

Isomerizations of C₈—C₁₂ cycloalkadienes catalyzed by titanocene derivatives

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The interaction of Cp₂TiH containing catalyst with C₁₀ and C₁₂ cycloalkadienes yields *n*-cycloalken-1-ylbis(cyclopentadienyl)titanium(III) compounds (*n* = 2—6) but only the stable allyl compounds are characterized by e.s.r. and electronic absorption spectra. All of them cooperate in transforming the substrate by stepwise double bond shifts into the equilibrium mixture of isomers. The conjugated cycloalkadienes constituted minor components in C₁₀ and C₁₂ equilibrium mixtures while in C₈ diene it was the only product.

При взаимодействии катализатора содержащего Cp₂TiH с C₁₀ и C₁₂ циклоалкадиенами, образуются производные *n*-циклоалкен-1-илбис(циклопентадиенил)титана(III), где *n* = 2—6. Стабильные аллилпроизводные охарактеризованы ЭПР и электронными абсорбционными спектрами. Все они участвуют в превращении субстрата в равновесную смесь изомеров путем ступенчатого передвижения двойной связи. Сопряженные циклоалкадиены составляют побочные компоненты в равновесных смесях C₁₀ и C₁₂, однако, в C₈ диене это был единственный продукт.

Titanium hydride complexes induce shifts of remote double bonds in diolefins to produce conjugated isomers [1, 2]. Complexes of the Cp₂TiR (Cp = C₅H₅, R = alkenyl) type have been assumed as intermediates [3] and the isomerization was ascribed to the tendency of these complexes to form allylic ligands. The efficient catalysts were generated in the reaction mixture of Cp₂TiCl₂ with LiAlH₄ in boiling olefins and by the thermolysis of μ -(η^5 : η^5 -fulvalene)-di- μ -hydrido-bis(η^5 -cyclopentadienyltitanium) (FHT) at temperatures higher than 140°C [1—4].

In the present paper the bis(η^5 -cyclopentadienyl)titanium(III) hydride containing compounds is prepared by the reaction of the bis(η^5 -cyclopentadienyl)titanium(III) chloride dimer (Cp_2TiCl)₂ with LiAlH_4 in benzene at room temperature. This catalyst precursor is useful for mechanistic studies since it reacts with olefins already at room temperature. Here, it is used for the catalytic isomerization of the thermally unstable (*E,Z*)-1,5-cyclodecadiene (1,5-CD) within the ring preservation. Since the isomerization of cycloalkadienes C_{10} and larger affords mainly nonconjugated isomers [5–8] we were also interested in the catalytic transformations of (*Z,Z*)-1,5-cyclooctadiene (1,5-COD) and (*E,E*)-1,5-cyclododecadiene (1,5-CDD).

Experimental

Chemicals

Cp_2TiCl_2 (Schuchardt, Munich) and LiAlH_4 (Metallgesellschaft A.G., Frankfurt am Main) were used as received.

(Cp_2TiCl)₂ was prepared by the reduction of Cp_2TiCl_2 with aluminium powder in THF and purified from AlCl_3 by repeated washing with diethyl ether followed by heating to 100°C *in vacuo*.

(*Z,Z*)-1,5-Cyclooctadiene (1,5-COD) (Fluka) and (*E,Z*)-1,5-cyclodecadiene (1,5-CD) (Fluka) were fractionated at lowered pressure and degassed.

(*E,E*)-1,5-Cyclododecadiene (1,5-CDD) was prepared by partial hydrogenation of (*E,E,E*)-1,5,9-cyclododecatriene (CDT) (Fluka). The saturated acetic acid solution was hydrogenated at atmospheric pressure using Pd/C catalyst (Pd content 3%). After diminution of CDT content to about 30% the hydrogenation was stopped, the hydrocarbon layer washed with water, separated and dried over Na_2SO_4 . The product contained about 40% of a mixture of (*Z*)- and (*E*)-cyclododecene and 1,5-CDD (30%). The olefin and diene were separated and isolated in pure form by liquid chromatography on a column (length 2 m, $d = 5$ cm) containing silica gel impregnated with AgNO_3 .

(*E,Z*)-1,3-Cyclododecadiene (1,3-CDD) was prepared by bromination of the above prepared mixture of (*E*)- and (*Z*)-cyclododecene with *N*-bromosuccinimide to 3-bromocyclododecene followed by dehydrobromination with quinoline [9].

