THE ISOMERIZATION CATALYST $(C_5H_5)_2TiCl_2$-LiAlH$_4$. INFLUENCE OF THE NATURE OF UNSATURATED HYDROCARBONS ON THE CATALYST ACTIVITY

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Summary

The reaction pathway between the components of the catalytic system Cp_2TiCl_2-LiAlH$_4$-unsaturated hydrocarbon, depends considerably on the nature of the reaction medium. In dienes which are able to form stable η^3-allyltitanocene derivatives, these represents the main reaction product; they are catalytically active in the double bond shifts. In dienes not forming stable η^3-allyltitanocene derivatives and in α-olefins, the catalytically-active η^1-alkenyl- and alkyl-titanocenes are transiently formed, deactivating rapidly to give the $[(C_5H_5)(C_5H_4)TiHAlR_2]_2$ complexes and minor amounts of η^3-allyltitanocene derivatives in a side reaction involving intermolecular hydrogen transfer. In all α-olefinic hydrocarbons, the formation of alkyl-, η^1-alkenyl- or η^3-allyl-titanocene derivatives is preceded by the hydroalumination reaction, yielding $Cp_2TiCl_2AlR_2$ complexes. In internal olefins, the hydroalumination reaction does not occur and the alkyltitanocenes which are formed catalyze the transformation of $(Cp_2TiCl)_2$ into μ-(η^5 : η^5-fulvalene)-di-μ-chlorobis(η^5-cyclopentadienyltitanium), thus inducing the self-deactivation of the system.

Introduction

The systems consisting of Cp_2TiCl_2 and an organometallic reducing agent are subject to increasing interest because of their catalytic activity in hydrometallations [1–3] and in isomerizations [4–8] of unsaturated hydrocarbons.

Recently, we have used the Cp_2TiCl_2-LiAlH$_4$ system for practical laboratory isomerizations of industrially-produced dienes, e.g. bicyclo[4.3.0]nona-3,7-diene [9], 1,5-cyclooctadiene [10], 4-vinylcyclohexene and 1,5-hexadienes [11], obtaining quantitatively the conjugated isomers. In all cases, a higher temperature ($\geqslant 60°C$)

was necessary to increase the rate of Cp_2TiCl_2 reduction with commercial, non-activated $LiAlH_4$. Although active $LiAlH_4$, which reduces Cp_2TiCl_2 at room temperature [12], can be obtained by evaporating an ether solution of $LiAlH_4$ in vacuo, the use of commercial $LiAlH_4$ makes the catalyst preparation simple and safe. This is also why we find it worthwhile to study this system in detail under the conditions of the isomerization experiment, i.e. at the boiling point of the unsaturated hydrocarbon, using commercial $LiAlH_4$ and Cp_2TiCl_2 and an argon atmosphere.

In this work we investigate the reactions which occur in the Cp_2TiCl_2-$LiAlH_4$ catalyst during isomerizations of some hydrocarbons containing the vinyl group, i.e. 1,5-hexadiene, 1,7-octadiene, 1-heptene, 1-octene and 4-vinylcyclohexene, and a comparison is made of the reactions proceeding in a mixture of internal heptenes. This study is complementary to our analogous study of the influence of internal and cyclic dienes, in which the presence of η^3-allyltitanocene-derivatives was found to be related to both the isomerization activity and the catalyst deactivation leading to μ-(η^5 : η^5-fulvalene)-di-μ-chlorobis(η^5-cyclopentadienyltitanium) [10]. Both studies are aimed at a general understanding of the catalysis by systems in which a titanocene hydride species is formed transiently in situ, and at explaining the differences in the catalyst behaviour, depending on the nature of unsaturated hydrocarbons.

Results and discussion

The Cp_2TiCl_2-$LiAlH_4$-unsaturated hydrocarbon systems were studied by ESR and electronic absorption spectroscopy (VIS) using samples removed from the reaction mixture under argon. Representative organometallic reaction products were isolated and identified by mass spectrometry and/or ^1H and ^{13}C NMR spectroscopy; other products of the same structural type were identified by the first two methods in the reaction solution immediately after the sample separation. The samples are denoted by a hydrocarbon number and indexed alphabetically by sampling order. All the spectroscopic data are collected in Table 1.
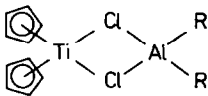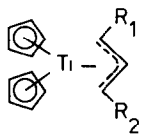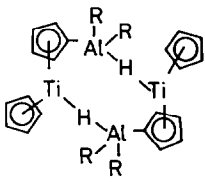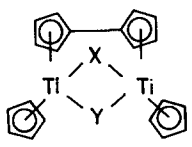
The behaviour of the catalytic systems was found to be different in α,ω-dienes forming stable η^3-allyltitanocene-derivatives (1,5-hexadiene (I), 1,7-octadiene (II)), in α-olefins (1-heptene (III), 1-octene (IV)), in dienes not forming stable η^3-allyltitanocene-derivatives (limonene (V), 4-vinylcyclohexene (VI)), and in internal olefins (a mixture of 2- and 3-heptenes (VII)). The results for particular systems are described in detail below.

1,5-Hexadiene (I)

The reduction of Cp_2TiCl_2 by $LiAlH_4$ proceeded slowly in boiling I ($\sim 60\,^\circ C$). The orange colour of Cp_2TiCl_2 turned to light green only after 5 h (sample I-a). Then the mixture suddenly started to boil vigorously and sample I-b was taken while the temperature of the solution was rising. The colour of the solution quickly turned to blue (I-c). During further boiling for 1 h the temperature rose to $80\,^\circ C$ but the blue colour did not change further (I-d).

