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THE CATALYTIC SYSTEM $[(C_5H_5)_2TiCl]_2/LiAlH_4$ IN AROMATIC SOLVENTS

I. FORMATION OF TITANOCENE HYDRIDE COMPLEXES; AN ESR STUDY

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Summary

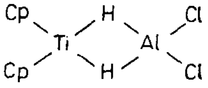
The reaction between $(Cp_2TiCl)_2$ and $LiAlH_4$ in aromatic solvents yields a stable complex compound which probably consists of linear, polynuclear form of Cp_2TiAlH_4 bearing Cp_2TiH side groups. It is characterized by a broad ESR single line ΔH 3.5–4.5 mT at $g = 1.990–1.991$. The binuclear complexes $Cp_2TiH_2AlCl_2$ (I), $Cp_2TiH_2Al(Cl)H$ (II) and $Cp_2TiH_2AlH_2$ (III) are successive formed as minor components. The ESR spectrum of II, consisting of 13 lines (a_{Al} 0.78 mT, a_H(bridge) 0.39 mT), and that of a new form of III (IIIb, a_{Al} 0.36 mT, a_H(bridge) 0.40 mT) were observed for the first time. Complexes I, II and IIIb show a superhyperfine splitting at low temperatures. Changes of the multiplicity of this splitting revealed that a_H(outer) is close to that of cyclopentadienyl-hydrogen atoms 0.056–0.058 mT. All these hydrides have an electronic absorption band (*d–d*) at λ_{max} 550 nm, $\varepsilon \sim 130$ (l cm mol^{-1}).

Introduction

Complex titanium aluminium hydrides, formed in the system $(Cp_2TiCl)_2/LiAlH_4$/benzene, have been used as catalysts for double bond shifts in medium size cyclic dienes [1] and for cyclization of 1,2-divinylcyclohexanes [2]. The closely related system $Cp_2TiCl_2/LiAlH_4$ also appears to be an effective catalyst for the double bond shifts in olefins and dienes [3,4]. Similar polymer-supported systems have been tested as catalysts for olefin isomerizations [5,6].

The homogeneous systems $Cp_2TiCl_2/LiAlH_4$ and $Cp_2TiCl/LiAlH_4$ in ethereal solvents have mainly been studied by spectroscopic means, and among the expected complexes I, II, and III the formation of I and III has been confirmed by ESR spectroscopy [7–10].

However, the necessity for ethereal solvents severely restricted use of these catalytic systems, and so we have used hydrocarbon media instead, both in catalytic tests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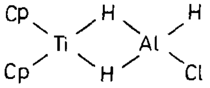
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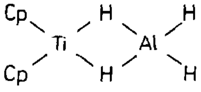
III

[1–4] and spectroscopic investigations [4]. In the present paper the reactions proceeding in the heterogeneous system $(Cp_2TiCl)_2/LiAlH_4$/toluene are investigated by means of ESR and electronic absorption spectra of complexes formed successively in the reaction mixture.

Results and discussion

It was known that the reaction of $(Cp_2TiCl)_2$ with $LiAlH_4$ in aromatic solvents proceeds in a complicated way [1], and does not yield the expected complex III. The structure and the origin of the final product IV, which is known to contain a reactive titanocene hydride species [1], was not clear, and so we studied the intermediates formed during the reaction using the ESR and electronic absorption spectra of samples of homogeneous solutions withdrawn from the reaction mixture. Representative samples, denoted A–D, correspond to those stages of the reaction in which particular intermediates were formed in high concentration; the yellow-green solution of $(Cp_2TiCl)_2$ turns progressively to reddish-blue (A), blue (B), dark green (C) and finally brown (D). A black precipitate is formed along with an almost colourless solution upon standing with $LiAlH_4$ for several days.

ESR spectra

The ESR spectra at room temperature revealed that in the course of the reaction the broad signal of $(Cp_2TiCl)_2$ (ΔH 9.2 mT) at $g = 1.977$ was replaced by another broad single line of slightly varying line width $\Delta H = 3.5$–4.5 mT and $g = 1.990$–1.991 (Fig. 1). These minor changes were partially due to overlapping spectra showing hyperfine splitting (hfs) patterns upon dilution of the sample solutions with toluene. The basic broad ESR line persisted throughout the reaction A–D and can therefore be ascribed to the final product IV.