μ -(η^5 : η^5 -Fulvalene)-di- μ -hydrido-bis(η^5 -cyclopentadienyl)titanium) (FHT) was prepared by the reduction of Cp_2TiCl_2 by LiAlH_4 (Ti : Al = 1 : 4) in boiling mesitylene [10].

Purification procedures

All handling with substrates and catalysts was performed in the sealed high vacuum apparatus without greased joints and stopcocks. Benzene, hexane, and cycloalkadienes were distilled on FHT *in vacuo*, the obtained solution was heated to 100°C for 3 h and the

hydrocarbon was distilled in ampoules equipped with breakable seals. They were used for the isomerization experiments only if the solution of FHT remained green after heating; when it turned yellow or brown the purification had to be repeated with fresh FHT.

Preparation of titanium hydride containing catalyst [Cp₂TiH]

Lithium aluminium hydride recrystallized from diethyl ether and dried at 100°C in high vacuum was mixed with the benzene solution of (Cp₂TiCl)₂. The yellow-green solution turned to blue and after 2 h it was poured away from the excess of LiAlH₄, concentrated, and precipitated with n-hexane. The dark crystalline material was dissolved in benzene and the solution was distributed into ampoules with break-seals.

Isomerizations

Benzene solutions of [Cp₂TiH] or FHT were evaporated *in vacuo* and cycloalkadiene was distilled-in to prepare titanium concentration [Ti] = 1×10^{-2} mol l⁻¹. The solutions were immediately distributed into e.s.r. sample tubes and u.v. cuvettes which were sealed off. These were kept at chosen temperatures and their e.s.r. and electronic absorption spectra were measured in time intervals. Finally they were opened to air and their content was distilled off to separate the hydrocarbon products from the decomposed catalysts. The course of isomerization was followed by g.l.c. Pure isomerized olefins were obtained by preparative g.l.c. (for CD) and by combination of preparative liquid chromatography on silica gel impregnated with AgNO₃ and the preparative g.l.c. (for CDD). Their identification was based upon the infrared and ¹H- and ¹³C-n.m.r. spectra analyses and g.l.c.—m.s. determination of oxidation cleavage products.

Methods

E.s.r. spectra were taken on an ERS-220 spectrometer (ZWG – DAW, Berlin) at room temperature in X-band. The quantitative determination of Cp₂TiR and other paramagnetic species was performed by double integration of the first derivative record using the heptane solution of DPPH as a standard.

Mass spectra were measured on a Jeol MS D-100 instrument coupled with the gas chromatograph (column SE-30, 3% on Chromosorb W).

Gas chromatographic analyses and preparations were carried out on a Perkin—Elmer F-21 preparative gas chromatograph using Carbowax M-20 (10% on Chromaton N-AW).

Infrared spectra of organic substances were taken on a UR-75 (Zeiss, Jena) spectrometer in thin layers.

The absorption electronic spectra were measured on a Varian Cary 17 D spectrometer using the sealed quartz cuvettes.

¹H- and ¹³C-n.m.r. spectra were taken on a Jeol FX-60 spectrometer at 60 MHz and 15.897 MHz — FT-mode, respectively.

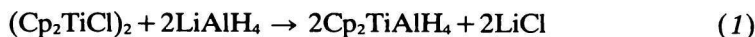
The oxidation of cycloalkadienes by KMnO_4 to two dicarboxylic acids and their esterification to obtain methyl esters was carried out according to the method described in [11].

Results and discussion

The $[\text{Cp}_2\text{TiH}]$ catalyst

The nature of the $[\text{Cp}_2\text{TiH}]$ catalyst is deduced from its genesis, spectroscopical investigations and from its reaction with dienes.

The first stage of the reaction between $(\text{Cp}_2\text{TiCl})_2$ and LiAlH_4 is the formation of the complex $\text{Cp}_2\text{TiAlH}_4$ according to the equation

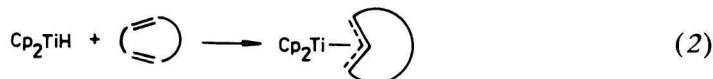


The quantitative e.s.r. measurement confirmed the complete conversion of $(\text{Cp}_2\text{TiCl})_2$ broad signal $\Delta H = 9.2$ mT at $g = 1.9777$ to the badly resolved eightline spectrum of $\text{Cp}_2\text{TiAlH}_4$ complex at $g = 1.9876$ (intensity ratios 1:3:4:4:4:4:3:1, $a_{\text{Al}} = a_{\text{H}} = 0.365$ mT). The low solvating ability of benzene is probably responsible for the broadening of lines, lower g values and lower hyperfine coupling constants to aluminium ($I = 5/2$) and two bridging hydrogen nuclei, in comparison with the literature data obtained in more polar solvents [12, 13].

