2]$ (1F) catalyzed the linear head-to-tail dimerization of 1-alkynes. A selectivity of better than 98% and a turnover number (TN) in the range 1200–1500 mmol of 1-alkyne per mmol of Ti was obtained after 14 d at 30°C for 1-pentyne, 1-hexyne, cyclohexylethyne, phenylethyne and trimethylsilylethyne. Among other complexes in the series, 1A–1D attained $TN \leqslant 25$ after 5 d at 30°C and produced mainly a mixture of 1,3,5- and 1,2,4-trisubstituted benzene derivatives. The complex $(C_5HMe_4)_2Ti[\eta^2\text{-}C_2(SiMe_3)_2]$ (1E) afforded ca. 20% of the head-to-tail dimers in addition to cyclotrimers but its activity was extremely low, corresponding to $TN \sim 7$. The rate of dimerization by 1F is controlled by the slow exchange rate of 1-alkynes with bis(trimethylsilyl)acetylene.

Keywords: Permethyltitanocene; Catalysis; Linear dimerization; 1-Alkynes; Bis(trimethylsilyl)acetylene complex

1. Introduction

The regioselective dimerization of 1-alkynes to head-to-tail dimers (2,4-disubstituted 1-buten-3-ynes) is known to be catalyzed by the $(C_5Me_5)_2TiCl_2/^iPrMgBr$ (Mg/Ti = 2) system in diethyl ether or in THF [1]. Conversions higher than 90% at an initial molar ratio of 1-alkyne/Ti = 50 after 30 min reaction time were obtained for 1-butyne, 1-pentyne, 1-hexyne, cyclohexylethyne, phenylethyne and trimethylsilylethyne. The mechanism of the dimerization has been proposed to involve a permethyltitanocene (Ti^{III}) acetylide as a catalytically active species. The catalytic cycle consisted of acetylene coordination followed by its insertion into the Ti–C σ-bond of the acetylide and replacement of the 2,4-disubstituted 1-buten-3-yne-1-yl thus formed by acetylide via a hydrogen transfer from a coordinating 1-alkyne molecule. The virtually absolute selectivity of the dimerization was attributed to steric congestion of the coordination space at the $(C_5Me_5)_2Ti(\eta^1\text{-}C\equiv CR)$ centre allowing only one mode of coordination of the 1-alkyne.

Subsequently, carbyls of permethylscandocene [2] and ytterbocene [3] have been found to act as catalysts in the head-to-tail dimerization of propyne. More recently, Heeres and Teuben studied the catalytic activity of bent permethylmetallocene carbyls $(C_5Me_5)_2MCH(SiMe_3)_2$ (M = Y, La, Ce) towards 1-alkynes in order to correlate the structure of the products with a change in the steric congestion due to the different ionic radii of the metals (Ti^{3+}, 0.67 Å; Sc^{3+}, 0.75 Å; Y^{3+}, 0.90 Å; Ce^{3+}, 1.01 Å; and La^{3+}, 1.03 Å) [4]. They found that the formation of the head-to-tail dimers was less selective as the ionic radius of the metal increased, and that the structure of the products depended on the bulkiness and electron donating/withdrawing effect of the acetylene substituent. Surprisingly, t-butylethyne always gave 2,4-t-butyl-1-buten-3-yne although it was unreactive in the presence of a permethyltitanocene catalyst [1]. NMR investigation of the homogeneous reaction mixtures at a molar ratio of 1-alkyne/M > 45 and a reaction time of 2–2.5 h allowed the conversion of the carbyls to acetylides to be monitored, leading to the formation of dimers or larger clusters, and the oligomerization of 1-alkynes. The results were discussed in terms of the above-mentioned catalytic cycle adapted for the permethylmetallocene (M^{III}) acetylide catalytic complex.

Here we report on the catalytic activity of a series of

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$(C_5H_{5-n}Me_n)_2Ti[\eta^2-C_2(SiMe_3)_2]$ $(n = 0-5)$ complexes (1A–1F) towards 1-alkynes and in particular an efficient head-to-tail dimerization induced by the $(C_5Me_5)_2Ti[\eta^2-C_2(SiMe_3)_2]$ complex 1F.

2. Experimental details

Handling of the titanium complexes, the purification of acetylenes and solvents, preparation of the catalytic reaction mixtures, and EPR and UV–vis measurements were carried out under vacuum using a vacuum line provided with metal valves and all-sealed glass devices equipped with breakable seals.

