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ISOMERIZATION OF OLEFINS ON HYDRIDE-HALIDE COMPOUNDS OF TITANIUM AND ALUMINIUM OF COMPOSITION L_mTiH_2AlXX' . THE ROLE OF THE COCATALYST AND THE GEOMETRY OF THE LIGAND ENVIRONMENT OF THE TITANIUM ATOM IN CATALYTIC HYDROGEN TRANSFER

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Summary

Using bimetallic complexes of the compositions $(C_5H_5)_2TiH_2MXX'$ and $(CH_2)_n(C_5H_4)_2TiH_2AlXX'$ ($M = B, Al; X, X' = H, Hal, Alk, n = 1-3$) as examples, the rate of homogeneous catalytic isomerization of α -olefins has been studied under the influence of the ligand environment, the nature of the transition metal, and the substituent at M. Only titanium and aluminium complexes with non-rigid ligand environments and involving terminal Al-H bonds show catalytic activity in the reaction. An alkyl isomerization mechanism at the heterobinuclear centre is suggested. The first reaction step involves coordination of an olefin at the six-coordinate Al atom followed by the insertion of the olefin molecule in the terminal Al-H bond.

Introduction

The structure of active centres (AC) of catalytic systems of the Ziegler-Natta type has not been studied comprehensively. The AC models and the reaction mechanism developed for the polymerization of olefins can with a few exceptions be divided into two groups: mono- and bi-metallic [1,2]. The AC is either a mononuclear moiety or contains an atom of a non-transition metal in the second coordination sphere. In the opinion of the proposers of the bimetallic model, this atom determines mainly the stereochemical aspects of substrate

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coordination, which to some extent draws the two standpoints together. Taking into account, however, the strong effect of the nature of the cocatalyst on the catalytic activity [1,2], one cannot rule out the bimetallic mechanism in the strict sense of the word, i.e. the participation in the catalytic process of other atoms, in particular of non-transition metals.

The fact that the mechanism of catalytic reactions in Ziegler-type systems is difficult to determine is caused by the multicomponent nature of the catalysts, which results in parallel and successive reactions, and by the extreme lability of the AC and its sensitivity to catalytic poisons. So-called "modelling with respect to the catalyst" may be the most effective method of investigation in this case, which consists of studying the catalytic activity of individual compounds of known composition and structure containing potentially catalytically active chemical bonds and functional groups.

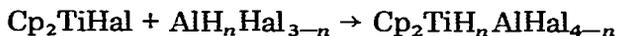
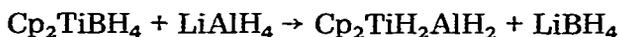
As such "monocomponent" catalysts we have chosen the previously studied [3-7] bimetallic hydride complexes of titanium and aluminium of composition L_mTiH_2AlXX' , where $L = C_5H_5$ ($m = 2$) and $(CH_2)_n(C_5H_4)_2$ ($m = 1, n = 1-3$); $X, X' = H, Hal$. Two types of metal-hydrogen bonds are present in these compounds: hydride bridges, TiH_2Al , and terminal $Al-H$ bonds [6,7]. Thus one would expect that these compounds would have catalytic activity in hydrogen transfer reactions, in particular, olefin isomerization.

The study of the catalytic properties of the first representative of the series, Cp_2TiAlH_4 , containing a TiH_2Al bridge, has shown that it catalyzes isomerization of α -olefins at a high rate [8], but that it is absolutely inactive in hydrogenation reactions [9]. Complex $(Cp_2Ti)_2AlH_4Cl$, obtained from the reaction between $(CpTiCl)_2$ and lithium aluminiumhydride ($Al:Ti = 1:2$), is active in both hydrogenation and isomerization [8]. The data on the stereospecificity and kinetics of 1-hexene isomerization on the complexes $(Cp_2Ti)_2AlH_4Cl$ [8] and $Cp_2TiH_2AlH_2$ unambiguously point to different natures of the AC and different mechanisms of isomerization on these compounds.

The aim of this work was to study the effect of ligand environment, the nature of the non-transition metal (cocatalyst), and the degree of binding of the cyclopentadienyl ligands at the titanium atom on the catalytic activity of hydride-halide complexes of titanium and aluminium in the homogeneous isomerization of olefins.

