ETHYL-SUBSTITUTED (η^5-CYCLOPENTADIENYL)-BIS(DIHALOALANEDI-μ-HALO)TITANIUM(III) AND (η^6-BENZENE)BIS(DIHALOALANEDI-μ-HALO)TITANIUM(II) CHLORO AND BROMO COMPLEXES

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Summary

Ethyl-substituted trinuclear complexes $CpTiAl_2Cl_{8-x}Et_x$ (x = 1—4) were prepared by the reaction of $CpTiCl_3$ with two equivalents of ethylaluminium compounds. The complexes were characterized by the half-width of their EPR single-line spectra, which decreased from 1.9 mT for x = 1 to 0.85 mT for x = 4, and by the position of their d—d absorption bands. From these data the composition of ethylated titanium complexes formed in the systems $CpTiAl_2$-Cl_8-$Et_{3-x}AlCl_x$ (x = 0, 1, 2) was determined.

In the system $C_6H_6 \cdot TiAl_2Cl_8$-$Et_{3-x}AlCl_x$ the formation of only the first two members of ethylated arenetitanium(II) series $C_6H_6 \cdot TiAl_2Cl_7Et$ and $C_6H_6 \cdot TiAl_2Cl_6Et_2$ could be observed. The latter complexes differed from the parent complex in the position of the charge transfer band $Ti^{II} \rightarrow C_6H_6$ and, after addition of an equimolar amount of cyclopentadiene, the EPR spectra of corresponding $CpTi^{III}$ trinuclear complexes were observed. In both, Ti^{III} and Ti^{II} series, the stability of the complexes decreased with increasing content of ethyl groups. The properties of $CpTi^{III}$ trinuclear complexes are compared with those of the binuclear complexes $Cp_2TiAlCl_{4-x}Et_x$ (x = 0, 1, 2). Results for the series of bromo complexes were mostly analogous.

Introduction

The parent complex of the $CpTi^{III}$ series $CpTiAl_2Cl_8$ (Ia) was prepared for the first time by the reduction of $CpTiCl_3$ with aluminium powder in the presence of $AlCl_3$, and its trinuclear structure I was deduced from the interaction of the Ti^{III} unpaired electron with the two equivalent aluminium nuclei observed in its EPR spectrum [1]. Recently, this complex was found to be formed in the redox reaction of (η^6-benzene)bis(dichloroalanedi-μ-chloro)titanium(II) (IIa)

with an equimolar amount of cyclopentadiene (CpH) [2]. Since the trinuclear structure II of arenetitanium(II) complexes has been confirmed by X-ray structural analysis of the hexamethylbenzene derivative [3], the formation of Ia from IIa supports the structure I. Moreover, the reaction of both types of complexes with a large excess of CpH yielded the well known binuclear Cp_2Ti^{III} complexes of type III [2]. The reactions of Ti^{II} complexes with CpH were used for the EPR determination of the distribution of halogen atoms between bridge and outer positions in benzenetitanium(II) complexes containing various numbers of chlorine and bromine atoms [4].

I II III
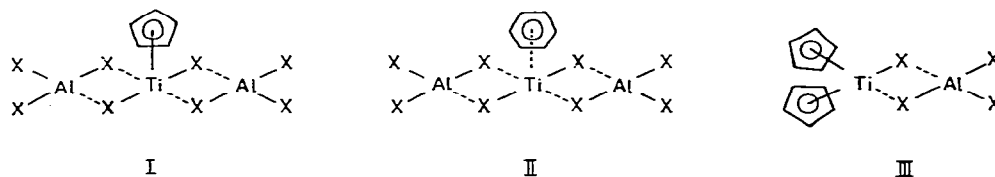
The chloro complex IIa is known to be a good catalyst for butadiene cyclotrimerisation [5], but its activity can be increased by the addition of organoaluminium compounds [6]. Dzierzgowski et al [6] suggested that the higher activity of these systems was brought about by the alkylation of IIa in its outer positions followed by a dissociation to yield a coordinatively unsaturated titanium ion. As the system containing $CpTiCl_3$ in combination with organoaluminium compounds is catalytically active in the polymerisation of olefins [7], the interactions of ethylaluminium compounds with titanium complexes of both types I and II seem worthy of study.

The aim of the investigation described below was to find conditions for formation of ethyl-containing complexes I and II, and to compare their stabilities and spectroscopic properties with those of Cp_2Ti^{III} complexes of type III.

