

The reaction of pentamethylcyclopentadiene with the titanium Ziegler–Natta catalysts, a tool for their investigation

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Abstract

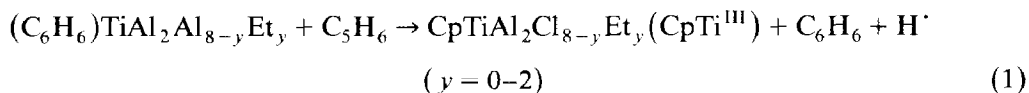
The reaction of the systems $\text{TiCl}_4 + \text{Et}_x\text{AlCl}_{3-x}$ ($x = 1-3$) with pentamethylcyclopentadiene (Cp^*H) yields $\text{Cp}^*\text{TiAl}_2\text{Cl}_{8-y}\text{Et}_y$ ($y = 0-4$) complexes in good-to-excellent yields (60–96%). The composition and yields of these complexes were determined from the ESR spectra of products. The reaction of the initially precipitated titanium chlorides with Cp^*H is complete after several days. The composition of the $\text{Cp}^*\text{TiAl}_2\text{Cl}_{8-y}\text{Et}_y$ complexes shows that the addition of triphenylphosphine (PPh_3) to the $\text{TiCl}_4 + \text{Et}_x\text{AlCl}_{3-x}$ systems affords more ethylated systems because PPh_3 removes the most chlorinated aluminium component of the system as a 1:1 complex. In the absence of free aluminium component the PPh_3 decomposes the $\text{Cp}^*\text{TiAl}_2\text{Cl}_{8-y}\text{Et}_y$ ($y = 0-4$) and $(\eta^6\text{-benzene})\text{TiAl}_2\text{Cl}_{8-y}\text{Et}_y$ ($y = 0-2$) complexes.

Introduction

The titanium-based Ziegler–Natta catalysts, largely derived from TiCl_4 or TiCl_3 and alkylaluminium compounds, are widely used to polymerize α -olefins and dienes on an industrial scale [1,2]. Similar catalysts, differing only in their component ratios, cyclooligomerize dienes [3,4] or acetylenes [5,6] or permit their cross-addition [7–9]. Alternatively, $(\eta^6\text{-arene})\text{titanium(II)}$ complexes, e.g., $(\text{C}_6\text{H}_6)\text{Ti}(\text{AlCl}_4)_2$ (Ia) either by themselves or with ethylaluminium compounds, were found to be superior catalysts for some of these reactions, such as the cyclotrimerization of butadiene to (Z, E, E) -1,5,9-cyclododecatriene (CDT) [10–12]. The formation of $(\eta^6\text{-C}_6\text{H}_6)\text{Ti}^{\text{II}}$ complexes in the $\text{TiCl}_4 + \text{Et}_x\text{AlCl}_{3-x}$ ($x = 1-1.5$) systems during the butadiene cyclotrimerization was recently shown by electronic absorption spectroscopy [13].

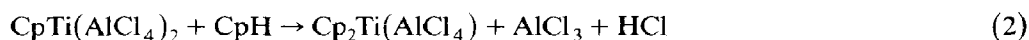
Interaction of Ia with ethylaluminium compounds involves the partial replacement of the outer chlorine ligands by Et groups, and consequently changes the catalytic properties of these systems [12]. The number of Et groups in $(\text{benzene})\text{Ti}^{\text{II}}$

complexes was determined from the shifts in the charge transfer band of Ia to longer wavelengths and from the line width of the ESR signals of CpTi^{III} (Cp = η⁵-C₅H₅) compounds, which were obtained from the (benzene)Ti^{III} complexes in the redox reaction, eq. 1 [14]; the line width decreases with rise in the number of Et groups [15].



Both methods give virtually identical results for the number of Et groups; the results showed that the equilibria in the Ia + *n* Et_{*x*}AlCl_{3-*x*} and CpTiAl₂Cl₈ + *n* Et_{*x*}AlCl_{3-*x*} (*x* = 1-3) systems are strongly shifted towards the more chlorinated aluminium titanium complexes compared to the free aluminium compounds [15].

Of the methylated cyclopentadienes, which all undergo reaction 1, pentamethylcyclopentadiene (Cp*H) and ethyltetramethylcyclopentadiene were found to have the following advantages over cyclopentadiene: (a) reaction 1 is more feasible because Cp*H is a stable monomer, (b) the Cp*Ti^{III} complexes obtained are stable —up to *y* = 4— which permits investigation of highly ethylated Ziegler-Natta catalysts, and (c) an excess of Cp*H does not replace the aluminate ligand in the Cp*Ti^{III} complexes as in reaction 2, which proceeds with less alkylated cyclopentadienes [15,16].



Here the interaction of the TiCl₄ + *n* Et_{*x*}AlCl_{3-*x*} (*x* = 1-3) systems with Cp*H was studied by ESR spectroscopy which gave the composition and yields of Cp*Ti^{III} complexes for various compositions and quantities of ethylaluminium compounds. The method was used to investigate the effect of the addition of triphenylphosphine (PPh₃) on the title systems.

