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Methyl-substituted cyclopentadienyl ligands: influence on the properties of titanocene chloro(ethyl)aluminates

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Abstract

The binuclear complexes $\bar{C}p_2TiCl_2AlCl_{2-x}Et_x$ ($\bar{C}p$ = Cp, MeCp, Me_3Cp, Me_4Cp and Me_5Cp; $x = 0$–2) were prepared from $\bar{C}p_2TiCl_2$ by reduction with ethylaluminium compounds Et_xAlCl_{3-x} ($x = 1$–3) and/or from $\bar{C}p_2TiCl$ by addition of aluminium compounds Et_xAlCl_{3-x} ($x = 0$–2). The reductive method did not yield the complexes $(Me_5Cp)_2Ti(AlCl_4)$ and $(Me_5Cp)_2Ti(AlCl_3Et)$ and gave only low yields of complexes containing 3 or 4 Me groups in the $\bar{C}p$ ligand and no or one Et group in the aluminate ligand. All these complexes were prepared by the addition method except $(Me_4Cp)_2Ti(AlCl_4)$ which reacted rapidly with excess $AlCl_3$ to give $(Me_4Cp)Ti(AlCl_4)_2$. On going from the Cp to Me_3Cp binuclear complexes the electronic effect of the Me groups decreased the rate of their formation in the reduction reaction, shifted their $\lambda_{max}(d\text{–}d)$ to shorter wavelengths, increased their g-value and the a_{Al} coupling constant and decreased the $a_{Ti(7/2)}$ coupling constant. It was suggested that the steric effect was responsible for a considerable deviation from these correlations in the Me_5Cp complexes, showing an extremely low g-value and $\lambda_{max}(d\text{–}d)$ at very long wavelengths.

Introduction

Recently we established that the methyl substituents on the cyclopentadienyl ligand influence the stability of the trinuclear complexes $\bar{C}pTiAl_2Cl_{8-x}Et_x$ ($\bar{C}p$ = Cp, MeCp, Me_3Cp, Me_4Cp and Me_5Cp; $x = 0$–4) and the parameters of their ESR and electronic absorption spectra [1]. A good correlation between the number of Me groups and the rate constant of reaction 1 was found, demonstrating that substitution by Me groups decreases the capability of the Ti^{IV}–Et intermediate complex to eliminate the Et group.

$$\bar{C}pTiCl_3 + 2\ Et_xAlCl_{3-x} \rightarrow \bar{C}pTiAl_2Cl_{8-2x+1}Et_{2x-1} + Et^{\cdot}\ (x = 1, 2) \quad (1)$$

$$\bar{C}p_2TiCl_2 + Et_xAlCl_{3-x} \rightarrow \bar{C}p_2Ti(AlCl_{4-x+1}Et_{x-1}) + Et^{\cdot}\ (x = 1\text{–}3) \quad (2)$$

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The analogous reaction 2 yielding the binuclear complexes $\bar{C}p_2Ti(AlCl_{4-x}Et_x)$ ($x = 0$–2) was thoroughly studied for unsubstituted titanocene dichloride in consequence of the discovery that the system Cp_2TiCl_2–Et_2AlCl had catalyzed the polymerization of ethylene as the first soluble titanium catalyst [2,3]. Formation of the intermediate Ti^{IV} complex $Cp_2Ti(Et)Cl_2Al(Et)Cl$ (I) in reaction 2 was deduced from the visible spectra of the reacting system Cp_2TiCl_2–Et_2AlCl [4]. The comparison of the ESR spectrum intensity with the kinetics of ethylene polymerization in the systems Cp_2TiCl_2–Et_2AlCl and $EtAlCl_2$ led to the conclusion that the polymerization proceeds by ethylene insertion into the Et–Ti bond of I while the ethyl elimination gives the Ti^{III}–Al binuclear complex [5]. The X-ray structure analysis proved that the Ti–Al bonding in $Cp_2TiCl_2AlEt_2$ is effected through two bridging chlorine atoms [6]. The ESR studies showed that the unpaired electron density is delocalized over the aluminium nucleus and that the extent of this delocalization is suppressed by the electron-donating effect of ethyl substituents in the aluminate ligand [7–11].