The ESR spectrum of A at room temperature showed six poorly resolved triplets (Fig. 2a), which on further dilution gave the superhyperfine splitting (shfs) pattern ascribed to I by Henrici-Olivé and Olivé [8]. Though we found slightly higher values of both the splitting constants (a_{Al}, a_H(bridge)) and the g-value (Table 1), we observed the same temperature dependent linewidth effect as was described for I in THF solution [8]. The lowest magnetic field triplet of I at −45°C is shown in Fig. 3a.

Sample B yielded a complex, almost symmetric ESR spectrum consisting of 17 hfs lines at $g = 1.9920$ (Fig. 2b). The high-resolution ESR spectrum recorded with a diluted solution at −45°C (Fig. 4) confirmed that the complex pattern arose from the superposition of a new 13-line spectrum and the weaker spectrum of I. The latter is clearly indicated by pairs of lines lying behind both edges of the 13-line spectrum (cf. Fig. 2a and 2b). The outer lines are split by 0.32 mT and show lower resolution of the $M_I = 0$ line of the 1/2/1 triplet (cf. Figs. 3a and 4). The average splitting in the 13-line spectrum is 0.39 mT and each line is split into shfs multiplets with a 0.058 mT. Both the number of lines and hf splitting fit to the coupling pattern

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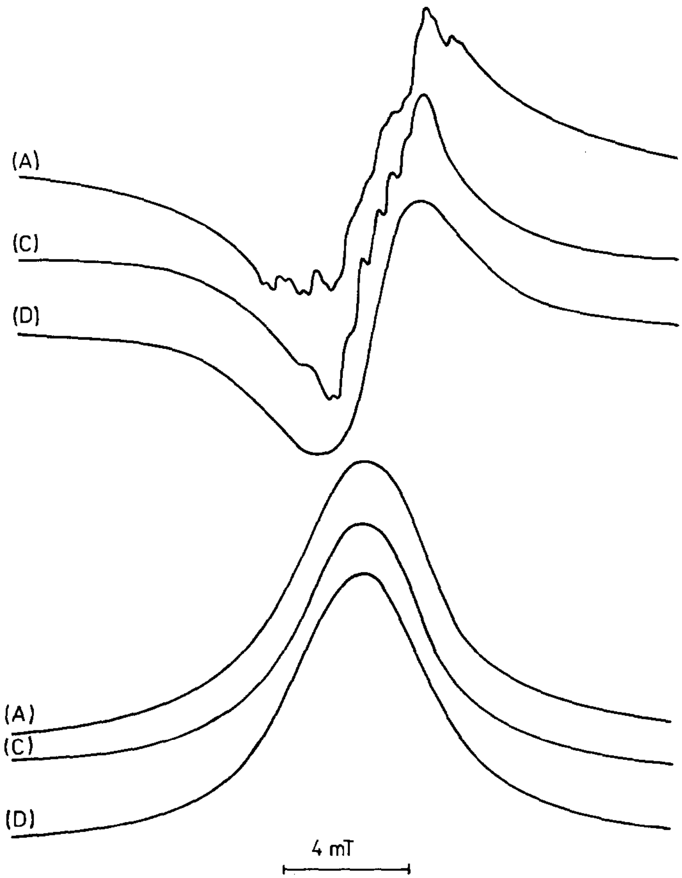

Fig. 1. The ESR spectra of samples A, C and D and their integrated forms (lower section) at room temperature.

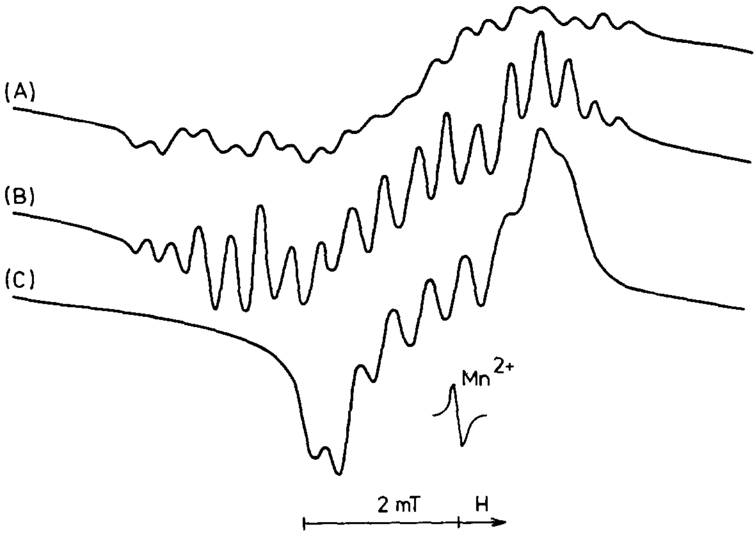

Fig. 2. The central sections of the ESR spectra of samples A, B and C recorded at room temperature with modulation amplitude 0.1 mT.