Experimental

General

The reactions of TiCl₄ with ethylaluminium compounds and simultaneously or subsequently with pentamethylcyclopentadiene, Me₅C₅H, (Cp*H) were carried out under vacuum in sealed glass devices and ampoules equipped with magnetically breakable seals. The molar ratio Cp*H/Ti was always 2.

Chemicals

TiCl₄ (Intern. Enzymes) was refluxed with copper turnings, degassed and distilled in vacuo. The colourless compound was diluted with dry benzene to give a 0.04 *M* solution. Benzene solutions of (C₆H₆)TiAl₂Cl₈ (Ia), EtAlCl₂, Et₂AlCl, and Et₃Al (0.1 or 1.0 *M*) were the same as those used in the catalytic systems for the butadiene cyclootrimerization [11,12]. The benzene solution of Cp*H (0.05 *M*) was the same as previously used [16].

Procedures

The solution of TiCl₄ (0.04 mmol in 1 ml) was mixed with solutions of ethylaluminium compounds in a bulb attached to an ESR sample tube and sealed

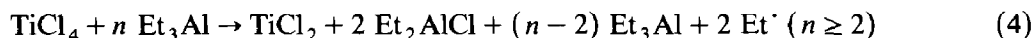
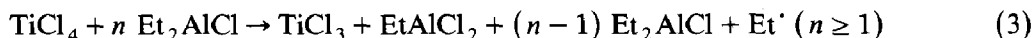
quartz cell to measure the electronic absorption spectra. The reaction mixtures were usually stirred at room temperature for 1 h and the solution of Cp*H (1.6 ml) was added with stirring. The ESR spectra of the reaction mixture were recorded before and after addition of Cp*H until no further changes occurred. The electronic absorption spectra of the final reaction solutions were recorded. In the instant experiments, Cp*H was first mixed with the ethylaluminium component and then TiCl₄ was added immediately. Weighed amounts of freshly recrystallized triphenylphosphine (PPh₃) were added to the reaction mixtures from an attached ampoule under vacuum. Reactions of Ia or the systems Ia + Et_xAlCl_{3-x} (x = 1–3) with PPh₃ and/or Cp*H were carried out as described previously [16].

Methods

The ESR spectra were recorded on an ERS-220 spectrometer (Centre for Production of Scientific Instruments, Ger. Acad. Sci., Berlin, GDR) in the X-band at room temperature. The *g* values were calibrated relative to the signal of a Mn²⁺ (*M*₁ = -1/2 line) standard at *g* = 1.9860. Magnetic fields were measured with a MJ 110-R magnetometer equipped with a proton NMR probe (Radiopan, Poznań, Poland). For quantitative measurements, the spectrum of the first derivative was integrated and the area of the ESR absorption spectrum was compared with that of a standard (Cp₂TiAlCl₃Et, 5.275 × 10⁻³ M in benzene). The concentration of the Cp*Ti^{III} complexes was determined to within ±5% of 1 × 10⁻² to 5 × 10⁻⁴ M. Electronic absorption spectra were recorded on a Varian Cary 17 D spectrometer in sealed quartz cells (*d* = 0.1 and 1.0 cm) (Hellma).

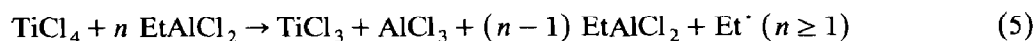
Results and discussion

The reduction of TiCl₄ with Et₂AlCl or Et₃Al in benzene involves the very rapid precipitation of most of the titanium as solid low-valent titanium chlorides. The reduction with Et₂AlCl almost quantitatively gives rusty-brown β-TiCl₃ [17,18], whereas the reduction with Et₃Al gives dark brown TiCl₂ [12] (eqs. 3 and 4).



Very weak ESR signals were observed near *g* ~ 1.970 and *g* ~ 1.930 in the spectra for the final, nearly colourless reaction solutions. The signals at *g* ~ 1.970 were stable, and those at *g* ~ 1.930 decreased in intensity with ageing. The signals at *g* ~ 1.970 fall within the range of *g*-values which characterize highly alkylated CpTiAl₂Cl_{8-y}Et_y complexes [16]; the formation of a small amount of these complexes can be expected because their formation in the above systems to produce organic fragments (ethyl radicals) is thermodynamically strongly favoured [19]. The signals at *g* ~ 1.930 are attributable to species which are probably similar in nature to the soluble species formed in TiCl₄ + EtAlCl₂ systems (vide infra).

The reduction of TiCl₄ with EtAlCl₂ is much slower than in the cases described; nevertheless, it has been shown [20] that an equimolar amount of EtAlCl₂ ensures the reduction of TiCl₄ according to eq. 5:



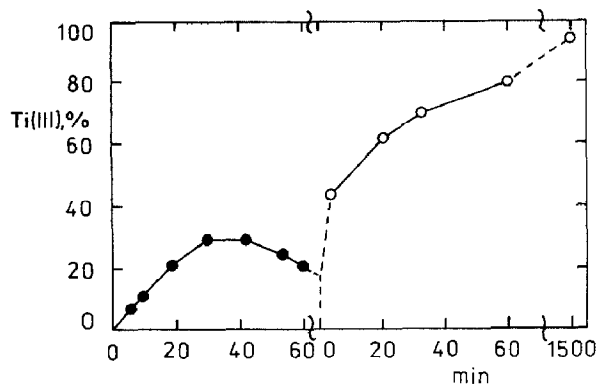


Fig. 1. The formation and decay of the soluble Ti^{III} species in the $\text{TiCl}_4 + 40 \text{ EtAlCl}_2$ system (●) and the formation of $\text{Cp}^*\text{Ti}^{\text{III}}$ complexes after addition of 2 equiv of Cp^*H (○). $[\text{Ti}]$ initially $1.54 \times 10^{-2} \text{ M}$, after addition of the Cp^*H solution, $1.52 \times 10^{-3} \text{ M}$.