The solution of I-a was poured away from the solid $LiAlH_4$, the solvent was distilled off in vacuo and the green material was extracted with hexane and crystallized at $-78\,^\circ C$. The mass spectrum of the crystalline solid (Table 1) showed peaks consistent with the formula $Cp_2TiCl_2Al(C_6H_{11})_2$ (A-I). The ESR and VIS spectra confirmed the binuclear structure of the complex, being analogous to that of

TABLE 1. SPECTROSCOPIC DATA ON TITANIUM COMPLEXES

Compounds, type		VIS ^{a}, ESR, MS and NMR data
(A)		VIS: A-I 661 nm, A-II not measured, all others 670–675 nm ESR: all compounds give singlet line $\Delta H = 0.8–1.1$ mT, $g = 1.977$
A-0	R = C_2H_5	MS: A-0, A-I and A-III fragment analo-
A-I	R = C_6H_{11}	gously: $[CpTiCl]^+$ (100%) > $[Cp_2TiCl]^+$ > $[Cp_2Ti]^+$
A-II	R = C_8H_{15}	~ $[RAlCl]^+$ > $[R_2AlCl]^+$ ≫ $[M - R]^+$ > $[M]^{+\cdot}$ (< 1%)
A-III	R = C_7H_{15}	Elemental composition of ions of A-0
A-IV	R = C_8H_{17}	(error in 10^{-3} of mass unit): $C_4H_{10}Al^{35}Cl$
A-V	R = $C_{10}H_{17}$	(+0.1), $C_{12}H_{15}TiAl^{35}Cl_2$ (+3.8),
A-VI	R = C_8H_{13}	$C_{14}H_{20}TiAl^{35}Cl_2$ (+4.9)
(B)		VIS: B-I 579 nm, B-II 565 nm ESR: all compounds give single line $\Delta H = 0.5–0.6$ mT, $g = 1.993$.
B-I	$R_1 = CH_3$ $R_2 = C_2H_5$	MS: B-I m/z 261.1108, error $+1.5 \times 10^{-3}$ for $[C_{16}H_{21}Ti]^+$; m/z 178.0259, error 2×10^{-4}
B-II–B-VII		for $[C_{10}H_{10}Ti]^+$
(C)		VIS: all compounds 400 (sh), 498 (s), 575 (s) nm ^{1}H NMR C-0: TiHAl -6.96 br s (1H); CH_3CH_2 0.72 q ($J = 7.3$ Hz, 2H), 0.96 q ($J = 7.3$ Hz, 2H), 1.43 t ($J = 7.3$ Hz, 3H), 1.55 t ($J = 7.3$ Hz, 3H);
C-0	R = C_2H_5	C_5H_4 4.37 s (1H), 4.98 s (1H), 5.88 s (1H),
C-III	R = C_7H_{15}	6.94 s (1H); C_5H_5 5.12 s (5H); (cf. ref. 17)
C-IV	R = C_8H_{17}	^{13}C NMR C-0: CH_3CH_2 4.6 t, 10.4 q, 10.7 q;
C-V	R = $C_{10}H_{17}$	C_5H_4 107.3 d, 109.9 d, 120.0 s, 132.8 d;
C-VI	R = C_8H_{13}	C_5H_5 102.1 d. Both NMR spectra indicate the inequivalence of the methyl groups [17]. The spectra of other compounds are identical as far as concerns the C_5H_5 and C_5H_4 ligands; also the TiHAl resonance is always in the -6.72 to -7.66 ppm range ^{b}.
(D)		VIS: D-1 538, D-2 468 and 640, D-3 432 and 828 nm (cf. ref. 10).
D-1	X = Y = Cl	
D-2	X = H, Y = Cl	
D-3	X = Y = H	

^{a} Electronic absorption spectra in visible range. ^{b} All compounds, except C-0, were not obtained in a crystalline form. They contained small amounts of paramagnetic impurities and hydrocarbons both of which prevented the resolution and assignment of spectra in the region of alkyl groups.

$Cp_2TiCl_2Al(C_2H_5)_2$ (A-0) [13]. The dark yellow substance remaining after the extraction was dissolved in benzene and identified by ESR and VIS as $(Cp_2TiCl)_2$ [12]. The hydrocarbon distilled off from I-a was unchanged I.

The vacuum distillation of the solvent from I-d left a greasy dark material which, after two recrystallizations from hexane, afforded a crystalline blue substance (B-I). The substance was identified as (1-methyl-3-ethyl-η^3-allyl)titanocene by its ESR, VIS and mass spectra (Table 1) [14,15]. Evidence for the quantitative transformation of A-I to B-I was obtained by ESR spectroscopy, as shown in Fig. 1.

The mass spectra of the crude greasy material revealed, besides B-I, the presence of trihexenylaluminium (indicated by ions at m/z 193 $[(C_6H_{11})_2Al]^+$) and its hexadiene homologues, characterized by ions at m/z 275.2345 (error $+4 \times 10^{-4}$ for $[C_{18}H_{32}Al]^{+\cdot}$, m/z 357 $[C_{24}H_{42}Al]^+$ and m/z 439 $[C_{30}H_{52}Al]^+$. Another peak at m/z 246.2344 (error $+3 \times 10^{-4}$ for $[C_{18}H_{30}]^{+\cdot}$ indicated the presence of the hexadiene trimer possessing probably the linear structure, because of the most abundant fragmentation to $[M - C_6H_{11}]^+$ (m/z 163).

The hydrocarbon present in the sample I-d was the mixture of geometrical isomers of 2,4-hexadiene described in ref. 11. The partial transformation of I into 1,4-hexadienes was already detected in the sample I-b.