Results and discussion

The formation of ethyl-containing complexes I in the systems $CpTiAl_2Cl_8$-$Et_{3-x}AlCl_x$ ($x = 0, 1, 2$) and ethyl-containing complexes II in systems C_6H_6 · $TiAl_2Cl_8$-$Et_{3-x}AlCl_x$ was studied by means of electronic absorption and EPR spectroscopy. For the application of the EPR method in the latter systems, the EPR inactive complexes of type II had first to be converted into the corresponding complexes of type I by treatment with CpH. The identification of specific complexes by EPR in both systems is thus based on comparison of their EPR spectra with those of the authentic compounds I obtained by the reaction of $CpTiCl_3$ with two equivalents of ethylaluminium compounds. For the identification of binuclear complexes of type III formed with an excess of CpH in both systems, and for a better understanding of the influence of ethyl substitution on the electronic and EPR spectra of the above complexes, the series of complexes $Cp_2TiAlCl_{4-x}Et_x$ ($x = 0, 1, 2$) was also prepared and examined by electronic and EPR spectroscopy. The spectroscopic data for all the chloro and analogous bromo complexes obtained in this study are collected in Table 1. Representative electronic absorption spectra of complexes Ia, IIa, and IIIa are shown in Fig. 1.

TABLE 1

SPECTRAL CHARACTERISTICS OF Ti-Al COMPLEXES

Complex	EPR (mT)				electronic (nm)	
	g	a_{Ti}	a_{Al}	ΔH	CT	$d-d$
Ia	1.9726	1.5	0.58	—	370, 415 sh	670
Ia-1	1.9728	1.5	—	1.9	365, 405 sh	690
Ia-2	1.9730	1.5	—	1.4	358, 400 sh	705
Ia-3	1.9730	1.5	—	1.2	350, 390 sh	715
Ia-4	1.9730	1.5	—	0.85		
Ib	1.988		—	3.8	395 [a]	690
Ib-1	1.990		—	2.7	370 [a]	705
Ib-2	1.990		—	2.4	360, 400 sh	712
IIa					398	560, 810
IIa-1					404	560, 810
IIa-2					411	560, 810
IIb					403	576, 856
IIb-1					410	576, 856
IIb-2					415	576, 856
IIIa	1.975	1.18	0.70	—		660
IIIa-1	1.976	1.18	0.35	—		675
IIIa-2	1.977	1.20	—	1.0 [b]		685
IIIb	1.985	1.18	0.78	—		660
IIIb-1	1.988	1.17	—	1.8 [b]		680
IIIb-2	1.990	1.17	—	0.9		690

ΔH, peak-to-peak in the 1st derivative spectrum.

sh, shoulder.

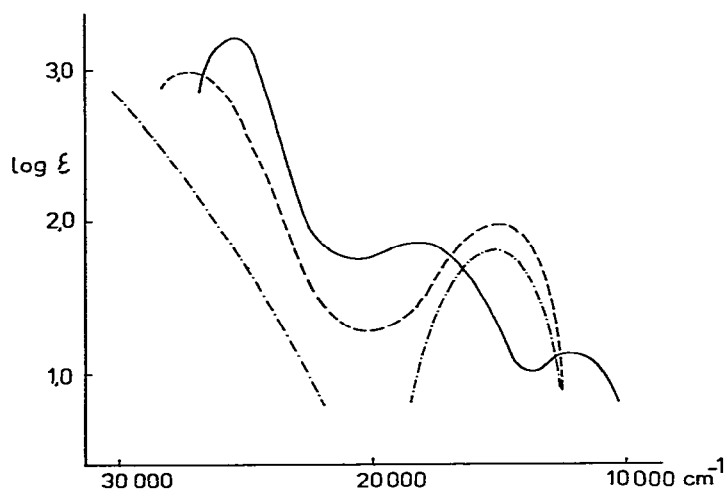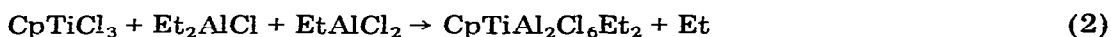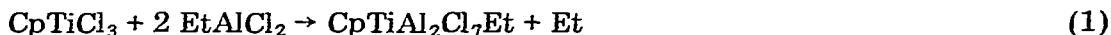[a] The band at 400 nm overlapped. [b] Badly resolved doublet.

