Effect of substituents on the catalytic properties of bis(cyclopentadienyl)zirconium dichloride complexes with polymethylaluminoxane and $AlBu^i_3/CPh_3B(C_6F_5)_4$ cocatalysts in ethylene polymerization

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The catalytic properties of the complexes $(RCp)_2ZrCl_2$ (R = H, Me, Pr^i, Bu^n, Bu^i, Me_3Si, *cyclo*-C_6H_{11}), and $Me_2SiCp^*NBu^tZrCl_2$ ($Cp^* = C_5(CH_3)_4$) combined with the $AlBu^i_3-CPh_3B(C_6F_5)_4$ cocatalyst in ethylene polymerization were studied. The specific activity of the substituted bis-cyclopentadienyl complexes decreases in the sequence: Me > Pr^i > Bu^n > Bu^i > Me_3Si > *cyclo*-C_6H_{11}, which corresponds to the activity sequence for these complexes activated by polymethylaluminoxane (MAO) but is 4—20 times lower in absolute value. Comparison of the polyethylene samples obtained in the presence of the same complexes with MAO and $AlBu^i_3-CPh_3B(C_6F_5)_4$ cocatalysts showed that polyethylene with much higher molecular mass, melting point, and crystallinity is formed in the presence of the ternary catalytic systems, and this indicates a different nature of the active sites of the catalytic systems. The effective activation energy of polymerization (~3.6 kcal mol^{-1}), first order with respect to monomer and ~0.4 order with respect to organoaluminum component, was found for the $(Pr^iCp)_2ZrCl_2-AlBu^i_3-CPh_3B(C_6F_5)_4$ catalytic system. It was proposed on the basis of the kinetic data that Al^iBu_3 enters into the composition of the active site to form a bridged heteronuclear cationic complex.

Key words: metallocene catalysts, zirconocenes, ethylene polymerization, kinetics of polymerization, active site, perfluorophenyl borates, polymethylaluminoxane, effect of substituents.

Metallocene complexes of group IVB L_2MX_2 (L are unsubstituted or substituted η-bound ligands, cyclopentadienyl (Cp), indenyl (Ind), and fluorenyl (Flu); M = Ti, Zr, Hf; X = Cl, Alk) combined with polymethylaluminoxane (MAO) are known to be highly efficient catalysts for olefin polymerization. It is widely accepted[1—5] that electron-deficient cationic complexes are formed in these catalytic systems under MAO action:

$$L_2MX_2 + MAO \longrightarrow L_2M^+Me...X\cdot MAO^-$$

Since MAO has been discovered as a highly efficient cocatalyst for metallocene complexes,[6] it remained the single efficient activator for the catalytic system for a long time. It has been found later[4,7—9] that cationic complexes exhibiting high activity in olefin polymerization are also formed as a result of interaction between perfluorophenyl boranes and borates and dimethyl derivatives of metallocenes.

$$L_2MMe_2 + B(C_6F_5)_3 \longrightarrow L_2M^+Me...MeB^-(C_6F_5)_3,$$

$$L_2MMe_2 + CPh_3B(C_6F_5)_4 \longrightarrow$$

$$\longrightarrow L_2M^+Me...B^-(C_6F_5)_4 + CPh_3Me$$

However, this approach to the formation of the active site has some limitations. First, it is necessary to preliminarily alkylate metallocene dichloride and to separate the cationic complex.[8—10] Sometimes such a cationic complex cannot be obtained in individual form. Second, a low thermal stability of dialkylmetallocenes and metallocene-borate complexes as compared to dichlorides results in poor reproducibility of experiments. In addition, high concentrations of metallocenes are required, 2—3 times higher than those of the complexes providing maximum activity during activation by MAO. Due to high reactivity of cationic complexes, side reactions with other components of a reaction medium (for instance, with neutral dimethyl deriva-

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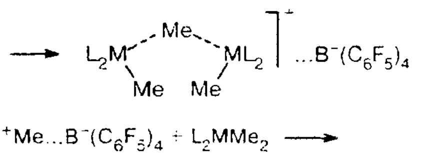
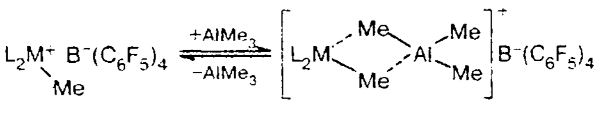
tives) occur, producing the dimeric cationic complexes[10—12]



The maximum activity of the complexes formed by MAO activation is observed at an excess of the cocatalyst (Al : Zr = 10^3—10^4), providing also elimination of the water admixture from the reaction medium. When perfluorophenyl boranes and perfluorophenyl borates are used, the reactions with the water admixture can result in fast deactivation of the cationic complexes. It has been reported previously[13] that the catalytically active complexes cannot be obtained at even very high concentrations of metallocene and trityl perfluorophenyl borate (~$1 \cdot 10^{-3}$ mol L^{-1}).