1,7-Octadiene (II)

The reaction course, as monitored by ESR and VIS spectra, was analogous to that found in the system containing I. The formation of the blue-green complex $Cp_2TiCl_2Al(C_8H_{15})_2$ (A-II) was accomplished after only 10 min boiling at 117°C. Both the formation of η^3-allyltitanocene derivatives (B-II) and the isomerization of II to the internal conjugated dienes [11] were completed after a further 25 min boiling at a maximum of 127°C.

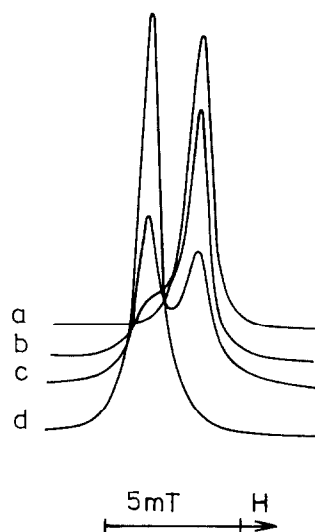It is highly probable that B-II consists of a mixture of η^3-allyltitanocene deriva-

Fig. 1. Integrated ESR spectra of the system $Cp_2TiCl_2 \cdot LiAlH_4$-1,5-hexadiene. Samples were taken after 300 min (I-a), 330 min (I-b), 360 min (I-c) and 460 min (I-d) from the reaction at 60–80°C

tives containing (1-methyl-3-butyl-η^3-allyl)titanocene and (1-ethyl-3-propyl-η^3-allyl)titanocene. These last compounds, prepared analogously at room temperature, absorb at 580 nm [16] which is the value found for (1,3-dialkyl-η^3-allyl)titanocenes [14]. The shift of the absorption band to 565 nm, found in B-II (Table 1), is due to presence of a minor amount of the complex $[(C_5H_5)(C_5H_4)TiHAl(C_8H_{15})_2]_2$ formed during preparation of B-II. The position of the absorption band of B-II is sensitive to the presence of a trace amount of the complex because the molar extinction coefficient of its most intense band at 498 nm is at least 10-times higher than that of B-II (ϵ(580 nm) ~ 2.6 l cm mol^{-1}). The components of B-II were not obtained in a crystalline form and, therefore, their structural determination was not attempted.

1-Heptene (III)

The reduction of Cp_2TiCl_2 in boiling III (94°C) yielded a blue-green solution (III-a) from which the hexane-soluble, crystalline complex $Cp_2TiCl_2Al(C_7H_{15})_2$ (A-III) was isolated. The dark yellow residue soluble in benzene was $(Cp_2TiCl)_2$. The subsequent rapid change of the colour to brown (III-b) and brown-red (III-c) was accompanied by the isomerization of III. In the ESR spectra of these samples (Fig. 2) the signal at $g = 1.993$ was observed, though in a one order of magnitude lower intensity than in the systems with I and II. Although this paramagnetic species could not be characterized by other methods, the ESR data are sufficient to assign it to an η^3-allyltitanocene derivative (B-III) [14–16]. Both species, A-III and B-III, decomposed further to give diamagnetic products. Among them, the red compound (C-III), well soluble in hexane, was isolated as the main component. The ^1H and ^{13}C NMR and VIS spectra confirmed that C-III is a heptyl analogue of the complex $[(C_5H_5)(C_5H_4)TiHAl(C_2H_5)_2]_2$ (C-0), prepared by heating $(Cp_2TiCl)_2$ with triethyl-
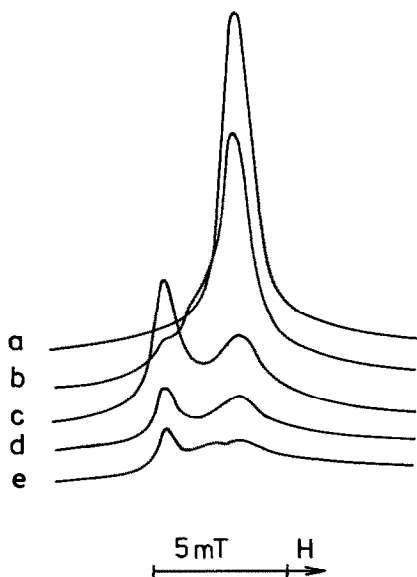

Fig. 2. Integrated ESR spectra of the system $Cp_2TiCl_2 \cdot LiAlH_4$-1-heptene. Samples were taken after 20 min (III-a), 25 min (III-b), 40 min (III-c), 50 min (III-d) and 100 min (III-e) from the reaction at 94–98°C.

aluminium in heptane [17] (Table 1). A large amount of 2-heptenes was already present in III-b and the final product, obtained after 2 h boiling, consisted of internal heptenes as follows: (E)-2- 32%, (E)-3- 38%, (Z)-2- 12%, (Z)-3- 8%.

1-Octene (IV)

This system behaved in all respects analogously to that containing III, except that all processes took place more rapidly at the boiling temperature 121–123°C.