During the contact with LiAlH_4 for several hours the blue solution of $\text{Cp}_2\text{TiAlH}_4$ ($\lambda_{\text{max}} = 680$ nm) changed to the dark blue colour due to a very broad absorption with the flat maximum at 540–550 nm. Simultaneously the broad e.s.r. signal grew at expense of the $\text{Cp}_2\text{TiAlH}_4$ signal intensity. This process of $\text{Cp}_2\text{TiAlH}_4$ decomposition was accomplished by evaporation of the benzene solution to dryness. After washing the black residue with n-hexane its benzene solution exhibited the broad e.s.r. signal $\Delta H = 4.0$ – 4.9 mT at $g = 1.989$. The absorption maximum and the e.s.r. signal width changed in the above-mentioned ranges depending apparently on little changes in the preparation and purification procedures. This observation shows that the catalyst is a mixture of rather similar complexes. These complexes do not react observably with electron donors, e.g. diethyl ether or triphenylphosphine but they all yield the same product by the reaction with 2,4-hexadiene. Upon addition of the latter the e.s.r. signal of $[\text{Cp}_2\text{TiH}]$ is quantitatively transformed to the sharp signal $\Delta H = 0.3$ mT at $g = 1.9937$ and correspondingly the broad absorption at $\lambda_{\text{max}} = 550$ nm ($\log \epsilon \sim 2.0$) is substituted by the distinct band at $\lambda_{\text{max}} = 580$ nm ($\log \epsilon \sim 2.7$). Both resulting data agree with those found for Cp_2TiR compounds prepared in ethereal solvents by the reduction of Cp_2TiCl_2 with allylmagnesium halides [14] or isopropylmagnesium halides in the presence of

dienes [15]. The obtained dark blue compound was isolated and its composition was confirmed mass spectrometrically: peaks m/z 261 ;1108 and 178 ;0259 fit ions $C_{16}H_{21}Ti$ (error + 1.5 mmass) and $C_{10}H_{10}Ti$ (error + 0.2 mmass), respectively (cf. [16]).

The addition of cycloalkadienes 1,5-CD, 1,5-CDD, and 1,3-CDD to Cp_2TiH induces the same spectral changes as the addition of 2,4-hexadiene. Therefore the formation of 1,3-dialkyl- η^3 -allylbis(cyclopentadienyl)titanium(III) compounds can be assumed to proceed according to the following equation (a large cycle simulates the dialkyl substitution)



The apparent higher rate of the Cp_2TiR formation observed with 1,3-CDD in comparison with 1,5-CD and 1,5-CDD is brought about by different concentrations of conjugated isomers. All prepared Cp_2TiR compounds were stable at room temperature, their solutions in 2,4-hexadiene and CDD were stable even at 100°C. In CD, Cp_2TiR changed by an intermolecular hydrogen transfer [3, 4] to a dienyl complex. The shifts of λ_{max} to 615 nm and of the e.s.r. g value to 1.9926 indicate that the dienyl complex has two double bonds in conjugation with the Ti—C bond [3]. However, upon prolonged heating the dienyl compound decomposed to diamagnetic products, too.

The formation of cyclodecatriene-like compound was proved by distilling hydrocarbons from the heated CD solution of Cp_2TiR onto fresh $[Cp_2TiH]$ — the dienyl compound was formed immediately at room temperature. The g.l.c.—m.s. analyses of the isomerized mixture of hydrocarbons showed the presence of hydrogen transfer products $CD \pm 2H$, $4H$ in amounts as low as the catalyst concentration, therefore they were neither isolated nor specified.

In 1,5-COD the signal of Cp_2TiR species at $g = 1.9934$ reached only by one order lower intensity than the above-mentioned signals, reflecting so the sterically induced instability of the Cp_2TiR compound with R derived from 1,3-COD [15].