The catalytically active complexes can be separated from metallocene dichlorides by their *in situ* alkylation with trialkylaluminum followed by generation of the cationic complex with the aid of perfluorophenyl borates.[14—16] This approach allows the catalytically active systems to be obtained at low concentrations of metallocene, a small excess of organoaluminum component, and a stoichiometric transition metal : borate ratio. Data are available in the literature[17—20] on the use of aluminum alkyls (for example, triisobutylaluminum ($AlBu^i_3$)) as cocatalysts for metallocenes supported on the surface of inorganic supports pretreated with MAO. However, data on the nature of the active sites formed in the ternary catalytic systems (metallocene dichloride—AlR_3—perfluorophenyl borates or boranes) are absent. AlR_3 are assumed to act only at the stage of preliminary alkylation of the dichloride complex or as reagents that purify the reaction medium from the water admixture. However, the participation of $AlBu^i_3$ in the reactions producing the catalytically active cationic complexes cannot consist only in alkylation of the dichloride complex. Thus, the equilibrium formation of catalytically active heteronuclear bridged complexes caused by AlR_3 (R = Me, Et) has been reported[11,21,22]:



M = Zr, Hf

The literature data on the effect of the organoaluminum compound on the catalytic properties of these ternary catalytic systems are scanty.[23,24]

In this work, the catalytic activity of zirconocene dichlorides Cp_2ZrCl_2 (Cp), $(MeCp)_2ZrCl_2$ (MeCp), $(Pr^iCp)_2ZrCl_2$ (Pr^iCp), $(Bu^nCp)_2ZrCl_2$ (Bu^nCp), $(Bu^tCp)_2ZrCl_2$ (Bu^tCp), $(Me_3SiCp)_2ZrCl_2$ (Me_3SiCp), $(CyCp)_2ZrCl_2$ (Cy = *cyclo*-C_6H_{11}, CyCp), and $Me_2SiCp^*NBu^tZrCl_2$ (Cp^* = Me_4C_5, Cp^*NBu^t) in ethylene polymerization with the use of $AlBu^i_3$ as an alkylating agent followed by the formation of the catalytically active cationic complexes with the aid of $CPh_3B(C_6F_5)_4$ were studied as well as the properties of polymers formed. The catalytic properties of the substituted non-bridging zirconocene dichlorides upon their activation by MAO and $AlBu^i_3$—$CPh_3B(C_6F_5)_4$ and the properties of the polyethylene samples obtained were compared.

Experimental

All preparations of catalysts were carried out in an argon atmosphere. The solvent (toluene) was purified according to a standard procedure. It was distilled over sodium, then twice over $LiAlH_4$, and stored under argon.

Zirconocenes[25] and $CPh_3B(C_6F_5)_4$[26] were synthesized according to known procedures. Triisobutylaluminum was used as a 25% solution in toluene (Aldrich). Argon and ethylene were dried by passing through a column with activated molecular sieves 5A.

Polymerization under ethylene pressure ≤1 atm was carried out in a glass reaction vessel. Toluene and $AlBu^i_3$ were placed into a thermostatted reactor equipped with a stirrer in an argon atmosphere at room temperature. Argon was removed and the solution was saturated with ethylene up to required pressure. After ethylene had been dissolved completely (in 5—10 min), the zirconocene complex was introduced. The solution was stirred for 5 min at room temperature, then the temperature and monomer pressure were increased up to specified values, and a solution of $CPh_3B(C_6F_5)_4$ in toluene was added. The introduction of the latter component of the cocatalyst was taken as the starting point of polymerization. The kinetics of polymerization was measured by consumption of ethylene at a constant monomer pressure. Polymerization was stopped by a 10% solution of HCl in ethanol. The polymer was filtered, washed with alcohol and water, and dried to a constant weight at 60 °C in a vacuum. Polymerization at an ethylene pressure above atmospheric was performed in a high-pressure thermostatted stainless-steel reactor equipped with a stirrer and a system for introducing the components of the catalytic system. The sequence of introducing the components and the feed of monomer were the same as in the runs in the glass reactor.