4-Isopropenyl-1-methylcyclohexene (V)

After boiling for 20 min at 178°C, the colour of the reaction solution turned to light green and a singlet ESR signal appeared at $g = 1.978$, showing the maximum content of the paramagnetic species (V-a). By analogy, this species can be assigned as the binuclear Ti–Al complex A-V, in which V is probably hydroaluminated at the isopropenyl group. While the overall content of the paramagnetic species decreased steadily during the further reaction, a new doublet ESR signal ($a = 0.6$ mT) at $g = 1.985$ was increasing, as shown in Fig. 3. Its intensity then decreased more slowly than that of A-V and therefore it became the main paramagnetic species in the sample V-c. The colour of the reaction solution turned from green, through brown, to red and, according to its VIS spectrum, the sample V-c contained mainly the diamagnetic compound C-V. The ESR singlet signal of very low intensity at $g = 1.993$ occurred transiently before all the paramagnetic species decayed (V-d). It can be ascribed to an η^3-allyltitanocene derivative, B-V, which could be formed by
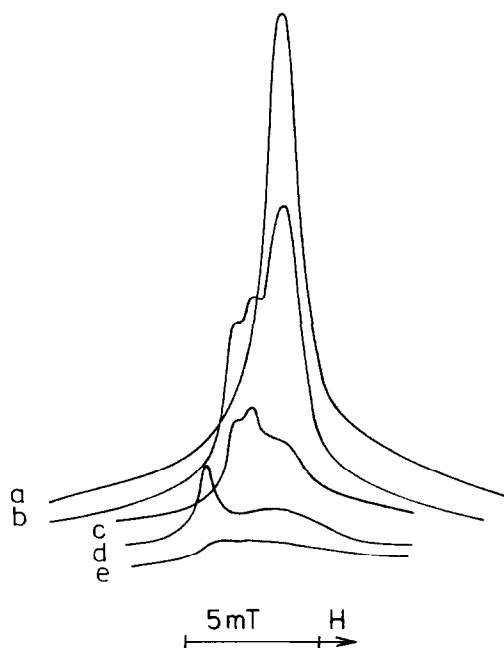

Fig. 3. Integrated ESR spectra of the system $Cp_2TiCl_2 \cdot LiAlH_4$-4-isopropenyl-1-methylcyclohexene. Samples were taken after 20 min (V-a), 40 min (V-b), 75 min (V-c), 100 min (V-d) and 140 min (V-e) from the reaction at 178°C. The record of V-c is amplified by 2, those of V-d and V-e by 4.

hydrogen transfer from V. The isomerization of V is hindered by the presence of tertiary carbon atoms in the molecule; no products of isomerization have been revealed by GC/MS.

The doublet ESR signal is attributed to a binuclear Ti–Al complex containing a μ-chloro-μ-hydrido- bridge, $Cp_2Ti(H)(Cl)AlR_2$, since the ESR spectrum is sufficiently characteristic of this species [18]. The formation of this type of complex was clearly detected during the transformation of A-0 into Cp_2TiAlH_4 under the action of solid $LiAlH_4$ in benzene solution [16]. In the other vinylic hydrocarbons used in this study, the μ-chloro-μ-hydrido-complexes did not occur because the hydrocarbons were more reactive towards the Ti–H–Al bond than V.

4-Vinylcyclohexene (VI)

The system using VI as the reaction medium behaved analogously to the preceding one, subsequently yielding compounds A-VI, B-VI and C-VI (Table 1), except that a higher concentration of B-VI was formed transiently in the earlier reaction stage. The isomerization, including the preferred shift of the vinyl group to give 4-ethylidenecyclohexene, commenced simultaneously with the occurrence of B-VI. The final product was practically pure 3-ethylidenecyclohexene as a 1 : 1 mixture of the (E)- and (Z)-isomers [11].

Internal heptenes (VII)

The mixture of internal heptenes obtained by the isomerization of III was used as the reaction medium to demonstrate the different behaviour of unsaturated hydrocarbons not possessing the vinyl double bond. In the first step of the Cp_2TiCl_2 reduction, $(Cp_2TiCl)_2$ was formed, giving a broad ESR signal $\Delta H = 9.2$ mT at $g = 1.977$ [10] (VII-a). When the reduction was completed (VII-b), the yellow-brown colour of the solution changed quickly to a very intense purple colour. This change was accompanied by the occurrence of a rather weak ESR signal at $g = 1.993$ corresponding to the η^3-allyltitanocene species (B-VII). Its intensity quickly reached a maximum and then decreased (see Fig. 4). During this process (samples VII-c–VII-e), $(Cp_2TiCl)_2$ decayed to give the purple diamagnetic μ-($\eta^5 : \eta^5$-fulvalene)-di-μ-chlorobis(η^5-cyclopentadienyltitanium) (D-1) [10]. Further boiling of the reaction mixture for 30 min yielded the green solution containing a mixture of μ-($\eta^5 : \eta^5$-fulvalene)-μ-chloro-μ-hydridobis(cyclopentadienyltitanium) (D-2) and μ-($\eta^5 : \eta^5$-fulvalene)-di-μ-hydridobis(cyclopentadienyltitanium) (D-3). This reaction course, leading to D-1–D-3, is typical for the reaction between Cp_2TiCl_2 and $LiAlH_4$ in the medium of internal and cyclic dienes and trienes at their boiling temperature (140–188°C) [10].

