

Polymethylcyclopentadienyltitanocene tetrahydridoaluminates and their reaction with butadiene; a spectroscopic study

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Abstract

The $\text{Cp}_2^*\text{TiAlH}_4$ complexes ($\text{Cp}^* = \text{Cp}, \text{MeCp}, \text{Me}_3\text{Cp}, \text{Me}_4\text{Cp}, \text{Me}_5\text{Cp}$ and EtMe_4Cp) were prepared from Cp_2^*TiCl and LiAlH_4 in toluene. On aging, all the $\text{Cp}_2^*\text{TiAlH}_4$ complexes, except for the peralkylated ones, formed paramagnetic clusters composed probably of the Cp_2^*TiH and $\text{Cp}_2^*\text{TiAlH}_4$ units. The clusters reacted with an excess of butadiene to give (1-methyl- η^3 -allyl)titanocenes and $\text{Cp}_2^*\text{TiAlH}_4$ complexes. The $\text{Cp}_2^*\text{TiAlH}_4$ complexes yielded the same allyltitanocene products, but in a slower subsequent reaction. Aging of the peralkylated $\text{Cp}_2^*\text{TiAlH}_4$ complexes led to the thus far unknown paramagnetic products which are unreactive to butadiene. The (1-methyl- η^3 -allyl)titanocenes were also prepared from Cp_2^*TiCl by reaction with LiAlH_4 in the toluene/butadiene mixture. The $\text{Cp}_2^*\text{TiAlH}_4$ complexes which formed transiently in these systems were found to have ESR parameters different from those obtained in pure toluene. The effects were established of the methyl substituents in the Cp^* ligands on the ESR and electronic absorption spectra of the $\text{Cp}_2^*\text{TiAlH}_4$ complexes and (1-methyl- η^3 -allyl)titanocenes.

Introduction

The electron-donating effect of the methyl substituents in the cyclopentadienyl ligands of the titanocene halide derivatives $\text{Cp}_2^*\text{TiCl}_2$ and Cp^*TiCl_3 depresses (i) their oxidation potential [1] and (ii) the ionization energy of the valence electrons [2–4]. Consequently, as the number of methyl substituents in the Cp^*TiCl_3 ($\text{Cp}^* = \text{Cp}, \text{MeCp}, \text{Me}_3\text{Cp}, \text{Me}_4\text{Cp},$ and Me_5Cp) compounds increases, so the rate of their reduction by ethylaluminium compounds decreases gradually. The Cp^*TiCl_3 compounds and the resulting products, the trinuclear complexes $\text{Cp}^*\text{TiAl}_2\text{Cl}_{8-x}\text{Et}_x$ ($x = 0-4$) showed approximate additivity of the methyl group effect on shifts of their CT and $d-d$ electronic absorption bands, and g -values [5]. The methyl group effect enhanced the stability of the trinuclear complexes containing highly ethylated

chloroaluminate ligands ($x = 3,4$), but decreased the stability of the tetrachloroaluminate complexes. In the $\text{Cp}_2^*\text{TiAlCl}_{4-x}\text{Et}_x$ ($x = 0-2$) series of binuclear complexes, prepared either by addition of $\text{Et}_x\text{AlCl}_{3-x}$ ($x = 0-2$) to Cp_2^*TiCl or by reduction of $\text{Cp}_2^*\text{TiCl}_2$ with $\text{Et}_x\text{AlCl}_{3-x}$ ($x = 1-3$), the peralkylated complexes containing the AlCl_4 or AlCl_3Et aluminate ligands could not be prepared by the same reduction [6]. This was probably due to steric hindrance in the transient $(\text{Me}_5\text{Cp})_2\text{TiCl}_2$ complexes EtAlCl_2 or Et_2AlCl , preventing transfer of the Et group to titanium. Steric hindrance was also assumed to be responsible for the deviation, away from correlations found for other Cp^* complexes, of the spectral parameters of the $(\text{Me}_5\text{Cp})_2\text{TiAlCl}_{4-x}\text{Et}_x$ ($x = 0-2$) complexes.

We found recently, that the high-temperature reduction of the $\text{Cp}_2^*\text{TiCl}_2$ compounds with LiAlH_4 in aromatic solvents yielded different products depending on the number of Me groups in the Cp^* ligand [7]. Considerations about the reaction pathways raised the question of stability of $\text{Cp}_2^*\text{TiAlH}_4$ complexes which were probably common intermediates in these systems. Of the $\text{Cp}_2^*\text{TiAlH}_4$ complexes, only $(\text{Me}_5\text{Cp})_2\text{TiAlH}_4$ has so far been obtained from the reaction of $(\text{Me}_5\text{Cp})_2\text{TiBH}_4$ with LiAlH_4 in ether [8].