The melting points of polymers were determined on a DSM-3 scanning calorimeter (heating rate 5 deg min^{-1}). The crystallinity of samples was calculated by referring the specific integral intensity of the heat-evolution peak to the specific melting heat of the polyethylene single crystal (PE)[27] (64.5 cal g^{-1}). The molecular mass of the polyethylene samples was estimated by measuring the viscosity of polymer solutions in decalin at a temperature of 135 °C. The coefficients in the Mark—Kuhn—Howink equation for polyethylene were K_η = $4.6 \cdot 10^{-4}$, α = 0.73.

Results and Discussion

All the complexes were active in ethylene polymerization in the presence of the $AlBu^i_3$—$CPh_3B(C_6F_5)_4$ cocatalyst. We did not observe monomer consumption and PE formation when only $AlBu^i_3$ was introduced in metallocene solutions at a concentration of the complex ≤$1 \cdot 10^{-5}$ mol L^{-1}.

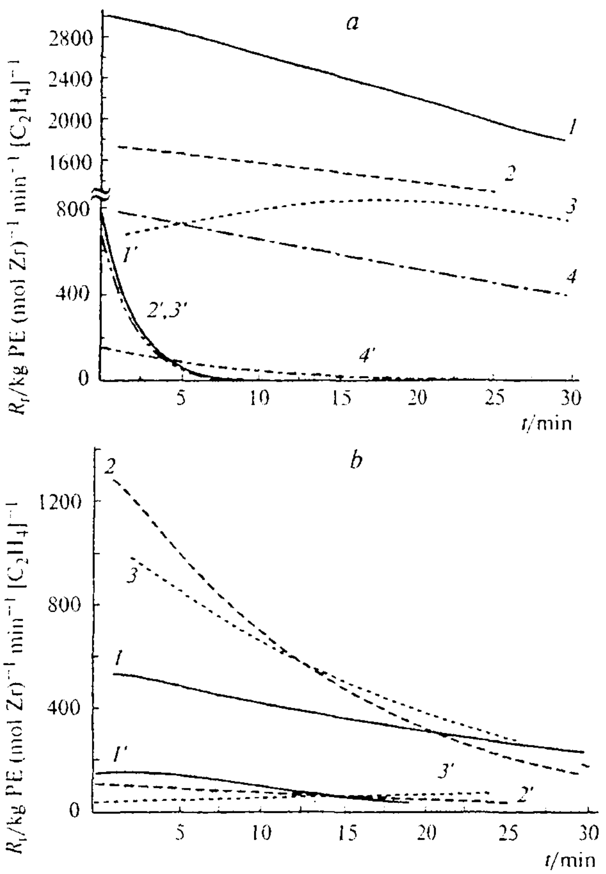


Fig. 1. Comparison of the consumption rates (R_r) of ethylene by the catalytic systems L_2ZrCl_2 with MAO (*1, 2, 3, 4*) ([Zr] = $2 \cdot 10^{-7}$ mol, Al : Zr = 2000, ethylene pressure, 0.54 atm, toluene, 30 °C)[28] and with $AlBu^i{}_3$—$CPh_3B(C_6F_5)_4$ (*1', 2', 3', 4'*) ([Zr] = $6 \cdot 10^{-7}$ mol, Al : Zr = 500, B : Zr = 1, ethylene pressure, 1 atm, toluene, 20 °C) as cocatalysts. Ligand: *a* — MeCp (*1, 1'*); Pr^{i}Cp (*2, 2'*); Bu^{n}Cp (*3, 3'*); Bu^{i}Cp (*4, 4'*); *b* — CpH (*1, 1'*) (the conditions of polymerization see in Table 1); Me_3SiCp (*2, 2'*); *cyclo*-C_6H_{11}Cp (*3, 3'*).