The Me substituents in the $\bar{C}p$ ligands of the $\bar{C}p_2TiCl_2$ compounds influence the energy of both the valence [12] and the inner shell electrons [13] through the inductive and hyperconjugation effects and as a result they decrease the oxidation potential e.g., in $(Me_5Cp)_2TiCl_2$ by as much as 0.5 V [13]. The greater bulkiness of the Me_5Cp ligands did not influence the angle contained by them in $(Me_5Cp)_2TiCl_2$ with respect to Cp_2TiCl_2 [14], however, there are indications of differing stereoselectivity of isomerization [15,16] and oligomerization reactions [17] catalyzed by low-valent, highly methylsubstituted titanocene derivatives.

Therefore we found it to be of interest to study the preparation of the $\bar{C}p_2Ti(AlCl_{4-x}Et_x)$ ($x = 0$–2) complexes according to reaction 2 or, where it failed, by addition of aluminium compounds to $\bar{C}p_2TiCl$, and to follow the influence of Me substituents on the ESR and electronic absorption spectra of the complexes in order to reveal the nature of the Me substituent effects.

Results and discussion

Formation of the $\bar{C}p_2Ti(AlCl_4{}_{-x}Et_x)$ ($x = 0$–2) complexes from $\bar{C}p_2TiCl_2$ by reduction with Et_xAlCl_{3-x} ($x = 1$–3)

The complexes $\bar{C}p_2Ti(AlCl_2Et_2)$, $\bar{C}p_2Ti(AlCl_3Et)$ and $\bar{C}p_2Ti(AlCl_4)$ were formed in high yields by the addition to the $\bar{C}p_2TiCl_2$ solution in benzene of equimolar quantities of Et_3Al, Et_2AlCl and $EtAlCl_2$, respectively, only if the $\bar{C}p_2TiCl_2$ compounds contained a low number of Me groups and/or the ethylaluminium compounds contained a low number of chlorine atoms. In cases where the binuclear complexes were not formed quantitatively they were accompanied by diamagnetic by-products only. This allowed us to follow the course of reaction 2 and to determine the yields of the binuclear complexes by quantitative ESR spectroscopy. The yields of complexes, rate constants for their formation and colours of the reaction solutions are listed in Table 1.

Reaction 2 proceeded stoichiometrically in all $\bar{C}p_2TiCl_2$–Et_3Al systems except that containing $(Me_5Cp)_2TiCl_2$. The reaction rates in 0.01 *M* solutions were generally very high so that the rate constant could be determined only for the slowest system $(Me_3Cp)_2TiCl_2$–Et_3Al. The reaction rates decreased from Cp_2TiCl_2

Table 1

Colours of the $\overline{\mathrm{Cp}}_2\mathrm{TiCl}_2$–$\mathrm{Et}_x\mathrm{AlCl}_{3-x}$ ($x = 1$–3) systems and rates of formation and yields of the $\overline{\mathrm{Cp}}_2\mathrm{Ti(AlCl}_{4-x}\mathrm{Et}_x)$ ($x = 0$–2) complexes therefrom [a]