Here we describe the preparation of the $\text{Cp}_2^*\text{TiAlH}_4$ complexes by treating Cp_2^*TiCl with LiAlH_4 in toluene or in the toluene/butadiene solutions at room temperature. Their stability, reaction with butadiene, and their ESR and electronic absorption spectra with regard to the number of Me groups in the $\bar{\text{Cp}}$ ligands have been studied.

Experimental

General

All preparations, manipulations, and measurements of the $\text{Cp}_2^*\text{TiAlH}_4$ complexes were carried out under a high vacuum which included the use of vacuum lines operated by metal valves and all-sealed glass devices equipped with magnetically breakable seals.

Reagents

The compounds Cp_2^*TiCl ($\text{Cp}^* = \text{C}_5\text{H}_5(\text{Cp})$, $\text{CH}_3\text{C}_5\text{H}_4$ (MeCp), $(\text{CH}_3)_3\text{C}_5\text{H}_2$ (Me_3Cp), $(\text{CH}_3)_4\text{C}_5\text{H}$ (Me_4Cp), $(\text{CH}_3)_5\text{C}_5$ (Me_5Cp) and $(\text{C}_2\text{H}_5)(\text{CH}_3)_4\text{C}_5$ (EtMe_4Cp)) were prepared from $\text{Cp}_2^*\text{TiCl}_2$ by reduction with Al powder in THF or by controlled reduction with LiAlH_4 in toluene as described elsewhere [6]. LiAlH_4 (Metallgesellschaft, Frankfurt a.M.) and LiAlD_4 ($\sim 98\%$ D) (German Acad. Sci., Berlin, GDR) were dissolved in ethyl ether and the solutions were placed in ampoules equipped with breakable seals. Butadiene (Fluka, puriss.) was treated with copper(I) trifluoroacetate and $\mu-(\eta^5:\eta^5\text{-fulvalene})\text{di-}\mu\text{-hydridobis}(\text{cyclopentadienyltitanium})$ (FHT) until the solution remained green [9]. Toluene was purified with sulphuric acid, dried over LiAlH_4 and stored as the FHT-containing solution.

Procedures

The ether solution of LiAlH_4 was evaporated in vacuo (finally at 100°C) and the toluene solution of Cp_2^*TiCl ($4-6 \times 10^{-3} \text{ M}$, 5 ml) was poured on to the freshly prepared, white, finely crystalline LiAlH_4 (~ 0.4 mmol). Consumption of Cp_2^*TiCl was indicated by a change of the yellow-green colour in the case of Cp_2TiCl and

(MeCp)₂TiCl (both forming dimers), or the intense blue colour of the more methylated titanocene monochlorides, into the pale blue colour of the Cp^{*}₂TiAlH₄ compounds (pale green in the case of the Me₅Cp and EtMe₄Cp complexes). During the reaction the solution was repeatedly filtered through silica wool into the ESR sample tube for measurement. The ESR and electronic absorption spectra of the Cp^{*}₂TiAlH₄ complexes were taken within 5 h after their preparation and then daily, or after even longer intervals. The same reactions were also carried out in the presence of butadiene (5 mmol). Gaseous butadiene (5 mmol) was also added to cooled solutions of the Cp^{*}₂TiAlH₄ complexes immediately after their preparation and after their two months of aging. The course of these reactions was monitored by ESR and electronic absorption spectroscopy.

Methods

ESR spectra were recorded on an ERS-220 spectrometer (Centre for Scientific Instruments, German Acad. Sci., GDR) in the X-band using a variable temperature unit operating in the range -140 to +30 °C. The magnetic field was calibrated with a proton magnetometer MJ-110 R (Radiopan, Poznań, Poland). *g*-Factors were relative to the Mn²⁺ signal standard of *g* = 1.9860.

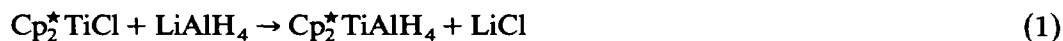
Electronic absorption spectra were measured on a Varian Cary 17 D spectrometer in the range of 300–2000 nm in 0.1 and 1.0 cm all-sealed quartz cuvettes (Hellma).

Mass spectra were recorded on a JEOL D-100 spectrometer. Samples in sealed capillaries were opened and inserted into the direct inlet under argon.

Results and discussion

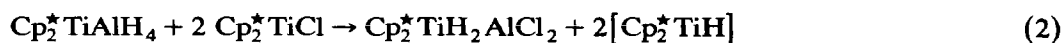
The Cp^{}₂TiCl / LiAlH₄ / toluene system*

Toluene solutions of Cp^{*}₂TiCl (Cp^{*} = Cp, MeCp, Me₃Cp, Me₄Cp, Me₅Cp and EtMe₄Cp) were treated with solid LiAlH₄ at room temperature to give the Cp^{*}₂TiAlH₄ complexes according to overall eq. 1.