Isomerizations with η^3-allyltitanocene derivatives

The catalytic activity of η^3-allyltitanocene compounds was proven by isomerizations of II and III in the presence of the η^3-allyltitanocene derivatives, B-II, derived from conjugated octadienes. The preliminary kinetic measurements revealed that the isomerization of III had an induction period, but that it was then independent of the concentration of III to about a 60% conversion (Fig. 5); the zero order with respect to the olefin was also found for the isomerization of 1-hexene with the Cp_2TiCl_2-$LiAlH_4$ system in an ether medium [7]. The rate of isomerization of II was approximately proportional to the square of its concentration (Fig. 5). The overall
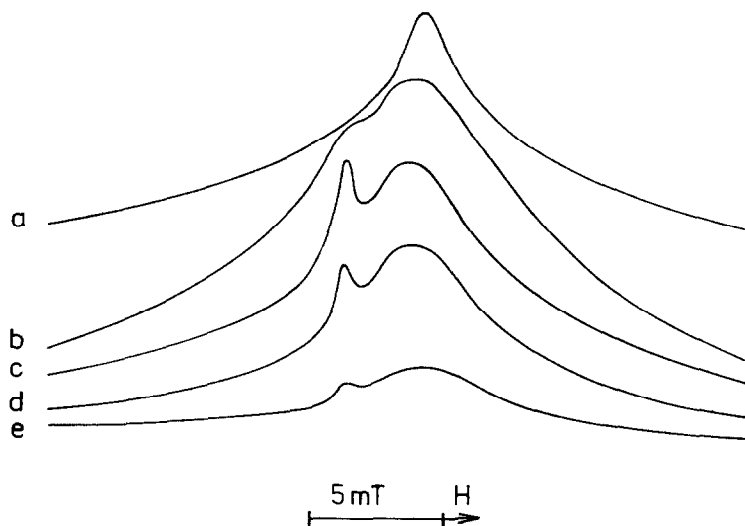
Fig. 4. Integrated ESR spectra of the system $Cp_2TiCl_2 \cdot LiAlH_4$-internal heptenes. Samples were taken after 15 min (VII-a), 27 min (VII-b), 31 min (VII-c), 40 min (VII-d) and 85 min (VII-e) from the reaction at 98 °C.

activation energies $E_A(II) = 23.7$ and $E_A(III) = 21.3$ kcal mol^{-1} were determined from the initial reaction rates and constant reaction rates, respectively. At the temperatures used (20–70 °C), the concentrations of B-II, according to ESR measurements, decreased slightly in the initial reaction stage but then they remained constant. The stability of η^3-allyltitanocene-derivatives depended on the solvent; in
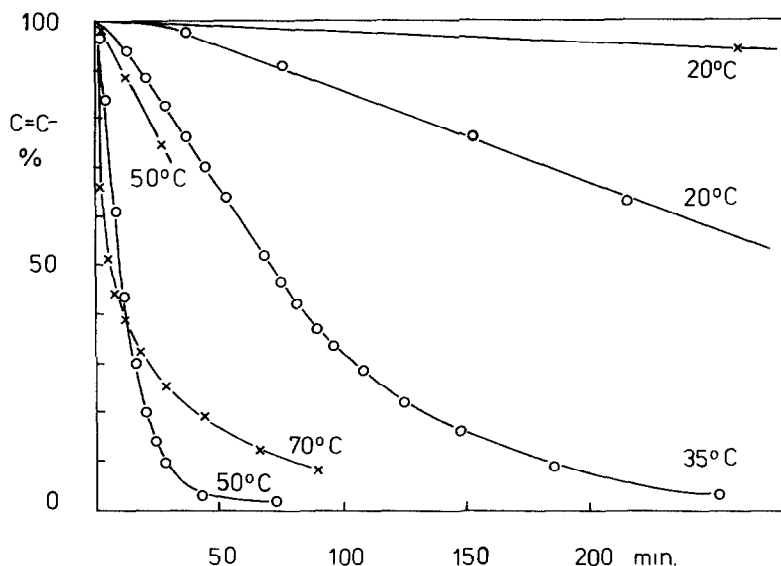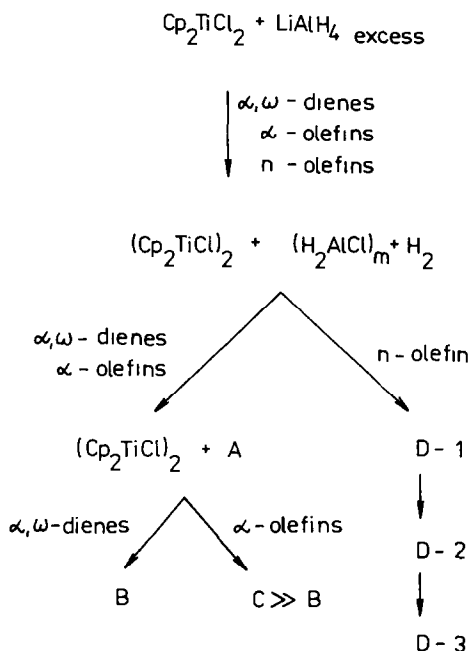

Fig. 5. Isomerization of 1-heptene (O) and 1,7-octadiene (×) by η^3-allyltitanocene derivatives B-II at different temperatures. The conversion curve of 1,7-octadiene at 20 °C is linear to 440 min (88.4%) and that at 50 °C was not completed. Initial concentration of B-II in both hydrocarbons was 3.275×10^{-3} M.

hexadienes and octadienes they were stable at 100°C for 1 h but in heptenes about 15% of them decomposed after 3 h at 100°C. The product of isomerization of III at 20°C for 7 days contained the following isomers: (E)-2- 65%, (Z)-2- 17%, (E)-3- 11% and (Z)-3- 7%.

*Mechanisms of the formation and decay of alkyl-, η^1-alkenyl- and η^3-allyl-titanocene derivatives*

The experimental results summarized in Scheme 1 show that the interaction

$$Cp_2TiCl_2 + LiAlH_4 \text{ excess}$$

α,ω - dienes
α - olefins
n - olefins

$$(Cp_2TiCl)_2 + (H_2AlCl)_m + H_2$$

α,ω - dienes
α - olefins

n - olefin

$(Cp_2TiCl)_2 + A$ D - 1

α,ω-dienes α-olefins

D - 2

B   C ≫ B

D - 3

SCHEME 1

between the catalyst components leads to three possible final organotitanium products, depending on the nature of the unsaturated hydrocarbon used as the reaction medium.

