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 $(C_5H_4i-Pr)_2Ni$ exhibits the highest catalytic activity in the dimerization of ethylene among the nickelocenes, $(C_5H_4R)_2Ni$ (R = H, Et, *n*-Pr, *i*-Pr, or *t*-Bu) and their analogs $(C_5H_4R)Ni(C_3H_5)$ (R = H, *i*-Pr). The higher activity is accompanied by lower selectivity with respect to 1-butene and with higher yields of 1-hexene. It is suggested that the introduction of an alkyl substituent in the cyclopentadienyl ring of nickelocene favors the generation of "hydride sites" involving the nickel atom. These sites participate in the process of ethylene dimerization.

Key words: substituted nickelocene; ethylene dimerization; butene; catalytic activity; selectivity.

The possibility of employing nickelocene as a multicomponent homogeneous catalyst in the dimerization of ethylene under rather rigorous conditions was for the first time demonstrated in 1967.¹ The product of nickelocene hydrogenation, $(C_5H_5)Ni(C_5H_7)$, exhibits higher activity and selectivity at a lower temperature.² The course of polymerization and oligomerization of ethylene in the presence of a zirconocene-methylalumoxane catalyst substantially depends on the nature of the substituent in the cyclopentadienyl moiety. $^{3-6}$ This fact prompted us to suggest that the introduction of alkyl groups in nickelocenes would affect the activity and selectivity of the catalyst. Therefore in this work we have studied the effect of the alkyl substituent R in $(C_5H_4R)_2Ni$ (R = H, Et, n-Pr, i-Pr, or t-Bu) and in their analogs, $(C_5H_4R)Ni(C_3H_5)$ (R = H, *i*-Pr), on the process of ethylene dimerization.

Results and Discussion

The introduction of a substituent in the cyclopentadienyl ring of nickelocene brings about a decrease in the induction period and an increase in the proportion of hexenes, as compared with butenes, in the reaction products (Fig. 1, Table 1). The selectivity of the catalyst diminishes in the following order of R: H > Et > n-Pr >*i*-Pr. The substitution of an allyl ligand for one of the cyclopentadienyl rings lowers the yield of dimerization products. The composition of the reaction products formed in the presence of $(C_5H_5)Ni(C_3H_5)$ is close to that obtained with $(C_5H_4i$ -Pr)₂Ni. The addition of EtAlCl₂ to $(C_5H_4i$ -Pr)₂Ni cuts the induction period to zero, and the dimerization of ethylene occurs in this case at a lower temperature and pressure. The amount of EtAlCl₂ exerts only a slight effect on the rate of dimerization; the data on reaction selectivity are given in Table 2.

The dimerization of olefins catalyzed by nickel compounds can proceed⁷ either as a synchronous coupling



Fig.1. The effect of the nickelocene structure on the kinetics of ethylene dimerization at $5 \cdot 10^{-2} M$ Ni, 423 K, $p_{C_2H_4} = 4$ MPa, 0.04 L of toluene. Nickelocenes: $(i-PrC_5H_4)_2Ni$ (*I*); $(n-PrC_5H_4)_2Ni$ (*2*); $(EtC_5H_4)_2Ni$ (*3*); $(C_5H_5)_2Ni$ (*4*); $(C_5H_5)Ni(C_3H_5)$ (*5*); $(i-PrC_5H_4)Ni(C_3H_5)$ (*6*).

Tab	le	1.	The	effe	ct of	f sub	stitut	ed	cycloj	penta	lieny	l ligan	ds (on
the	sel	ect	tivity	of	nick	eloce	ene-o	catal	lyzed	ethyl	ene o	limeriz	zati	on
(423	3 K	; 1	V = 4	40 m	L, <i>p</i>	СлНа	= 4	MF	Pa)					

Catalyst	The composition of the products (%)						
(2.0 mmol)	1-Butene	cis-2- Butene	trans-2- Butene	1-Hexene			
$\overline{(C_5H_5)_2N_i}$	98.0	0.9	1.1				
$(EtC_5H_4)_2Ni$	86.0	6.4	3.7	3.9			
$(n-\Pr C_5 H_4)_2 Ni$	81.5	7.6	5.4	5.5			
$(i-\Pr C_5 H_4)_2 Ni$	30.6	7.3	7.0	55.1			
$(C_5H_5)Ni(\overline{C_3H_5})$	26.4	2.7	2.2	68.7			
$(i-\Pr C_5H_4)Ni(C_3H_5)$) 40.7	31.7	25.9	1.7			
$(t-BuC_5H_4)_2Ni$	No rea	No reaction					

(a) or as degenerate polymerization (b). In the first case two ethylene molecules are coordinated simultaneously to a nickel atom, with subsequent formation of a metalcontaining ring.



According to the mechanism of degenerate polymerization, the dimerization involves the formation of some "nickel hydride sites" caused by the transfer of a hydrogen atom from the cyclopentadienyl ring or the alkyl groups attached to it to the metal atom. The insertion of an olefin molecule into the Ni-H bond to form the NiEt moiety is followed by the coordination of a second C_2H_4 molecule, its insertion into the Ni-C bond to produce a NiBu moiety, and β -hydride transfer from the methylene group to the metal atom with the formation of butene.