Due to substantial difference in the kinetics of ethylene consumption, it is impossible to compare the activities of the catalytic systems in the presence of various activators in conventional units, the weight of PE (mol Zr)$^{-1}$ (h atm)$^{-1}$ or with respect to the specific yield of polyethylene. In our opinion, the initial rates of ethylene consumption can be used as characteristics of the catalytic properties of the systems studied. The complexes with alkyl substituents in the cyclopentadienyl ring (MeCp, Pr^{i}Cp, Bu^{n}Cp, Bu^{i}Cp) activated by $AlBu^i{}_3$—$CPh_3B(C_6F_5)_4$ (Table 1) exhibited high initial activity that rapidly dropped in several minutes (Fig. 1, *a*). In the system with unsubstituted zirconocene (Cp) and the complexes with non-alkyl substituents in the ring (Me_3SiCp, CyCp), ethylene was consumed more slowly (see Fig. 2, *b*). The initial rates of ethylene consumption in the catalytic systems activated by MAO[28] (Table 2) are significantly higher for both unsubstituted Cp_2ZrCl_2 and for the complexes with substituents in the cyclopentadienyl ring. These differences are likely due to a different nature of the active sites, which determines the reactivity of the metal—carbon bond.

The formation of PE in a toluene suspension considerably differs. In the presence of the first three complexes, a gelatinous polymeric product was formed instantly over the whole reaction volume. In the case of the remaining four complexes, the PE particles were formed gradually such as in the catalytic systems with MAO as cocatalyst. We suppose that a sharp decrease in the polymerization rates in the presence of the first three zirconocenes and $AlBu^i{}_3$—$CPh_3B(C_6F_5)_4$ as cocatalyst is not due to only deactivation of the cationic complexes. The catalytic systems in which the rates of ethylene consumption drastically decreased retained their activity even after 24 h. The most probable reason for this behavior is the encapsulation of the active sites by the gelatinous polymer formed and, as a consequence, the appearance of diffusion limitations for the monomer approach to the active site.

Table 1. Ethylene polymerization in the presence of the catalytic systems zirconocene dichloride—$AlBu^i{}_3$—$CPh_3B(C_6F_5)_4$ and some characteristics of the PE samples

Run	Complex	Ligand	σ^{*} [a]	E_s^0 [b]	T_p [c] /°C	p /atm	Al : Zr	R_r^0 [d]	Y/g [e] (t_r/min)	M_η	M.p. [f] /°C
1	$(MeCp)_2ZrCl_2$	Me	−0.5	−0.3	20	1.0	500	780	0.13(8)	397000	134
2	$(Pr^iCp)_2ZrCl_2$	Pr^i	−0.7	−1.1	30	1.0	500	672	0.10(5)	734000	133
3	$(Pr^iCp)_2ZrCl_2$	Pr^i	−0.7	−1.1	30	1.0	400	652	0.07(5)	808000	131
4	$(Pr^iCp)_2ZrCl_2$	Pr^i	−0.7	−1.1	30	1.0	300	600	0.07(4)	709000	131
5	$(Pr^iCp)_2ZrCl_2$	Pr^i	−0.7	−1.1	30	1.0	200	472	0.07(5)	655000	131
6	$(Pr^iCp)_2ZrCl_2$	Pr^i	−0.7	−1.1	30	1.0	100	350	0.04(5)	535000	133
7	$(Pr^iCp)_2ZrCl_2$	Pr^i	−0.7	−1.1	−20	1.0	500	239	0.07(5)	1000000	136
8	$(Pr^iCp)_2ZrCl_2$	Pr^i	−0.7	−1.1	0	1.0	500	307	0.13(5)	727000	135
9	$(Pr^iCp)_2ZrCl_2$	Pr^i	−0.7	−1.1	20	1.0	500	663	0.12(5)	519000	137
10	$(Pr^iCp)_2ZrCl_2$	Pr^i	−0.7	−1.1	20	10.0	500	292	2.1(5)	509000	134
11	$(Pr^iCp)_2ZrCl_2$	Pr^i	−0.7	−1.1	20	0.6	500	223	0.13(25)	314000	—
12	$(Pr^iCp)_2ZrCl_2$	Pr^i	−0.7	−1.1	20	0.3	500	147	0.05(25)	230000	—
13	Cp_2ZrCl_2	H	0	0	20	1.0	100	160	0.15(14)	380000	134