Experimental

All operations in the synthesis and the study of the catalytic activity of hydride-halide complexes were carried out in an atmosphere of dry argon. The solvents were dehydrated by refluxing and distillation over $LiAlH_4$. The solutions of the complexes were prepared by following the known procedures [5] according to the reactions:



Binuclear complexes containing coordinated Cp rings were prepared in a similar way [7].

TABLE 1

ISOMERIZATION OF 1-HEXENE ON HYDRIDE-HALIDE COMPLEXES L_mTiH_2AlXX'

Catalyst	Rate of transformation (mol C_6H_{12} /g-at Ti min)	<i>f</i> (at a given degree of 1-hexene transformation, %)		
		40	60	90
Cp_2TiAlH_4	20.0	5.5	4.8	4.7
$(Cp_2TiAlH_3Cl)_2$	6.1	3.8	4.1	5.2
Cp_2TiAlH_3Br	1.9	5.3	5.8	—
$Cp_2TiAlH_2Cl_2$	0	—	—	—
Cp_2TiBH_4	0	—	—	—
$CH_2(C_5H_4)_2TiAlH_4$	0	—	—	—
$(CH_2)_2(C_5H_4)_2TiAlH_4$	0.03 ^a	—	—	—
$(CH_2)_3(C_4H_5)_2TiAlH_4$	0.4 ^a	—	—	—

^a The reaction does not go to completion.

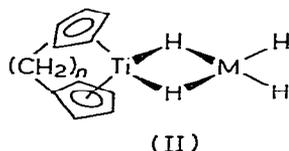
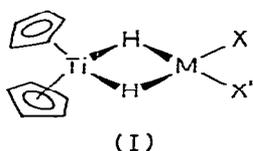
The elemental analyses for Ti, Al, Cl, and Br was performed as described [6]. The EPR spectra of the solutions were recorded at room temperature on a Varian-E-3 radiospectrometer of 3 cm range with a B4-modulation frequency of 100 KHz and Mn^{2+} as a reference.

The isomerization of 1-hexene was carried out at 22°C in a thermostated vessel, fitted with a stirrer and a tube for sampling, in an ether-benzene mixture. The reaction was terminated by contact with air. The composition of the isomerization products was determined on a XM-8M chromatograph (capillary column 30 m in length, tricresylphosphate as a liquid phase, flame-ionization detector). The titanium concentration in the solution was within the range 0.01--0.03 mol/l, the substrate:titanium ratio was 50—150. The total solution volume amounted to 30—40 ml. The results of 1-hexene isomerization on the catalysts under consideration are given in Table 1.

Results and discussion

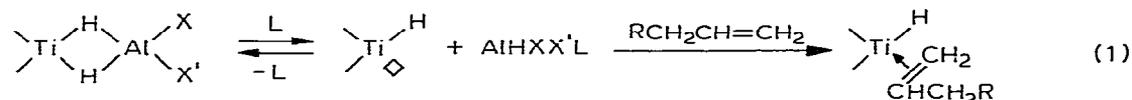
Table 1 illustrates the result of hexene-1 isomerization on the hydride-halide complexes L_mTiH_2AlXX' . Up to a transformation degree of 80% the rate of 1-hexene transformation almost in all cases does not depend on its concentration. Therefore, the initial reaction rate was chosen as a measure of catalyst activity. As is seen from the Table, the stereospecificity factor ($f = trans/cis$ hexene-2) for all the compounds under study is almost the same and exceeds considerably the equilibrium value ($f = 3.4$ [10]), whereas the isomerization rates differ greatly. A strong effect from the number and nature of the substituents at the aluminium atom on the catalytic activity points unambiguously to the heterometallic character of the AC, whose structure is apparently similar for all the compounds L_mTiH_2AlXX' .