The Cp^{*}₂TiAlH₄ complexes were identified from their ESR spectra which showed the hyperfine splittings due to interaction of the unpaired electron of Ti^{III} with the aluminium nucleus (*I* = 5/2) and two equivalent bridging hydrogen atoms (vide infra). The corresponding coupling constants *a*_{Al} and *a*_H were previously established for the parent compound of the series, Cp₂TiAlH₄ [10–13].

The quantitative ESR measurements proved that reaction 1 went to completion when an excess of LiAlH₄ was used. However, during the reaction, the presence of the intermediate complexes Cp^{*}₂TiH₂AlCl₂ and Cp^{*}₂TiH₂AlCl(H) was detected, and in several cases their ESR parameters were, at least approximately, determined. The formation of these complexes shows that reaction 2 in solution is faster than reaction 1 between solute and solid.



The transient product [Cp^{*}₂TiH] was not detected by ESR spectroscopy; it may have formed a diamagnetic dimer [14] or an oligomer [15]. The overall stoichiometry of reaction 1 can be fulfilled by successive reactions, as in eq. 3.

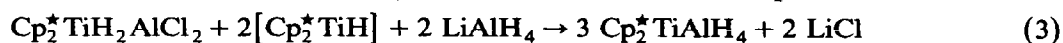


Table 1

ESR spectra of the $\text{Cp}_2^*\text{TiAlH}_4$ and $\text{Cp}_2^*\text{TiAlD}_4$ complexes and their products after aging ^a

Cp^*	g	a_{Al} (mT)	A_{H} (mT)	$a_{\text{Ti}(7/2)}$ (mT)	$a_{\text{H}(\text{Cp}^*)}$ (mT)	No. of lines ^b	ΔH (mT)
Cp X ^c	1.991	0.53	0.53			8	
Y ^c	1.9888	0.36	0.40		0.056	8	
	1.9896	0.47	0.37			8	
aged	1.991					1	3.5-4.0
MeCp	1.9877	0.49	0.38			8	
(D ₄)	1.9877	0.475		0.61		6	
aged	1.9915					1	2.6
Me ₃ Cp	1.9870	0.56	0.28			13	
(D ₄)	1.9870	0.54		0.55		6	
aged	1.9880					1	3.0
Me ₄ Cp	1.9867	0.57	0.285		0.095	39	
(D ₄)	1.9867	0.56				6	
aged	1.9864					1	3.3
Me ₅ Cp	1.9851	0.61	0.305			13	
(D ₄)	1.9851	0.59		0.49		6	
aged	1.9844					3	$a = 0.47$
EtMe ₄ Cp	1.9853	0.60	0.30			13	
(D ₄)	1.9853	0.59		0.49		6	
aged	1.9843					3	$a = 0.47$

^a Spectra were recorded between -20 and $+20^\circ\text{C}$ in toluene solution; g -factors were negligibly temperature-dependent in this region. Samples were aged for 2 months. ^b Multiplet intensities were: 6×1 , $1/3/4 \times 4/3/1$, $1/11 \times 2/1$. ^c Taken from ref. 13.

In the parent system of the series, $\text{Cp}_2\text{TiCl}/\text{LiAlH}_4/\text{toluene}$, the complexes $\text{Cp}_2\text{TiH}_2\text{AlCl}_2$, $\text{Cp}_2\text{TiH}_2\text{AlCl}(\text{H})$ and a mixture of the two $\text{Cp}_2\text{TiAlH}_4$ complexes differing in their ESR parameters (see X, Y in Table 1) were successively formed [13]. The superposition of ESR spectra of the two $\text{Cp}_2\text{TiAlH}_4$ complexes gave a slightly unsymmetrical eight-line spectrum, for which the overall parameters are given in Table 1. Within a few hours the $\text{Cp}_2\text{TiAlH}_4$ complexes turned into a compound which was thought to be a cluster composed of the Cp_2TiH and $\text{Cp}_2\text{TiAlH}_4$ units; its ESR spectrum consisted of a broad line at $g = 1.990-1.991$ [13] (Table 1).

The system $(\text{MeCp})_2\text{TiCl}/\text{LiAlH}_4$ is similar in all respects to that of $\text{Cp}_2\text{TiCl}/\text{LiAlH}_4/\text{toluene}$. The complexes, $(\text{MeCp})_2\text{TiH}_2\text{AlCl}_2$ ($g = 1.9918$, sextuplet of triplets, a_{Al} 1.13 mT, a_{H} 0.33 mT) and $(\text{MeCp})_2\text{TiH}_2\text{AlCl}(\text{H})$ ($g = 1.9918$, 13 lines $1/(11 \times 2)/1$, a_{Al} 0.84 mT, a_{H} 0.42 mT), were subsequently formed in the reacting system and their ESR parameters were close to those of the Cp complexes (cf. ref. [13]). The eight-line spectrum of $(\text{MeCp})_2\text{TiAlH}_4$ (Fig. 1, A and Table 1) was very similar to that obtained for the $\text{Cp}_2\text{TiCl}/\text{LiAlH}_4$ system and thus it is probably formed by the superposition of the spectra of two magnetically inequivalent complexes, such as in the parent system.