TABLE I

ESR PARAMETERS OF TITANOCENE HYDRIDE COMPLEXES

Complex	g-value	a_{Al} (mT)	a_H(bridge) (mT)	a_H(outer,Cp) (mT)	Multiplicity		References
					hfs	shfs	
I	1.9920	1.06	0.32	0.058	$6\times(1/2/1)$	odd	This work
	1.993	1.08	0.31	0.057	$6\times(1/2/1)$	odd	8
	1.990	1.00	0.34	–	$6\times(1/2/1)$	–	9
II	1.9919	0.78	0.39	0.058	$1/(11\times2)/1$	even	This work
IIIa	1.991	0.53	0.53	–	$1/3/(4\times4)/3/1$	–	This work
	1.991	0.50	0.50	–	$1/3/(4\times4)/3/1$	–	10
	1.989	0.50	0.50	–	$1/3/(4\times4)/3/1$	–	7
IIIb	1.9888	0.36	0.40	0.056	$1/3/(4\times4)/3/1$	odd	This work
I-d_2	1.9922	1.04	–	0.055	6×1	odd	This work
	1.990	1.00	–	–	6×1	–	9
II-d_3	1.9919	0.78	–	0.058	6×1	–	This work
IIIa-d_4	1.9887	0.56	–	–	6×1	–	This work
	1.991	0.50	–	–	6×1	–	10
IIIb-d_4	1.9882	0.36	–	0.060	6×1	[a]	This work
IV	1.990–1.991 [b]	$\Delta H = 3.5$–4.5 mT [b]			–	–	This work

[a] Probably odd. [b] IV-d gives the same parameters.

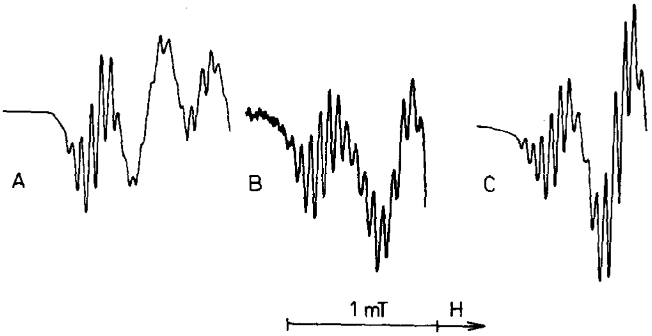

Fig. 3. The low magnetic field edges of the high resolution ESR spectra of complexes I (sample A) (A), II (sample taken between B and C, containing IIIa and no I) (B), IIIb in n-hexane (isolated from C) (C). The spectra were recorded with modulation amplitude 0.01 mT at temperatures −40°C A, B and −60°C C.

1/(11 × 2)/1 expected for the complex II provided a_{Al} (0.78 mT) = 2 a_{H}(bridge) (0.39 mT). The superposition with the spectrum of I modulates the hfs line intensities considerably, e.g. the higher intensities of the 3rd and the 9th line result from exact summation with $M_{\mathrm{I}} = 0$ lines of I, while other lines of I are subtracted to different extents (Fig. 2b). This superposition also accounts for the slight variation of the splitting between particular hfs lines (0.38–0.40 mT) and for the changes in the multiplicity of the shfs patterns of hf lines in the order: even, even, odd, even, odd, even, odd and so on symmetrically. The overall symmetry of the experimental spectrum confirms that the g-values of complexes I and II are practically identical. The even number of shfs lines in the ESR spectrum of II was confirmed by the measurement of a sample which had been taken from the reaction mixture between samples B and C and in which I was already absent. This sample showed superposition of the eight-line spectrum of IIIa (see below) and the spectrum of II, the first low-field hfs line of which (Fig. 3b) was observed uncontaminated. We did not find any reaction stage at which pure II could be obtained; it was always accompanied by either I or IIIa.

