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Effects of methyl substituents at the cyclopentadienyl ligand on the properties of $C_5H_5TiCl_3$ and $C_5H_5TiAl_2Cl_{8-x}(C_2H_5)_x$ ($x = 0$–4) complexes

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Abstract

The methyl substituents in the series of $\bar{C}pTiCl_3$ compounds ($\bar{C}p$ = Cp, MeCp, Me_3Cp, Me_4Cp, Me_5Cp and $EtMe_4Cp$) shift the position of their CT absorption band from $\lambda = 384$ nm to max. 438 nm and decrease the rate of reduction of $\bar{C}pTiCl_3$ by ethylaluminium compounds yielding the trinuclear $\bar{C}pTiAl_2Cl_{8-x}Et_x$ ($x = 0$–4) complexes. In the $\bar{C}pTiCl_3$/excess Et_2AlCl systems the rate of reduction was controlled by pseudomonomolecular decomposition of the proposed octahedral intermediate $\bar{C}pTiEt(Cl_2AlEt_2)(Cl_3AlEt)$. The rate constants for reduction decreased in the above series of $\bar{C}pTiCl_3$ compounds from 1.10×10^{-3} to 6.15×10^{-5} s^{-1}. The methyl substituents in the $\bar{C}pTiAl_2Cl_{8-x}Et_x$ complexes shifted the charge transfer bands to longer wavelengths, the *d*–*d* transition to shorter wavelengths and the ESR *g*-value away from the free electron value. The opposite shifts were induced by the replacement of the outer chlorine atoms in the chloroaluminate ligands by ethyl groups. On going from Cp to Me_5Cp the thermal stability of the $\bar{C}pTiAl_2Cl_8$ complexes decreased while the complexes $\bar{C}pTiAl_2Cl_4Et_4$ became stable even with the excess of Et_3Al. The $\bar{C}pTiAl_2Cl_{8-x}Et_x$ complexes were also formed in the redox reaction of non-dimerizing methylcyclopentadienes (Me_3CpH/$EtMe_4CpH$) with bis(di-μ-chloroalane)(benzene)titanium(II) complexes $C_6H_6 \cdot TiAl_2Cl_{8-x}Et_x$ ($x = 0$–2). The reaction was found stoichiometric except for the perchloro complexes forming diamagnetic byproducts.

Replacement of the cyclopentadienyl ligand (Cp) by the pentamethylcyclopentadienyl ligand (Me_5Cp) in metallocene derivatives leads to increased stability of complexes owing to the inductive and hyperconjugation effects of the methyl group and to the extended sterical shielding of the coordination space about the central metal atom [1–3]. The inductive and hyperconjugation effects influence the chemical and physical properties of the complexes by increasing the electron density at the metal atom, and decreasing the ionisation potential of the Cp ligand [4,5].

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In the titanocene dihalide series the substitution of Cp with Me_5Cp lowered the oxidation potential by 0.5–0.6 V and decreased the binding energies of the Ti(2p) inner shell electrons by 0.8 eV [6]. The ^{49}Ti NMR chemical shift showed remarkable downfield shifts on going from Cp to Me_5Cp derivatives, thus following the inverse halogen-dependence found for titanocene dihalides [7]. The methyl substituents have a substantial effect on the energy of valence electrons in titanocene dihalides [8] and cyclopentadienyltitanium trihalides [9] as observed by photoelectron spectroscopy. In the latter compounds the lowest vertical ionisation energy band was strongly shifted to lower energy by the methyl substitution; this indicated that the HOMO electrons reside mostly at the Cp ligand. The other two low-ionisation energy bands were related to electrons of mostly halogen atom orbitals.

The effects of methyl substitution have so far been studied for mono- and pentamethylcyclopentadienyl titanium complexes [6–9] and no experimental data have confirmed the additivity of effects throughout the series of methyl substituted derivatives. Thus we thought it would be interesting to examine the methyl substitution effects on the electronic absorption spectra of $\bar{C}pTiCl_3$ compounds ($\bar{C}p = C_5H_5$ (Cp), $CH_3C_5H_4$ (MeCp), $(CH_3)_3C_5H_2$ (Me_3Cp), $(CH_3)_4C_5H$ (Me_4Cp, $(CH_3)_5C_5$ (Me_5Cp) and $(C_2H_5)(CH_3)_4C_5$ ($EtMe_4Cp$)), and electronic absorption and ESR spectra of $\bar{C}pTiAl_2Cl_{8-x}Et_x$ ($x = 0$–4) complexes. The latter complexes were prepared from $\bar{C}pTiCl_3$ and ethylaluminium compounds as previously described for $CpTiCl_3$ [10,11]. The methyl substituent effect on the reducibility of the $\bar{C}pTiCl_3$ compounds has been confirmed by rates at which they are reduced by an excess Et_2AlCl.

The formation of the $\bar{C}pTiAl_2Cl_{8-x}Et_x$ complexes by the reaction of (benzene)titanium(II) complexes $C_6H_6 \cdot TiAl_2Cl_{8-x}Et_x$ ($x = 0$–2) with highly methylated cyclopentadienes has also been studied. The use of these non-dimerizing cyclopentadienes makes this reaction, found earlier for monomeric cyclopentadiene [10,11], more convenient for investigation of the titanium Ziegler-Natta catalysts.