Stable, soluble intermediates of Ti^{III} were observed by Adema et al. [21] in these and in the $\text{TiCl}_4 + \text{Et}_2\text{AlCl}$ systems [22] in heptane solution for Al/Ti molar ratios ≤ 1 , at concentrations of about 1% of the aluminium concentration. The more abundant species at $g = 1.925$ was assigned to $\text{TiCl}_3 \cdot (\text{AlCl}_2\text{Et})_2$, and the minor species at $g = 1.933$ to $\text{TiCl}_3 \cdot \text{AlCl}_2\text{Et}$ [21].

Throughout this work, ethylaluminium compounds were used in at least a two-fold molar excess relative to TiCl_4 , the minimum ratio which is required for the stoichiometric formation of the $\text{Cp}^*\text{TiAl}_2\text{Cl}_{8-y}\text{Et}_y$ ($y = 0-4$) complexes. Under these conditions, the soluble Ti^{III} species ($g \sim 1.93$) are not stable and decompose rapidly in the $\text{TiCl}_4 + \text{Et}_2\text{AlCl}$ systems and more slowly in the $\text{TiCl}_4 + \text{EtAlCl}_2$ systems. With a 40-fold molar excess of EtAlCl_2 , the maximum concentration of soluble Ti^{III} species attained 30% of the overall titanium concentration and then diminished (Fig. 1). The decrease in the ESR signal intensity coincides with the onset of TiCl_3 precipitation.

*The reaction of the $\text{TiCl}_4 + \text{Et}_x\text{AlCl}_{3-x}$ ($x = 1-3$) systems with Cp^*H*

The addition of Cp^*H to both aged and instant $\text{TiCl}_4 + \text{Et}_x\text{AlCl}_{3-x}$ systems yielded green, soluble products which were identified from their ESR and electronic absorption spectra as the complexes $\text{Cp}^*\text{TiAl}_2\text{Cl}_{8-y}\text{Et}_y$ ($y = 0-4$). The composition of the complexes was deduced from the line widths of their ESR signals by use of recently published values of ΔH for $\text{Cp}^*\text{TiAl}_2\text{Cl}_{8-y}\text{Et}_y$ complexes, differing in the number of Et groups [16]. The line width falls as the number of Et substituents (y) in the outer positions of the complexes rises owing to the electron donating ability of the Et groups [23]. Differences in ΔH between the complexes with y values differing by 1 are not large ($\sim 0.4 \text{ mT}$) so that the change in ΔH is virtually continuous with the change in the composition and the approximate abundance of the complexes can be derived from the calibration curve depicted in Fig. 2. This simple method is not applicable to complexes with effective y values of less than 1, which give the composite spectra of an eleven-line multiplet for $\text{Cp}^*\text{TiAl}_2\text{Cl}_8$ and a single line spectrum for $\text{Cp}^*\text{TiAl}_2\text{Cl}_7\text{Et}$. The ΔH data are consistent with a small shift in the g -value of the complexes to a higher value as y increases. The values of ΔH and g and the effective values of y obtained from the calibration graph for ΔH