In light of the present results, the assignment of the 17-line ESR spectrum at $g = 1.989$ observed by Bulychev et al. [7,9] in the system $Cp_2TiCl_2/LiAlH_4$ (1/1)/

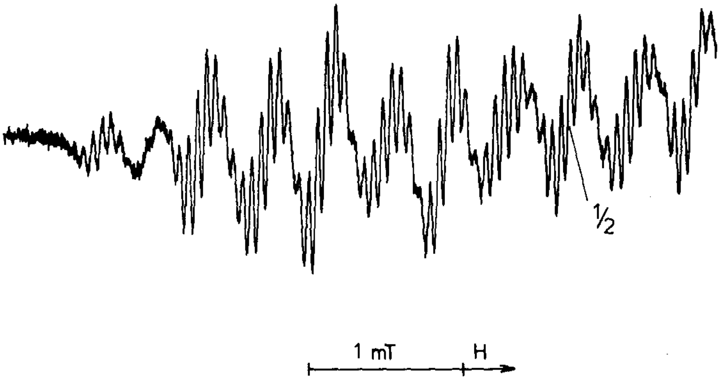

Fig. 4. The low-field half of the ESR spectrum of sample B at −40°C recorded with modulation amplitude 0.01 mT.

ether/benzene to a dimer of II seems doubtful. On the other hand, the parameters of the 13-line spectrum which they observed for $Cp_2TiH_2Al(Br)H$ [9] agree with our assignment.

The green sample (C) exhibited the unsymmetric eight-line ESR spectrum (Fig. 2c) resembling the known spectrum of III [7,9]. Comparison of ESR spectra of samples collected between B and C showed that they were composed of two eight-line spectra and a continuously decreasing spectrum of II, which was finally absent in C. The transient complex, more abundant at the beginning of transformation II → III, is denoted IIIa. It could not be obtained pure and therefore its ESR parameters $g = 1.991$ and $a_{Al} = a_H(\text{bridge}) = 0.53$ mT were only approximately determined. The second intermediary complex, denoted IIIb, was prepared in a pure state by evaporating C in vacuo and extracting the gray-green solid with n-hexane. The blue hexane solution exhibited an eight-line multiplet 1/3/(4 × 4)/3/1 at $g = 1.9888$ with hf splitting $a = 0.36$ mT between inner four lines of equal intensity and $a = 0.40$ mT between outer lines. The diluted solution of IIIb yielded further shf splitting $a = 0.056$ mT of all hf lines at −65°C (Fig. 5). This shf splitting is nearly the same as that observed in complexes I and II; in all cases it may be brought about by the interaction of the unpaired electron with η^5-cyclopentadienyl protons [8,11]. The odd multiplicity of shf splitting was observed for hf lines having intensities 1 and 4, while the two lines of the intensity 3 possessed even multiplicity. This variation of multiplicities agrees well with the varying values of hf splitting, and can be explained in terms of the difference between the coupling to inner hydride protons $a_H = 0.40$ mT and that to the aluminium nucleus. Since the difference $a_H - a_{Al} = 0.040$ mT is sufficiently close to the shf splitting 0.056 mT, the even multiplicity of hf lines of intensity 3 is caused by the superposition of two odd multiplets shifted by the value of shfs, as is shown in the hfs pattern of Fig. 5.

The ageing of samples A and B led to a further change in the composition of the complexes, I being converted into II and II into III simultaneously with the decrease in their contribution to the total paramagnetic absorption which, however, remained constant. The fall of the contribution of IIIb continued slowly (for days) in sample B and more rapidly in C and in the reaction mixture. The brown solution of D formed