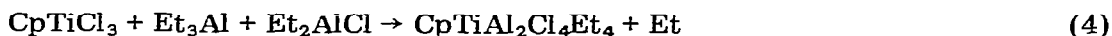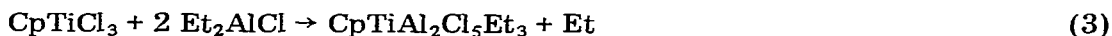Fig. 1. Electronic absorption spectra of benzene solutions of Ia — — —, IIa ————, and IIIa · — · — ·.

Ethyl-substituted (η^5-cyclopentadienyl)bis(dihaloalanedi-μ-halo)titanium(III) complexes

Complexes of this type were readily obtained by the stoichiometric reduction of $CpTiCl_3$ in the presence of two equivalents of ethylaluminium compounds. This method, mentioned also by Dzhabiev and Shilov [8], gave the pure compounds $CpTiAl_2Cl_7Et$ (Ia-1) and $CpTiAl_2Cl_6Et_2$ (Ia-2) quantitatively according to equations 1 and 2.

$$CpTiCl_3 + 2\ EtAlCl_2 \rightarrow CpTiAl_2Cl_7Et + Et \qquad (1)$$

$$CpTiCl_3 + Et_2AlCl + EtAlCl_2 \rightarrow CpTiAl_2Cl_6Et_2 + Et \qquad (2)$$

Both compounds were obtained as green crystals by cooling of their n-hexane solutions.

The compounds $CpTiAl_2Cl_5Et_3$ (Ia-3) and $CpTiAl_2Cl_4Et_4$ (Ia-4) were obtained in benzene solution according to equations 3 and 4.

$$CpTiCl_3 + 2\ Et_2AlCl \rightarrow CpTiAl_2Cl_5Et_3 + Et \qquad (3)$$

$$CpTiCl_3 + Et_3Al + Et_2AlCl \rightarrow CpTiAl_2Cl_4Et_4 + Et \qquad (4)$$

The dirty green benzene solution of Ia-3 was indefinitely stable at room temperature, but after evaporation of the benzene in vacuo or addition of a large amount of n-hexane, a red precipitate, insoluble in n-hexane and in benzene, was obtained. The formation of Ia-4 was accompanied by partial decomposition even in benzene solution. The original green colour of the solution turned quickly to brown and after several hours brown and red precipitates appeared on the ampoule walls. The complex decomposed quantitatively during evaporation of the benzene or upon the addition of n-hexane. The electronic and EPR spectra were taken as soon as possible after the preparation of the complex. The green-brown solution examined after 20 min showed absorption bands characteristic of other complexes of the series, though the exact positions could not be determined because they are overlapped by the continuous absorption which decreases in intensity towards longer wavelengths. No change of the EPR spectrum was observed during 40 min after the preparation of the complex.

The EPR spectra of the ethylated complexes derived from Ia appeared at $g = 1.9726$—1.9730 and the coupling to aluminium nuclei, well resolved in Ia, decreased sharply upon ethyl substitution. For complexes Ia-1—Ia-4 only single-line EPR spectra were observed, differing in their half-width from $\Delta H = 1.9$ mT for Ia-1 to $\Delta H = 0.85$ mT for Ia-4 (see Fig. 2 and Table 1). All these complexes were further characterized by coupling to ^{47}Ti (nat. abund. 7.7%, $I = 5/2$) and ^{49}Ti (nat. abund. 5.5%, $I = 7/2$) nuclei observed in about 30-times weaker wings of the EPR spectra. The constant value of $a_{Ti} = 1.5$ mT for both isotopes was found in all complexes derived from Ia.

In the electronic absorption spectra of complexes Ia-1—Ia-4 the d—d absorption band at about 700 nm is gradually shifted to longer wavelengths and broadened. Simultaneously the charge transfer bands occuring in Ia at 370 nm and 415 nm are shifted to shorter wavelengths (Table 1).