Results and discussion

Effects of methyl substituents on the properties of $CpTiCl_3$

The methyl substituents in the $\bar{C}pTiCl_3$ compounds influenced the position of their charge transfer (CT) electronic absorption band and their reducibility by the action of ethylaluminium compounds.

The CT band of $CpTiCl_3$ at 384 nm gradually shifted to longer wavelengths on going to $(Me_5Cp)TiCl_3$ as given in Table 1. The differences in energies of the electronic transition between the methyl homologues were found to be approximately constant, amounting ca. 0.08 eV per Me group. Since the differences in energy of the HOMO orbitals amounted to about 0.18 eV per Me group, as found from the photoelectron spectra of the Cp, MeCp and Me_5Cp derivatives [9], the addition of the electronic transition energy to the HOMO energy shows (Fig. 1) that the LUMO energy increases in the series of $\bar{C}pTiCl_3$ compounds by ca. 0.10 eV per Me group. This behaviour is compatible with both the hyperconjugation effect raising the energy of predominantly Cp e-type HOMO [9] and the methyl inductive effect increasing the energy of LUMO with large metal d-orbital character (see MO scheme in ref. 9).

Table 1

Electronic absorption bands of C̄pTiCl$_3$ compounds and reduction rates of C̄pTiCl$_3$ with Et$_2$AlCl in excess [a]

C̄p	C̄pTiCl$_3$ [b]		C̄pTiCl$_3$ + 100 Et$_2$AlCl [b]		Rate constant of C̄pTiCl$_3$ reduction, k (s^{-1}) [c]
	λ_{max} (nm)	eV	λ_{max} (nm)	eV	
EtMe$_4$Cp	438	2.831	448	2.767	–
Me$_5$Cp	438	2.831	448	2.767	6.15×10^{-5}
Me$_4$Cp	426	2.910	436	2.844	1.56×10^{-4}
Me$_3$Cp	415	2.987	426	2.910	3.85×10^{-4}
MeCp	392	3.163	400	3.099	8.37×10^{-4}
Cp	384	3.228	388	3.195	1.10×10^{-3}

[a] [Ti] = 0.01 M, [Et$_2$AlCl] = 1.0 M, solvent benzene, temperature 26±0.5 °C. [b] $\epsilon = 2\text{–}3 \times 10^3$ cm^2 mmol^{-1}. [c] $k = \ln 2/t_{1/2}$.

The fact that the change of reducibility of CpTiCl$_3$ depends on the degree of methylation of the Cp ligand was observed during preparation of the C̄pTiAl$_2$Cl$_{8-x}$Et$_x$ (x = 0–4) complexes (C̄pTi^{III}) from C̄pTiCl$_3$ and ethylaluminium compounds. An excess of EtAlCl$_2$ led to the formation of the C̄pTi^{III} complexes after a number of days, at temperatures ranging from 20 to 70 °C. The effect of methyl substitution on the reducibility of C̄pTiCl$_3$ compounds was evaluated by measuring the rates of formation of the C̄pTi^{III} complexes in the presence of a 100-fold excess of Et$_2$AlCl in benzene solution at 26 °C by ESR.

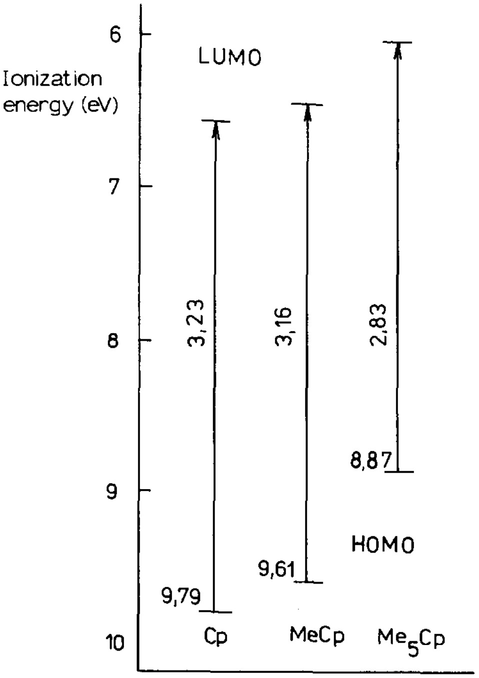


Fig. 1. Energy levels of the HOMO and LUMO as determined by photoelectron spectroscopy [9] and electronic absorption spectroscopy.

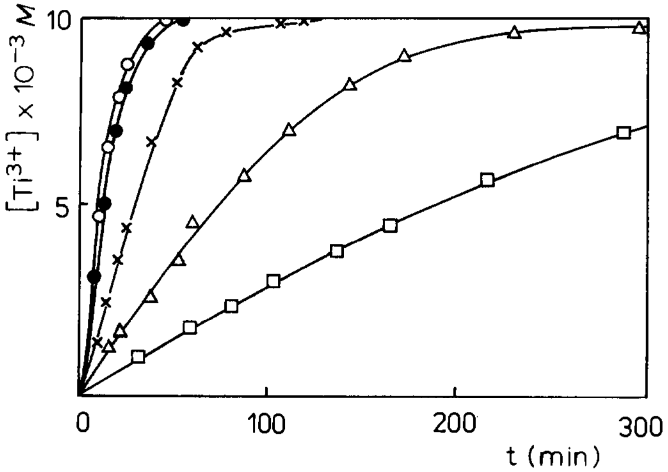


Fig. 2. The kinetics of formation of the $\bar{\mathrm{C}}\mathrm{pTi^{III}}$ complexes in the systems $\bar{\mathrm{C}}\mathrm{pTiCl_3} + 100\ \mathrm{Et_2AlCl}$ ($[\mathrm{Ti}] = 1 \times 10^{-2}$ *M*, solvent benzene, temperature $26 \pm 0.5\,^\circ\mathrm{C}$).