The first reaction step common to all hydrocarbon media is the reduction of titanium(IV) to titanium(III). Since $LiAlH_4$ is insoluble in hydrocarbons its at least two-fold utilization in the reduction of Cp_2TiCl_2, according to eq. 1, is highly probable.

$$2\,Cp_2TiCl_2 + LiAlH_4 \rightarrow (Cp_2TiCl)_2 + AlH_2Cl + LiCl + H_2 \tag{1}$$
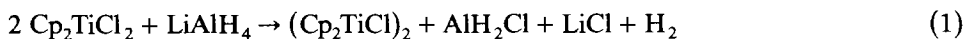
The transient formation of $Cp_2TiAlCl_4$ was observed in internal dienes at high temperatures, thus indicating even the full utilization of the reducing capacity of $LiAlH_4$ [10].
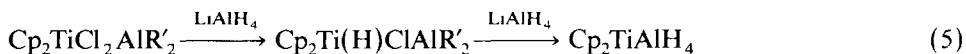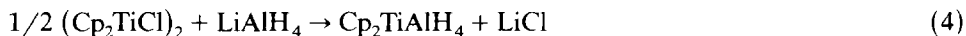
The formation of the A-type compounds in vinyl containing hydrocarbons is brought about by the hydroalumination reaction of the vinyl groups with the binuclear Ti–Al complexes which are probably present in equilibria similar to (2).

$$(Cp_2TiCl)_2 + AlH_2Cl \rightleftharpoons 1/2\ (Cp_2TiCl)_2 + Cp_2Ti(H)_2AlCl_2 \tag{2}$$
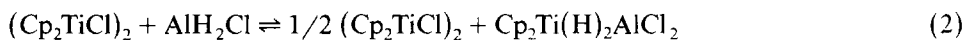
The hydroalumination probably proceeds on the activated bridge hydrogen bond, and the alkyl groups are exchanged to outer positions to give stable compounds of the A-type according to eq. 3.

$$Cp_2Ti(H)_2AlCl_2 + 2C{=}C{-}R \rightarrow Cp_2TiCl_2AlR'_2\ (R' = {-}C{-}C{-}R) \tag{3}$$

It has been established that both the $(Cp_2TiCl)_2$ and $Cp_2TiCl_2AlR'_2$ complexes react with the active $LiAlH_4$ in toluene at room temperature according to eqs. 4 and 5 [16].

$$1/2\ (Cp_2TiCl)_2 + LiAlH_4 \rightarrow Cp_2TiAlH_4 + LiCl \tag{4}$$

$$Cp_2TiCl_2AlR'_2 \xrightarrow{\text{LiAlH}_4} Cp_2Ti(H)ClAlR'_2 \xrightarrow{\text{LiAlH}_4} Cp_2TiAlH_4 \tag{5}$$

In the presence of α,ω-dienes and at the high reaction temperatures used in the present isomerization systems, both products of the reaction 5 add rapidly to the double bonds and, as a result, stable (1,3-dialkyl-η^3-allyl)titanocenes are formed by the subsequent double bond shifts. The dissolved aluminium hydride compounds are probably catalytically alkylated to give R'_3Al compounds as long as vinylic hydrocarbons are present in the systems. The evidence for the presence of hexenyl-aluminium compounds in the system with I was obtained by MS. On the other hand there was no indication of the solid $LiAlH_4$ alkylation.

α-Olefins and dienes, such as V and VI which do not form stable B-type complexes add to both products of the reaction 5 to give alkyl- and η^1-alkenylti-tanocenes, which are unstable at ambient temperature [19]. In the isomerization systems, their life-time is very short and they decay rapidly to C-type complexes. The latter conversion can be brought about by the subsequent alkylation of the Cp_2TiAlH_4 complex followed by the elimination of alkane, as shown in Scheme 2. Though the
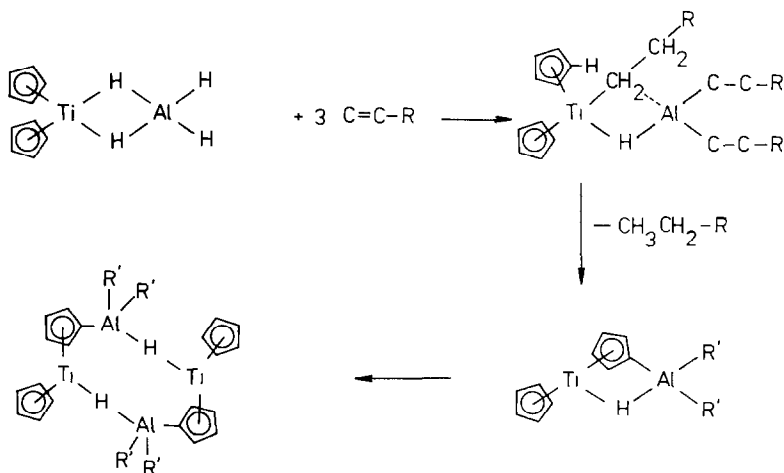

SCHEME 2

formation of C-type complexes from Cp_2TiR and AlR_3, as expected in the preparative method [17], cannot be excluded, we suggest that the addition of olefin to

$Cp_2Ti(H)_2AlR'_2$ destabilizes the complex, and this destabilization results in the elimination of the alkyl group accompanied by hydrogen abstraction from the cyclopentadienyl ligand. Instead of the hydrogen bridge, the new bridging η^5-(Ti): η^1-(Al)-cyclopentadienide ligand C_5H_4 is formed, partially stabilizing the binuclear complex (for stabilization of a Ti–Ti complex through this ligand see ref. 20). The stabilization process is completed by the dimerization of the latter intermediate to give the C-type complex.