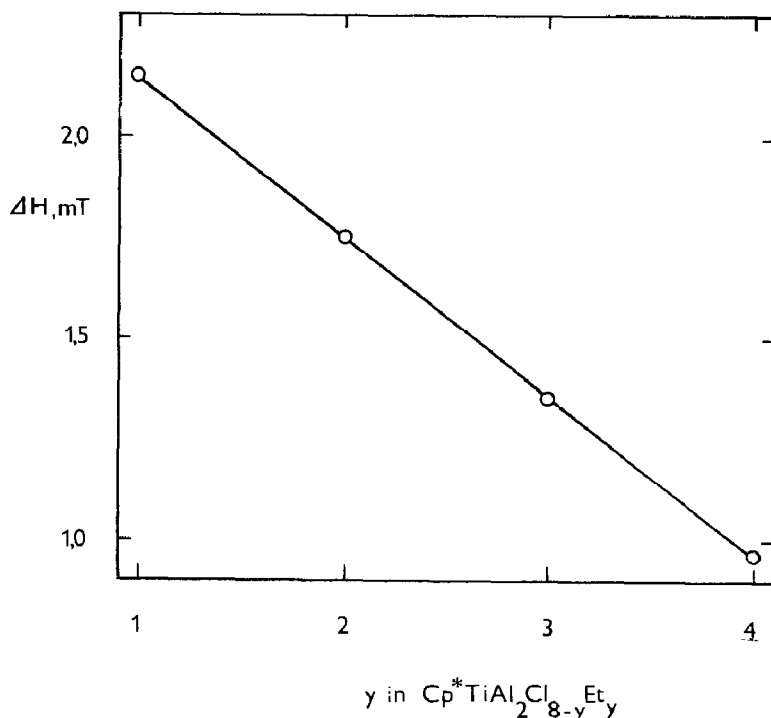


Fig. 2. Plot of the ESR signal line width (ΔH peak-to-peak) against the composition of the $\text{Cp}^*\text{TiAl}_2\text{Cl}_{8-y}\text{Et}_y$ complexes (from ref. 16). $y=1$, $\Delta H=2.15$ mT; $y=2$, $\Delta H=1.75$ mT; $y=3$, $\Delta H=1.36$ mT; $y=4$, $\Delta H=0.97$ mT.

(Fig. 2) for representative systems are given in Table 1. The composition of the complexes are roughly consistent with their electronic absorption spectra, which show a broad $d-d$ absorption band at 660–690 nm and charge transfer bands at 420 and 485 nm for $\text{Cp}^*\text{TiAl}_2\text{Cl}_8$ which are shifted to shorter wavelengths by each additional ethyl group [16]. However, the background absorption in the 300–500 nm region attributable to by-products makes this spectral method unreliable.

Addition of 2 equiv. of Cp^*H to the $\text{TiCl}_4 + 40 \text{ EtAlCl}_2$ system that had been aged for 1 h led to immediate conversion of the soluble Ti^{III} species (vide supra) into $\text{Cp}^*\text{Ti}^{\text{III}}$ complexes (see Figs. 1 and 3). The quantitative transformation of precipitated TiCl_3 into the same product required a further 20 h for completion (Table 1, No. 1). The observed eleven-line multiplet in the ESR spectrum of the reaction mixture (Fig. 3) indicated the presence of $\text{Cp}^*\text{TiAl}_2\text{Cl}_8$ in a mixture containing $\text{Cp}^*\text{TiAl}_2\text{Cl}_7\text{Et}$. The electronic absorption spectrum of the final solution showed the bands of the $\text{Cp}^*\text{Ti}^{\text{III}}$ complexes [16] and increased absorption in the 300–500 nm region, indicating the presence of a diamagnetic by-product, which was probably produced by the interaction of Cp^*H with traces of AlCl_3 . A similar effect was observed earlier in the spectrum of $\text{Cp}^*\text{TiAl}_2\text{Cl}_8$ obtained from the reaction of Ia with Cp^*H [16]. Therefore, two equivalents of Cp^*H were used in place of one in this work to ensure that sufficient amounts of Cp^*H were present for the formation of the $\text{Cp}^*\text{Ti}^{\text{III}}$ complexes. When the system was aged for 4 h, the soluble Ti^{III} species largely decomposed to TiCl_3 , which resulted in much slower formation of the $\text{Cp}^*\text{Ti}^{\text{III}}$ complexes upon addition of Cp^*H . The conversion of TiCl_3 was complete

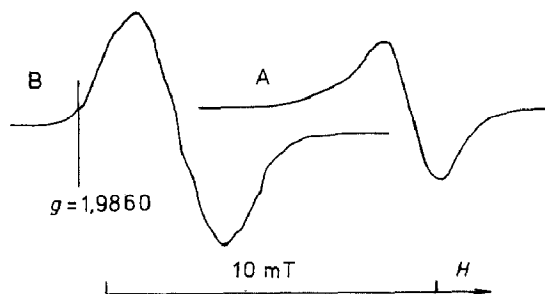


Fig. 3. ESR spectra of the $\text{TiCl}_4 + 40 \text{ EtAlCl}_2$ system before (A) and after (B) addition of 2 equiv of Cp^*H .

only after 5 d; the yield and composition of the $\text{Cp}^*\text{Ti}^{\text{III}}$ complexes were practically the same as in the preceding experiment. The lower yield of $\text{Cp}^*\text{Ti}^{\text{II}}$ complexes in the $\text{TiCl}_4 + 5 \text{ EtAlCl}_2$ system (Table 1, No. 2) is probably attributable to competitive cationically induced consumption of Cp^*H in a strongly Lewis-acid system [13].

The $\text{TiCl}_4 + \text{Et}_2\text{AlCl}$ systems upon laying gave $\text{Cp}^*\text{Ti}^{\text{III}}$ complexes in high yields. The rate of their formation (from TiCl_3) was generally lower than those in the $\text{TiCl}_4 + \text{EtAlCl}_2$ systems. The reaction required a maximum of 9 d for completion in the $\text{TiCl}_4 + 2 \text{ Et}_2\text{AlCl}$ system, but an excess of Et_2AlCl shortened the reaction time to 3 d (Table 1, Nos. 3, 5–8). An example of the kinetics of the formation $\text{Cp}^*\text{Ti}^{\text{III}}$ is depicted in Fig. 4.