In contrast to the general stability of Cp_2TiR compounds in the parent diolefins, the $[Cp_2TiH]$ complexes decomposed at 100°C in benzene solution to give the nonparamagnetic black solid — probably metallic titanium and hydrogen. These are also the final products of $(Cp_2TiCl)_2$ reduction by $LiAlH_4$ excess in conditions described above provided the reaction time is prolonged for one day. This mode of $[Cp_2TiH]$ decomposition is due to the presence of aluminium hydride either complexed or free; otherwise any Cp_2TiH agglomerates should decompose to give FHT as it was demonstrated for the Cp_2TiH dimer [17] and polymer [18].

The results of rather preliminary investigations of the $[Cp_2TiH]$ catalyst show that it is a mixture of Cp_2TiH and AlH_3 complexed in agglomerates of unknown structure. The content of aluminium is likely higher than 50% of all metal atoms as

the final catalyst is formed from intermediate $\text{Cp}_2\text{TiAlH}_4$ complex in the presence of solid LiAlH_4 and the ability of $\text{Cp}_2\text{TiAlH}_4$ to coordinate another molecule of AlH_3 has been proved recently [12]. Although the titanium reduction can go to $\text{Ti}(0)$ the catalyst is isolated from LiAlH_4 in the stage when no decrease of $\text{Ti}(\text{III})$ is indicated by the e.s.r. method and then its benzene solution is stable (at 20–30°C). The large width of e.s.r. signal of $[\text{Cp}_2\text{TiH}]$ can be explained by the interaction of $\text{Ti}(\text{III})$ unpaired electron with more than one aluminium nucleus (*cf.* e.s.r. of $\text{CpTi}(\text{AlX}_4)_2$ complexes [19]) or by the Ti—Ti interaction similar to that in $(\text{Cp}_2\text{TiCl})_2$ [10]. From the catalytic point of view it is important that during the reaction of $[\text{Cp}_2\text{TiH}]$ catalyst with inner dienes aluminium hydrides do not interfere with the formation of Cp_2TiR compounds though the formation of alkylaluminium compounds can be expected with vinyl containing diolefins [20].

Isomerization of cycloalkadienes

Isomerization of cycloalkadienes started immediately after mixing $[\text{Cp}_2\text{TiH}]$ catalyst with substrates at room temperature but the rates of isomerization differed in the order 1,5-COD > 1,5-CD > 1,5-CDD ~ 1,3-CDD (Table 1). The isomerization of 1,5-COD to 1,3-COD was completed after 15 min at 20°C though the concentration of Cp_2TiR was at least ten times lower than that found by e.s.r. in CD and CDD. In 1,5-CD at 20°C the stable isomers (*Z,Z*)-1,6-CD and (*Z,Z*)-1,3-CD were accompanied by a considerable amount of (*Z,Z*)-1,4-CD. However, the latter compound disappeared following the disappearance of (*Z,E*)-1,5-CD. The increase of the reaction temperature to 100°C shortened the time necessary to obtain the equilibrium mixture though the catalyst was destroyed considerably during the heating. The products of isomerization at 100°C, after being separated from titanium compounds by vacuum distillation, could be heated to 200°C without any change of their composition. On the other hand, the addition of FHT to this mixture followed by heating to 140°C for 1 h resulted in the transformation of all CD isomers into mainly the mixture of *cis*- and *trans*-1,2-divinylcyclohexanes. The *cis* isomer is the product of thermally induced Cope rearrangement [21] and the *trans* isomer is the product of its isomerization induced by FHT. These results show that in the presence of FHT, yielding the alkyltitanocene-like species upon heating to 140°C [2], the exchange equilibrium between isomers with different positions of double bonds is restored and the 1,5-isomer is irreversibly removed to give *cis*-1,2-divinylcyclohexane.