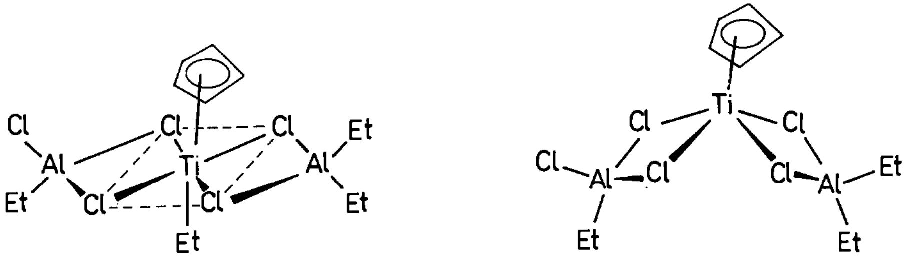
The kinetic curves for all the $\bar{\mathrm{C}}\mathrm{pTiCl_3}$ compounds showed similar shapes (Fig. 2). They deviate slightly from the rate equation for the monomolecular reaction, and show a slower initial rate, followed by an acceleration which levelled off during the reaction. This kinetic behaviour can be tentatively explained by the two step formation of the $\bar{\mathrm{C}}\mathrm{pTi^{III}}$ complexes (eqs. 1 and 2).

$$\bar{\mathrm{C}}\mathrm{pTiCl_3} + (\mathrm{Et_2AlCl})_2 \rightleftharpoons \bar{\mathrm{C}}\mathrm{pTiCl_3} \cdot 2\mathrm{Et_2AlCl} \rightleftharpoons \bar{\mathrm{C}}\mathrm{pTiEt(Cl_3AlEt)(Cl_2AlEt_2)}\ (\mathrm{I}) \tag{1}$$

$$\mathrm{I} \xrightarrow{k} \bar{\mathrm{C}}\mathrm{pTi(Cl_3AlEt)(Cl_2AlEt_2)} + \mathrm{Et}^{\cdot} \tag{2}$$

The formation of the $\bar{\mathrm{C}}\mathrm{pTiCl_3}$ complexes with $\mathrm{Et_2AlCl}$ was indicated by the distinct red shift of the CT band of $\bar{\mathrm{C}}\mathrm{pTiCl_3}$ immediately after mixing the reaction components (Table 1). No additional change in the spectra occurred except the growing features of the $\bar{\mathrm{C}}\mathrm{pTi^{III}}$ spectra (see later) and it can thus be assumed that equilibrium 1 is rapidly established. The only information about the composition of equilibrium 1 which can be deduced from the spectra is that it contains less than 5% of $\bar{\mathrm{C}}\mathrm{pTiCl_3}$. By analogy with the $\mathrm{Cp_2TiCl_2/(Et_2AlCl)_2}$ systems which transiently yield the $\mathrm{Cp_2TiCl(Et) \cdot EtAlCl_2}$ complex [12], it can be assumed that equilibrium 1 is strongly shifted in favor of I. The structure of complex I, which undergoes homolytic dissociation in step 2, is presumed to be an axially distorted octahedron with the η^5-$\bar{\mathrm{C}}$p groups and η^1-Et group at its apices (Fig. 3).

The rapid formation of the equilibrium 1 implies that the overall kinetics of the $\bar{\mathrm{C}}\mathrm{pTi^{III}}$ formation is controlled by the slow pseudomonomolecular decomposition of I. The deviation from the first order kinetics is probably due to equilibrium 1 which lowers the concentration of I. The evaluation of the constant of formation of I from the kinetics of $\bar{\mathrm{C}}\mathrm{pTi^{III}}$ formation was, however, impossible because of insufficient precision of the ESR measurement. For comparative purposes the rate constants for formation of the $\bar{\mathrm{C}}\mathrm{pTi^{III}}$ complexes were calculated from the half-time of the reaction. Values of the rate constants decreased with increasing number of methyl



(I) (II)

Fig. 3. The suggested structures of the intermediate complex $\mathrm{CpTiEt(Cl_3AlEt)(Cl_2AlEt_2)}$ (I) and the reaction product $\mathrm{CpTiAl_2Cl_5Et_3}$ (II).

groups in $\overline{\mathrm{Cp}}\mathrm{TiCl_3}$ (see Table 1). The differences in log k between the methyl homologues were higher for highly methylated compounds than for $\mathrm{CpTiCl_3}$ and $\mathrm{(MeCp)TiCl_3}$.