The $\text{TiCl}_4 + n \text{ Et}_3\text{Al}$ systems upon aging afforded the highest yields of $\text{Cp}^*\text{Ti}^{\text{III}}$ complexes, largely $\text{Cp}^*\text{TiAl}_2\text{Cl}_4\text{Et}_4$, for $n = 2$, although still only 65% (Table 1, No. 11). The low yield was attributable to incomplete dissolution of the precipitated TiCl_2 and to the formation of a diamagnetic by-product whose presence was indicated by increased background absorption in the spectrum at $\lambda < 500 \text{ nm}$. Higher or lower amounts of Et_3Al gave even poorer yields. An equimolar excess of Et_3Al led to the complete decomposition of $\text{Cp}^*\text{TiAl}_2\text{Cl}_4\text{Et}_4$ to give ESR-inactive

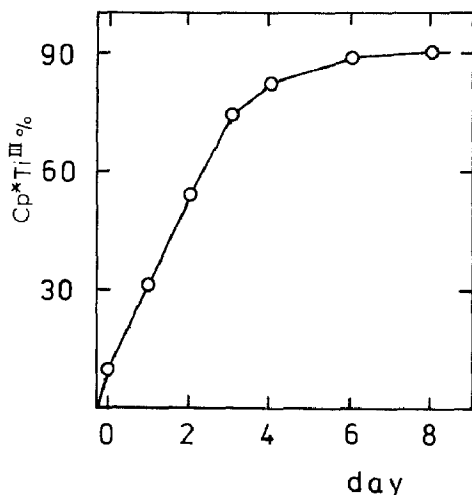
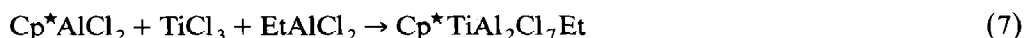


Fig. 4. The kinetics of the formation of $\text{Cp}^*\text{Ti}^{\text{III}}$ complexes in the $\text{TiCl}_4 + 2 \text{ Et}_2\text{AlCl} + 2 \text{ Cp}^*\text{H}$ system (the system was aged for 1 h before addition of Cp^*H ; $[\text{Ti}] 1.18 \times 10^{-2} \text{ M}$).

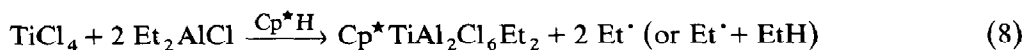
products. Addition of Et_2AlCl to these systems improved the yields (Table 1, No. 10).

It was of interest from a mechanistic and practical viewpoint to examine the reaction between TiCl_4 and $\text{Et}_x\text{AlCl}_{3-x}$ in the presence of Cp^*H . In this case, the $\text{TiCl}_4 + n \text{Et}_2\text{AlCl}$ systems initially produce a large amount of $\text{Cp}^*\text{Ti}^{\text{III}}$ complexes (about 20–40%) together with the TiCl_3 precipitate. The reaction then required shorter reaction times for completion than when all the TiCl_3 was precipitated before addition of Cp^*H (Table 1, No. 4). In the $\text{TiCl}_4 + 2 \text{Et}_3\text{Al}$ system, the presence of Cp^*H during mixing prevented the formation of a precipitate and within 10 min the reaction mixture became a green solution, which gave $\text{Cp}^*\text{TiAl}_2\text{Cl}_4\text{Et}_4$ in higher yields (Table 1, No. 12). The $\text{TiCl}_4 + 40 \text{EtAlCl}_2$ system in the presence of Cp^*H immediately produces the $\text{Cp}^*\text{Ti}^{\text{III}}$ complexes and TiCl_3 in intensely yellow-coloured mixtures. Although the system gave $\text{Cp}^*\text{Ti}^{\text{III}}$ complexes in 85% yield after 1 d, it should contain large amounts of diamagnetic by-products from the acidic conversion of Cp^*H .

The results obtained from the aged and the instant systems show that the limiting step in the formation of the $\text{Cp}^*\text{Ti}^{\text{III}}$ complexes is the dissolution of the TiCl_3 or TiCl_2 precipitates. The rapid conversion to $\text{Cp}^*\text{Ti}^{\text{III}}$ complexes in the $\text{TiCl}_4 + (2 \text{Et}_3\text{Al} + 2 \text{Cp}^*\text{H})$ system indicates that TiCl_2 at onset of formation and in the presence of the solvating ethylaluminium component (Et_2AlCl) is able to undergo a very rapid redox reaction with Cp^*H , similar to that of the (arene) Ti^{II} complexes (eq. 1). In the other systems, in which the reduction to Ti^{II} cannot be achieved by the action of the ethylaluminium compound itself, two reaction pathways can be considered. The first is based on exchange reactions of Cp^*H with the ethylaluminium moiety and of the $\text{Cp}^*\text{-Al}$ compound that forms with TiCl_3 (e.g., eqs. 6 and 7).



The second pathway probably involves the reduction of TiCl_3 to an intermediate Ti^{II} species followed by a rapid redox reaction with Cp^*H . Such a reduction yielding (benzene) Ti^{II} complexes was established in the $\text{TiCl}_3 + \text{EtAlCl}_2 + \text{benzene} + \text{butadiene}$ system, in which the presence of butadiene is essential [13,24]. That 2 equiv. of Et groups are involved in the formation of $\text{Cp}^*\text{Ti}^{\text{III}}$ complexes from TiCl_4 in either pathway was confirmed by experiments 3 and 4 (Table 1) which yielded the $\text{Cp}^*\text{Ti}^{\text{III}}$ complex as outlined in eq. 8.