Since conversion of Cp_2TiCl_2 to C-type complexes is nearly quantitative the overall reaction can be expressed by the eq. 6.

$$2Cp_2TiCl_2 + 4LiAlH_4 \xrightarrow{\alpha\text{-olefin}} C + 2AlR_3 + 4LiCl + 2RH + H_2 \qquad (6)$$
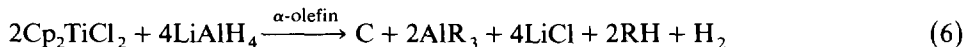
Nevertheless, a small fraction of the alkyl- and η^1-alkenyl-titanocene species avoids the above reaction path, as evidenced by the presence of minor amounts of η^3-allyltitanocene species in these systems. These B-type complexes arise during the olefin exchange process if the dissociating alkyl group abstracts a hydrogen atom from a coordinating olefin molecule. The isomerization of the η^1-alkenyltitanocene compounds thus formed affords more stable B-type complexes. However, even the latter should be transformed to C-type complexes in the presence of AlR_3 at temperatures of at least 100 °C.

In internal olefins, no products of the hydroalumination reaction have been observed; this is in line with results obtained in ethereal solvents [1–3]. The characteristic feature of the reaction route is the conversion of $(Cp_2TiCl)_2$ into D-1 commencing simultaneously with the occurrence of a small amount of B-type compounds. Their occurrence indicates the transient presence of highly reactive alkyltitanocenes which catalyzes both the isomerization of olefins and the hydrogen transfer from the cyclopentadienyl ligand of $(Cp_2TiCl)_2$ to the olefin, thus enabling the formation of the fulvalene ligand [10]. In such a way, the major part of Cp_2TiCl_2 does not participate actively in the catalysis of the isomerization, provided the reaction temperature is lower than 140 °C. At higher temperatures, the complexes D-2 and D-3 catalyze the intramolecular hydrogen shifts and intermolecular hydrogen transfer reactions in unsaturated hydrocarbons with an unexpectedly high activity and life-time [21].
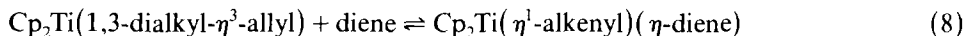
Isomerization activity and selectivity

The catalytic activity of the $Cp_2TiCl_2 \cdot LiAlH_4$ system in unsaturated hydrocarbon media can be explained by the presence of alkyl-, η^1-alkenyl- and η^3-allyltitanocene derivatives. Though the first two species are unstable under isomerization conditions, their life-time is enhanced in the presence of the parent olefin or diene because of a shift of the equilibrium 7 to the right.

$$Cp_2TiH + R_1-CH=CH-R_2 \rightleftharpoons Cp_2Ti-CH(R_1)-CH_2-R_2 \qquad (7)$$
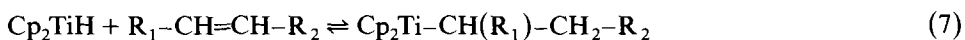
The high rate of alkyl–olefin or η^1-alkenyl–diene exchange is responsible for the high rate of isomerization in the reaction stage when alkyl- or η^1-alkenyl titanocenes are formed according to eq. 7. The exchange reactions proceed either by the β-hydrogen elimination mechanism [22], involving unstable titanocene hydride species (for stability of titanocene hydride species see ref. 23, or by a substitution mechanism in which an alkyl ligand is displaced by the coordinating olefin [24].

The isomerization of α, ω-dienes proceeds mainly by the substitution mechanism, since η^3-allyltitanocene derivatives of the B-type are stable in appropriate dienes up to 100°C. Since the B-type complexes are coordinatively saturated [14], the η^3-allyl–diene exchange should include an η^3-allyl to η^1-alkenyl isomerization 8, induced by the π-coordination of the diene molecule.

$$Cp_2Ti(1,3\text{-dialkyl-}\eta^3\text{-allyl}) + diene \rightleftharpoons Cp_2Ti(\eta^1\text{-alkenyl})(\eta\text{-diene}) \qquad (8)$$

The isomerization of α-olefins with B-type compounds requires the existence of an equilibrium 9, which involves the π-coordination of the olefin analogous to 8.

$$Cp_2Ti(1,3\text{-dialkyl-}\eta^3\text{-allyl}) + olefin \rightleftharpoons Cp_2Ti(alkyl) + diene \qquad (9)$$
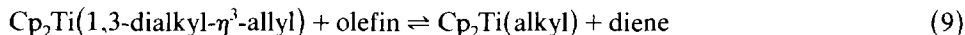
The equilibrium 9 is shifted strongly to the left, as demonstrated by a constant concentration of B-II during the isomerization of III at 20–50°C. The observed initial decrease of the B-II concentration ($< 5\%$) was comparable in isomerizations of both II and III and, therefore, it was due to the reaction of B-II with impurities.

The products of the isomerizations are in all cases the thermodynamically more stable isomers [25]. The differences in composition of n-heptenes obtained at 20°C and 100°C are brought about by different activation energies of isomerizations of 1- to 2-heptenes and 2- to 3-heptenes. Other examples of titanium-catalyzed temperature-controlled isomerizations are given in refs. 21 and 26. The influence of the structure of the titanium catalyst on the product composition has been established only in the case of the $[C_5(CH_3)_5]_2TiCl_2 \cdot Na^+ C_{10}H_8^-$ catalyst yielding selectively 2-olefins from 1-olefins [8]. However, the relevance of this effect to the present systems is not clear, since the reported isomerization is assumed to take place on titanium(II) species, and the effect is probably induced by steric hindrance due to the permethylated Cp ligands [8].