The stabilization of the Ti–Et bond by methyl substituents on the $\overline{\mathrm{Cp}}$ ligand is probably because their electron donation to titanium decreases the propensity of $\mathrm{Ti^{IV}}$ to receive an electron by breaking the Ti–Et bond. On the other hand, the Ti–Et bond is destabilized by the presence of di-μ-chloroalane ligands since the compound $\mathrm{CpTiCl_2Et}$ was found to be stable at room temperature [13]. The apparent large difference in the rates of the reduction of $\overline{\mathrm{Cp}}\mathrm{TiCl_3}$ by $\mathrm{Et_2AlCl}$ and $\mathrm{EtAlCl_2}$ is tentatively compatible with the Olivés' assumption [14] that electron donation by the ethyl substituents through the chloroaluminate bridges destabilizes the Ti–Et bond, as was found in complexes of the type $\mathrm{Cp_2TiCl(Et)\cdot AlCl_{3-n}Et_n}$ ($n = 1, 0$).

The electronic effects of highly methylated $\overline{\mathrm{Cp}}$ ligands may be combined with their steric effect, probably bending the di-μ-chloralane ligands in the direction of the Ti–Et bond. A similar pyramidal structure is without doubt common to all the $\overline{\mathrm{Cp}}\mathrm{Ti^{III}}$ complexes (Fig. 3). The Al–Ti–Al angle in structurally analogous (arene)bis(dichloroalanedi-μ-chloro)titanium(II) complexes was found to be 108° and 113° in the hexamethylbenzene and benzene derivatives [15,16] and hence, a similar value of the Al–Ti–Al angle is to be expected in the $\overline{\mathrm{Cp}}\mathrm{Ti^{III}}$ complexes and should be only slightly dependent on the number of methyl substituents.

Preparation of $\overline{\mathrm{Cp}}\mathrm{TiAl_2Cl_{8-x}Et_x}$ ($x = 0$–4) complexes and the effect of methyl substituents on their chemical properties

The trinuclear $\overline{\mathrm{Cp}}\mathrm{Ti^{III}}$ complexes can be prepared by adding two molar equivalents of ethylaluminium compound to $\overline{\mathrm{Cp}}\mathrm{TiCl_3}$ as described previously for $\mathrm{CpTiCl_3}$ [10]. In this way the complexes $\overline{\mathrm{Cp}}\mathrm{TiAl_2Cl_7Et}$, $\overline{\mathrm{Cp}}\mathrm{TiAl_2Cl_5Et_3}$ and $\overline{\mathrm{Cp}}\mathrm{TiAl_2Cl_4Et_4}$ were prepared in the benzene solution according to equations 3, 4 and 5, respectively.

$$\overline{\mathrm{Cp}}\mathrm{TiCl_3} + 2\ \mathrm{EtAlCl_2} \rightarrow \overline{\mathrm{Cp}}\mathrm{TiAl_2Cl_7Et} + \mathrm{Et^{\cdot}} \qquad (3)$$

$$\overline{\mathrm{Cp}}\mathrm{TiCl_3} + 2\ \mathrm{Et_2AlCl} \rightarrow \overline{\mathrm{Cp}}\mathrm{TiAl_2Cl_5Et_3} + \mathrm{Et^{\cdot}} \qquad (4)$$

$$\overline{\mathrm{Cp}}\mathrm{TiCl_3} + \mathrm{Et_2AlCl} + \mathrm{Et_3Al} \rightarrow \overline{\mathrm{Cp}}\mathrm{TiAl_2Cl_4Et_4} + \mathrm{Et^{\cdot}} \qquad (5)$$

All the complexes were identified from their ESR spectra, and from their electronic absorption spectra in benzene solutions. The spectroscopic data indicated that the 100-fold excess of $\mathrm{EtAlCl_2}$ and $\mathrm{Et_2AlCl}$, used for the measurement of the reduction kinetics, only led to formation of minor amounts of the more ethylated complexes $\bar{\mathrm{C}}\mathrm{pTiAl_2Cl_6Et_2}$ and $\bar{\mathrm{C}}\mathrm{pTiAl_2Cl_4Et_4}$, respectively. This is consistent with the previously observed preference for the morechlorinated $\mathrm{CpTi^{III}}$ complexes in equilibria 6 and 7 [10].

$$\bar{\mathrm{C}}\mathrm{pTiAl_2Cl_7Et} + \mathrm{EtAlCl_2} \rightleftharpoons \bar{\mathrm{C}}\mathrm{pTiAl_2Cl_6Et_2} + \mathrm{AlCl_3} \qquad (6)$$

$$\bar{\mathrm{C}}\mathrm{pTiAl_2Cl_5Et_3} + \mathrm{Et_2AlCl} \rightleftharpoons \bar{\mathrm{C}}\mathrm{pTiAl_2Cl_4Et_4} + \mathrm{EtAlCl_2} \qquad (7)$$

The complexes $\bar{\mathrm{C}}\mathrm{pTiAl_2Cl_8}$ were prepared by the reaction of $\bar{\mathrm{C}}\mathrm{pTiCl_3}$ with two equivalents of $\mathrm{EtAlCl_2}$ at 70 °C until the formation of $\bar{\mathrm{C}}\mathrm{pTiAl_2Cl_7Et}$ complexes was complete as seen from their electronic absorption spectra (maximum two weeks for the $\mathrm{Me_5Cp}$ and $\mathrm{EtMe_4Cp}$ derivatives). Then the reaction mixture was treated with an excess of fine crystals of $\mathrm{AlCl_3}$. The aluminium trichloride partly dissolved and the resulting solution showed an ESR eleven-line spectrum differing from that of $\mathrm{CpTiAl_2Cl_8}$ [11] only by its poorer resolution. This was probably due to the presence of trace amounts of the $\bar{\mathrm{C}}\mathrm{pTiAl_2Cl_7Et}$ complex.