In the systems containing polymethylated Cp^* ligands the formation of the $\text{Cp}_2^*\text{TiH}_2\text{AlCl}_2$ and $\text{Cp}_2^*\text{TiH}_2\text{AlCl}(\text{H})$ complexes was transient and was revealed by the wing spectra accompanying the ESR spectrum of $\text{Cp}_2^*\text{TiAlH}_4$. As judged from the positions of their outermost lines the g -values of these complexes were about 0.003 higher than those of the corresponding $\text{Cp}_2^*\text{TiAlH}_4$ complexes and a_{Al}

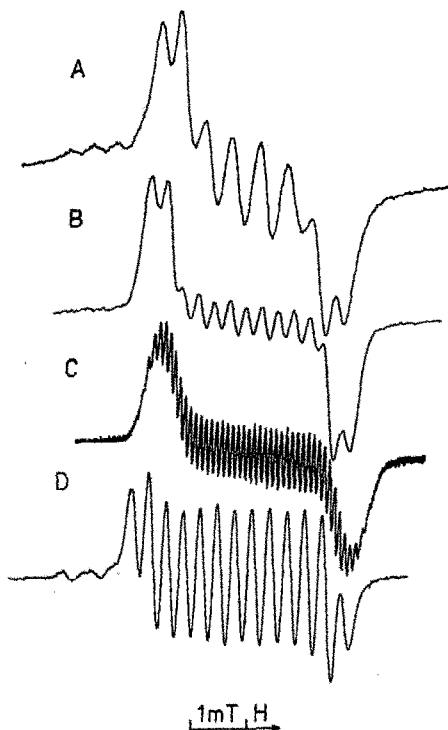


Fig. 1. ESR spectra of $\text{Cp}_2^*\text{TiAlH}_4$ complexes in toluene solution (temperature, modulation amplitude): $(\text{MeCp})_2\text{TiAlH}_4$ (A) 0°C , 0.02 mT; $(\text{Me}_3\text{Cp})_2\text{TiAlH}_4$ (B) -20°C , 0.04 mT; $(\text{Me}_4\text{Cp})_2\text{TiAlH}_4$ (C) -20°C , 0.01 mT; $(\text{Me}_5\text{Cp})_2\text{TiAlH}_4$ (D) -40°C , 0.04 mT.

coupling constants were lower than in the Cp and MeCp complexes. The $\text{Cp}_2^*\text{TiAlH}_4$ complexes mainly gave rise to the 13-line spectra (multiplet $1/(11 \times 2)/1$) which require $a_{\text{Al}} = 2a_{\text{H}}$ (Fig. 1, B–D and Table 1). Additional splitting, apparently due to the cyclopentadienyl protons ($a_{\text{H}(\text{Cp}^*)}$), was observed only in the spectrum of $(\text{Me}_4\text{Cp})_2\text{TiAlH}_4$ (Fig. 1, C). The spectrum shows 39 lines caused by the triplet splitting (2 equivalent Cp^* protons) of each line of the 13-line multiplet. The equal intensities of all the lines may arise from relatively large linewidth compared with $a_{\text{H}(\text{Cp}^*)}$. The large value of $a_{\text{H}(\text{Cp}^*)}$ in $(\text{Me}_4\text{Cp})_2\text{TiAlH}_4$ compared with that of $\text{Cp}_2^*\text{TiAlH}_4$ (see Table 1) implies that the methyl substitution at the Cp ligand increases the unpaired electron density at the remaining protons. Besides these two cases the Cp^* proton splitting was not observed probably because of line broadening owing to (i) small unresolved splitting contributions of the Me protons and (ii) from the presence of inequivalent Cp^* protons.

The assignment of coupling constants was confirmed by the ESR spectra of the $\text{Cp}_2^*\text{TiAlD}_4$ complexes. The deuterated complexes display six-line spectra arising from interaction with the aluminium nucleus. The values of a_{Al} thus obtained were close to those obtained from the hydride complexes. The resolved, weak, wing spectra of the $\text{Cp}_2^*\text{TiAlD}_4$ complexes allowed determination of the $a_{\text{Ti}(7/2)}$ coupling constant in most cases (Table 1). On the other hand, the Cp^* proton splitting in the

Table 2

Electronic absorption spectra of $\text{Cp}_2^*\text{TiAlH}_4$ complexes ^a and (1-methyl- η^3 -allyl)titanocenes ^b