The mol ratio of unsaturated hydrocarbon to Cp_2TiCl_2 of $\sim 10^3$ used in practical isomerizations [9–11] ensures both the complete isomerization and a reasonably short time for the Cp_2TiCl_2 reduction. The present results show that this ratio can be increased by several orders of magnitude for the isomerizations of α,ω-dienes and cyclic and internal dienes which form stable η^3-allyltitanocene derivatives. In these cases, the life-time of the B-type catalytic complexes is very high and the ratio substrate/Cp_2TiCl_2 is limited mainly by the amount of poisoning impurities in the system. However, the main portion of the hydrocarbon should be added to the reaction mixture in the stage when the B-type complexes are forming, for the initial dilution would slow down the Cp_2TiCl_2 reduction. In the other hydrocarbons studied, a large increase of the substrate/Cp_2TiCl_2 ratio is limited by the rapid deactivation of alkyl- and η^1-alkenyl-titanocenes and by a low concentration of the B-type products. In any case, the presence of the B-type compounds, which can be detected easily by ESR [9–11,21,25], indicates the isomerization capability of the Cp_2TiCl_2-based systems.

Experimental

High-vacuum conditions were used throughout this work for all operations with organometallic compounds, except the isomerization reactions with the $Cp_2TiCl_2 \cdot$ LiAlH$_4$ system. In the latter case an argon atmosphere and apparatus equipped with greased joints were used to follow the conditions of the laboratory isomerization

procedure [11]. In other cases, all-sealed devices equipped with breakseals and sealed spectroscopic cells and sample tubes were used.

Chemicals

Cp$_2$TiCl$_2$ (Schuchardt, München) and LiAlH$_4$ (Metallgesellschaft A.G., Frankfurt a. M.) were used without purification. Cp$_2$TiCl$_2$AlEt$_2$ was prepared by mixing (Cp$_2$TiCl)$_2$ (1 mmol) with Et$_2$AlCl (2 mmol) in heptane, and purified by crystallization at low temperature [13]. [(C$_5$H$_5$)(C$_5$H$_4$)TiHAlEt$_2$]$_2$ was obtained by heating (Cp$_2$TiCl)$_2$ (5 mmol) with AlEt$_3$ (15 mmol) in heptane, and purified by crystallization at low temperature [17]. All hydrocarbons (Fluka) were purified by standing over LiAlH$_4$, followed by vacuum distillation and by heating of their solutions containing D-3 to 120°C. The latter procedure, followed by vacuum distillation, was repeated with fresh D-3 until the solution remained light green.

Isomerizations with the Cp$_2$TiCl$_2$ · LiAlH$_4$ system

The purified olefin or diene (60 ml) was added to Cp$_2$TiCl$_2$ (0.5 g, 2 mmol) and LiAlH$_4$ (0.3 g, 8 mmol) in a three-necked vessel sealed to the vacuum-argon line and equipped with a thermometer, magnetic stirrer and a sampling device. The reactions were run under argon, usually at the boiling temperature of the unsaturated hydrocarbon. Six samples of the reaction mixture ($\sim$ 5 ml) were transferred to the break-seal ampoules during the reaction, using a siphon controlled by argon pressure. The samples were degassed and clear solutions were separated from the black sediment for spectroscopic measurements and isolation of complexes. The final reaction mixture was poured into a break-seal ampoule, the hydrocarbon was distilled off in vacuo, and the organometallic products were isolated by extraction of the residue with hexane or benzene.

Isomerizations with (1,3-dialkyl-η^3-allyl)titanocenes

A mixture of (1-methyl-3-butyl-η^3-allyl)titanocene and (1-ethyl-3-propyl-η^3-allyl)titanocene (B-II) was obtained in the standard experiment using, however, the isomerized mixture of internal octadienes in order to minimize the amount of organoaluminium compounds. The dark product was evaporated and dissolved in n-hexane to give a blue solution. The solution was distributed into break-seal ampoules (0.5 ml) and stored in the dark at -20°C. Hexane was replaced by 2 ml of II or III and the solution was poured into a quartz cuvette (2 mm) sealed to an ESR tube and this device was sealed off. It was thermostatted and the disappearance of the vinyl group absorption at 1640 nm was measured. The concentration of B-II before (3.275×10^{-3} M) and after isomerization was monitored by the ESR method.

Identification of products

Representative products of type-A and type-C compounds were isolated and their identification was carried out by comparison of their MS or ^{1}H and ^{13}C NMR spectra with the spectra of ethyl derivatives of the same type (A-0, C-0) prepared by literature methods [13,17]. The B-type compounds were characterized by ESR and VIS spectra (B-I also by MS spectrum). The ESR and VIS spectra of A-type and C-type compounds are practically insensitive to the nature of the alkyl or η^3-allyl substituents and therefore these methods were used for identification of the titanium products in freshly separated samples. All the spectroscopic data are listed in Table

1. The composition of isomerized 1-heptene was determined by ^{13}C NMR using (E)-2-heptene and (E)-3-heptene as standards and literature data for the (Z)-isomers.

Methods

Electronic absorption (VIS) spectra and ESR spectra were measured as described elsewhere [12]. Mass spectra of organometallic compounds were obtained on a JEOL-JMS D-100 mass spectrometer using a direct inlet. Capillaries containing samples were opened and inserted into the direct inlet under a nitrogen atmosphere. ^1H and ^{13}C NMR spectra were obtained on a JEOL-FX-60 spectrometer at 60 and 15.036 MHz, FT-mode. Compounds of C-type were dissolved in benzene-d_6 and measured in sealed NMR sample tubes.

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