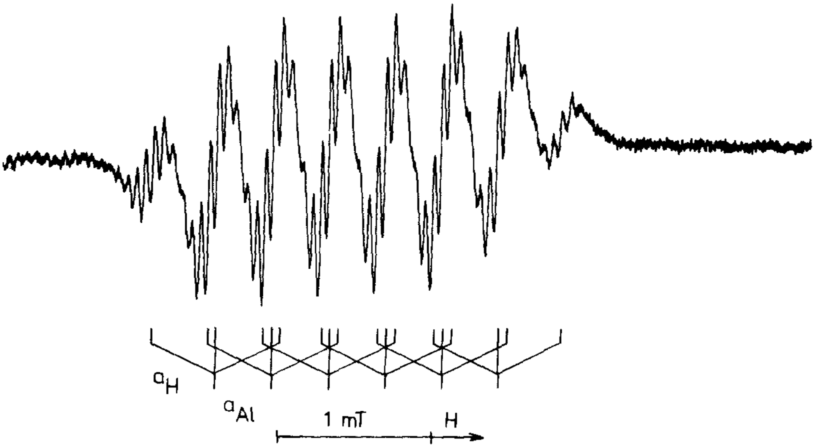

Fig. 5. The high resolution ESR spectrum of IIIb in n-hexane at −60°C solution recorded with modulation amplitude 0.01 mT.

after several hours gave the broad ESR line of IV without any hfs structure. Its total paramagnetic absorption was, however, lower by 5–10% than that of preceding samples.

The assignment of coupling constants of complexes I–III was confirmed by using deuterium labelled analogues, which also yielded some indication of the structure of IV. The ESR spectra of complexes I-d_2, II-d_3 and III-d_4, formed in the reaction of $(Cp_2TiCl)_2$ with $LiAlD_4$, showed deuterium atoms did not exchange with the cyclopentadienyl protons or with toluene. The ESR spectra of all the complexes consisted of six lines of equal intensity due to the interaction of unpaired electron with aluminium nucleus ($I = 5/2$). The values of a_{Al} obtained from deuterated binuclear complexes agreed with those obtained from the hydride derivatives (Table 1). The complex II-d_3 was observed as a minor component only in combination with I-d_2 or with both I-d_2 and IIIa-d_4, showing that II-d_3 may be even less stable than II. On standing, IIIa-d_4 is slowly converted into IIIb-d_4, this transformation changing the sextet with $a \sim 0.5$ mT into another with $a \sim 0.4$ mT. The shf splitting was observed at low temperatures for I-d_2, II-d_3 and IIIb-d_4, but the shfs multiplicity (odd) could be established only for I-d_2. The complex IIIb-d_4 in hexane exhibited slightly asymmetric shfs ESR spectrum at −60°C, with a notably poorer resolution than was observed with IIIb. The line width of the broad ESR line of IV does not change in the deuterated samples, showing that the large line half-width is not due to any unresolved coupling to hydrogen atoms.

The coupling constants a_{Al} and a_H(bridge) in the complete series I–III (Table 1) show a dependence on the nature of outer substituents on the aluminium atom. An increase in the number of hydrogen atoms in outer positions leads to a decrease in a_{Al} and an increase, though less pronounced, in a_H(bridge), reflecting the lower electron affinity of hydrogen than of chlorine atoms.

The changes of the multiplicity of the shf splitting from odd for I to even for II and odd for IIIb indicate the contribution of the outer hydride protons of II and IIIb to the shf splitting exhibited by ten equivalent cyclopentadienyl protons. The good resolution of shfs multiplets in all complexes allows us to conclude that the values of coupling constants of the outer hydride protons are close to those of the cyclopentadienyl protons, i.e., 0.056–0.058 mT.

Electronic absorption spectra

The electronic absorption spectra of the reddish-blue sample A and the blue sample B are very similar, showing a weak, very broad band with λ_{max} 540–550 nm, which replaced the original absorption bands of $(Cp_2TiCl)_2$ (CT band 455 nm, log $\varepsilon \sim 3$, *d–d*-band 690 nm, log $\varepsilon \sim 2$). The appearance of the spectra of A and B is very similar to that of hexane solution of IIIb (λ_{max} 550 nm, $\varepsilon \sim 130$) (Fig. 6). This weak absorption band is tentatively assigned to the *d–d* transition analogous to the same transition of $Cp_2TiAlCl_4$ at 660 nm [12]. The reddish colour of A is due to the presence of an absorption shoulder near 500 nm. As it is known in the binuclear complexes $Cp_2TiCl_2AlR_{2-x}Cl_x$ (R = ethyl, $x = 0$–2) the *d–d* transition at 700 nm is shifted towards shorter wavelengths with increasing x, the shoulder at 500 nm may reflect the presence of I in A. Since we know from the ESR measurements that the species IV giving the broad ESR signal is by far the major paramagnetic component in samples A and B, we assume that its absorption spectrum is very similar, if not identical, with that of B and IIIb.