to be continued

Table 1. *continued*

Run	Complex	Ligand	σ^* [a]	E_s^0 [b]	T_p [c] /°C	p /atm	Al : Zr	R_r^0 [d]	Y/g [e] (t_r/min)	M_η	M.p. [f] /°C
14	$(Bu^nCp)_2ZrCl_2$	Bu^n	−0.6	−0.8	20	1.0	500	651	0.11(5)	665000	137
15	$(Bu^iCp)_2ZrCl_2$	Bu^i	−0.6	−1.4	20	1.0	500	189	0.12(30)	398000	133
16	$(Me_3SiCp)_2ZrCl_2$	Me_3Si	−0.8	−3.7	25	1.0	500	107	0.13(25)	828000	134
17	$(CyCp)_2ZrCl_2$	Cy	−0.6	−1.4	0	1.0	500	11	0.02(30)	582000	—
18	$(CyCp)_2ZrCl_2$	Cy	−0.6	−1.4	20	1.0	500	21	0.04(30)	193000	—
19	$(CyCp)_2ZrCl_2$	Cy	−0.6	−1.4	30	1.0	500	72	0.09(25)	600000	—
20	$(CyCp)_2ZrCl_2$	Cy	−0.6	−1.4	40	1.0	500	279	0.09(10)	598000	—
21	$Me_2SiCp^*NBu^tZrCl_2$	Cy	−0.6	−1.4	30	11.5	260	46	7.9(30)	>2000000	137
22	$Me_2SiCp^*NBu^tZrCl_2$	Cy	−0.6	−1.4	70	11.5	260	51	5.8(30)	1820000	136
23	$Me_2SiCp^*NBu^tZrCl_2$	Cy	−0.6	−1.4	90	11.5	260	705	7.6(9)	127000	113

Note. The conditions of polymerization: toluene, $[Zr] = 3.0 \cdot 10^{-5}$ mol L^{-1}. [a] The Taft inductive constant. [b] The Palm steric constant. [c] Temperature of polymerization. [d] The initial rate of ethylene consumption, kg PE (mol Zr)$^{-1}$ (min $[C_2H_4]$)$^{-1}$. [e] Polymer yield for the reaction time indicated. [f] Melting point according to the DSC data.

Table 2. Ethylene polymerization in the presence of the catalytic system zirconocene dichloride—MAO and some characteristics of the PE samples[28]

Run	Complex	A [a]	R_r^0 [b]	M_w [c]	M_n [c]	M.p. [d] /°C	α [d] (%)
24	$(MeCp)_2ZrCl_2$	6470	3030	345500	133800 [e] 49600		
25	$(Pr^iCp)_2ZrCl_2$	4555	1730	291200	67000	135	57
26	$(Bu^nCp)_2ZrCl_2$	2235	830	323300	59600	134	53
27	$(Me_3SiCp)_2ZrCl_2$	2049	1290	654700	101100	138	59
28	$(Bu^iCp)_2ZrCl_2$	1658	780	272900	68700	133	62
29	$(CyCp)_2ZrCl_2$	1265	990	196600	74900		

Note. The conditions of polymerization: toluene, 20 mL; $[Zr] = 2 \cdot 10^{-7}$ mol L^{-1}; cocatalyst, Al : Zr = 2000; temperature of polymerization, 30 °C; ethylene pressure, 0.54 atm. [a] Catalytic activity, kg PE (mol Zr h)$^{-1}$. [b] The initial rate of ethylene consumption, kg PE (mol Zr)$^{-1}$ (min $[C_2H_4]$)$^{-1}$. [c] According to the data of gas-vapor chromatography. [d] According to the data of DSC; α is the degree of crystallinity. [e] Bimodal distribution.

With respect to the initial reaction rates and the polymer yield, all the complexes activated by $AlBu^i_3$—$CPh_3B(C_6F_5)_4$ can be arranged in the sequence of decreasing activity: MeCp > Pr^iCp > Bu^nCp > Bu^iCp > Me_3SiCp > CyCp. This sequence as a whole corresponds to that found by us[28] for the complexes activated by MAO: MeCp > Pr^iCp > Bu^nCp > Me_3SiCp > Bu^iCp > CyCp (see Table 2). We have shown previously[28] that the logarithm of the specific catalytic activity closely matches the inductive Taft constant (σ^*) and the steric Palm constant (E_s^0).[29] A similar linear dependence of the potentials of electrochemical reduction on the combined effect of substituents has been found for the series of titanocenes substituted in the cyclopentadienyl ring.[30] Since both processes, polymerization and electrochemical reduction, reflect the reactivity of the bond between transition metal and σ-bound ligand, the transition state should be sensitive to the electronic and steric effects of substituents. We found for the ternary catalytic systems studied in this work that the logarithm of the ratio of the initial consumption rates (R^0) for ethylene in the presence of the substituted and unsubstituted complexes is connected with the constants σ^* and E_s^0 by a linear relation

$$\ln(R^0_{CpR}/R^0_{Cp}) = \rho\sigma^* + \delta E_s^0,$$

where $\rho = -4.23$, $\delta = 1.18$. As can be seen in Fig. 2, the logarithms of normalized initial rates linearly increase with an increasing combined effect of substituents. The active site formed in the ternary catalytic systems is significantly more sensitive to the electronic effect of substituents than that formed under the action of MAO.[28]