Cp [*]	$\bar{\text{Cp}}_2^*\text{TiAlH}_4$, λ_{max} (nm)			$\text{Cp}_2^*\text{Ti}(1\text{-methyl-}\eta^3\text{-allyl})$ λ_{max} (nm) ^f
	A ^d	B ^e	C	
Cp ^c		550		538
MeCp	360 sh	530	640 sh	530
Me ₃ Cp	380 sh	550	640 sh	508
Me ₄ Cp	395	550	640 sh	518
Me ₅ Cp	408	590	670 sh	518
EtMe ₄ Cp	408	590	670 sh	518

^a In toluene solution; solutions were pale blue, except for the Me₅Cp and EtMe₄Cp complexes, solutions of which were light green. ^b In hexane solution; solutions were purple. ^c Taken from ref. 13 and 20. ^d $\epsilon \sim 600\text{--}750 \text{ cm}^2 \text{ mmol}^{-1}$. ^e $\epsilon \sim 70\text{--}90 \text{ cm}^2 \text{ mmol}^{-1}$. ^f $\epsilon \sim 300\text{--}400 \text{ cm}^2 \text{ mmol}^{-1}$.

Me₄Cp complex was smeared by the unresolved splitting contributions from the bridge deuteride nuclei.

The ESR coupling constants listed in Table 1 show that the methyl substitution in the Cp ring brings about a slight increase of the unpaired electron density at the Al nucleus while its density is decreased at the Ti atom. The simultaneous shift of *g*-factor to lower values is compatible with the electron density shift from the Cp^{*} ligand to the aluminate group. The analogous *g*-factor shifts were also observed in the series of complexes $\text{Cp}^*\text{TiAl}_2\text{Cl}_{8-x}\text{Et}_x$ ($g = 1.9696\text{--}1.9730$; $a_{\text{Ti}} \sim 1.5 \text{ mT}$) [5] and $\text{Cp}_2^*\text{TiAlCl}_{4-x}\text{Et}_x$ ($g = 1.9755\text{--}1.9772$; $a_{\text{Ti}} = 1.03\text{--}1.19 \text{ mT}$) [6]. When these three series of complexes are compared we see that values of the *g*-factor are roughly inversely proportional to a_{Ti} (cf. Table 1), in agreement with the literature data [16]. On the other hand, the *g*-factor shift induced by the Me groups in the $\text{Cp}_2^*\text{TiAlH}_4$ complexes is proportional to $a_{\text{Ti}(7/2)}$ (see Table 1). This is consistent with the observations [5,6] that electron donation from the Cp^{*} ligands affects the spectral parameters of the titanium complexes in a different way than the electron donation induced by alkyl groups in the aluminate ligands.

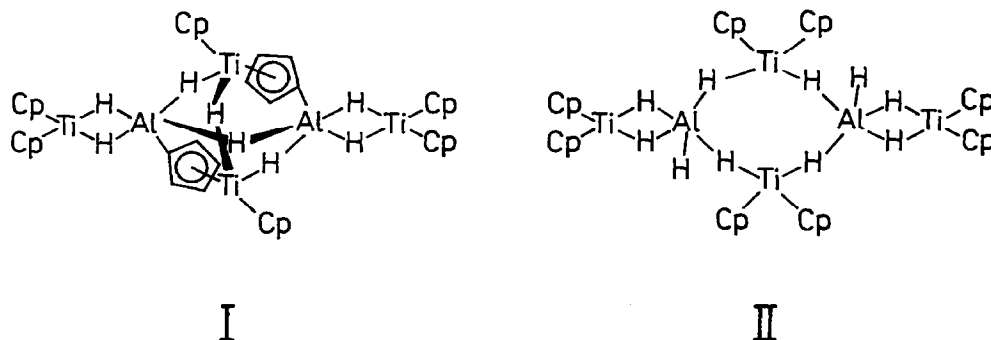
The electronic absorption spectra of the $\text{Cp}_2^*\text{TiAlH}_4$ complexes showed a nearly regular shift of the charge transfer band (A) to longer wavelengths but the *d*–*d* transitions (B,C) were unaffected by the methyl substituents except for the pentaalkylated complexes (Table 2). The increase of λ_{max} (A) is connected with increase in energy of the HOMO induced by the methyl substituents [2–5]. The extraordinary spectral parameters found in the $(\text{Me}_5\text{Cp})_2\text{TiAlCl}_{4-x}\text{Et}_x$ ($x = 0\text{--}2$) complexes [6] were thought to be because of sterical hindrance, but this is hardly justified in case of the AlH₄ ligand [8]. Hence, we suggest that the shift of the *d*–*d* transitions to longer wavelengths in the pentaalkylated derivatives is false and results from the presence of a minor diamagnetic byproduct which is strongly absorbing near 600 nm.