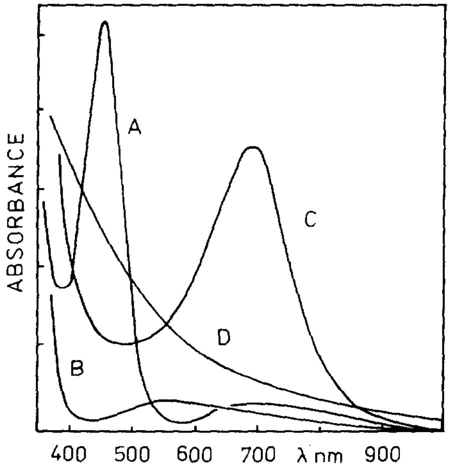

Fig. 6. The electronic absorption spectra of the system $(Cp_2TiCl)_2/LiAlH_4$/toluene: $(Cp_2TiCl)_2$ in toluene (A), sample B (B), sample C (C) and sample D (D).

The formation of complexes IIIa and IIIb, which was simultaneously followed by ESR, was accompanied by the appearance of a strong absorption band with λ_{max} 690 nm, which was responsible for the green colour of sample C. This completely obscured the weak absorption band of both complexes IV and IIIb, the presence of which was, however, proved by the ESR spectra and by the isolation of IIIb. Since we did not observe any change in the ESR spectra to which the appearance of the green compound could be attributed, and since the total ESR absorption did not observably decrease, we suggest that an intermediate diamagnetic decomposition product is responsible for the absorption band at 690 nm which has a molar extinction coefficient of at least 10^3. In the later stage of the reaction the green colour of C is replaced by an intense continuous absorption, the intensity of which decreases from 300 nm to longer wavelengths, giving the brown colour of D (Fig. 6). The weak absorption band of IV is hidden behind this continuous absorption.

Comparison with the ether-containing system

Since the reported formation of III in the system $Cp_2TiCl/LiAlH_4$/diethyl ether/benzene [7] was not consistent with the reaction course observed in the toluene medium, while the presence of species IIIa and a strong absorption band at 600–700 nm seemed to be common to both systems, we investigated the former system under comparable conditions. In the homogeneous system $Cp_2TiCl/LiAlH_4$ (1/1)/diethyl ether/benzene (1/2), complexes I and II were not detected but complex IIIa showing $a_{Al} = a_H = 0.5$ mT at $g = 1.991$ was formed as the only paramagnetic species. The electronic absorption spectra revealed that the absorption of IIIa, probably near 550 nm, was accompanied by a quickly increasing absorption band with a maximum which shifted to the reported value 660 nm attributed erroneously to III [7] and later to 690 nm. Therefore we suggest that the green diamagnetic product has the same structure in both systems, and that in toluene it is formed only by decomposition of IIIa. In toluene a puzzling problem is posed by the presence of two species IIIa and IIIb. The occurrence of shfs in the ESR spectra of complexes I, II and IIIb places them in one series, while complex IIIa, which does not exhibit shf splitting, has been predominantly observed in ethereal solvents. It cannot be excluded that the small amount of IIIa formed in the system under study is due to traces of diethyl ether incorporated into the crystalline $LiAlH_4$, despite degassing at 100°C for 1 h at 10^{-4} Torr.

The formation and suggested structure of the titanocene hydride-containing product IV

The spectroscopic study showed that complex IV was accompanied by complexes I, II and III in samples A, B and C, respectively, and by the diamagnetic decomposition products in samples C and D. The presence and structures of the binuclear complexes give indications of the reactions proceeding in the heterogeneous reaction system. Since $LiAlH_4$ is nearly insoluble in toluene, the conversion of $(Cp_2TiCl)_2$ to I and IV, as found in A, has to include a two-fold utilization of the primarily formed complex III according to equations 1–3.

$$1/2(Cp_2TiCl)_2 + LiAlH_4 \rightarrow LiCl + Cp_2TiAlH_4 \quad (1)$$

$$1/2(Cp_2TiCl)_2 + Cp_2TiAlH_4 \rightarrow Cp_2TiH + Cp_2TiAlH_3Cl \quad (2)$$

$$1/2(Cp_2TiCl)_2 + Cp_2TiAlH_3Cl \rightarrow Cp_2TiH + Cp_2TiAlH_2Cl_2 \quad (3)$$