The stability of the $\bar{\mathrm{C}}\mathrm{pTiAl_2Cl_8}$ complexes in the solid state depends on the number of methyl substituents. The light-green crystalline $\mathrm{(MeCp)TiAl_2Cl_8}$, which was obtained after all volatiles including free aluminium compounds had been evaporated off in high vacuo, was sublimed without decomposition, similar to that for $\mathrm{CpTiAl_2Cl_8}$ [11]. However, the more methylated complexes, although they form crystalline materials (green $\mathrm{Me_3Cp}$ and $\mathrm{Me_4Cp}$, green-brown $\mathrm{Me_5Cp}$ and $\mathrm{EtMe_4Cp}$ derivatives) after all volatile impurities had been removed in high vacuo at room temperature, they decomposed during sublimation at 140 °C to give the red-to-purple $\bar{\mathrm{C}}\mathrm{pTiCl_2}$ compounds [17].

All complexes containing the ethylaluminium ligands formed green (Cp–$\mathrm{Me_4Cp}$ derivatives) or green-yellow ($\mathrm{Me_5Cp}$ and $\mathrm{EtMe_4Cp}$ derivatives) oily liquids after all volatile components had been removed. The $\mathrm{Me_3Cp}$–$\mathrm{Me_5Cp}$ complexes of the $\bar{\mathrm{C}}\mathrm{pTiAl_2Cl_4Et_4}$ series showed surprising stability at ambient temperature and remarkable resistance to reaction with excess $\mathrm{Et_3Al}$; the $\mathrm{Me_5Cp}$ and $\mathrm{EtMe_4Cp}$ derivatives were stable in benzene solutions in the presence of as much as a 6-fold excess of $\mathrm{Et_3Al}$. This contrasts sharply with the instability of the ethylated cyclopentadienyl complexes; $\mathrm{CpTiAl_2Cl_4Et_4}$ was unstable in the benzene solution and $\mathrm{CpTiAl_2Cl_5Et_3}$ decomposed to give red, insoluble $\mathrm{CpTiCl_2}$ after hexane had been added to its concentrated benzene solution [10].

All complexes $\bar{\mathrm{C}}\mathrm{pTiAl_2Cl_{8-\mathit{x}}Et_{\mathit{x}}}$ ($x = 0$–4) decomposed when a small amount of THF vapour was added, and gave the red-to-purple precipitates of the $\bar{\mathrm{C}}\mathrm{pTiCl_2}$ compounds which dissolved in liquid THF. The green-to-blue THF solutions of the $\bar{\mathrm{C}}\mathrm{pTiCl_2 \cdot THF}$ complexes showed gradual shifts from a very broad, low-intensity *d–d* band to shorter wavelengths on going from the Cp (680–900 nm) to the $\mathrm{Me_5Cp}$ derivatives (580–670 nm). The position of the band for $\mathrm{CpTiCl_2 \cdot THF}$ was consistent with published data [18].

ESR and electronic absorption spectra of the $\bar{\mathrm{C}}\mathrm{pTiAl_2Cl_{8-\mathit{x}}Et_{\mathit{x}}}$ *($x = 0$–4) complexes*

The ESR *g*-values, splitting constants or half-widths of signals are listed in Table 2 and the electronic absorption spectra of all complexes are collected in Table 3.

Table 2

ESR spectra of complexes $\bar{\mathrm{C}}\mathrm{pTiAl_2Cl_{8-x}Et_x}$ ($x = 0, 1, 3, 4$) [a]

$\bar{\mathrm{C}}$p	$\bar{\mathrm{C}}\mathrm{pTiAl_2Cl_8}$ [b]		$\bar{\mathrm{C}}\mathrm{pTiAl_2Cl_7Et}$		$\bar{\mathrm{C}}\mathrm{pTiAl_2Cl_5Et_3}$		$\bar{\mathrm{C}}\mathrm{pTiAl_2Cl_4Et_4}$	
	g	a(Al)	g	ΔH	g	ΔH	g	ΔH
$\mathrm{EtMe_4Cp}$	1.9697	0.575	1.9701	2.20	1.9705	1.36	1.9707	0.98
$\mathrm{Me_5Cp}$	1.9696	0.575	1.9700	2.15	1.9705	1.36	1.9708	0.97
$\mathrm{Me_4Cp}$	1.9706	0.575	1.9709	2.06	1.9712	1.28	1.9715	0.95
$\mathrm{Me_3Cp}$	1.9718	0.575	1.9715	2.03	1.9717	1.25	1.9720	0.94
MeCp	1.9724	0.580	1.9725	1.92	1.9726	1.13	1.9728	0.92
Cp	1.9726	0.580	1.9728	1.90	1.9730	1.07	1.9730	0.85

[a] g-values are to within ±0.0003, and ΔH are to within ±2%. [b] Eleven-line multiplet.