Aging of the $\text{Cp}_2^\text{TiAlH}_4$ complexes and reaction with butadiene*

All the $\text{Cp}_2^*\text{TiAlH}_4$ complexes were unstable on a time scale of weeks. All of them except pentaalkylated ones gave rise to cluster compounds analogous to the parent, the formation of which was previously observed in the $\text{Cp}_2\text{TiCl}/\text{LiAlH}_4/\text{toluene}$ [13]. All these compounds were characterized by a broad ESR signal with

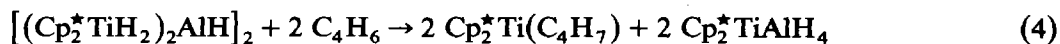
approximately the same g -value as the resolved spectra of corresponding $\text{Cp}_2^*\text{TiAlH}_4$ complexes (Table 1). The electronic absorption spectra of the cluster compounds remained the same as those of the $\text{Cp}_2^*\text{TiAlH}_4$ complexes except that the long wavelength shoulder at 640 nm (C) was shifted to 595 nm in all compounds. This coincidence of most of the spectroscopic parameters points to very similar titanium ligand field environments in both types of complex.

Earlier we found that the cluster obtained in the $\text{Cp}_2^*\text{TiCl}/\text{LiAlH}_4$ system reacts rapidly with dienes to give a mixture of the $(\eta^3\text{-allyl})\text{titanocene}$ derivative (Cp_2TiA) and $\text{Cp}_2\text{TiAlH}_4$. The latter then reacts slowly with the diene to give the same Cp_2TiA compound. In view of this observation we have suggested that the cluster is composed of the Cp_2TiH and $\text{Cp}_2\text{TiAlH}_4$ units [13]. Evidence of the validity of our suggestion was given by an X-ray diffraction study carried out previously on the minor product (I) of the reaction between Cp_2TiCl and LiAlH_4 in TMEDA/toluene [17]. We think that this is the product of hydrogen elimination from the cluster which in turn rapidly reacts with dienes. Accordingly, this cluster should contain the Al-H-Ti bonds and two non-bridged Al-H bonds as shown in the structure II instead of the $\eta^1:\eta^5\text{-C}_5\text{H}_4$ bridges between Ti and Al atoms in I. The



pentahydridoaluminate group was confirmed by X-ray crystallography of I and of complex $[(\text{Me}_5\text{Cp})_2\text{TiH}_2]_2\text{AlH}$ [8]. If the cluster has structure I then Cp_2TiA and the Natta's complex $[(\text{C}_5\text{H}_5)(\text{C}_5\text{H}_4)\text{TiHAlR}_2]_2$ should have been formed in equal amounts, the latter being easily recognizable by the strong absorption band at 498 nm [18]. The compound $(\text{Cp}_2\text{TiH}_2)_2\text{AlCl}$ [19], which is also probably formed in the $\text{Cp}_2\text{TiCl}/\text{LiAlH}_4/\text{toluene}$ system, in addition to Cp_2TiA should yield a very stable complex $\text{Cp}_2\text{TiCl}_2\text{AlR}_2$ ($\text{R} = \text{allyl}$ derived from the diene) which is easily detected by the ESR method (single line at $g = 1.977$) [18].

In agreement with the behaviour of the Cp cluster (probably II) all clusters containing methyl-substituted Cp^* ligands reacted with an excess of butadiene to give (1-methyl- $\eta^3\text{-allyl}$)titanocenes according to eq. 4 and 5.



The ESR spectra of the reaction mixtures after completion of reaction 4 consisted of a single line at $g = 1.9903\text{--}1.9930$ due to (1-methyl- $\eta^3\text{-allyl}$)titanocene (vide infra) and a multiplet of the $\text{Cp}_2^*\text{TiAlH}_4$ complex in comparable intensities. The final

Table 3

ESR spectra of the $\text{Cp}_2^*\text{TiAlH}_4^1$ complexes which were formed in the presence of (1-methyl- η^3 -allyl)titanocenes

Cp^*	$\text{Cp}_2^*\text{TiAlH}_4^1$				No. of lines
	g	a_{Al}	a_{H}	$a_{\text{H}(\text{C}^*\text{p})}$	
MeCp	1.9886	0.49	0.41		8
Me ₃ Cp	1.9876	0.53	0.39		8
Me ₄ Cp ^a	1.9866	0.55	0.33	0.11	33
Me ₅ Cp	1.9850	0.54	0.35		8 ^b

^a Recorded at -5°C ; other complexes were measured at 20°C . ^b Approximate intensities were $1/2/4 \times 1/2/1$ with the 4 inner lines split; $a_{\text{Ti}(7/2)} = 0.485$ mT.

reaction solution contained only a trace of $\text{Cp}_2^*\text{TiAlH}_4$ in accord with the excess of butadiene in the equilibrium 5. The equilibrium constant of equation 5 was estimated to be 5 for the $\text{Cp}_2\text{TiAlH}_4/2,4$ -hexadiene system in *n*-hexane [20].