2.1. Chemicals

The $(C_5H_{5-n}Me_n)_2Ti[\eta^2-C_2(SiMe_3)_2]$ $(n = 0-5)$ complexes (1A–1F) were the same as those whose characterization was discussed in a preceding paper [5]. Hexane was dried by refluxing over $LiAlH_4$ and stored as solutions of dimeric titanocene $(C_{10}H_8)$ $[(C_5H_5)-Ti(\mu-H)]_2$ [6]. Compounds 1A–1F were used as 0.1 M solutions in hexane and 1F was also used as a 0.005 M solution in the same solvent. Terminal acetylenes, 1-pentyne, 1-hexyne, trimethylsilylethyne, t-butylethyne, phenylethyne and cyclohexylethyne (Aldrich) were purified by vacuum distillation and by storage for several hours as a solution of dimeric titanocene. They were then distilled on a vacuum line into a storage ampule. Portions (1–3 ml) were distilled into the reaction ampules with an attached ampule containing the catalytic complex. The reaction ampules were sealed off after their contents had been cooled to liquid nitrogen temperature. $(C_5HMe_4)_2Ti(\eta^1-C\equiv CSiMe_3)_2$ was obtained by the reaction of $(C_5HMe_4)_2TiCl_2$ with 2 mol equiv. of $LiC\equiv CSiMe_3$ in toluene. MS [direct inlet, 80°C, 70 eV, m/z (%)]: 484 (0.6, M$^{+\cdot}$); 386 (19.1); 290 (100); 179 (6.6); 166 (11.9); 83 (6.3); 73 (14.7). ^{1}H NMR (C_6D_6) δ: 0.198 (18H, s, 2 × SiMe₃); 1.761 (12H, s, 4 × Me); 2.269 (12H, s, 4 × Me); 4.991 [2H, s, H(Cp)] ppm. ^{13}C NMR (C_6D_6) δ: 0.78 (q, 6C); 14.51 (q, 4C); 15.16 (q, 4C); 109.90 (d, 2C); 122.03 (s, 2C); 122.06 (s, 2C); 129.14 (s, 2C); 181.15 (s, 2C) ppm. IR (hexane) (cm^{-1}): 2017 $\nu(C\equiv C)$. Its preparation in detail will be published elsewhere.

2.2. Methods

Proton 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 and were referred to the solvent signal. UV–vis spectra were measured in the range 270–2000 nm on a Varian Cary 17D spectrometer using all-sealed quartz cuvettes (Hellma). Infrared spectra were obtained on a UR-75 instru-

ment (Ziess, Jena, Germany). The 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 Chromaton N-AW-DMCS column. Analogous GC–MS analyses were carried out on a Hewlett Packard gas chromatograph (5890 series II) equipped with a mass spectrometric detector (5971 A) and a capillary column SPB-1 (length 30 m; Supelco). The GC determination of the dimer obtained from the reaction mixture was carried out by integrating the peak areas of the dimer and of dodecane whose standard solution in hexane was added to a sample of the reaction mixture.

2.3. Catalytic conversion of terminal acetylenes by 1A–1F

Solutions of 1A–1F in hexane (0.1 M, 3 ml) were mixed with 1-alkyne (15–17 mmol; molar ratio 1-alkyne/Ti = 50–56), cooled with liquid nitrogen and sealed off in an ampule. The homogeneous reaction mixtures were then thermostatted to 30°C for 5 d. After opening to air, a sample of the reaction solution (< 0.1 ml) was used for the chromatographic determination of the product yield. The main portion was poured through a 7-cm length column of silica gel and was eluted with hexane. Yellow titanium-containing products were trapped in the column and a colourless solution was obtained. The hexane was evaporated on a rotary evaporator and the remaining product was weighed and analyzed by GC and GC–MS methods. The maximum conversion of 1-alkynes with 1F after 14-d reaction time was determined similarly using 2 ml of a 0.005 M solution of 1F in hexane and 20–25 mmol of 1-alkyne (molar ratio of alkyne/Ti = 2000–2550). Yields of 2,4-substituted 1-buten-3-ynes ranged from 6.0–7.5 mmol corresponding to a turnover number of 1200–1500 mmol of 1-alkyne per 1 mmol of 1F. The dimer yields were poorly reproducible and depended strongly on the purity of the acetylenes. When the conversion was lower than about 12 mmol, the acetylene was purified once more with dimeric titanocene using the procedure described above. In all cases other than t-butylethyne, the yields were improved. t-Butylethyne, however, failed to dimerize despite such purification. After evaporation of most of the hexane and t-butylethyne, GC–MS analysis revealed the minor presence of a head-to-tail dimer in addition to two more abundant cyclotrimers. The overall turnover number was about 30 mmol of acetylene per one mmol of Ti.