The influence of Et groups in the chloroaluminate ligands on the ESR and electronic absorption spectra of the complexes was found to be the same as those found previously for the $\mathrm{CpTiAl_2Cl_{8-x}Et_x}$ complexes [10]. The eleven-line ESR spectra of the $\bar{\mathrm{C}}\mathrm{pTiAl_2Cl_8}$ complexes, showing clearly the interaction of the $\mathrm{Ti^{III}}$ unpaired electron with two equivalent Al nuclei ($I_{\mathrm{Al}} = 5/2$) [19], collapsed to a broad singlet in the $\bar{\mathrm{C}}\mathrm{pTiAl_2Cl_7Et}$ compounds. The further replacement of outer chlorine atoms by Et groups leads to gradual narrowing of the ESR signal. This effect, together with a slight shift of the g-value to the free electron value indicate that a release of the electron density from the Al nuclei to the $\bar{\mathrm{C}}$p ligand has taken place. The introduction of ethyl groups also considerably shifted the positions of the CT bands (A and B in Table 3) to shorter wavelengths and the position of the d–d band (C in Table 3) to longer wavelengths.

The methyl substituents in the Cp ligand displayed opposite effects in all the $\bar{\mathrm{C}}\mathrm{pTi^{III}}$ complexes. They shifted the g-value away from the free electron value and slightly broadened the ESR signals which indicate an increase of electron density at the aluminium nuclei. In the electronic absorption spectra the methyl substituents shifted the CT bands to longer wavelengths for all the compounds by approximately the same amounts as those for the $\bar{\mathrm{C}}\mathrm{pTiCl_3}$ compounds, and shifted the d–d band to shorter wavelengths.

All the spectroscopic data confirm that the electron donation induced by the Et group attached to the aluminium and that induced by the Me group of the $\bar{\mathrm{C}}$p

Table 3

Electronic absorption spectra of complexes $\bar{\mathrm{C}}\mathrm{pTiAl_2Cl_{8-x}Et_x}$ ($x = 0, 1, 3, 4$) [a]

$\bar{\mathrm{C}}$p	$\bar{\mathrm{C}}\mathrm{pTiAl_2Cl_8}$			$\bar{\mathrm{C}}\mathrm{pTiAl_2Cl_7Et}$ [b]			$\bar{\mathrm{C}}\mathrm{pTiAl_2Cl_5Et_3}$ [b]			$\bar{\mathrm{C}}\mathrm{pTiAl_2Cl_4Et_4}$ [b]		
	A	B	C	A	B	C	A	B	C	A	B	C
$\mathrm{EtMe_4Cp}$	420	485sh	660	415	475sh	670	405	460sh	685	390	450sh	690
$\mathrm{Me_5Cp}$	420	485sh	660	415	475sh	670	405	460sh	685	390	450sh	695
$\mathrm{Me_4Cp}$	410	480sh	660	405	465sh	670	395	455sh	690	385	440sh	700
$\mathrm{Me_3Cp}$	405	460sh	665	395	450sh	675	385	440sh	695	370	430sh	705
MeCp	375	–	670	365	–	680	355	410sh	705	350	–	710
Cp	370	415sh	670	360	405sh	690	350	390sh	710	not stable		

[a] Wavelengths in nm; A, B – CT bands, C – d–d band. [b] Bands A – $\epsilon \sim 700$–$900\ \mathrm{cm^2\ mmol^{-1}}$; bands C – $\epsilon \sim 90$–$100\ \mathrm{cm^2\ mmol^{-1}}$.

ligand influence the ESR g-value as well as the positions of the electronic absorption bands in opposite directions. Further physico-chemical investigations of the $\bar{\mathrm{C}}\mathrm{pTi}^{\mathrm{III}}$ complexes aimed at obtaining structural information and the quantum chemical modelling of the effects are under way.

Formation of the $\bar{\mathrm{C}}\mathrm{pTi}^{\mathrm{III}}$ complexes by the redox reaction of (benzene)titanium(II) complexes with non-dimerizing methylcyclopentadienes

Previously we found that the complexes $\mathrm{CpTiAl_2Cl_{8-x}Et_x}$ were also formed in the redox reaction of (η^6-benzene)-bis(dichloroalanedi-μ-chloro)titanium(II) and its ethyl derivatives with monomeric cyclopentadiene (CpH) according to eq. 8 [10,11].

$$\mathrm{C_6H_6 \cdot Ti^{II}Al_2Cl_{8-x}Et_x + CpH \rightarrow CpTi^{III}Al_2Cl_{8-x}Et_x + C_6H_6 + H^{\cdot}} \qquad (8)$$

An excess of CpH led to the formation of binuclear complexes in which an $\mathrm{AlCl_{4-x}Et_x}$ ligand is replaced by Cp, shown schematically in eq. 9.

$$\mathrm{CpTiAl_2Cl_{8-x}Et_x + CpH \rightarrow Cp_2TiAlCl_{4-x}Et_x + H(AlCl_{4-x}Et_x)} \qquad (9)$$

The complete transformation of $\mathrm{CpTi^{III}}$ to $\mathrm{Cp_2Ti^{III}}$ complexes required a large excess of CpH which polymerized in a side reaction. Reaction 8 opened a new way for the investigation of the Ziegler-Natta catalysts containing $\mathrm{Ti^{II}}$ species, however, its application was hampered by both the difficulty of dosing unstable CpH from the gas phase, and by the mixtures of products obtained.