As no free $(Cp_2TiCl)_2$ was observed in A, the further reaction with $LiAlH_4$ must proceed via equilibration of the alanate and chloroalanate ligands, according to equations 4 and 5, subsequently yielding complexes II and III.

$$Cp_2TiAlH_2Cl_2 + LiAlH_4 \rightarrow Cp_2TiAlH_3Cl + LiCl + AlH_3 \quad (4)$$

$$Cp_2TiAlH_3Cl + LiAlH_4 \rightarrow Cp_2TiAlH_4 + LiCl + AlH_3 \quad (5)$$

If titanocene hydride Cp_2TiH, formed according to equations 2 and 3, were monomeric and reactive, it should react with AlH_3 to give III according to equation 6, the overall result would be constant with equation 1.

$$Cp_2TiH + AlH_3 \rightarrow Cp_2TiAlH_4 \quad (6)$$

The experimental results show, however, that III is not formed by reaction 6, and this may be accounted for by unexpected stability of the titanocene hydride species and by the oligomerization of alane [13]. Instead, the ageing of all samples A–C results in the decay of the binuclear complexes while IV remains the only stable product.

In regard to the structure of IV, the positions and intensities of the *d–d* transition and the *g*-values show that the ligand fields around the titanium atoms are very similar in the binuclear complexes I–III and the species IV. The large line width of the ESR signal of IV, which was found not to vary upon replacement of hydrides by deuterides, indicates the titanium–titanium electron exchange interaction, similar to that occurring in the dimer of Cp_2TiCl [14]. The difference between the line halfwidth for IV (3.5–4.5 mT) and that for $(Cp_2TiCl)_2$ (9.2 mT) is qualitatively consistent with the difference in efficiencies of the electron exchange interactions through –H–Al–H and di-μ-chloro bridges. In both cases, however, the exchange interaction does not lead to observable spin pairing, as confirmed by quantitative transformation of their ESR signals into the ESR signals of monomeric species, e.g., allyltitanocene derivatives [1] and Cp_2TiCl [4].

We suggest that the initial formation of the Cp_2TiH species (equations 2 and 3) initiates the growth of linear polynuclear complexes rather than binuclear complexes I–III. These complexes must be capable of further binding of Cp_2TiH species through the alane moiety, as schematically shown in Fig. 7. The stability of the complexed Cp_2TiH must be the result of occupation of the free coordination site on the titanium atom by the bridging hydrogen atom and by the steric hindrance which lowers the reactivity at the relatively free Ti–H bond, since titanocene hydride was reported to be stable only at low temperature in the form of a dimer [15].

The suggested structure is supported by reactions of IV with unsaturated hydrocarbons. All the olefins and dienes examined reacted with IV, forming alkyl- and allyl-titanocene derivatives in addition to IIIb. The release of the Cp_2TiH species from IV by the reaction with the double bond brings about the decomposition of the polynuclear complex IV into binuclear complexes IIIb. Following this relatively fast process, IIIb reacts with sterically unhindered dienes to give quantitatively allyltitanocene derivatives, while with sterically hindered dienes and internal olefins IIIb was quite stable. The high reactivity of IV thus provides evidence for the presence of a Cp_2TiH species more reactive than IIIb. A full account of the reactions of IV and IIIb with unsaturated hydrocarbons will be the subject of a forthcoming communication.

Properties of the product IV

Compound IV isolated from the reaction stage corresponding to sample B was previously used for the preparation of allyltitanocene compounds derived from 1,3-cyclodecadiene and 1,3-cyclododecadiene and for the isomerization of these hydrocarbons [1]. The concentrated blue benzene solution of IV was precipitated with n-hexane to give a black-blue crystalline material, the solubility of which in benzene decreased with the time of standing in the solid state. The supernatant n-hexane/benzene contained IV in much lower concentration than the original solution; IIIb was present only when the precipitated compound was freshly prepared. No significant amounts of aluminium hydrides could be detected after evaporation of the supernatant solution in vacuo, showing that alane oligomers were co-precipitated with IV. From the green sample C the dark product was isolated as a solid in the same way. It dissolved in benzene to give a brown solution, which reacted with olefinic hydrocarbons in the same way as IV isolated from B.