The purity of isolated 2-propyl-1-hepten-3-yne, 2-butyl-1-octen-3-yne, 2,4-cyclohexyl-1-buten-3-yne, 2,4-diphenyl-1-buten-3-yne and 2,4-bis(trimethylsilyl)-1-buten-3-yne was checked by GC–MS and the ^{1}H and

^{13}C NMR spectra of these compounds in CDCl$_3$ were in good agreement with literature data [1].

2.4. Spectroscopic investigation of the catalytic systems

Complexes **1A**, **1E** and **1F** in hexane solution (0.1 M, 3 ml) were mixed with trimethylsilylethyne (TMSE) (1 ml, 7.0 mmol) and the UV–vis and EPR spectra recorded until the initial complex disappeared, or in the case of **1F** for 5 d. All volatiles were then distilled in vacuum at 25°C into a trap cooled with liquid nitrogen. The volatiles were examined by GC–MS for the presence of bis(trimethylsilyl)acetylene (BTMSA), trimethylsilylethyne (TMSE), 2,4-bis(trimethylsilyl)-1-buten-3-yne, and 1,3,5- and 1,2,4-tris(trimethylsilyl)benzenes. The residue was dissolved in hexane and the solution characterized by IR spectroscopy.

3. Results and discussion

3.1. Catalytic oligomerization of 1-alkynes by 1A–1F

Complexes **1A–1F** were examined as catalysts for the conversion of 1-pentyne, 1-hexyne, cyclohexylethyne, phenylethyne and trimethylsilylethyne. Typical results for 1-hexyne at a molar ratio of acetylene/Ti = 56 are listed in Table 1. Of the complexes studied, only **1F** afforded the pure head-to-tail dimer (2-butyl-1-buten-3-yne) in virtually 100% yield. Complexes **1A–1D** gave mixtures of products dominated by 1,3,5- and 1,2,4-tributylbenzenes, but in low yield corresponding to turnover numbers $\leqslant 25$. The dimers formed in trace amounts in the **1A–1C** systems were different from the head-to-tail isomer. Minor amounts of dibutylbenzenes in the **1A** and **1B** systems indicated some unexpected activity of these catalysts in the dealkylation of tributylbenzenes. Complex **1E**, which is close in number of Me groups to **1F**, showed extremely

low activity but the products contained 20% of the head-to-tail dimer in addition to cyclic trimers. All the other acetylenes resembled 1-hexyne in their reactivity towards **1A–1F**. The product types were the same and the product yields were very similar to those obtained from 1-hexyne.

The above results show that only **1F** is interesting catalytically for the selective formation of the head-to-tail dimers. To establish the synthetic potential of **1F**, the dimerization experiments were carried out at an initial molar ratio of 1-alkyne/**1F** in the range 2000–2550. After 14 d reaction time at 30°C, all the acetylenes attained conversions corresponding to turnover numbers of 1200–1500 and the head-to-tail dimer was obtained with better than 98% selectivity. Differences in reactivity between the acetylenes were not established because their conversions were poorly reproducible, depending strongly on the purity of the acetylene and the overall purity in the system. An attempt to catalyze the dimerization of t-butylethyne by **1F** under these conditions was unsuccessful. The products corresponding to a turnover number of about 30 contained only 20% of 2,4-bis(t-butyl)-1-buten-3-yne in addition to a mixture of cyclic trimers.

The kinetics of the dimerization reaction with **1F** were not established because separation of the samples during the reaction under vacuum conditions required sealing them off. This must be avoided since the catalyst is rapidly deactivated by the products of the pyrolysis of 1-alkynes. Sampling from the reaction vessel under argon appeared to be not viable on a time scale of 14 d. These circumstances precluded comparison of the activity of **1F** with that of the $(C_5Me_5)_2TiCl_2/^iPrMgBr$ system where a turnover number of 2.0 and 4.5 for diethyl ether and THF, respectively, has been reported for a reaction time of 1 min at a molar ratio of 1-alkyne/Ti = 50 [1]. Some features of the catalysis by **1A**, **1E** and **1F** can be drawn, however, from a careful spectroscopic investigation of the sealed catalytic systems.