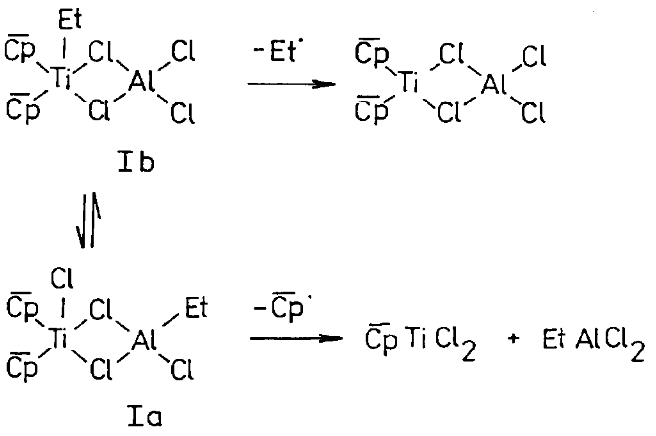
$\overline{\mathrm{Cp}}$	EtAlCl_2		$\mathrm{Et}_2\mathrm{AlCl}$			$\mathrm{Et}_3\mathrm{Al}$		
	Colour	Yield [b] (%)	Colour	Rate constant k [c]	Yield [b] (%)	Colour	Rate constant k [c]	Yield [b] (%)
Cp	blue	100	blue	1.8×10^{-2}	100	blue	V	100
MeCp	blue	100	blue	1.0×10^{-3}	100	blue	V	100
$\mathrm{Me}_3\mathrm{Cp}$	brown	20	green	1.4×10^{-4}	85	blue	0.14	100
$\mathrm{Me}_4\mathrm{Cp}$	brown	20	green	1.4×10^{-4}	85	turqoise	Λ	100
$\mathrm{Me}_5\mathrm{Cp}$	brown [d]	0	yellow green	—	0	green	Λ	85

[a] [Ti] = 0.01 M, $\{\mathrm{Et}_x\mathrm{AlCl}_{3-x}\} = 0.01$ M, solvent benzene, temperature 23±0.5 °C. [b] Determined by the ESR method within an accuracy of ±5%. [c] The rate constant k determined from the half-life of reaction 2: $k = 1/(\tau_{1/2}\cdot[\mathrm{Ti}]^n)$ 1 mol^{-1} s^{-1} ($n < 1$). [d] Purple oily precipitate was separated on glass walls.

to $(\mathrm{Me}_3\mathrm{Cp})_2\mathrm{TiCl}_2$, however, the rates for the $\mathrm{Me}_4\mathrm{Cp}$ and $\mathrm{Me}_5\mathrm{Cp}$ derivatives were considerably higher. This is in sharp contrast to the regularly decreasing rates from the Cp to $\mathrm{Me}_5\mathrm{Cp}$ derivatives in the analogous reaction 1 of the $\overline{\mathrm{Cp}}\mathrm{TiCl}_3$ compounds yielding the trinuclear complexes [1].

The reactions of $\overline{\mathrm{Cp}}_2\mathrm{TiCl}_2$ with $\mathrm{Et}_2\mathrm{AlCl}$ yielded the $\overline{\mathrm{Cp}}_2\mathrm{Ti(AlCl}_3\mathrm{Et)}$ complexes in all cases except the $\mathrm{Me}_5\mathrm{Cp}$ derivative. The rate constants decreased from the Cp to the $\mathrm{Me}_3\mathrm{Cp}$ compound but the rate constants for the $\mathrm{Me}_4\mathrm{Cp}$ and $\mathrm{Me}_3\mathrm{Cp}$ derivatives were practically the same. The $(\mathrm{Me}_5\mathrm{Cp})_2\mathrm{TiCl}_2$–$\mathrm{Et}_2\mathrm{AlCl}$ system gave very rapidly a mixture of two paramagnetic substances in about 50% yield. These substances formed a single line at $g = 1.9705$, resembling the spectrum of $(\mathrm{Me}_5\mathrm{Cp})_2\mathrm{Ti(AlCl}_2\mathrm{Et}_2)$ (see later) and a sextuplet at $g = 1.9750$, $a_{\mathrm{Al}} = 1.0$ mT. The latter species was not the product of disproportionation of $(\mathrm{Me}_5\mathrm{Cp})_2\mathrm{Ti(AlCl}_3\mathrm{Et)}$ because its a_{Al} was much higher than that of $(\mathrm{Me}_5\mathrm{Cp})_2\mathrm{Ti(AlCl}_4)$ (see below).