Systems $CpTiAl_2X_8$-$Et_{3-x}AlX_x$ ($X = Cl$, Br)

The exchange reaction of the ethylaluminium compounds Et_2AlCl, Et_3Al
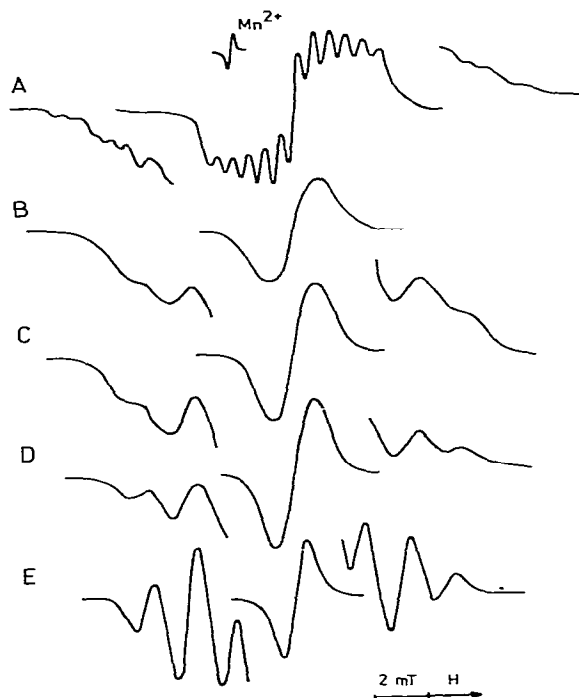
Fig. 2. EPR spectra of CpTi^{III} complexes: Ia, A; Ia-1, B; Ia-2, C; Ia-3, D; and Ia-4, E (g(Mn^{2+}) = 1.980, wing spectra amplified by factor 32).

and EtAlCl$_2$ with Ia gives rise to the ethylated compounds characterized above and therefore their equilibrium composition can be estimated from the ΔH of their EPR spectra and from the positions of their $d–d$ absorption bands.

The interaction between Ia and Et$_2$AlCl at ratios of <1 resulted in the gradual replacement of Ia by Ia-1, as observed by overlapping of eleven-line and single-line signals in the EPR spectra of reacting solutions. At an Al/Ia ratio of 1, only the single-line EPR spectrum of ΔH = 1.9 mT was observed, showing that Ia-1 was formed according to equation 5.

$$Ia + Et_2AlCl \rightarrow Ia\text{-}1 + EtAlCl_2 \tag{5}$$

The complete transformation of Ia into Ia-2 required a considerable excess of Et$_2$AlCl over the stoichiometry shown in equation 6.

$$Ia + 2\ Et_2AlCl \rightarrow Ia\text{-}2 + 2\ EtAlCl_2 \tag{6}$$

An Al/Ia ratio of 4 was necessary to reach the narrowing of the EPR line to half-width ΔH = 1.4 mT appropriate to Ia-2. The further addition of Et$_2$AlCl up to a 100-fold excess changed ΔH to 1.35 mT, indicating the possible presence of a minor amount of Ia-3.

The addition of one equivalent of Et$_3$Al to Ia yielded a mixture of Ia-1 and Ia-2 according to equilibrium 7.

$$Ia + Et_3Al \rightarrow Ia\text{-}1 + Et_2AlCl \rightleftharpoons Ia\text{-}2 + EtAlCl_2 \tag{7}$$

At an Et_3Al/Ia ratio of 2, the complex Ia-2 contained some Ia-3 formed in the equilibrium 8.

$$Ia + 2Et_3Al \rightarrow Ia\text{-}2 + 2\ Et_2AlCl \rightleftharpoons Ia\text{-}3 + Et_2AlCl + EtAlCl_2 \tag{8}$$
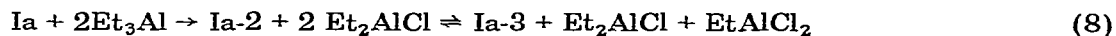
The optimum Et_3Al/Ia ratio for obtaining Ia-2 was about 1.8. The complex Ia-3 was obtained at an Et_3Al/Ia ratio of 3, according to equation 9.

$$Ia + 3\ Et_3Al \rightarrow Ia\text{-}3 + 3\ Et_2AlCl \tag{9}$$
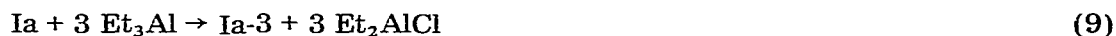
At an Et_3Al/Ia ratio of 4 the narrowing of ΔH to 0.85 mT proved the presence of Ia-4, but the solution was unstable; it quickly turned brown, and brown material precipitated slowly from solution.