Table 1
Yields and composition of products from the oligomerization of 1-hexyne catalyzed by $Cp'_2Ti[\eta^2\text{-}C_2(SiMe_3)_2]$ complexes [a]

Cp'	Total yield (%)	Composition of products (%)				
		Dimers		Cyclotrimers		
		Head-to-tail	Others	A [b]	B [c]	DBB [d]
C$_5$Me$_5$	100	> 98	0	0	0	0
C$_5$Me$_5$	59 [e]	> 98	0	0	0	0
C$_5$HMe$_4$	7	21	0	30	49	0
C$_5$H$_2$Me$_3$	49	3	0	45	52	0
C$_5$H$_3$Me$_2$	45	0	1	48	51	0
C$_5$H$_4$Me	43	0	2	62	32	2
C$_5$H$_5$	42	0	1	50	42	7

[a] [Ti] = 0.06 M, [1-hexyne] = 3.4 M, hexane 3 ml, 1-hexyne 2 ml, 30°C for 5 d (1-hexyne/Ti = 56). [b] 1,3,5-Tributylbenzene. [c] 1,2,4-Tributylbenzene. [d] DBB = dibutylbenzenes. [e] Experiment carried out at [Ti] = 0.002 M, [1-hexyne] = 5.1 M, hexane 2 ml, 1-hexyne 3 ml, 30°C for 14 d (1-hexyne/Ti = 2550).

3.2. Spectroscopic investigation of the interaction of trimethylsilylethyne with 1A, 1E and 1F

The interaction of 1A, 1E and 1F with trimethylsilylethyne (TMSE) in hexane at a molar ratio of TMSE/Ti = 24 was followed by monitoring the absorption band of the BTMSA complexes in the region 900–1100 nm [5]. The presence of paramagnetic intermediates or products in the initially diamagnetic systems was checked by EPR spectroscopy at room temperature. The final volatile products were determined by GC analysis and the organometallic residue was characterized by infrared spectroscopy. In the 1A–TMSE system, the yellow colour of 1A changed to red within 30 min and, accordingly, the absorption band of 1A at 1060 nm disappeared. After 2 h the solution turned green. Volatiles contained mainly cyclic trimers of TMSE, unreacted TMSE and released BTMSA in nearly quantitative yield. The residual green titanium complex in hexane did not show any absorption band in the 1500–2200 cm^{-1} region but rather a strong absorption band at 1240 cm^{-1} which is characteristic of the trimethylsilyl group. This means that TMSE had been incorporated into this catalytically inactive complex. Among known products of the interaction of titanocene species with acetylenes, the dimeric compound [(C$_5$H$_5$)$_2$Ti(μ-η^1 : η^2-C≡CSiMe$_3$)]$_2$ of type I shows a strong absorption band at 1798 cm^{-1} [7,8] and hence cannot be present in the above system. On the other hand, titanacyclopentadiene complexes of type II [9–11] or dimeric complexes of type III [8,12] do not exhibit IR bands in the above-mentioned region and hence the presence of these compounds derived from TMSE is possible.

Complex 1E disappeared (as indicated by the disappearance of the absorption band at 920 nm) after 2 d to give a brown solution which did not exhibit any distinct absorption band in the visible region. Volatiles contained cyclic trimers, 2,4-bis(trimethylsilyl)-1-buten-3-yne, unreacted TMSE and quantitatively released BTMSA. The infrared spectrum of the catalyst residue in hexane showed a broad strong band at 1880 cm^{-1} and a sharp strong band at 2017 cm^{-1}. The latter band may be attributed to (C$_5$HMe$_4$)$_2$Ti(η^1-C≡CSiMe$_3$)$_2$ based on the coincidence of the wavenumber and line width with the infrared absorption band of the authentic compound. The band at 1880 cm^{-1} cannot be assigned to any titanocene–acetylene compounds known to date.