The pathways could differ in the yields of the recombination products of Et radicals but no attempt was made to solve this problem.

The effect of PPh_3 on the composition of the catalytic systems

The addition of PPh_3 to the Ziegler–Natta systems listed in Table 1 influenced the composition of the resulting $\text{Cp}^*\text{Ti}^{\text{III}}$ complexes so that more strongly ethylated complexes were produced. The same results were obtained independently of the order of addition of Cp^*H and PPh_3 . Changes in the compositions of the $\text{Cp}^*\text{TiAl}_2\text{Cl}_{8-y}\text{Et}_y$ complexes after addition of PPh_3 show that $\text{AlCl}_3 \cdot \text{PPh}_3$ is

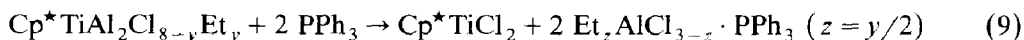
Table 1

Reaction of the $\text{TiCl}_4 + \text{Et}_x\text{AlCl}_{3-x}$ ($x = 1-3$) systems with Cp^*H and the change in the composition of the $\text{Cp}^*\text{TiAl}_2\text{Cl}_{8-y}\text{Et}_y$ complexes induced by addition of PPh_3 ^a

Exp. No.	System: $\text{TiCl}_4 +$	Ageing before addition of Cp^*H , h	$\text{Cp}^*\text{TiAl}_2\text{Cl}_{8-y}\text{Et}_y$ complexes ^b			
			Yield, %/d	g	ΔH , mT	y
1	40 EtAlCl_2	1	96/1	1.9697	^c	<1
1a	40 $\text{EtAlCl}_2 + 2 \text{PPh}_3$	—	96	1.9698	^c	<1
2	5 EtAlCl_2	1	60/10	1.9697	^c	<1
2a	5 $\text{EtAlCl}_2 + 2 \text{PPh}_3$	—	85/13	1.9698	1.97	1.5
3	2 Et_2AlCl	1	85/9	1.9700	1.82	1.9
3a	2 $\text{EtAlCl}_2 + 2 \text{PPh}_3$	—	0	—	—	—
4	2 Et_2AlCl	0	85/3	1.9700	1.82	1.9
5	3 Et_2AlCl	1	88/7	1.9700	1.76	2.0
6	5 Et_2AlCl	1	92/3	1.9701	1.68	2.2
7	6 Et_2AlCl	1	92/3	1.9702	1.64	2.3
7a	6 $\text{EtAlCl}_2 + 2 \text{PPh}_3$	—	92	1.9706	1.02	3.8
8	30 Et_2AlCl	1	94/3	1.9703	1.50	2.6
9	$\text{Et}_3\text{Al} + 2 \text{Et}_2\text{AlCl}$	0	94/1	1.9704	1.30	3.1
9a	$\text{Et}_3\text{Al} + 2 \text{Et}_2\text{AlCl} + 1 \text{PPh}_3$	—	90	1.9706	1.02	3.8
10	2 $\text{Et}_3\text{Al} + \text{Et}_2\text{AlCl}$	1	70/9	1.9706	1.00	3.9
11	2 Et_3Al	1	60/9	1.9707	0.97	4.0
11a	2 $\text{Et}_3\text{Al} + 1 \text{PPh}_3$	—	35	1.9707	0.97	4.0
12	2 Et_3Al	0	70/0.01	1.9707	0.97	4.0

^a TiCl_4 (0.04 mmol in 1 ml of benzene solution) and $\text{Et}_x\text{AlCl}_{3-x}$ (0.1 M solution in benzene) were mixed and aged, usually for 1 h. Then Cp^*H (0.08 mmol in 1.6 ml of benzene solution) was added with stirring. In instant experiments Cp^*H was mixed with the ethylaluminium component and then the TiCl_4 solution was added. Weighed amounts of PPh_3 were added to the reaction mixture from evacuated ampoules with breakable seals after the yields and composition of the $\text{Cp}^*\text{TiAl}_2\text{Cl}_{8-y}\text{Et}_y$ complexes changed no further. ^b Accuracy of the measurements: line width $\Delta H \pm 0.02$ mT; $y \pm 0.05$. ^c An eleven line multiplet $a = 0.575$ mT of $\text{Cp}^*\text{TiAl}_2\text{Cl}_8$ is overlapped by a single line spectrum.

formed in the $\text{TiCl}_4 + \text{EtAlCl}_2$ systems (cf. Nos. 1,1a and 2,2a, Table 1) and $\text{EtAlCl}_2 \cdot \text{PPh}_3$ in the $\text{TiCl}_4 + \text{Et}_2\text{AlCl}$ systems (cf. Nos. 7,7a and 9,9a). Their formation implies that PPh_3 is bonded to the most chlorinated aluminium component present in the system to give a stable 1:1 complex. The existence of only 1:1 complexes with PPh_3 was established for AlCl_3 [25] as well as for Me_3Al [26]. Although a comparison of the stabilities of the PPh_3 complexes for the series of the $\text{Et}_x\text{AlCl}_{3-x}$ ($x = 0-3$) compounds is not available, the observed order of the affinity of PPh_3 for aluminium compounds: $\text{AlCl}_3 > \text{EtAlCl}_2 > \text{Et}_2\text{AlCl}$ is consistent with the order of their Lewis acidities. Addition of PPh_3 to the system containing no free aluminium components (Table 1, No. 3a) results in the stoichiometric decomposition of the $\text{Cp}^*\text{Ti}^{\text{III}}$ complex to give ESR-inactive products (eq. 9) or if added before Cp^*H it prevents the formation of the $\text{Cp}^*\text{Ti}^{\text{III}}$ complex.