The use of stable methylcyclopentadienes $\mathrm{Me_3CpH}$, $\mathrm{Me_4CpH}$, $\mathrm{Me_5CpH}$ or $\mathrm{EtMe_4CpH}$ in reaction 8 has now made it possible to study the stoichiometry of this reaction and behaviour of the $\bar{\mathrm{C}}\mathrm{pTi}^{\mathrm{III}}$ complexes with respect to an excess of cyclopentadiene. The reaction was carried out by mixing benzene solutions of both reactants, the formation of the $\bar{\mathrm{C}}\mathrm{pTi}^{\mathrm{III}}$ complexes being quantitatively determined by ESR spectroscopy. The composition of complexes was confirmed by the electronic absorption and ESR spectra, using the data of Tables 2 and 3. The rate of the reaction was immeasurably fast on the time scale of 10^1 seconds even with the least acidic $\mathrm{Me_5CpH}$ (pK_a 26.1 against 18.0 for CpH) [20].

The titration of the 0.1 M solutions of $\mathrm{C_6H_6 \cdot Ti^{II}Al_2Cl_{8-x}Et_x}$ ($x = 1, 2$) with 0.05 M solutions of the $\bar{\mathrm{C}}\mathrm{pH}$ hydrocarbons showed that the reagents reacted according to the stoichiometry of eq. 8. The same reaction, but with $\mathrm{C_6H_6 \cdot TiAl_2Cl_8}$ required 1.1–1.2 molar equivalents of $\bar{\mathrm{C}}\mathrm{pH}$ to reach to optimum, but with less than stoichiometric yields of the $\bar{\mathrm{C}}\mathrm{pTiAl_2Cl_8}$ complexes. Solutions of the latter complexes displayed well-resolved eleven-line ESR spectra which implied that only diamagnetic by-products had formed. As judged from yields of the $\bar{\mathrm{C}}\mathrm{pTiAl_2Cl_8}$ complexes the content of by-products increased in the series from $\mathrm{Me_3CpH}$ to $\mathrm{Me_5CpH}$ and $\mathrm{EtMe_4CpH}$. By-products were responsible for the brownish coloration of the otherwise green or yellow-green solutions of the $\bar{\mathrm{C}}\mathrm{pTi}^{\mathrm{III}}$ complexes. The excess of methylcyclopentadienes enhanced the decomposition of all $\bar{\mathrm{C}}\mathrm{pTiAl_2Cl_8}$ complexes to diamagnetic by-products, and in contrast to CpH did not lead to formation of the binuclear complexes $\bar{\mathrm{C}}\mathrm{p_2TiAlCl_4}$. Only the $\mathrm{C_6H_6 \cdot TiAl_2Cl_8}$/$\mathrm{Me_3CpH}$ or $\mathrm{Me_4CpH}$ (Ti: $\bar{\mathrm{C}}\mathrm{pH} = 1:10$) systems produced traces of these complexes, which were detected by ESR ($g = 1.9755$, $a_{\mathrm{Al}} = 0.7$ mT, $a_{\mathrm{Ti}} = 1.05$ mT) after all trinuclear complexes had disappeared during prolonged warming to 70 °C.

The preliminary experiments confirmed that reaction 8 can be applied for semiquantitative determination of the active titanium(II) species by using non-dimerizing $\bar{\mathrm{C}}\mathrm{pH}$, in the catalysis of butadiene cyclotrimerization based on either (benzene)titanium(II) complexes or $TiCl_4$, both combined with ethylaluminium chlorides in excess. The content of the $\overline{\text{Cp}}\text{Ti}^{\text{III}}$ complexes which was obtained within several minutes after $\overline{\text{Cp}}\text{H}$ addition could be related to the catalytically active Ti^{II} species presumably having the trinuclear structure of the (benzene)titanium(II) complexes [21].

Experimental

General

Titanocene dichloride derivatives were prepared under argon. Preparations of methyl substituted cyclopentadienyltitanium trichlorides, their reactions with ethylaluminium compounds and reactions of (benzene)titanium(II) complexes with the methyl substituted cyclopentadienes were performed under vacuum using all-sealed glass devices, equipped with magnetically breakable seals, for handling and filling the ESR tubes, and all-sealed quartz cuvettes.