Reaction 5 also proceeded when an excess of butadiene was added to freshly prepared $\text{Cp}_2^*\text{TiAlH}_4$ complexes in toluene solution, but induction periods were observed for reactions of $(\text{Me}_4\text{Cp})_2\text{TiAlH}_4$ and $(\text{Me}_5\text{Cp})_2\text{TiAlH}_4$. The parameters of ESR spectra of all $\text{Cp}_2^*\text{TiAlH}_4$ complexes changed to those listed in Table 3 after a certain portion of the original $\text{Cp}_2^*\text{TiAlH}_4$ complex (see Table 1) was converted to (1-methyl- η^3 -allyl)titanocene. The complexes with changed ESR parameters are denoted as $\text{Cp}_2^*\text{TiAlH}_4^1$.

Among the $\text{Cp}_2^*\text{TiAlH}_4$ complexes only $(\text{Me}_5\text{Cp})_2\text{TiAlH}_4$ and $(\text{EtMe}_4\text{Cp})_2\text{TiAlH}_4$ behaved in a different manner on aging. They did not form the clusters described but gave rise to paramagnetic complexes characterized by an ESR triplet spectrum (Table 1). These compounds did not react with butadiene and the ESR triplet splitting was not changed in the compounds obtained from deuterated aluminates. The paramagnetic compounds were stable up to 150°C but upon heating to 200°C in vacuo they released the titanocene derivatives containing the dimethylenecyclopentenyl ligand, $(\text{Me}_5\text{C}_5)(\text{Me}_3\text{C}_5(\text{CH}_2)_2)\text{Ti}$ [21] and $(\text{EtMe}_4\text{C}_5)(\text{EtMe}_2\text{C}_5(\text{CH}_2)_2)\text{Ti}$. The electronic absorption spectra (λ_{max} 580 nm) and mass spectra (m/z 316 M^+ (100%) and m/z 330 M^+ (100%), respectively) were in agreement with those of authentic samples [7]. The same paramagnetic compounds were also formed as intermediate products in the high-temperature reduction of peralkylated $\text{Cp}_2^*\text{TiCl}_2$ complexes with LiAlH_4 [7] and their structure is currently under study.

The systems $\text{Cp}_2^\text{TiCl}/\text{LiAlH}_4/\text{toluene}/\text{butadiene}$*

The reactions that took place in these systems were strongly affected by the nature of the Cp^* ligand. In all these systems except for those containing $(\text{Me}_5\text{Cp})_2\text{TiCl}$ and $(\text{EtMe}_4\text{Cp})_2\text{TiCl}$, the Cp_2^*TiA compounds were initially formed along with the $\text{Cp}_2^*\text{TiAlH}_4^1$ complexes. $(\text{MeCp})_2\text{TiCl}$ was completely consumed to give a mixture of both products in which $(\text{MeCp})_2\text{Ti}(\text{C}_4\text{H}_7)$ predominated. In the Me_3Cp and Me_4Cp systems the Cp_2^*TiA compounds initially formed, disappeared and pure $\text{Cp}_2^*\text{TiAlH}_4^1$ complexes were transiently obtained. The $\text{Cp}_2^*\text{TiAlH}_4^1$ complexes were slowly transformed into the Cp_2^*TiA compounds over a period of several days. The $\text{Cp}_2^*\text{TiAlH}_4^1$ complexes observed in these systems had the same ESR parameters (Table 3) as the $\text{Cp}_2^*\text{TiAlH}_4^1$ complexes that were generated during

the reaction of butadiene of the freshly prepared $\text{Cp}_2^*\text{TiAlH}_4$ complexes or their clusters (vide supra). Only $(\text{Me}_5\text{Cp})_2\text{TiCl}$ and $(\text{EtMe}_4\text{Cp})_2\text{TiCl}$ were initially converted to the $\text{Cp}_2^*\text{TiAlH}_4$ complexes without transient formation of Cp_2^*TiA . Their ESR spectra were identical with those listed in Table 1. However, when these complexes began to react with butadiene under formation of Cp_2^*TiA the parameters of ESR spectra changed to those listed in Table 3.

The above results indicate that reaction 2, followed by very rapid addition of butadiene to the $[\text{Cp}_2^*\text{TiH}]$ species, applies in the initial stages of all but the peralkylated systems. The absence of the initial formation of Cp_2^*TiA in the peralkylated systems may point to low reactivity of the Cp_2^*TiH species or the absence of reaction 2 in the presence of butadiene.