The reactions of $\overline{\mathrm{Cp}}_2\mathrm{TiCl}_2$ with EtAlCl_2 were very slow at room temperature and therefore after 4 days the reaction mixtures were warmed to 70 °C for 20 h. The initial reaction rates were in the order Cp > MeCp > $\mathrm{Me}_3\mathrm{Cp} \sim \mathrm{Me}_4\mathrm{Cp}$ but while the Cp and MeCp complexes were formed quantitatively, the final yields of the $\mathrm{Me}_3\mathrm{Cp}$ and $\mathrm{Me}_4\mathrm{Cp}$ complexes were as low as 20%. In these cases, the absence of ESR spectra of the $\overline{\mathrm{Cp}}_2\mathrm{Ti(AlCl}_3\mathrm{Et)}$ complexes, which were formed in the initial period of the reaction because of the large excess of EtAlCl_2 over AlCl_3, showed that all the EtAlCl_2 was consumed. Only a very weak ESR signal (10%) was obtained in the system $(\mathrm{Me}_5\mathrm{Cp})_2\mathrm{TiCl}_2$–$\mathrm{EtAlCl}_2$, resembling the signal of $(\mathrm{Me}_5\mathrm{Cp})_2\mathrm{Ti(AlCl}_2\mathrm{Et}_2)$ by the g-value and the line shape. Since the binuclear complexes are either blue or green, (see Table 2), the brown colour of the systems with highly methyl-substituted $\overline{\mathrm{Cp}}$ ligands was due to the presence of diamagnetic by-products. In addition, a purple oily precipitate separated in the system $(\mathrm{Me}_5\mathrm{Cp})_2\mathrm{TiCl}_2$–$\mathrm{EtAlCl}_2$, indicating formation of $(\mathrm{Me}_5\mathrm{Cp})\mathrm{TiCl}_2$ [1]. The by-products probably arose from a different mode of decomposition of the $\mathrm{Ti}^{\mathrm{IV}}$ intermediate $\overline{\mathrm{Cp}}_2\mathrm{TiCl}_2 \cdot \mathrm{EtAlCl}_2$ containing bulkier $\overline{\mathrm{Cp}}$ ligands. The formation of $(\mathrm{Me}_5\mathrm{Cp})\mathrm{TiCl}_2$ points to a cleavage of the $\overline{\mathrm{Cp}}$–Ti bond induced by coordination of EtAlCl_2 or AlCl_3 to $\overline{\mathrm{Cp}}_2\mathrm{TiCl}_2$ [18,19]. The transfer of an Et group from Al to Ti to give Ib (Scheme 1) is probably hindered by



Scheme 1

the presence of bulky $\bar{\mathrm{Cp}}$ ligands and competing decomposition of Ia then lowers or prevents formation of the $\bar{\mathrm{Cp}}_2\mathrm{Ti(AlCl_4)}$ complexes.

Formation of the $\bar{\mathit{Cp}}_2\mathit{Ti(AlCl_{4-x}Et_x)}$ *complexes from* $\bar{\mathit{Cp}}_2\mathit{TiCl}$ *and* $\mathit{Et_xAlCl_{3-x}}$ $(x = 0\text{–}2)$

The binuclear highly methyl-substituted complexes $\bar{\mathrm{Cp}}_2\mathrm{Ti(AlCl_4)}$ and $\mathrm{(Me_5Cp)_2Ti(AlCl_3Et)}$ which could not be prepared by reaction 2 and $\mathrm{(MeCp)_2Ti(AlCl_4)}$ and $\mathrm{(Me_5Cp)_2Ti(AlCl_2Et_2)}$ were prepared according to the stoichiometry of reaction 3.

$$\bar{\mathrm{Cp}}_2\mathrm{TiCl} + \mathrm{Et}_x\mathrm{AlCl}_{3-x} \rightarrow \bar{\mathrm{Cp}}_2\mathrm{Ti(AlCl}_{4-x}\mathrm{Et}_x) \ (x = 0\text{–}2) \qquad (3)$$