In the system $Ia\text{-}EtAlCl_2$ the eleven-line EPR spectrum of Ia was only partially overlapped by the single line of Ia-1 at a 20-fold excess of $EtAlCl_2$. This means that the equilibrium 10 is shifted strongly to the left hand side.

$$Ia + EtAlCl_2 \rightleftharpoons Ia\text{-}1 + AlCl_3 \tag{10}$$

In these systems, exchange of ethyl groups of organoaluminium compounds for chlorines of titanium trinuclear complexes and exchange of free and complexed ethylaluminium chlorides is proposed. The former process proceeds readily when the number of ethyl groups in the free organoaluminium compounds and on each aluminium atom in the titanium complex differ by at least two. The latter processes governs the final composition of the trinuclear complexes, because the aluminium compounds containing fewer ethyl groups after the exchange are stronger electron acceptors and are more strongly bound to titanium ions than more ethylated aluminium compounds. For example, ethylaluminium dichloride formed in reaction 6 prevents the further exchange with an excess of diethylaluminium chloride which would lead to Ia-3.

In the series of bromo complexes derived from $CpTiAl_2Br_8$ (Ib) the results of the exchange reactions with Et_2AlBr and Et_3Al were analogous in part. Though there was no direct comparison with independently prepared ethylated $CpTi^{III}$ complexes, both the narrowing of EPR signals and the corresponding shifts of the $d\!-\!d$ absorption band upon addition of ethylaluminium compounds gave reliable evidence for formation of Ib-1 and Ib-2. After addition of an equimolar amount of Et_2AlBr to Ib the original EPR broad line of $\Delta H = 3.8$ mT was replaced by a single line of $\Delta H = 2.7$ mT probably from Ib-I. A further narrowing of the EPR signal accompanied by the shift of the $d\!-\!d$ band observed at higher Al/Ib ratio may indicate the presence of Ib-2 (see Table 1). On the other hand, under conditions suitable for formation of the complex $CpTiAl_2Br_5Et_3$ (Ib-3), e.g. for $Et_3Al/Ib = 2\!-\!3$, the badly resolved multiline EPR spectrum overlapped the single-line spectrum and for $Et_3Al/Ib = 3\!-\!4$ the complex $Cp_2Ti\text{-}AlBr_2Et_2$ (IIIb-2) was observed as the main paramagnetic product and the formation of a red-brown precipitate was observed. The explanation of the multiline spectrum and the confirmation of what is probably a disproportionation of the trinuclear tetraethyl complex, e.g. according to equation 11, would require further study.

$$2\ CpTiAl_2Br_4Et_4 \rightarrow Cp_2TiAlBr_2Et_2 + TiBr_3 + 3\ Et_2AlBr \tag{11}$$

Ethyl-substituted (η^6-benzene)bis(dihaloalanedi-μ-halo)titanium(II) complexes

Ethyl derivatives of complexes $C_6H_6 \cdot TiAl_2Cl_8$ (IIa) and $C_6H_6 \cdot TiAl_2Br_8$ (IIb) were formed in the exchange reaction of the parent complexes with ethyl-aluminium compounds. Since the ethylated complexes could not be isolated, the evidence for their formation was obtained from the measurement of electronic absorption spectra of reaction mixtures and from the EPR measurement of CpTi^{III} complexes of type I obtained by treating the above reaction mixtures with CpII.

Ethyl substitution changed the colour of benzene solutions of IIa (purple) and IIb (blue) towards green because of the shift of the $Ti^{II} \rightarrow C_6H_6$ charge transfer band ($\epsilon \sim 10^3$) at 400 nm [9] to longer wavelengths (see Table 1). The positions of the d—d absorption bands at 560—570 nm ($\epsilon \sim 70$) and at 810 nm ($\epsilon \sim 10$) were not sensitive to the presence of ethyl groups.

The indirect EPR method used the redox reaction of arenetitanium^{II} complexes with an equimolar amount of CpH [2] to convert the EPR inactive complexes of type II into complexes of type I, which are easily identified by EPR, by the reaction shown in equation 12.

$$II + CpH \rightarrow I + C_6H_6 + H \tag{12}$$

It can be assumed that the extent of ethyl substitution in complexes of type II does not differ from that in appropriate complexes of type I, since the red shifts of the charge transfer band of the former complexes correspond with the narrowing of the EPR spectra of the latter. The results obtained from the EPR and electronic spectra of the system IIa-Et$_2$AlCl-CpH were identical with those obtained from the system Ia-Et$_2$AlCl at the same Al/Ti ratios, and so the electronic spectra observed in the system IIa-Et$_2$AlCl at Al/IIa ratios of 1 and 4 (see Table 1) can be ascribed to complexes $C_6H_6 \cdot TiAl_2Cl_7Et$ (IIa-1) and $C_6H_6 \cdot TiAl_2Cl_6Et_2$ (IIa-2), respectively. The dark green benzene solutions of this system were stable up to 50°C even at a 100-fold excess of Et$_2$AlCl. However, all attempts to precipitate these complexes by addition on n-hexane resulted in the decomposition of both complexes. After precipitation and washing with n-hexane the dark material was insoluble in benzene. The same complexes were also obtained upon addition of Et$_3$Al at Al/Ti ratios indicated above for the formation of Ia-1 and Ia-2. The addition of two or more equivalents of Et$_3$Al led to the decomposition of arenetitanium(II) complexes, yielding a brown precipitate. This means that the arenetitanium(II) complexes containing more than two ethyl groups are not stable in benzene solution at room temperature.