According to the data from EPR and dielectrometry [3—5,7], the majority of the above compounds and the similar borohydrides, $L_mTiH_2BH_2$ [11], are monomeric in solution and their structure is described by the structural formulae I and II, where $M = Al, B$; $X, X' = H, Cl, Br$. Only $(Cp_2TiH_2AlHCl)_2$ ob-



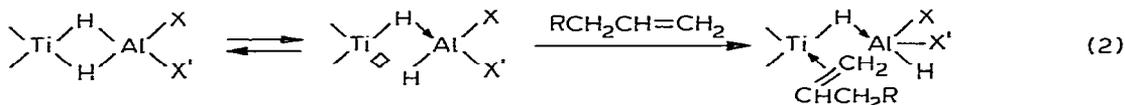
tained at room temperature is the exception; if, however, the temperature of the synthesis is lowered to -60°C , it also forms a monomeric molecule I. As follows from the results of quantum-chemical calculations on Cp_2ML_n molecules [12], the three valent orbitals of the titanium (III) atom are occupied by electrons from two hydrogen atoms and an unpaired electron. Consequently, coordination of an olefin in the classical way, namely via the atom of the transition metal (TM) (titanium), is in this case impossible without destruction of the very stable structure I or II. This evidently explains why no catalytic activity is observed in the reaction of olefin hydrogenation on $\text{Cp}_2\text{TiH}_2\text{AlH}_2$ [8] and other complexes with double hydrogen bridges TiH_2M , where $\text{M} = \text{Li}, \text{Na}, \text{Mg}$ [13].

Consider now the possible ways of insertion of an olefin into a bimetallic hydride complex $\text{L}_m\text{TiH}_2\text{AlXX}'$. The most evident route, consisting of homolytic cleavage of the TiH_2Al fragment with the formation of L_mTiH , with a vacancy at the titanium atom (eq. 1), must be ruled out, since firstly, no solvates of



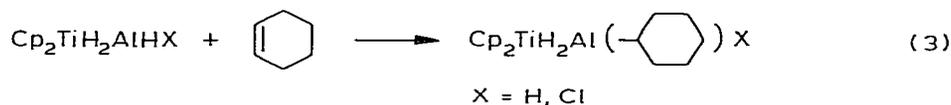
haloidalanes of the composition $\text{AlH}_{3-n}\text{X}_n\text{L}$ are found in the reaction products; secondly, the activities in the series of hydride-halide complexes differ considerably; and, thirdly, the Cp_2TiH fragment formed in reaction 1 is, an effective catalyst of hydrogenation [13] whereas the compounds under study are inactive in this reaction.

A partial dissociation of the TiH_2Al bridge with the formation of the vacancy at the titanium atom (eq. 2) is also possible.

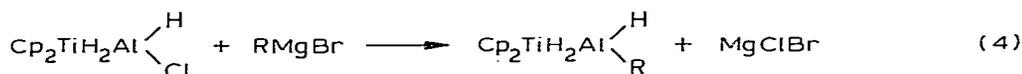


The decrease in catalytic activity of the complexes studied (Table 1) agrees with the increase in the strength of the TiH_2Al bond in the series $\text{Cp}_2\text{TiH}_2\text{AlH}_2 < \text{Cp}_2\text{TiH}_2\text{AlHHal} < \text{Cp}_2\text{TiH}_2\text{AlHal}_2$ (according to the EPR data [3–6]) and $(\text{CH}_2)_3(\text{C}_5\text{H}_4)_2\text{TiAlH}_4 < (\text{CH}_2)_2(\text{C}_5\text{H}_4)_2\text{TiAlH}_4 < \text{CH}_2(\text{C}_5\text{H}_4)_2\text{TiAlH}_4$ (by analogy with the corresponding borohydrides [11]) and may confirm the assumption. In this case, however, no explanation can be given of the complete absence of activity of $\text{CH}_2(\text{C}_5\text{H}_4)_2\text{TiAlH}_4$ and $\text{Cp}_2\text{TiH}_2\text{AlHal}_2$ which differ insignificantly from their nearest neighbours in the series. It should also be noted that, if coordination of the olefin follows reaction 2, the activities of the complexes $\text{Cp}_2\text{-TiH}_2\text{AlHCl}$ and $\text{Cp}_2\text{TiH}_2\text{AlHBr}$ must be similar since the a_{H} and a_{Al} constants in the EPR spectra, which characterize the electron density on the bridging hydro-