As indicated by the ESR spectra of the reaction solutions all complexes were prepared quantitatively except $\mathrm{(Me_3Cp)_2Ti(AlCl_4)}$ and $\mathrm{(Me_4Cp)_2Ti(AlCl_4)}$. A little $\mathrm{(Me_3Cp)Ti(AlCl_4)_2}$ was formed during formation of $\mathrm{(Me_3Cp)_2Ti(AlCl_4)}$ but its amount did not increase on prolonged contact with solid $\mathrm{AlCl_3}$. The complex $\mathrm{(Me_4Cp)_2Ti(AlCl_4)}$, however, turned rapidly and completely into $\mathrm{(Me_4Cp)Ti(AlCl_4)_2}$ upon prolonged contact of the reaction solution with solid $\mathrm{AlCl_3}$. The experiments attempting the preparation of both the $\mathrm{Me_3Cp}$ and $\mathrm{Me_4Cp}$ complexes were repeated

Table 2

Colours of the solid complexes $\bar{\mathrm{Cp}}_2\mathrm{Ti(AlCl}_{4-x}\mathrm{Et}_x)$ $(x = 0\text{–}2)$ and their *d–d* absorption bands in *n*-hexane solution

$\bar{\mathrm{Cp}}$	$\bar{\mathrm{Cp}}_2\mathrm{Ti(AlCl_4)}$		$\bar{\mathrm{Cp}}_2\mathrm{Ti(AlCl_3Et)}$		$\bar{\mathrm{Cp}}_2\mathrm{Ti(AlCl_2Et_2)}$	
	Colour	λ_{max}(nm)	Colour	λ_{max}(nm) [a]	Colour	λ_{max}(nm)
Cp	blue	660	blue	675	blue	675
MeCp	blue	650	blue	670	blue	680
$\mathrm{Me_3Cp}$	green	650, 740 sh	turquoise	660, 750 sh	blue	680
$\mathrm{Me_4Cp}$	green	–	turquoise	650, 740 sh	turquoise	670
$\mathrm{Me_5Cp}$	green	670, 770 sh	green	680, 780 sh	green	700, 790 sh

[a] The molar extinction coefficient of the *d–d* band at λ_{max} increased from 75 to 110 $\mathrm{cm^2\ mmol^{-1}}$ on going from the Cp to the $\mathrm{Me_4Cp}$ complex.

3 times using the same $\mathrm{AlCl_3}$ samples and high-vacuum conditions with reproducible results. On the other hand, the complexes $\mathrm{(MeCp)_2Ti(AlCl_4)}$ and $\mathrm{(Me_5Cp)_2Ti(AlCl_4)}$ were stable on contact with solid $\mathrm{AlCl_3}$ for days and the complexes $\mathrm{(Me_5Cp)_2Ti(AlCl_3Et)}$ and $\mathrm{(Me_5Cp)_2Ti(AlCl_2Et_2)}$ were stable in the presence of excess $\mathrm{EtAlCl_2}$ and $\mathrm{Et_2AlCl}$, respectively.

The substitution of the $\overline{\mathrm{Cp}}$ ligand by the $\mathrm{AlCl_4}$ group had previously been observed for $\mathrm{Cp_2Ti(AlCl_4)}$ in the presence of $\mathrm{AlCl_3}$ and hydrogen chloride (equation 4) [20].

$$\mathrm{Cp_2Ti(AlCl_4) + H^+(AlCl_4)^- \rightarrow CpTi(AlCl_4)_2 + CpH} \qquad (4)$$

In our systems the formation of catalytic amounts of protonic acids from interaction of $\mathrm{AlCl_3}$ with the glass surface cannot be excluded but the acids should be quenched by the released $\overline{\mathrm{Cp}}$ ligand. The reason for the minor formation of $\mathrm{(Me_3Cp)Ti(AlCl_4)_2}$ is not clear. The smooth formation of $\mathrm{(Me_4Cp)Ti(AlCl_4)_2}$ in the presence of excess $\mathrm{AlCl_3}$ can be explained by the exchange reaction 5.

$$\mathrm{(Me_4Cp)_2Ti(AlCl_4) + 2\ AlCl_3 \rightarrow (Me_4Cp)Ti(AlCl_4)_2 + (Me_4Cp)AlCl_2} \qquad (5)$$