In the system IIa-EtAlCl$_2$ no shift of the charge transfer band was observed at Al/IIa = 1 and at the 20-fold excess of EtAlCl$_2$ this band only moved from 398 nm for IIa to 400 nm. Together with the minor amount of Ia-1 observed after CpH treatment, this shows that the initial components are prefered in the equilibrium mixture.

The systems IIb-Et$_2$AlBr and Et$_3$Al behaved analogously to those derived from IIa. The formation of IIb-1 and IIb-2 was proved both by the observation of EPR signals ascribed to Ib-1 and Ib-2 after treatment with CpH and by red shifts of the charge transfer band similar (Table 1) to those of IIa-1 and IIa-2.

Ethyl-substituted bis(η^5-cyclopentadienyl(dihaloalanedi-µ-halo)titanium(III) complexes and their formation in the reaction of complexes I and II with an excess of CpH

The complexes $Cp_2TiAlCl_4$ (IIIa), $Cp_2TiAlCl_3Et$ (IIIa-1), and $Cp_2TiAlCl_2Et_2$ (IIIa-2) and their bromo analogues IIIb, IIIb-1, and IIIb-2 were prepared by the reduction of Cp_2TiCl_2 and Cp_2TiBr_2, respectively, by equivalent amounts of ethylaluminium compounds [10,11,12], e.g. according to equation 13.

$$Cp_2TiCl_2 + Et_3Al \rightarrow Cp_2TiAlCl_2Et_2 + Et \qquad (13)$$
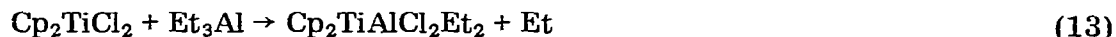
The parameters of EPR spectra of all complexes are given in Table 1. The EPR spectra of all chloro complexes and IIIb agree with those described in the literature [10—12]; the spectra of IIIb-1 and IIIb-2, which have not previously been described, show the usual characteristic of a narrowing of the EPR signals with increasing ethyl substitution. In the electronic spectra of the binuclear complexes, ethyl substitution moved the *d—d* band to longer wavelengths as described for complexes of type I. The main difference between these two types of complexes was the considerable shift of the charge transfer band in type III to shorter wavelengths (see Fig. 1).

A knowledge of properties of type III complexes was necessary for the study of the transformation of ethyl-substituted trinuclear complexes into binuclear ones by reaction with a large excess of CpH. The replacement of the tetrahaloalane ligand by the cyclopentadienyl ligand yielded free aluminium halide and hydrogen halide according to equation 14 [2].

$$CpTiAl_2Cl_8 + CpH \rightarrow Cp_2TiAlCl_4 + AlCl_3 + HCl \qquad (14)$$
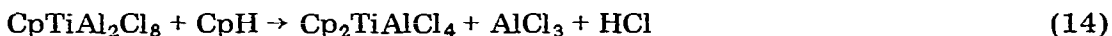
With ethyl-substituted complexes the hydrogen chloride formed will cleave ethyl groups from the binuclear complexes, and so complex IIIa is expected to be formed from Ia-1 and Ia-2 according to equation 15.

$$CpTiAl_2Cl_6Et_2 + CpH \rightarrow Cp_2TiAlCl_4 + EtAlCl_2 + EtH \qquad (15)$$

In fact, the transformation of Ia-1 to IIIa proceeded as with Ia when about a one hundred-fold excess of CpH was used; a much of the CpH polymerised under the catalytic action of $AlCl_3$ and HCl. The green solution of Ia-1 turned to a yellow viscous liquid, showing the strong absorption band at 420 nm due to cyclopentadiene cationic species. The EPR spectrum of the solution showed the six-line signal of IIIa. For the transformation of Ia-2 its more diluted solution in benzene (10^{-4} M) had to be used since a much faster polymerisation of CpH occurred in this system. The transformation was usually complete when the stirred solution of Ia-2 turned to a gelatinous solid. After standing overnight a nearly colourless liquid was released by the gel. Both the liquid as well as the gel showed the EPR spectrum of IIIa with only traces of IIIa-1. Exactly the same results were obtained with the corresponding complexes IIa-1 and IIa-2, and analogous results with the bromo complexes.