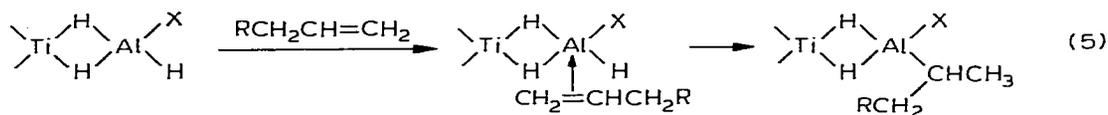
gen atoms and on the aluminium atom (i.e. the strength of the TiH_2Al bond), coincide for both compounds. However, from Table 1 it is seen, that the rate of isomerization in the presence of a chloro-substituted complex exceeds that in the presence of bromo-substituted complex by a factor of 4–5. This allows the conclusion to be reached that insertion of an olefin into the compounds under consideration follows another mechanism. The experimental data indicate that the activity of $\text{Cp}_2\text{TiH}_2\text{AlXX}'$ depends mainly on the number of terminal hydrogen atoms (Table 1). Earlier [8] it was shown that treatment of a solution of $\text{Cp}_2\text{TiH}_2\text{AlH}_2$ with cyclohexene results in transformation of the initial well-resolved octet (Fig. 1,a) into a poorly-resolved octet (Fig. 1,b) corresponding to the formation of a hydride-alkyl complex (eq. 3); this means that under mild conditions hydrometallation takes place. $\text{Cp}_2\text{TiH}_2\text{AlHCl}$ reacts with cyclohexene in a similar way (reaction 3).



The formation of $\text{Cp}_2\text{TiH}_2\text{AlRX}$ complexes via reaction 3 is confirmed by the similarity between their EPR spectra and spectra of these complexes obtained by the independent synthesis via the exchange reaction (eq. 4).



Addition of olefins to the M–H bond in mononuclear aluminium hydrides, contrary to boron hydrides, proceeds under rather rigid conditions ($t = 110\text{--}120^\circ\text{C}$ for LiAlH_4) [15]. Taking into account the above considerations as well as the coordinative unsaturation of the aluminium atom (maximum coordination number is 6) in $\text{L}_m\text{TiH}_2\text{AlHX}$, one may assume that incorporation of olefins into these complexes takes place along the Al–H bond and proceeds, apparently, via preliminary coordination at the aluminium atom (eq. 5).



The fact that $\text{Cp}_2\text{TiH}_2\text{BH}_2$ is catalytically inactive (the coordination number of the B atom is 4) confirms the assumption about the preliminary coordination. (Earlier the formation of unstable π -complexes of aluminium hydrides with olefins [16] and aromatic hydrocarbons [17] had been assumed). The proposed model (reaction 5) explains the (about 50%) decrease in activity of monohalide-substituted compounds as compared with $\text{Cp}_2\text{TiH}_2\text{AlH}_2$ and the absence of activity for $\text{Cp}_2\text{TiH}_2\text{AlHal}_2$. The nature of the substituent, in particular its bulk, plays a great role in the olefin coordination, which agrees with the experimental data on the isomerization in the presence of $\text{Cp}_2\text{TiH}_2\text{AlHCl}$ and $\text{Cp}_2\text{TiH}_2\text{AlHBr}$.