The presence of equimolar amounts of $\mathrm{(Me_5Cp)AlCl_2}$ and excess $\mathrm{AlCl_3}$ did not show a smearing effect on the eleven-line ESR spectrum of $\mathrm{(Me_4Cp)Ti(AlCl_4)_2}$ because the $\overline{\mathrm{Cp}}\mathrm{Ti^{III}}$ species tend to coordinate more chlorinated aluminate ligands [1,21]. Reaction 5 does not occur in the system $\mathrm{(Me_5Cp)_2Ti(AlCl_4)}$–$\mathrm{AlCl_3}$ probably because of the steric hindrance preventing coordination of $\mathrm{AlCl_3}$ to the binuclear complex. This does not contradict the easy cleavage of the $\mathrm{(Me_5Cp)}$–$\mathrm{Ti^{IV}}$ bond in the $\mathrm{(Me_5Cp)_2TiCl_2}$–$\mathrm{EtAlCl_2}$ system since no steric hindrance was found in the molecular structure of $\mathrm{(Me_5Cp)_2TiCl_2}$ [14] which would prevent formation of the transient complex $\mathrm{(Me_5Cp)_2TiCl_2 \cdot EtAlCl_2}$.

Properties of the binuclear complexes

The pure complexes formed crystalline materials except $\mathrm{(MeCp)_2Ti(AlCl_3Et)}$ and $\mathrm{(MeCp)_2Ti(AlCl_2Et_2)}$ which have a waxy consistence. $\mathrm{(Me_5Cp)_2Ti(AlCl_4)}$ differed from the other complexes in its lower solubility in n-hexane. The colours of the solid complexes are listed in Table 2 together with positions of the *d–d* absorption bands in the visible region of their n-hexane solutions. The *d–d* band position was shifted to longer wavelengths by the presence of the Et group(s) in the chloroaluminate ligand as found earlier for the Cp derivatives [21]. Correlation of the *d–d* band position with the number of Me groups in the $\overline{\mathrm{Cp}}$ ligands was partly obscured by distinct shoulders which occurred in the highly methyl-substituted complexes on the long-wavelength slope of the broad *d–d* absorption band. The propensity of Me groups to shift $\lambda_{\mathrm{max}}(d\text{–}d)$ to shorter wavelengths, recently observed in the similar trinuclear complexes [1], was convincingly traced only in the series of $\overline{\mathrm{Cp}}_2\mathrm{Ti(AlCl_3Et)}$ complexes except the $\mathrm{Me_5Cp}$ one. All $\mathrm{Me_5Cp}$ complexes displayed their *d–d* band at considerably longer wavelengths than other complexes of the same series containing an identical aluminate ligand (see Table 2).

The ESR spectra of the series of complexes $\overline{\mathrm{Cp}}_2\mathrm{Ti(AlCl_4)}$, $\overline{\mathrm{Cp}}_2\mathrm{Ti(AlCl_3Et)}$ and $\overline{\mathrm{Cp}}_2\mathrm{Ti(AlCl_2Et_2)}$ differed in the value of the a_{Al} coupling constant, decreasing sharply with the number of Et groups in the aluminate ligand (Fig. 1). This is in accordance with earlier studies on the Cp derivatives [7–1,21]. This decrease in a_{Al}