The same procedure with complexes Ia-3 and Ia-4 led to the solidification of solutions due to the formation of CpH polymer, though the EPR spectra revealed the presence of the original trinuclear complexes with only a minor admixture of IIIa-1. It is suggested that these trinuclear complexes are very efficient catalysts for CpH polymerisation, so that all the CpH is polymerized

before replacing the $AlCl_4$ ligand. The formation of IIIa-1 is probably the termination of the catalytic polymerisation process.

Comparison of properties of complexes

The stabilities of the three types of complexes can be estimated from their behavior in the solid state and in benzene solution. They increase in the order II < I < III and within each type of complexes they decrease with increasing number of ethyl groups, as shown graphically in Fig. 3 for chloro complexes. Judging from the behavior of complexes I containing more than two ethyl groups, the bromo complexes must be less stable than the chloro complexes. The fact that the complexes Ia-3, Ia-4, IIa-1 and IIa-2 are stable only in benzene solution may be the result of coordination of a benzene molecule in the position opposite to the π-bonded ligand. This benzene molecule is easily removed by dilution with n-hexane, and the complexes decompose.

The nearly constant *g*-values in the series of complexes I and III, respectively, prove that the ethyl groups enter only the outer positions of the complexes. This conclusion can be extended to the type II complexes, because their cyclopentadienylation does not change the structural frame of the complex [4]. The electron donating ability of ethyl groups lowers the unpaired electron density on aluminium atoms [10], as is demonstrated by narrowing of EPR spectra of both types of ethylated complexes I and III. While the coupling of the unpaired electron to aluminium nuclei ($I = 5/2$) can be observed in complexes Ia, IIIa, IIIa-1, and IIIb as multiline spectra, in all other ethylated complexes this coupling is responsible for the different half-widths of their single-line spectra. In complexes giving sufficiently narrow EPR lines the coupling constants for ^{47}Ti and ^{49}Ti nuclei could be determined from the measurement of the approximately 30-times weaker wing spectra (Fig. 2). Their values given in Table 1 indicate that the electron density on the titanium nucleus is higher in trinuclear ($a_{Ti} \sim 1.5$ mT) than in binuclear complexes ($a_{Ti} \sim 1.2$ mT). The lower a_{Ti} and higher *g*-value in binuclear complexes can be accounted for in terms of the greater delocalisation of the unpaired electron in the second Cp ligand, but there was only a poor linear reciprocal correlation between g_{av} and a_{Ti} values in the series of axially distorted Ti^{III} complexes [13]. Comparing complexes IIIa and IIIb gave no correlation, as g(IIIb) was much higher than g(IIIa) while a_{Ti} was the same in both series of complexes. Complexes Ib probably yield the poorest agreement with the g_{av}/a_{Ti} correlation because

$Cp_2TiAlCl_{4-x}Et_x$

$CpTiAl_2Cl_{8-x}Et_x$

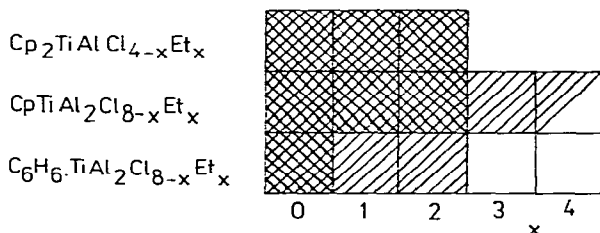$C_6H_6.TiAl_2Cl_{8-x}Et_x$

0 1 2 3 4

x

Fig. 3. Stabilities of titanium chloro complexes: crossed area, stable in benzene solution and in solid state; linked area, stable in benzene solution and decomposed by the precipitation with n-hexane; blank area, unstable in benzene solution.

g-values for IIIb and Ib complexes are nearly the same but a_{Ti} in Ib complexes are estimated from the broad spectral wings to be in the range 1.5 mT, as in Ia complexes.