Preparation of reagents

1,2,3-Trimethylcyclopent-2-enone and 3-ethyl-2,4,5-trimethylcyclopent-2-enone were prepared by the PbO_2 oxidation of 2-butanone and 3-pentanone [22], tetramethylcyclopent-2-enone was obtained by condensation of 3-pentanone with acetaldehyde according to the published procedure [23]. Mixtures of isomeric 1,2,3-trimethylcyclopentadienes (Me_3CpH), tetramethylcyclopentadienes (Me_4CpH), ethyltetramethylcyclopentadienes ($EtMe_4CpH$) and pentamethylcyclopentadiene (Me_5CpH) were obtained by reacting the ketones with $LiAlH_4$ or MeMgI in ether followed by iodine-catalyzed water elimination [24]. The corresponding cyclopentadienyllithium compounds were prepared as slurries in ethyl ether by the addition of the parent hydrocarbon to butyllithium (BuLi). $(MeCp)_2TiCl_2$ was prepared as described elsewhere [25]. The other titanocene dichlorides were obtained from $TiCl_3$ (which had been prepared by treating $TiCl_4$ in THF with one equivalent of BuLi and refluxing for a short while). The $TiCl_3$ solution was added to a slurry containing 2.2 equivalents of $\overline{\text{Cp}}\text{Li}$. The ethyl ether was then distilled off by gentle warming and the mixture was stirred and boiled under reflux for 24 h. During the reaction, the white cakes of $\overline{\text{Cp}}\text{Li}$ disappeared, to give a brown solution and a white sediment of LiCl. This mixture was poured into 2 *N* HCl and titanocene dichloride separated as crystals. The mother liquor was extracted with $CHCl_3$, the organic phase was dried with Na_2SO_4, and evaporated to dryness. The crude product collected was crystallized from $CHCl_3$ CH_3OH mixture, and then recrystallized from toluene. $(Me_3Cp)_2TiCl_2$ and $(Me_4Cp)_2TiCl_2$ formed red, $(Me_5Cp)_2TiCl_2$ and $(EtMe_4Cp)_2TiCl_2$ red-brown crystals. The purity of all compounds was checked by mass spectrometry.

Cyclopentadienyltitanium trichlorides $\overline{\text{Cp}}\text{TiCl}_3$ were obtained from the reaction of $TiCl_4$ with the corresponding titanocene dichloride (1 : 1), by heating at 140 °C for 4 h. The product was twice sublimed in vacuo and its purity was checked by mass spectrometry. The concentrations of the approximately 0.1 *M* solutions in benzene were determined by ESR spectroscopy to within $\pm 5\%$, after the $\overline{\text{Cp}}\text{TiCl}_3$ had been transformed into $\overline{\text{Cp}}\text{Ti}^{\text{III}}$ complexes (mostly $\overline{\text{Cp}}\text{TiAl}_2\text{Cl}_5\text{Et}_3$) by the reaction with approximately 10 equivalents of Et_2AlCl. The (benzene)titanium(II) complexes $C_6H_6 \cdot TiAl_2Cl_{8-x}Et_x$ ($x = 0$–2) and Et_3Al, Et_2AlCl, $EtAlCl_2$ and

$\mathrm{AlCl_3}$ were prepared with or without purification as described previously [10]. The cyclopentadienes $\mathrm{Me_3CpH}$, $\mathrm{Me_4CpH}$, $\mathrm{Me_5CpH}$ and $\mathrm{EtMe_4CpH}$, which were used for the reaction with the (benzene)titanium(II) complexes, were fractionated in vacuo, subsequently stored over $\mathrm{LiAlH_4}$ and dimeric titanocene, distilled to known volumes, and diluted with benzene to give 0.05 *M* solutions.

Procedures

The complexes $\overline{\mathrm{Cp}}\mathrm{TiAl_2Cl_{8-x}Et_x}$ ($x = 0$–4) were obtained by mixing either 0.1 *M* benzene solutions of $\overline{\mathrm{Cp}}\mathrm{TiCl_3}$ with a minimum of two equivalents of the ethylaluminium compound (0.1 *M* solution in benzene) or 0.1 *M* solutions of the $\mathrm{C_6H_6 \cdot TiAl_2Cl_{8-x}Et_x}$ ($x = 0$–2) complex with 1.0–1.2 equivalents of $\overline{\mathrm{Cp}}\mathrm{H}$ (0.05 *M* solution in benzene). For the kinetic measurements, $\overline{\mathrm{Cp}}\mathrm{TiCl_3}$ (0.02 mmol) in benzene was placed in a bulb equipped with an ESR sample tube, benzene was evaporated in vacuo and $\mathrm{Et_2AlCl}$ (2 ml of 1.0 *M* solution in benzene) was added. Mixing and the ESR measurements were carried out in a room thermostatted to $26 \pm 0.5\,^\circ\mathrm{C}$.

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. The *g*-values are to within ± 0.0003 of the difference in magnetic fields of the sample and the $\mathrm{Mn^{2+}}$ standard ($g = 1.9860$) signals. Magnetic fields were measured with a MJ 110-R magnetometer using proton NMR probe (Radiopan, Poznan, Poland). For quantitative measurements the spectrum of the first derivative was integrated twice and the areas of the absorption ESR spectra were compared with those of the standard $\mathrm{Cp_2TiAlCl_3Et}$ (5.275×10^{-3} *M* in benzene). The determination of $\overline{\mathrm{Cp}}\mathrm{Ti^{III}}$ concentration was in the range 1×10^{-2}–5×10^{-4} *M*, $\pm 5\%$.

Electronic absorption spectra were recorded on a Varian Cary 17 D spectrometer using sealed quartz cuvettes ($d = 0.1$ and 1.0 cm) (Hellma).

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