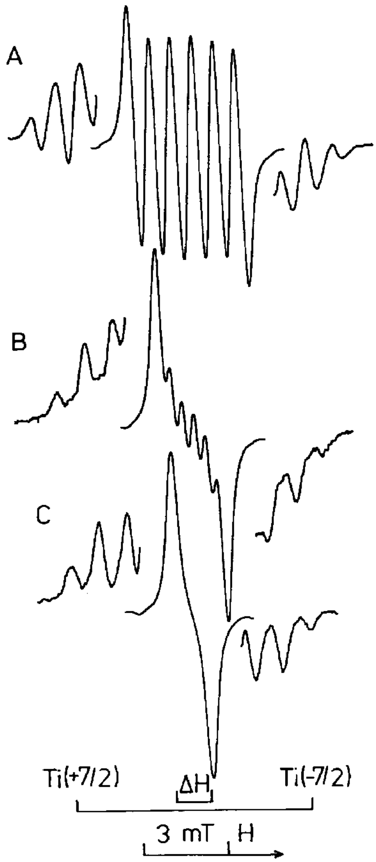


Fig. 1. ESR spectra of $(Me_4Cp)_2Ti(AlCl_4)$ (A), $(Me_4Cp)_2Ti(AlCl_3Et)$ (B) and $(Me_4Cp)_2Ti(AlCl_2Et_2)$ (C) (room temperature, modulation amplitude 0.06 mT, wings amplified 20 times).

was accompanied by only a small increase in the $a_{Ti(7/2)}$ coupling constant and by a slight increase in the g-value (see Table 3).

Methyl substitution in the $\bar{C}p$ ligands exerted qualitatively opposite effects. It increased the value of a_{Al} and decreased considerably the value of $a_{Ti(7/2)}$. The

Table 3

ESR parameters of the $\bar{C}p_2Ti(AlCl_{4-x}Et_x)$ ($x = 0$–2) complexes in benzene solution [a]

$\bar{C}p$	$\bar{C}p_2Ti(AlCl_4)$			$\bar{C}p_2Ti(AlCl_3Et)$			$\bar{C}p_2Ti(AlCl_2Et_2)$		
	g	a_{Al}	a_{Ti}	g	a_{Al}	a_{Ti}	g	ΔH	a_{Ti}
Cp	1.9755	0.70	1.18	1.9765	0.35	1.18	1.9772	1.08	1.19
MeCp	1.9754	0.70	1.13	1.9763	0.35	1.13	1.9770	1.10	1.15
Me_3Cp	1.9753	0.73	1.08	1.9760	0.38	1.08	1.9765	1.25	1.10
Me_4Cp	1.9756	0.77	1.03	1.9762	0.41	1.03	1.9770	1.35	1.05
Me_5Cp	1.9703	0.76	1.03	1.9709	0.41	1.04	1.9712	1.40	1.05

[a] In hexane solution the g-values were lower by 0.0005–0.0010 and the resolution of hyperfine splitting was not improved by temperature lowering below room temperature; highly methylated complexes displayed better resolved spectra in n-hexane while those of the Cp and MeCp complexes were resolved better in the benzene solution. The values of a and ΔH in mT (= 10 G).

g–value displayed a slight decrease on going from the Cp to $\mathrm{Me_3Cp}$ complexes but the $\mathrm{Me_4Cp}$ complexes gave irregularly higher g-values.

The exception in all the series of complexes was the $\mathrm{Me_5Cp}$ derivative which gave extremely low g-values and a_{Al} and $a_{\mathrm{Ti}(7/2)}$ coupling constants, usually very similar to those of the $\mathrm{Me_4Cp}$ complexes. Their g-values fell into the range of g-values appropriate for the trinuclear $\overline{\mathrm{Cp}}\mathrm{Ti^{III}}$ complexes [1] but the appearance of their ESR spectra, and the values of a_{Al} and $a_{\mathrm{Ti}(7/2)}$ indicated unequivocally that their structure was binuclear. In comparison, the $\overline{\mathrm{Cp}}\mathrm{Ti^{III}}$ complexes gave typical values of $a_{\mathrm{Ti}(7/2)}$ 1.5 mT and no hyperfine resolution in complexes containing mono- and diethyl-substituted aluminate ligands [1].