The next stage of the catalytic cycle may be a migration of the alkyl group

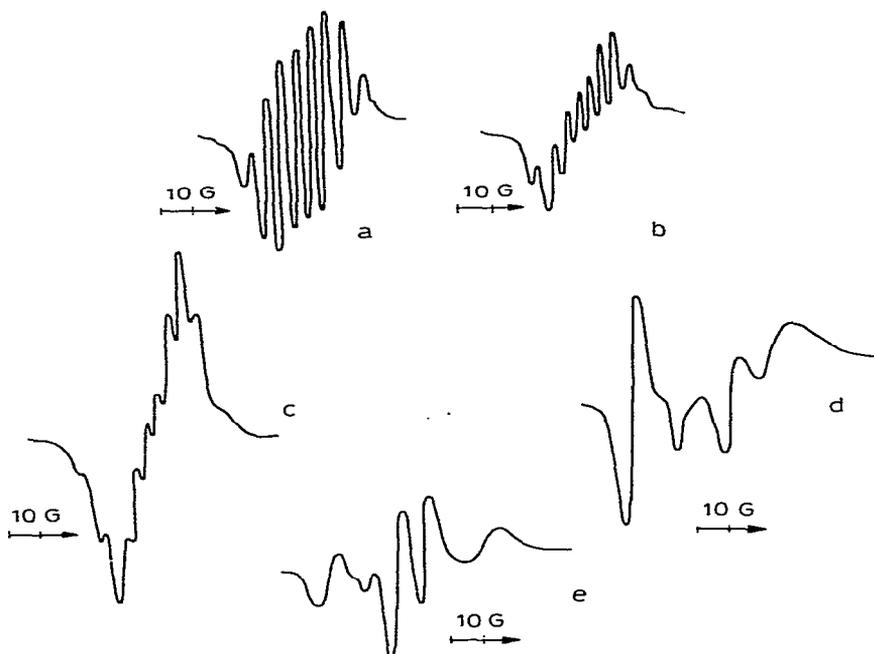
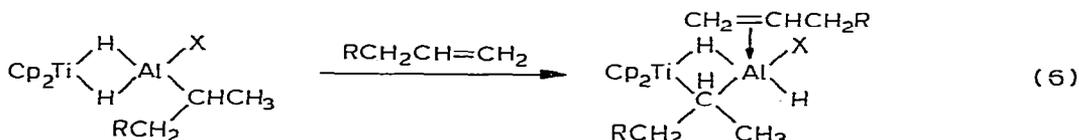
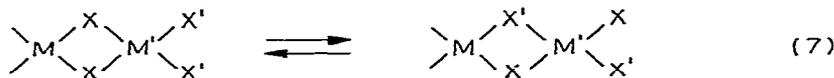


Fig. 1. EPR spectra of a) $\text{Cp}_2\text{TiH}_2\text{AlH}_2$, b) $\text{Cp}_2\text{TiH}_2\text{AlH}_2$ + cyclohexene, c) $\text{Cp}_2\text{TiH}_2\text{AlH}\text{-sec.-C}_6\text{H}_{13}$, d) $\text{Cp}_2\text{TiH}_2\text{AlH}\text{-sec.-C}_6\text{H}_{13}$ + 1-heptene, e) $\text{Cp}_2\text{TiH}_2\text{AlH}_2$ + 1-hexene.

from the terminal to the bridging position with the formation of the Ti—C—Al bond (eq. 6)

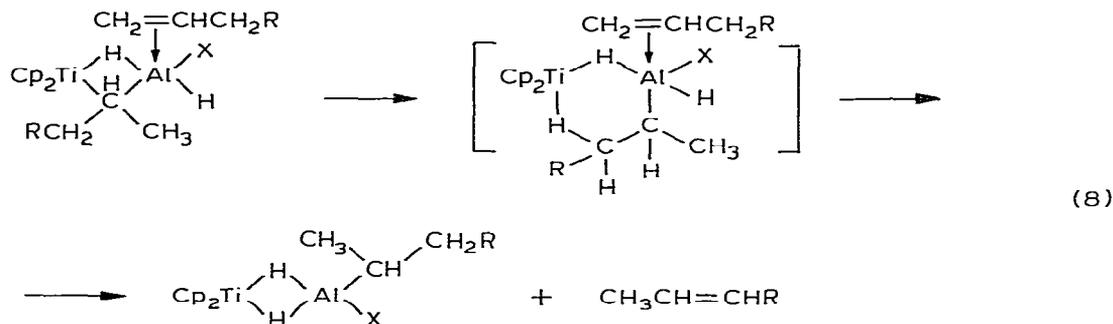


A fast intramolecular exchange of bridging and terminal ligands is observed, as a rule, in the NMR spectra of binuclear hydride and alkyl complexes (eq. 7).