The isomerization of cyclododecadienes, starting both from 1,5-CDD and 1,3-CDD to check the achievement of the equilibrium composition of isomerized products, proceeded more slowly in comparison with cyclodecadienes. With $[\text{Cp}_2\text{TiH}]$ catalyst the equilibrium composition was not achieved after 14 h at

Table 1

Isomerization of cycloalkadienes with $[\text{Cp}_2\text{TiH}]$ catalyst
 $([\text{Ti}] = 1 \times 10^{-2} \text{ mol l}^{-1})$

Cycloalkadiene	Reaction conditions	Product composition ^a		
1,5-COD	20°C, 15 min	(Z,Z)-1,3-COD 100%		
1,5-CD	20°C, 3 days	(Z,Z)-1,3- 6%,	(1,5-CD + (Z,Z)-1,6-) 72%,	(Z,Z)-1,4- 14%
	20°C, 22 days	(Z,Z)-1,3- 19%,	(Z,Z)-1,6- 69%,	(Z,Z)-1,4- 5%
	60°C, 4 h	(Z,Z)-1,3- 14%,	(Z,Z)-1,6- 76%,	(Z,Z)-1,4- 4%
	100°C, 4 h	(Z,Z)-1,3- 8%,	(Z,Z)-1,6- 89%,	(Z,Z)-1,4- 1%
1,5-CDD ^b	100°C, 14 h	(E,Z)-1,3- 17%,	I — 54%, II — 24%,	III — 4%
1,3-CDD ^b	100°C, 14 h	(E,Z)-1,3- 44%,	I — 33%, II — 19%,	III — 4%
1,5-CDD ^c	180°C, 3 h	(E,Z)-1,3- 10%,	I — 46%, II — 38%,	III — 6%
1,3-CDD ^c	180°C, 3 h	(E,Z)-1,3- 12%,	I — 43%, II — 39%,	III — 6%

a) Compounds (Z,Z)-1,6-CD, (E,Z)-1,5-CD, and (E,Z)-1,3-CDD were identified by comparison of their infrared spectra with the spectra obtained by Wilke, G. and Heimbach, P. published in *D.M.S. Collection of Infrared Spectra* No. 15017, 15018, and 15019; the infrared spectrum of (Z,Z)-1,3-CD agreed with the published record [22]. The structure of (Z,Z)-1,4-CD was established from its infrared spectrum (Table 2), ¹³C-n.m.r. spectrum: 20.5 t, 25.4 t, 27.0 t (2C), 30.1 t (2C), 128.3 d (2C), and 129.5 d (2C) and ¹H-n.m.r. spectrum triplet at 2.78 p.p.m. (*J* = 7.8 Hz) due to methylene group in between two double bonds. Chromatographic peaks I, II, and III are shown in the typical g.l.c. record in Fig. 1.

b) $[\text{Ti}] = 2 \times 10^{-3} \text{ mol l}^{-1}$.

c) Catalyst FHT, $[\text{Ti}] = 2 \times 10^{-3} \text{ mol l}^{-1}$.

100°C though no decomposition of Cp_2TiR compound was detected by the e.s.r. method. The nearby equilibrium was reached by heating FHT solutions in both 1,5-CDD and 1,3-CDD to 180°C for 3 h (Table 1) since g.l.c. records of both mixtures became very similar (Fig. 1). The obtained mixtures were so complex that

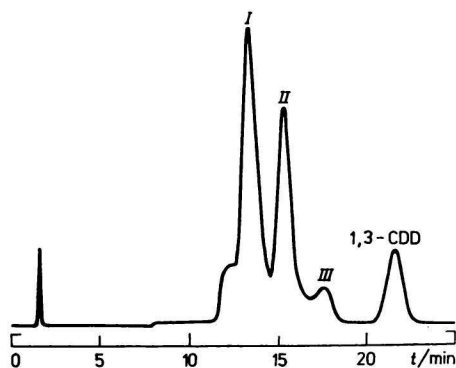


Fig. 1. The g.l.c. separation of products of 1,5-CDD isomerization catalyzed by FHT at 180°C for 3 h.

we failed in an effort to determine their composition. However, some major components were isolated by the combined use of liquid chromatography on $\text{AgNO}_3/\text{silica}$ gel column and preparative g.l.c. on Carbowax 20 M column. The obtained samples were subjected to oxidative cleavage to establish the positions of double bonds and (*E*)- or (*Z*)-configurations at double bonds were determined by infrared analysis. The chromatographic peak *I* (Fig. 1) contained large amount of (*E,E*)-1,5-CDD, the isomers (*E,Z*)-1,5-CDD and (*E,Z*)-1,6-CDD were the main components of (*II*) and the peak *III* was mainly due to (*Z,Z*)-1,7-CDD. Even these chromatographically isolated compounds contained minor amounts of other isomers so that the above assignments and their infrared spectra collected in Table 2 ought to be considered tentative. Also, the attempt to use the oxidative cleavage method for obtaining the distribution of positional isomers in the equilibrium mixtures failed as the abundance of methyl esters of lower dicarboxylic acids was always much higher than that of their higher counterparts.