From a catalytic point of view, it was of interest to study the influence of PPh_3 on (benzene) Ti^{II} complexes on the basis of the reaction with Cp^*H . The results are listed in Table 2 and show that the addition of PPh_3 to Ia leads to its immediate decomposition (eq. 10)

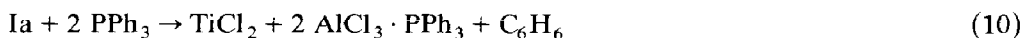


Table 2

Reaction of the $(C_6H_6)TiAl_2Cl_8$ (Ia) + Et_xAlCl_{3-x} ($x=1-3$) systems with Cp^*H and PPh_3 ^a

Exp. No.	The components added to Ia	Data for $Cp^*TiAl_2Cl_{8-y}Et_y$ complexes			
		Yield, %	<i>g</i>	ΔH , mT	<i>y</i>
1	2 PPh_3	0	—	—	—
2	1 PPh_3	50	1.9696	^b	0
3	4 $EtAlCl_2$	100	1.9696	^c	<1
3a	4 $EtAlCl_2$ + 4 PPh_3	100	1.9699	1.81	1.9
4	2 Et_2AlCl	100	1.9698	2.05	1.2
4a	2 $EtAlCl_2$ + 2 PPh_3	100	1.9702	1.72	2.1
5	3 Et_2AlCl	100	1.9698	1.91	1.7
5a	3 $EtAlCl_2$ + 2 PPh_3	100	1.9700	1.71	2.1
6	5 Et_2AlCl	100	1.9700	1.71	2.1
6a	5 $EtAlCl_2$ + 5 PPh_3	90	1.9705	1.07	3.7
7	4 Et_3Al	80 ^e	1.9706	0.98	3.95
8	(Cp^*H) ^d + 4 Et_3Al	100	1.9707	0.97	4.0
8a	(Cp^*H) ^d + 4 Et_3Al + 2 PPh_3	50	1.9707	0.97	4.0

^a Components were mixed in the following order: Ia (0.04 mmol in 2.4 ml of benzene solution), the component indicated in Table, Cp^*H (0.08 mmol in 1.6 ml of benzene solution) and the additional component indicated in Exp. (No. (a)). ^b Eleven-line multiplet $a = 0.575$ mT of $Cp^*TiAl_2Cl_8$. ^c The eleven-line multiplet overlaps a single line. ^d Cp^*H added before Et_3Al . ^e After 8 d.

A black precipitate of $TiCl_2$ separates from the solution which contains the $AlCl_3 \cdot PPh_3$ complex, as indicated by preliminary ^{27}Al NMR spectrometric measurements [27]. $TiCl_2$ did not react with Cp^*H in the absence of free ethylaluminum chlorides (Table 2, No. 1). The presence of unchanged Ia after reaction (experiment 2, Table 2) was observed in the electronic absorption spectrum of the system (for the spectrum see ref. 11). Ia yielded $Cp^*TiAl_2Cl_8$ after the addition of Cp^*H . In the systems containing an excess of Et_xAlCl_{3-x} ($x = 1, 2$), the composition of the $Cp^*TiAl_2Cl_{8-y}Et_y$ complexes obtained after addition of Cp^*H (eq. 1) changed on addition of PPh_3 in the same way as described above, indicating the formation of $EtAlCl_2 \cdot PPh_3$ in experiments 4–6 (Table 2). The reaction of Ia with 4 equiv. of Et_3Al led to quantitative precipitation of $TiCl_2$ [12], which only slowly and incompletely reacted with the added Cp^*H (Table 2, No. 7). On the other hand, addition of 4 equiv. of Et_3Al to the Ia + Cp^*H system quantitatively converted the $Cp^*TiAl_2Cl_8$ complex formed into $Cp^*TiAl_2Cl_4Et_4$ (Table 2, No. 8). Subsequent addition of 2 equiv. of PPh_3 resulted in the partial decomposition of $Cp^*TiAl_2Cl_4Et_4$, apparently as a result of the presence of Et_3Al , which was formed by the disproportionation of Et_2AlCl and removal of $EtAlCl_2$ with PPh_3 (Table 2, No. 8,8a). Generally, the results obtained for the Cl:Et composition of the Cp^*Ti^{III} complexes after addition of PPh_3 can be applied to the composition of (benzene) Ti^{II} complexes after the same treatment with PPh_3 , except that the latter decompose when they contain more than 2 Et groups [12,15].