Under normal conditions the equilibrium (according to EPR) is shifted to the left, i.e. the TiH_2Al bridge is retained. An excess of the olefin shifts the equilibrium towards formation of the alkyl bridge, which may be a result of coordination of a second olefin molecule. In the EPR spectrum this process is reflected in the appearance of the typical set of signals identical for all hydride-halide complexes of titanium and aluminium active in the isomerization reactions, but with different ratio of intensities. This means that in all cases the ligand environment of the titanium atom in the AC is similar. At the same time, β -elimination of the hydrogen atom, elimination of the isomerized olefin, and regeneration of the active centre take place in the bridging alkyl group (eq. 8).

It may be assumed that β -elimination is facilitated by the formation of an intermediate six- rather than four-membered cycle, which results in the predominant formation of the *trans* isomer of 2-hexene in the mixture.



The titanium atom, whose ligand environment plays a great role, participates in this stage of the catalytic cycle. Aluminohydrides with rigidly bonded cyclopentadienyl rings, $(\text{CH}_2)_n(\text{C}_5\text{H}_4)_2\text{TiH}_2\text{AlH}_2$ (II), are either inactive ($n = 1$), or exhibit a weak catalytic activity which grows with increasing length of the hydrocarbon chain which connects the rings. It goes without saying that in this case the reaction is blocked not because of titanium atom being too crowded for the transformations described to take place. The titanium atom is coordinatively unsaturated, especially in the complexes with methylene-bonded rings: the angle Cp-ring centre—Ti—Cp-ring centre is a minimum (121°) for $\text{CH}_2(\text{C}_5\text{H}_4)_2\text{TiCl}_2$ and increases in the series $\text{CH}_2(\text{C}_5\text{H}_4)_2\text{TiCl}_2(121^\circ) < (\text{CH}_2)_2(\text{C}_5\text{H}_4)_2\text{TiCl}_2(128^\circ) < \text{Cp}_2\text{TiCl}_2(130^\circ) < (\text{CH}_2)_3(\text{C}_5\text{H}_4)_2\text{TiCl}_2(133^\circ)$ [18]. Therefore, we may assume that a decrease in the activity in this case is related either to an increase in the strength of the intermediate bridged alkyl complexes due to the reduction of steric hindrance or (which is more probable) to the necessity of formation of a wedge-sandwich structure with a pseudotetrahedral titanium atom during the process of β -elimination, which becomes more as the rigidity of the cyclopentadienyl rings increases.

The proposed mechanism for olefin isomerization on the complexes $\text{L}_m\text{TiH}_2\text{-AlXX}'$ (reactions 5, 6, 8) is confirmed by the fact that olefins are readily hydrometallated by the terminal Al—H bonds and by the results of studying the interaction of heptene-1 with the model complex $\text{Cp}_2\text{TiH}_2\text{AlH-sec-C}_6\text{H}_{13}$ obtained by an independent synthesis (reaction 4). Thus, treatment of solutions of the latter (Fig. 1,c) with a small excess of heptene-1 results in the appearance in the EPR spectrum of a set of signals (Fig. 1,d) similar to that observed for the mixture $\text{Cp}_2\text{TiH}_2\text{AlH}_2 + \text{hexene-1}$ (Fig. 1,e) and in the formation of 2-hexene and 3-hexene, along with 2-heptene, in the reaction mixture. The *trans/cis* isomer ratio is the same for both olefins. All the above points undoubtedly to the participation of the terminal alkyl groups in the isomerization process.

It is quite possible that the proposed mechanism for the isomerization is not the only one. For instance, the very weak hydrogenating activity of $\text{Cp}_2\text{TiH}_2\text{-AlCl}_2$ can be attributed to the fact that reaction 2 proceeds only partially. The experimental data, however, prove convincingly the heterometallic mechanism

of catalytic isomerization on the aluminohydrides L_mTiH_2AlHX ; they also point to the important role of the non-transition metal (cocatalyst) and the terminal ligands bond to it in the process and indicate that the process is affected by the stereochemical rigidity of the ligand environment of the transition metal atom. It is quite clear that a change in the number and basicity of the substituents at the aluminium atom (even in the terminal position) must be an effective tool for controlling the catalytic activity of such compounds.

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