The reaction mixture of TMSE with 1F remained unchanged visually for 7 d and the absorption band of 1F at 916 nm decreased only negligibly. Volatiles only contained 2,4-bis(trimethylsilyl)-1-buten-3-yne and a trace of BTMSA. The residue in toluene showed characteristic infrared absorption bands for 1F at 1560, 1596 and 1636 cm^{-1} [5], a medium intensity band at 1880 cm^{-1} and a very weak and sharp band at 2011 cm^{-1}. The band at 2011 cm^{-1} may be attributed to (C$_5$Me$_5$)$_2$Ti(η^1-C≡CSiMe$_3$)$_2$ based on the 6-cm^{-1} decrease in wavenumber from the band position of (C$_5$HMe$_4$)$_2$Ti(η^1-C≡CSiMe$_3$)$_2$ and on the same band half-width (12 cm^{-1}). The band at 1880 cm^{-1} probably has the same origin as in the 1E system.

In all of these experiments EPR signals were not observed in any meaningful intensity, although identification of the titanocene diacetylides in the 1F and 1E systems implies the presence of appropriate titanocene monoacetylide intermediates. The presence of Ti^{III} in a form of (C$_5$H$_{5-n}$Me$_n$)$_2$Ti(η^1-C≡CSiMe$_3$) could not be observed by EPR spectroscopy for $n = 0$ as it forms a diamagnetic dimer [(C$_5$H$_5$)$_2$Ti(η^1-C≡CSiMe$_3$)]$_2$ [11,12] of type I and its absence follows from the absence of its IR band at 1798 cm^{-1}. The complex (C$_5$Me$_5$)$_2$Ti(η^1-C≡CSiMe$_3$) should be present in the 1F/TMSE system since it is an intermediate in the pathway to (C$_5$Me$_5$)$_2$Ti(η^1-C≡CSiMe$_3$)$_2$ (vide supra). This complex should also be a catalytic centre for the TMSE head-to-tail dimerization provided the catalytic mechanism proposed by Nakamura et al. [1] operates. It should be capable of observation by spectroscopic means since a similar (C$_5$Me$_5$)$_2$Ti(η^1-C≡CMe) complex is known to be monomeric, being characterized by the EPR signal at $g = 1.941$ ($\Delta H = 49$ G) and by the IR band at 2080 cm^{-1} [13]. However, judging from the low intensity of the infrared band of the deactivation product at 2011 cm^{-1}, the concentration of its intermediate is likely to be low and below the sensitivity limits for EPR and IR measurements. The complex (C$_5$HMe$_4$)$_2$Ti(η^1-C≡CSiMe$_3$) is probably also monomeric as the analogous trimethylstannyl complexes [(C$_5$H$_{5-n}$Me$_n$)$_2$Ti(η^1-C≡CSnMe$_3$)]$_2$ are only

I   II   III
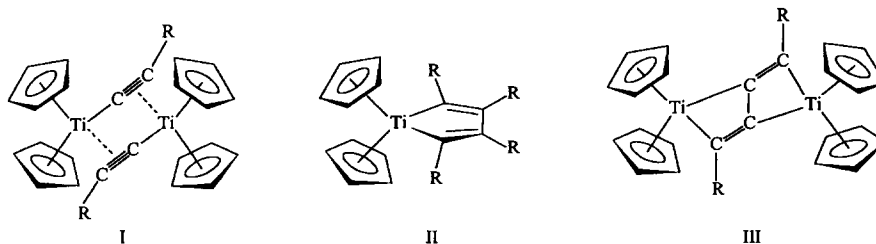
dimeric for $n = 0$–2 [14]. This complex was neither observed in the reacting system by EPR spectroscopy nor in the completely deactivated **1E**/TMSE system by IR spectroscopy.

The present results do not enable any conclusions to be drawn regarding the nature of the catalytic particles connected with the cyclotrimerization of 1-alkynes in the **1A–1E** systems.

3.3. Implications for the mechanism of 1-alkyne dimerization

The mechanism for head-to-tail dimerization by **1F** may be plausibly described by the catalytic cycle shown in Scheme 1.