The transformation of both systems, $TiCl_4 + Et_xAlCl_{3-x}$ (+ PPh_3) and Ia + Et_xAlCl_{3-x} (+ PPh_3), into the complexes $Cp^*TiAl_2Cl_{8-y}Et_y$ yields information on the composition of soluble Ti^{II} complexes which are formed in the former systems in the presence of unsaturated hydrocarbons, e.g., butadiene [11,12,13], cycloheptatriene [7], or bis(trimethylsilyl)acetylene [8,9], and which are carriers of the catalytic activity. In the most thoroughly studied cyclotrimerization of butadiene,

addition of PPh_3 changed the catalytic activity and selectivity of the $\text{TiCl}_4 + n \text{EtAlCl}_2$ ($n = 4-10$) systems so that more ethylated catalytic systems were obtained, in general agreement with the results of this work. The extent of ethylation, as reflected in the catalytic properties, corresponds not only to the removal of AlCl_3 but also to the disproportionation of EtAlCl_2 to give Et_2AlCl and $\text{AlCl}_3 \cdot \text{PPh}_3$ [28].

References

- 1 R. Feld and P.L. Cowe, *The Organic Chemistry of Titanium*, Butterworth, London-Washington, D.C., 1965.
- 2 N.G. Gaylord and H. Mark, *Linear and Stereoregular Addition Polymers*, Interscience Publishers, Inc., New York, 1959; M.M.T. Khan and A.E. Martell, *Homogeneous Catalysis by Metal Complexes*, Vol. II, Academic Press, London-New York, 1974.
- 3 P. Heimbach, *Angew. Chem.*, 85 (1973) 1035.
- 4 S. Kitazume and H. Morikawa, *J. Synth. Org. Chem. Japan*, 41 (1983) 154; H. Yasuda and A. Nakamura, *Rev. Chem. Intermed.*, 6 (1986) 365.
- 5 N.E. Schore, *Chem. Rev.*, 88 (1988) 1081.
- 6 F. Calderazzo, F. Marchetti, G. Pampaloni, W. Heller, H. Antropiusová and K. Mach, *Chem. Ber.*, in press.
- 7 K. Mach, H. Antropiusová, L. Petrusová, V. Hanuš, F. Tureček and P. Sedmera, *Tetrahedron*, 40 (1984) 3295.
- 8 K. Mach, H. Antropiusová, L. Petrusová, F. Tureček, V. Hanuš, P. Sedmera and J. Schraml, *J. Organomet. Chem.*, 289 (1985) 331.
- 9 K. Mach, F. Tureček, H. Antropiusová and V. Hanuš, *Organometallics*, 5 (1986) 1215.
- 10 S. Dzierzgowski, R. Gieżyński, S. Pasykiewicz and M. Niżyńska, *J. Mol. Catal.*, 2 (1977) 243.
- 11 J. Poláček, H. Antropiusová, V. Hanuš, L. Petrusová and K. Mach, *J. Mol. Catal.*, 29 (1985) 165.
- 12 J. Poláček, H. Antropiusová, L. Petrusová and K. Mach, *J. Mol. Catal.*, in press.
- 13 J. Poláček, H. Antropiusová, L. Petrusová and K. Mach, *J. Mol. Catal.*, submitted.
- 14 K. Mach, H. Antropiusová and J. Poláček, *J. Organomet. Chem.*, 172 (1979) 325.
- 15 K. Mach, H. Antropiusová and J. Poláček, *J. Organomet. Chem.*, 194 (1980) 285.
- 16 K. Mach, V. Varga, H. Antropiusová and J. Poláček, *J. Organomet. Chem.*, 333 (1987) 205.
- 17 E.J. Arlman and J.P. de Jong, *Rec. Trav. Chim. Pays-Bas*, 79 (1960) 910, 1319.
- 18 L.I. Zakharkin and V.M. Akhmedov, *Zh. Org. Khim.*, 2 (1966) 998.
- 19 H. Roehl, E. Lange, T. Golsal and G. Roth, *Angew. Chem.*, 74 (1962) 155.
- 20 A. Malatesta, *Can. J. Chem.*, 37 (1959) 1176.
- 21 E.H. Adema, H.J.M. Bartelink and J. Smidt, *Rec. Trav. Chim. Pays-Bas*, 81 (1962) 73.
- 22 E.H. Adema, H.J.M. Bartelink and J. Smidt, *Rec. Trav. Chim. Pays-Bas*, 80 (1961) 173.
- 23 G. Herici-Olivé and S. Olivé, *Angew. Chem. Int. Ed.*, 6 (1967) 790.
- 24 J. Poláček, K. Mach and L. Petrusová, *Coll. Czech. Chem. Commun.*, 50 (1985) 2041.
- 25 W.H.N. Vriezen and F. Jellinek, *Rec. Trav. Chim. Pays-Bas*, 89 (1970) 1306.
- 26 D.A. Wierda and A.R. Barron, *Polyhedron*, 8 (1989) 831.
- 27 Z. Černý, personal communication.
- 28 J. Poláček, H. Antropiusová, L. Petrusová and K. Mach, *Coll. Czech. Chem. Commun.*, submitted.