The changed parameters of the $\text{Cp}_2^*\text{TiAlH}_4$ complexes, which were observed only after the Cp_2^*TiA compounds had formed in the systems, should be due either to changed solvation of the complexes or to butadiene insertion into outer Al-H bonds in the $\text{Cp}_2^*\text{TiAlH}_4$ complexes. Similar changes of ESR parameters were induced by the addition of various unreactive unsaturated hydrocarbons to the toluene or hexane solutions of $\text{Cp}_2\text{TiAlH}_4$ [20]. In the present case, the formation of the same peralkylated $\text{Cp}_2^*\text{TiAlH}_4$ complexes in toluene and the toluene/butadiene mixture excludes the solvation with butadiene possibility. The problem remains open since no detailed study was performed on possible butadiene products formed in the presence of the Cp_2^*TiA compounds and no method was available to prove the absence or presence of butenyl groups in the $\text{Cp}_2^*\text{TiAlH}_4$ complexes.

Properties of the (1-methyl- η^3 -allyl)titanocenes

The Cp_2^*TiA compounds were obtained pure by evaporation of reaction solutions to dryness and subsequent extraction with n-hexane. The identity and purity of all compounds (evaporated hexane solutions) was checked by mass spectrometry: $(\text{MeCp})_2\text{Ti}(\text{C}_4\text{H}_7)$ m/z 261 M^+ , 206 (100%); $(\text{Me}_3\text{Cp})_2\text{Ti}(\text{C}_4\text{H}_7)$ m/z 317 M^+ , 262 (100%); $(\text{Me}_4\text{Cp})_2\text{Ti}(\text{C}_4\text{H}_7)$ m/z 345 M^+ , 290 (100%). The peralkylated (1-methyl- η^3 -allyl)titanocenes were not pure monomers from the mass spectra. In addition to the parent compounds, e.g., $(\text{Me}_5\text{Cp})_2\text{Ti}(\text{C}_4\text{H}_7)$ m/z 373 M^+ , 318 (100%), minor amounts of their analogues $M + 28$ (CH_2CH_2) + C_4H_6 + C_4H_6 + C_4H_6 were detected at higher temperatures of the sample as judged from $(M')^{++}$ ions. Formation of these compounds requires butadiene disproportionation-addition reaction which is difficult to rationalize. This reveals yet another extraordinary catalytic property of the peralkylated titanocene derivatives [22,23].

The ESR spectra of methyl substituted Cp_2^*TiA compounds showed a single line signal at temperatures below 30°C. Only the pentaalkylated compounds displayed a poorly resolved triplet splitting which coalesced to a single line below -60°C. This behaviour seems to be typical for the pentaalkylated Cp_2^*TiA compounds and is not due to the presence of the high molecular weight impurities (vide supra). The hyperfine splitting due to the allyl group protons, which is diagnostic for the structure of the Cp_2TiA derivatives [20], or for protons of a partially substituted cyclopentadienyl ring was not observed in either case. The methyl substituents at the Cp^* rings caused the g -values to fall slightly, as is usual in all the known derivatives (Table 1 and ref. 5,6). The anisotropic g -tensors (Table 4) did not indicate any differences in the structures of the methylated Cp_2^*TiA compounds from those of the known Cp_2TiA [20,24].

Table 4

ESR spectra of (1-methyl- η^3 -allyl)titanocenes (Cp_2^*TiA)^a

Cp^*	Cp_2^*TiA					
	g_{iso}^b	ΔH	g_z	g_y	g_x	\bar{g}_{av}
MeCp	1.9930	0.63	2.0019	1.9939	1.9868	1.9942
Me ₃ Cp	1.9925	0.59	2.0010	1.9930	1.9857	1.9933
Me ₄ Cp	1.9921	0.60	2.0010	1.9932	1.9846	1.9929
Me ₅ Cp	1.9903	^c	2.0018	1.9900	1.9840	1.9920

^a Anisotropic g -tensors were determined from the frozen toluene/butadiene solution at -130°C ; g_{iso} and ΔH (mT) were obtained at room temperature 22 – 25°C . ^b Isotropic g -values were slightly temperature dependent $g(-65^\circ\text{C}) - g(25^\circ\text{C}) = 0.009 (\pm 5 \times 10^{-5})$. ^c The ESR spectrum forms a poorly resolved triplet a 0.29 mT; it coalesced to a singlet ΔH 0.69 mT below -60°C .

The electronic absorption spectra of the Cp_2^*TiA compounds showed one absorption band in the visible region, similar to that in the spectra of Cp_2TiA compounds [20,25]. Its wavelength decreased on going from the Cp to the Me₃Cp compound but this trend was not followed by the higher analogues (see Table 2). The similar, though less-pronounced dependence was also found in the series of the $\text{Cp}_2^*\text{TiAlCl}_{4-x}\text{Et}_x$ series of compounds [6]. These effects may be connected with only partial d - d character of transitions as evidenced by the high molar extinction coefficient, especially in the Cp_2^*TiA series.

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