Replacement of BTMSA by 1-alkyne is followed by its oxidative addition, the insertion of another molecule of 1-alkyne accompanied by a proton transfer, and the reductive elimination of 2,4-disubstituted 1-buten-3-yne. The present observations indicate that the replacement of BTMSA is very slow, probably as a result of steric hindrance in a transient complex, and that the enyne does not effectively compete with 1-alkyne in the replacement of BTMSA. The turnover numbers do not differ substantially for reactive 1-alkynes having different proton acidity (increasing in the series alkyl < Ph < SiMe$_3$ [15]) and different substituent size. This is understandable if it is assumed that **1F** is always attacked by the unsubstituted side of the acetylene and that the rate of replacement of BTMSA is controlled by steric congestion in a transient complex, which is the same for all the reactive 1-alkynes. Approximately equal turnover numbers also imply that a similar steric hindrance must
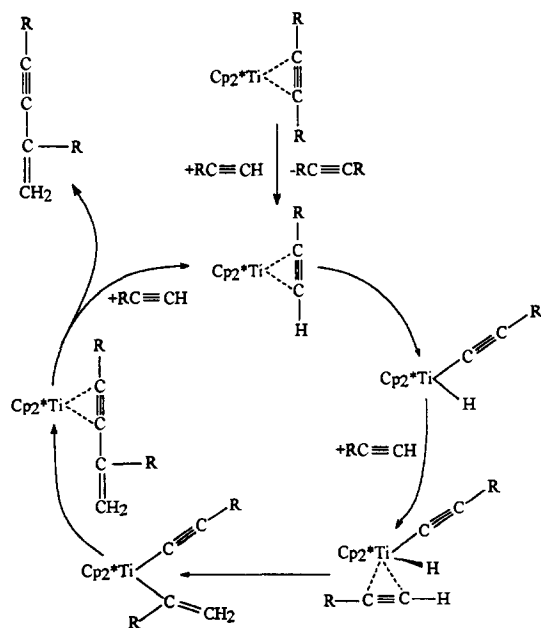
occur in the slowest step of the catalytic cycle and thus equalize the reaction rate for all the reactive 1-alkynes. The size of substituent only plays a decisive role in t-butylethyne where the bulky t-butyl group probably prevents the formation of the transient complex with **1F** and thus dimerization of t-butylethyne. On the other hand, TMSE is capable of forming the transient complex probably because the SiMe$_3$ group is more distant from the triple bond [$d(\equiv C\text{–}CMe_3) = 1.498$ Å and $d(\equiv C\text{–}SiMe_3) = 1.825$ Å] [16].

The striking difference in the catalytic activity and selectivity of **1F** and **1E** towards 1-alkynes is probably associated with the smaller space for coordination at the $(C_5Me_5)_2Ti$ fragment compared to that at $(C_5HMe_4)_2Ti$. Comparison of crystal structures of **1F** [17] and **1E** [5] revealed that the dihedral angle ϕ contained by the least-squares planes of cyclopentadienyl rings is smaller in **1F** ($41.1°$) than in **1E** ($50.0°$). This arises from steric hindrance between the Me substituents of the C_5Me_5 ligands in positions where the ligands approach each other in a staggered conformation. This steric hindrance is absent in **1E** as the relevant positions are occupied by hydrogen atoms. The small value of the angle ϕ in **1F** implies a decrease in the coordination space on the open side of a bent titanocene skeleton. Some steric congestion of the BTMSA ligand in **1F** seems to be reflected in a longer Ti–C$_{ac}$ distance [av. 2.124(3) Å] compared to that in **1E** [2.106(3) Å]. In contrast, a marginally longer C$\equiv$C distance in **1F** [1.309(4) Å against 1.303(5) Å in **1E**] is in accord with a stronger Ti–BTMSA coordination in **1F** as follows from **1F** exhibiting the largest ^{13}C NMR δ (C$\equiv$C) shifts and infrared ν(C$\equiv$C) vibration of all the **1A–1F** complexes [5]. Steric congestion in transient complexes is apparently the reason for the low reactivity of **1F** towards 1-alkynes (as exemplified for TMSE), and consequently for the high selectivity in the dimerization of 1-alkynes. The much faster reaction of **1E** and **1A** with TMSE resulted in their rapid deactivation.

An alternative mechanism for the dimerization based on a permethyltitanocene acetylide as a catalytic centre [1] is supported by the results obtained with lanthanide carbyls [4]. The presence of complex permethyltitanocene (Ti^{III}) acetylides with magnesium acetylides (tweezer-type complexes with Mg embedded between the acetylide arms, e.g. [(C$_5$Me$_5$)$_2$Ti(η^1-C$\equiv$C–R)$_2$]$^-$[Mg(THF)Cl]$^+$ [18]) in the (C$_5$Me$_5$)$_2$TiCl$_2$/^{i}PrMgCl/HC$\equiv$CR systems and their catalytic activity in the dimerization of 1-alkynes has recently been demonstrated by us [19]. Our present knowledge does not allow us to prefer the presence of either Ti^{III} or Ti^{II} in the catalytic complex. Intermediacy of (C$_5$Me$_5$)$_2$-Ti^{III}(C$\equiv$CR) probably occurs in the deactivation pathway of **1F** whereas the formation of a Ti^{II} compound in the reaction of a tweezer complex with 1-alkyne cannot be excluded. An example of such unexpected behaviour