In view of the results obtained from EPR spectra it is interesting that the replacement of the haloalane ligand in complexes of type I by Cp ligand does not induce any notable shift of the d—d absorption band, though the ethyl substitution in outer positions of complexes I and III shifts this band observably to longer wavelengths. In complexes of type II, ethyl substitution resulted in a red shift of the charge transfer band which must reflect the enhanced electron-donating ability of Ti^{II} [9] and loosening of the Ti^{II}-C_6H_6 bond. This accounts for the easy decomposition of ethylated complexes of type II upon dilution of their benzene solutions by aliphatic hydrocarbons. The different electron donor abilities of a series of Ti^{II} complexes could not be followed by measuring of the rate of electron transfer to CpH because this was too fast, but a simultaneous kinetic study of butadiene cyclotrimerisation revealed that initial rates of butadiene consumption increased with increasing Et_2AlCl/IIa ratio. This result can be considered as evidence for higher electron donation of ethylated arenetitanium(II) complexes on the assumption that the initial step of the butadiene cyclotrimerisation involves the electron transfer $Ti^{II} \rightarrow$ butadiene.

Experimental

Chemicals

Cp_2TiCl_2 (Schuchardt, München) and $CpTiCl_3$ (Pierce Inorganic) were used without purification. Cp_2TiBr_2 was prepared by the reaction of $TiBr_4$ with CpNa in THF and crystallised from toluene. $AlCl_3$ was prepared by heating fine aluminium turnings in CCl_4 vapour and sublimed in vacuo. A white product was obtained after melting $AlCl_3$ with aluminium powder in sealed ampoule. EtAl-Cl_2, Et_2AlCl, Et_2AlBr and Et_3Al were prepared by standard methods using argon and vacuum lines [14] and their purity was checked by infrared spectroscopy [15]. Benzene and n-hexane were refluxed with $LiAlH_4$, treated with IIa and stored on a vacuum line as solutions of "dimeric titanocene". CpH was obtained by thermolysis of dicyclopentadiene and stored on vacuum line as a solution of "dimeric titanocene" at liquid nitrogen temperature.

Procedures

The high-vacuum technique was used for all operations and determinations of electronic absorption and EPR spectra.

Complexes IIa and IIb were prepared as described elsewhere [9]. Complexes Ia and Ib were prepared by adding equivalent amounts of gaseous CpH to benzene solutions (10^{-2} M) of IIa and IIb. Their purity was checked by EPR and electronic spectra, the absence of IIIa and IIIb being specifically confirmed.

Complexes Ia-1—Ia-4 used as standards were prepared by mixing of benzene solutions of $CpTiCl_3$ and two equivalents of ethylaluminium compounds. The following organoaluminium compounds were used for preparations: 2 $EtAlCl_2$, Ia-1; $EtAlCl_2$ + Et_2AlCl, Ia-2; 2 Et_2AlCl, Ia-3; and Et_2AlCl + Et_3Al, Ia-4.

Complexes IIIa-1, IIIa-2, IIIb-1 and IIIb-2 were obtained by the reduction of

Cp_2TiCl_2 and Cp_2TiBr_2, respectively, with equimolar amounts of Et_2AlCl, Et_2-$AlBr$ and Et_3Al in benzene. Complexes were purified by removing all the benzene in vacuo and crystallisation from n-hexane at $-70°C$. Complexes IIIa and IIIb were prepared by mixing benzene solutions of IIIa-1 or IIIb-1, with an excess of aluminium halide to avoid reduction by $EtAlX_2$ [10]. Products were crystallized by adding n-hexane to their concentrated benzene solutions.

Systems IIa, IIb-ethylaluminium compounds were treated with the equimolar amounts of gaseous CpH as described earlier [2] and complexes of type I were formed immediately. Additions of an 100—1000-fold excess of CpH to benzene solutions ($10^{-2}—10^{-4}$ M) of complexes Ia-1—Ia-4, systems Ia, Ib-ethylaluminium compounds or systems IIa, IIb-ethylaluminium compounds were carried out with rapid stirring with a glass-covered magnetic stirrer. The reactions took several hours to reach equilibrium, depending on the amount of CpH polymerised.

Methods

EPR spectra were measured on an ERS-220 spectrometer (Centre for Production of Scientific Instruments, German Acad. Sci., Berlin, GDR) in the X-band at room temperature. For the measurement of the half-widths of signals the solutions of complexes were diluted to 10^{-3} M.

Electronic absorption spectra were recorded on an Optica Milano CF-4N spectrometer in the 320—1000 nm region using sealed quartz cells.

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