The blue compound IV slowly decomposes in sunlight in solution and in the solid

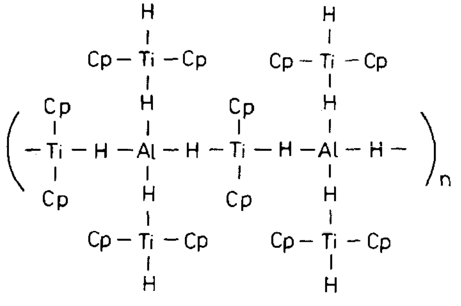

Fig. 7. The suggested structure of IV.

state. The blue or red-blue solid is precipitated on the ampoule walls, and the solid IV becomes less soluble when exposed to direct sunlight. In the dark it is thermally stable in both forms. Only 22% of IV decomposed after heating the benzene solution (10^{-2} *M*) to 100°C for 4 h as estimated from the decay of its ESR signal. However, no individual compound or significant decomposition product could be volatilized off from solid IV in the mass spectrometer up to 200°C. We suggest that polynuclear complexes containing bridging cyclopentadienyl ligands, similar in structure to Natta's complexes [16,17], can be formed both thermally and photolytically.

The addition of diethyl ether to the toluene solution of IV (1/1) caused only a slight increase in the concentration of IIIb in freshly prepared IV. The addition of triphenylphosphane had no effect upon the ESR or the electronic absorption spectrum of IV. The reaction of IV with anhydrous methanol afforded a crystalline green-blue compound. The ESR spectrum of its toluene solution consisted of six equal lines split by 0.46 mT at $g = 1.980$; these data match the complex $Cp_2TiAl(OCH_3)_4$ with bridging methoxy groups [11]. The controlled addition of anhydrous HCl yielded the complex $Cp_2TiAlCl_4$ as the only paramagnetic product [12].

Experimental

Chemicals

$(Cp_2TiCl)_2$ was prepared by the reduction of Cp_2TiCl_2 (Fluka) with aluminium powder in THF [14]. Aluminium chloride was removed by repeating washing of the product with ether and $(Cp_2TiCl)_2$ was sublimed in vacuo. $LiAlH_4$ (Fluka) and $LiAlD_4$ (99.4 ± 0.1%, Centr. Inst. Isotop. Radiat., Leipzig, GDR) were dissolved in ether and portions of the clear solutions were transferred to ampoules under vacuo. Toluene, benzene and ether were refluxed with $LiAlH_4$ then degassed, and green solutions in them of dimeric titanocene [4] were stored on a vacuum line.

Procedures

High-vacuum techniques using breakable seals were used for all operations and measurements of ESR and electronic absorption spectra.

The reaction between $(Cp_2TiCl)_2$ and $LiAlH_4$ or $LiAlD_4$, was started by adding the toluene solution of $(Cp_2TiCl)_2$ (10^{-2} *M*) to solid $LiAlH_4$ ($LiAlD_4$) which had been dried in vacuo and degassed at 100°C and 10^{-4} Torr for 1 h. The course of the reaction was followed by spectral measurements of samples of solution separated from the reaction mixture.

Compound IV was prepared in the same manner in benzene solution. Benzene (30 ml) was distilled onto $(Cp_2TiCl)_2$ 1 g (4.7 mmol) and the saturated solution was poured onto $LiAlH_4$ 0.4–0.8 g which had been degassed as described. The yellow-green solution turned blue on contact with $LiAlH_4$. The solution was repeatedly poured onto the remaining solid $(Cp_2TiCl)_2$ and then back to $LiAlH_4$ until all the $(Cp_2TiCl)_2$ had dissolved and the solution was a clear blue colour. The solution was filtered through quartz wool, then concentrated to saturation and poured into n-hexane (40 ml), to give finely crystals of the blue compound IV. After washing with hexane and drying in vacuo, about 0.9 g IV was obtained, corresponding to 90% yield if the overall composition $(C_5H_5)_2TiAlH_4$ is assumed.

Methods

ESR spectra were measured on an ERS-220 spectrometer (Centre for Production of Scientific Instruments, German Acad. Sci., Berlin, GDR) in the X-band. The measurements at low temperatures were carried out using a variable temperature unit STT-3. The g-values were related to the Mn^{2+} standard ($g = 1.9860$). The quantitative determination of paramagnetic species was performed by double integration of the first derivative record using the heptane solution of DPPH as a standard.

Electronic absorption spectra were taken on a Varian Cary 17 D spectrometer using sealed quartz cells.

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