Scheme 1. Catalytic cycle for head-to-tail dimerization of 1-alkynes by **1F**.

for the Ti^{III}-containing system in the presence of monomer is known. The $EtAlCl_2/TiCl_4/$butadiene $(Al/Ti \geqslant 40)$ system used for the selective trimerization of butadiene to (Z,E,E)-1,5,9-cyclododecatriene contained largely $(\eta^6\text{-arene})Ti^{II}(AlCl_4)_2$ after the butadiene feed had been stopped [20].

An investigation of the catalytic activity of **1F** under the most rigorous conditions is being undertaken.

Acknowledgement

References

[1] H. Akita, H. Yasuda and A. Nakamura, *Bull. Chem. Soc. Jpn.*, *57* (1984) 480.

[2] M.E. Thompson, S.M. Baxter, A.R. Bulls, B.J. Burger, M.C. Nolan, B.D. Santarsiero, W.P. Schaefer and J.E. Bercaw, *J. Am. Chem. Soc.*, *109* (1987) 203.

[3] K.H. den Haan, Y. Wielstra and J.H. Teuben, *Organometallics*, *6* (1987) 2053.

[4] H.J. Heeres and J.H. Teuben, *Organometallics*, *10* (1991) 1980.

[5] V. Varga, K. Mach, M. Polášek, P. Sedmera, J. Hiller, U. Thewalt and S.I. Troyanov, submitted to *J. Organomet. Chem.*

[6] H. Antropiusová, A. Dosedlova, V. Hanuš and K. Mach, *Transition Met. Chem.*, *6* (1981) 90.

[7] G.L. Wood, C.B. Knobler and M.F. Hawthorn, *Inorg. Chem.*, *28* (1989) 382.

[8] U. Rosenthal, A. Ohff, M. Michalik and H. Görls, *J. Organomet. Chem.*, *468* (1994) C4.

[9] V.B. Shur, E.G. Berkovich, M.E. Vol'pin, B. Lorenz and M. Wahren, *J. Organomet. Chem.*, *228* (1982) C36.

[10] K. Sonogashira and N. Hagihara, *Bull. Chem. Soc. Jpn.*, *39* (1966) 1178.

[11] M.D. Rausch, W.H. Boon and E.A. Mintz, *J. Organomet. Chem.*, *160* (1978) 81.

[12] D.G. Sekutowski and G.D. Stucky, *J. Am. Chem. Soc.*, *98* (1976) 1376.

[13] G.A. Luinstra, L.C. ten Cate, H.J. Heeres, J.W. Pattiasina, A. Meetsma and J.H. Teuben, *Organometallics*, *10* (1991) 3227.

[14] V. Varga, K. Mach, J. Hiller, U. Thewalt, P. Sedmera and M. Polášek, *Organometallics*, *14* (1995) 1410.

[15] R.E. Dessy, Y. Okuzumi and A. Chen, *J. Am. Chem. Soc.*, *84* (1962) 2899; C. Eaborn, B.A. Skinner and D.R.M. Walton, *J. Organomet. Chem.*, *6* (1966) 438.

[16] W. Zeil, J. Haase and M. Dakkouri, *Discuss. Faraday Soc.*, *47* (1969) 149.

[17] V.V. Burlakov, A.V. Polyakov, A.I. Yanovsky, Yu.T. Struchkov, V.B. Shur, M.E. Vol'pin U. Rosenthal and H. Görls, *J. Organomet. Chem.*, *476* (1994) 197.

[18] S.I. Troyanov, V. Varga and K. Mach, *Organometallics*, *12* (1993) 2820.

[19] K. Mach, V. Varga and R. Gyepes, *Abs. Book, XVIth Int. Conf. Organomet. Chem.* University of Sussex, UK, July 1994, OB 17.

[20] J. Poláček, H. Antropiusová, L. Petrusová and K. Mach, *J. Mol. Catal.*, *70* (1991) 9.