It can be concluded that qualitatively the same effects of Me substituents on the g–values, a_{Al} and $\lambda_{\mathrm{max}}(d–d)$ were observed in the $\overline{\mathrm{Cp}}\mathrm{Ti^{III}}$ trinuclear and $\overline{\mathrm{Cp}}_2\mathrm{Ti^{III}}$ binuclear complexes ($\overline{\mathrm{Cp}} = \mathrm{Cp–Me_3Cp}$) and that in both cases only electronic effects of Me substituents can be considered. Large opposite shifts of the g-value and $\lambda_{\mathrm{max}}(d–d)$ which were observed in the $\mathrm{(Me_5Cp)_2Ti(AlCl_{4-x}Et_x)}$ complexes should be connected with some steric hindrance which would change the ligand field geometry and consequently the d-orbital energy in these complexes. The values of a_{Al} and $a_{\mathrm{Ti}(7/2)}$ for these complexes, which do not fit the dependences due to electronic effects of Me substituents in the $\mathrm{Cp–Me_3Cp}$ series, demonstrate the steric hindrance effect on the unpaired electron density distribution over the complex frame.

Experimental

Chemicals

Titanocene dichlorides $\overline{\mathrm{Cp}}_2\mathrm{TiCl_2}$ ($\overline{\mathrm{Cp}} = \mathrm{C_5H_5}$ (Cp), $\mathrm{CH_3C_5H_4}$ (MeCp), $\mathrm{(CH_3)_3C_5H_2}$ ($\mathrm{Me_3Cp}$), $\mathrm{(CH_3)_4C_5H}$ ($\mathrm{Me_4Cp}$) and $\mathrm{(CH_3)_5C_5}$ ($\mathrm{Me_5Cp}$)), ethylaluminium compounds and $\mathrm{AlCl_3}$ were obtained as described previously [1]. Titanocene monochlorides $\overline{\mathrm{Cp}}_2\mathrm{TiCl}$ were prepared from $\overline{\mathrm{Cp}}_2\mathrm{TiCl_2}$ by reduction with both aluminium powder in THF at room temperature and $\mathrm{LiAlH_4}$ in boiling toluene. They were purified by washing with ethyl ether and by crystallization from n-hexane, respectively. Their purity was checked by mass spectrometry. Benzene and n-hexane were refluxed over $\mathrm{LiAlH_4}$ and stored as a solution of μ-(η^5 : η^5-fulvalene)di-μ-hydridobis(cyclopentadienyltitanium).

Procedures

A high-vacuum technique based on completely sealed glass devices and breakable seals was used throughout the preparation and purification of complexes and during measurement of their ESR and electronic absorption spectra. The complexes $\overline{\mathrm{Cp}}_2\mathrm{Ti(AlCl_{4-x}Et_x)}$ ($x = 0–2$) were prepared either by reduction of $\overline{\mathrm{Cp}}_2\mathrm{TiCl_2}$ with equivalent molar amounts of $\mathrm{EtAlCl_2}$, $\mathrm{Et_2AlCl}$ and $\mathrm{Et_3Al}$, respectively, or by addition of $\mathrm{AlCl_3}$, $\mathrm{EtAlCl_2}$ or $\mathrm{Et_2AlCl}$ to $\overline{\mathrm{Cp}}_2\mathrm{TiCl}$. All the components were dosed as benzene solutions except $\mathrm{AlCl_3}$ which was present in excess as a solid. The titanium concentration in the reaction mixtures was usually 0.01 *M*. The rate of formation of the $\overline{\mathrm{Cp}}_2\mathrm{Ti(AlCl_{4-x}Et_x)}$ complexes was followed by the ESR measurement using an ESR sample tube attached to the reaction bulb. The complexes were purified as follows. All the benzene was evaporated from the reaction mixture, a minimum amount of n-hexane was condensed on to the residue and a clear solution was poured off from the brown sediment eventually remaining and cooled to −70 °C. The mother liquor was poured off from the solid, usually crystalline complexes and these were dissolved in n-hexane for the measurement of electronic absorption spectra.

Methods

The ESR spectra were recorded on an ERS-220 spectrometer (Centre for Production of Scientific Instruments, German Acad. Sci., Berlin, GDR) in the X-band at room temperature and evaluated as described previously [1]. Electronic absorption spectra were taken on a Varian Cary 17 D instrument using sealed quartz cuvettes ($d = 0.1$ and 1.0 cm) (Hellma).

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