At 200°C and higher temperatures the formation of 5,6,7,8,9,10-hexahydrobenzocyclooctene (BCO) easily detectable by g.c.—m.s. indicated the increasing participation of intermolecular hydrogen transfer reaction. This compound was previously obtained by the isomerization of 1,5,9-CDT isomers by the system $\text{Cp}_2\text{TiCl}_2\text{—LiAlH}_4$ [4] and its formation is brought about by the easy hydrogen release from the intermediate bicyclo(6.4.0)dodeca-9,11-diene. In the present study, therefore, the occurrence of BCO proves the intermediate formation of CDT by the intermolecular hydrogen transfer. Also hydrogenated products — cyclododecenes and other products of CDT isomerization — tricyclo(7.3.0.0^{2.6})dodec-7-enes [4] were detected by the g.l.c.—m.s. method.

Results of isomerization reflect the changing properties of middle size cycloalkadienes. While C_8 ring affords only one product — 1,3-COD as also shown earlier with similar titanium catalyst [23], the C_{10} and C_{12} ring yields mixtures of isomers. Surprising is the tendency of C_{10} ring to form exclusively (*Z,Z*)-isomers since a relatively high content of (*E,E*)-1,6-CD was obtained under the action of $\text{Fe}(\text{CO})_5$ at u.v. photolysis [5]. The uncomplete results for CDD isomerization allow to confirm the tendency of larger rings to form (*E,Z*)-configurations in addition to (*E,E*)- or (*Z,Z*)-configuration for the isomer with the most distant double bonds [6—8]. As long as the comparison is possible the titanium catalysts are superior to the so far reported catalysts, e.g. acetylacetonates of transition metals — $\text{Al}(\text{C}_2\text{H}_5)_3$ at 60°C for 1,5-CD [5] or $\text{B}(\text{C}_2\text{H}_5)_3$ at 200°C for 1,5-CDD [8], both in activity and selectivity.

The catalysis of stepwise shifts of double bonds proceeds by the olefin displacement mechanism (3) rather than in the dissociation equilibrium (4)

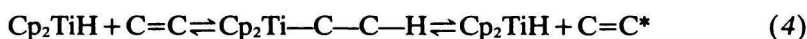
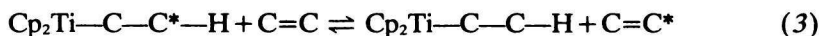


Table 2

Infrared spectra of isolated cycloalkadienes

Mode of vibration	(Z,Z)-1,4-CD	(E,Z)-1,5-CDD	(E,Z)-1,6-CDD	(Z,Z)-1,7-CDD
$\nu(=C-H)$	3065 w	3030, 3066 w	3028 sh, 3058 sh	3062 w
$\nu(C=C)$	1647 sh, 1653	1648 sh, 1654	1646	1647 sh, 1654
$\delta(C-H)$	1472, 1442	1450	1450	1462, 1442
$\delta(C=C-H) (E)$		994 m, 976 s, 969 vs	972 vs	
$\delta(C=C-H) (Z)$	708 vs	702 vs	711 s	720 vs
Other bands	1042 m, 974 m 926 s, 870 s 795 m, 772 s 578 m, 569 m	994 m, 859 m 596 w, 540 w 502 w, 486 w	1345 m, 770 m 746 m, 728 m 669 m, 586 m	938 m, 859 m 830 m, 810 m 703 s, 689 s 584 w, 561 w 541 m

This is supported by the observation that Cp_2TiR allyl compounds are generally stable to $100^\circ C$ in the medium of appropriate diene (if not labilized by steric hindrance, e.g. in COD) [1, 3] while isomerizations proceed at room temperature. In large cycloalkadienes the isomerization to nonconjugated isomers proves the existence of n -cycloalken-1-ylbis(cyclopentadienyl)titanium(III) compounds ($n > 3$) so far not detected by spectroscopic methods. Their concentration is low in comparison with the stable Cp_2TiR allyl compounds, however, they are responsible for bringing the cycloalkadiene systems to equilibria.

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