The Ni—H, Ni—Et, and Ni—Bu fragments can interact not only with C_2H_4 , but with butenes and hexenes as well; the occurence of these reactions would account for the lowering of the reaction selectivity. The easy formation of the metal-hydride species is probably the factor that determines the high rate of dimerization. In the case of unsubstituted nickelocene the formation of the Ni—H bond by means of hydrogen transfer from the ring to the metal atom occur only with difficulty; hence,

Table 2. Dimerization of ethylene catalyzed by the homogeneous system $(i-\text{PrC}_5\text{H}_4)_2\text{Ni}-\text{AlC}_2\text{H}_5\text{Cl}_2$ in toluene (343 K, $p_{\text{C}_2\text{H}_4} = 0.3$ MPa; $V_{\text{tot}} = 0.04$ L; 0.375 mmol of AlEtCl₂)

	The composition of the products (%)								
Al/Ni	1-Butene	<i>cis</i> -2- Butene	<i>trans</i> -2- Butene	Butene	1-Hexene				
2.0	2.6	58.2	30.8	0.1	8.3				
3.1	3.9	67.0	16.0	0.2	12.9				
5.3	2.3	55.2	32.1	0.1	10.3				
10.1	1.8	64.0	22.8	0.3	11.1				
12.3	2.4	61.6	19.1	0.15	16.8				
20.8	51.9	12.8	19.3		16.0				
47.4	49.4	16.2	13.4		21.0				

the reaction is more likely to proceed according to the simultaneous coupling mechanism.

The Ni—H bonds in alkyl substituted nickelocenes may arise upon activation of the C—H bonds in the alkyl groups. Examples of such processes have been reported.^{8,9} In the dimerization of ethylene catalyzed by $(C_5H_4R)_2Ni$ (R = Et, *n*-Pr, *i*-Pr) the compound with R = *i*-Pr is most active. This may be due to the ready formation of the Ni—H bonds.

Whereas dimerization catalyzed by the parent nickelocene proceeds predominantly as synchronous coupling, in the case of its alkyl substituted derivatives the contribution of the degenerate polymerization mechanism increases. This results in the reduction of the selectivity with respect to dimeric products. Notice that in the binary system $(C_5H_4i-Pr)_2Ni-EtAlCl_2$ the Ni-Et moiety forms first as a result of the transfer of the ethyl group, whereas the Ni-H bond arises after at least one catalytic cycle.

$$Ni-Et + C_2H_4 \rightarrow Ni-Bu \rightarrow Ni-H + C_4H_8.$$

Thus, the rate and selectivity of the dimerization of ethylene catalyzed by nickelocenes is governed by a number of factors, the most important of which is probably the ability of the nickelocene to form "hydride sites" with the participation of the alkyl groups of its cyclopentadienyl ligands.

Experimental

The compounds to be studied were prepared by known procedures.¹⁰ Cp₂Ni for ethylene dimerization was purified by sublimation at 130 °C (10⁻¹ Torr). According to the mass-spectrometric analysis its purity was no less than 99 %. The alkyl substituted nickelocenes $(C_5H_4R)_2Ni$ (R = Et, *n*-Pr, *i*-Pr, and *t*-Bu) were purified by vacuum distillation at 80–120 °C (10⁻¹ Torr), the resulting specimens were no less than 98 % purity (according to the mass-spectrometric analysis).

The reaction kinetics were studied using an UVD-150 vacuum high-pressure device. The composition of the reaction products was analyzed on a LKhM-8D chromatograph equipped with a 3 m column (inner diameter 4 mm) packed with 15 % of dimethylsulfolane on Chromaton (granulation $0.2\div0.35$ mm);

the temperature of the column was -20 °C, the detector current was 110 mA, and the rate of the carrier gas (helium) was 60 mL min⁻¹.

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Synthesis and properties of the dissymmetrical dinuclear complex of cobalt(III) with *o*-carborane(12) derivatives

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Dinuclear dicobaltacarborane with three different carborane fragments, $[(C_2B_9H_{11})Co(C_2B_8H_{10})Co(C_2B_8H_{10})]^{2-}$, has been synthesized, and its properties have been studied by means of DTA and IR, UV, ¹H and ¹¹B NMR spectroscopy techniques. It has been found that at 138 °C this complex undergoes thermal isomerization associated with the migration of a carbon atom in the $(CoC_2B_8H_{10})^+$ fragment to a position with a lower coordination number.

Key words: cobaltacarboranes; polyhedral compression; thermal isomerization.

Earlier, a dinuclear dicobaltacarborane,

 $[(1,2-C_2B_9H_{11})_2Co_2(1,2-C_2B_8H_{10})]^{2-}$ (1), containing two 1,2-dicarbollyl $(C_2B_9H_{11})^{2-}$ fragments and one 1,2dicarbacanastide $(C_2B_8H_{10})^{4-}$ moiety, has been synthesized¹ from mononuclear $[(1,2-C_2B_9H_{11})_2Co]^-$ cobaltacarborane by partial degradation of one of the dicarbollyl polyhedra by aqueous alkali and subsequent interaction with the Co(II) ion and one more dicarbollyl anion. As a result of this process, a sandwich-like chain system is formed where the carborane ligands are interconnected by Co(III) ions.

A point of interest about such a chain system is the high degree of electron delocalization in the cobaltacarborane fragments. However, up to now little was known about the chemical properties of this dicobaltacarborane.

The aim of the present study was to perform the reaction of "polyhedral compression" at one of the terminal $(C_2B_9H_{11})^{2-}$ fragments in the dicobaltacarborane 1 anion and investigate the properties of the asymmetrical dinuclear Co(III) complex (2). It was expected that two stoichiometrically analogous $(C_2B_8H_{10})$ fragments (a bidentate $(C_2B_8H_{10})^{4-}$ ligand, and a terminal $(C_2B_8H_{10})^{2-}$ ligand) should be present in the structure of this complex.