Comparison of the Arrhenius dependences for ethylene polymerization in the systems containing zirconocene $(Pr^iCp)_2ZrCl_2$ activated by MAO and $AlBu^i_3$—$CPh_3B(C_6F_5)_4$ showed that the values of the effective activation energy (E_{eff}) are close: 5.5±1.1 kcal mol^{-1} and 3.6±0.9 kcal mol^{-1}, respectively (Fig. 3). Such low

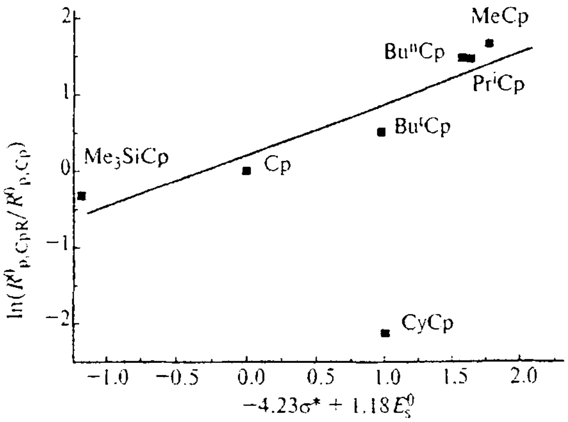


Fig. 2. Dependence of the logarithms of the reduced initial rates (R_p^0) of ethylene polymerization on the combined effect of substituents for a series of monosubstituted zirconocenes activated by $\mathrm{AlBu^i_3{-}CPh_3B(C_6F_5)_4}$. The conditions of polymerization: toluene, 20 mL; 20 °C; $[\mathrm{Zr}] = 6 \cdot 10^{-7}$ mol; Al : Zr = 500; B : Zr = 1; ethylene pressure, 1 atm.

E_{eff} values are typical of ethylene polymerization in the presence of cationic complexes of group IVB elements, whereas the E_{eff} values for the series of complexes studied by us and activated by MAO, including sterically hindered disubstituted zirconocene $\mathrm{Cy_2Cp}$, are less than 8—10 kcal mol^{-1}. The significantly higher E_{eff} value for the $\mathrm{(CyCp)_2ZrCl_2}$ complex activated by $\mathrm{AlBu^i_3{-}CPh_3B(C_6F_5)_4}$ (21.0±1.5 kcal mol^{-1}) suggests that in this case formation of the active cationic complex under the action of $\mathrm{AlBu^i_3{-}CPh_3B(C_6F_5)_4}$ is a rate determining step.

An abnormal dependence of the molecular parameters of the PE samples on the reaction temperature (T_r) was observed for the ternary catalytic systems. The M_w—T_r function for samples prepared in the presence of $\mathrm{Pr^iCp_2ZrCl_2{-}AlBu^i_3{-}CPh_3B(C_6F_5)_4}$ passes through a minimum in the region of 15—20 °C and the M_w value increases again at 30 °C (see Table 1, runs *2, 7—9*). These findings are reproducible for the PE samples prepared with the use of CyCp and $\mathrm{AlBu^i_3{-}CPh_3B(C_6F_5)_4}$ (see Table 1, runs *17—20*). This anomaly is likely due to the participation of $\mathrm{AlBu^i_3}$ in the formation of the various active sites, depending on the reaction conditions.

We attempted to examine this assumption with the example of the catalytic system $\mathrm{(Pr^iCp)_2ZrCl_2{-}AlBu^i_3{-}CPh_3B(C_6F_5)_4}$ by studying the effect of concentrations of the monomer and organoaluminum compound on the kinetics of polymerization. The reaction has the first order with respect to the monomer and the effective order ~0.4 with respect to $\mathrm{AlBu^i_3}$. When the molar ratio Al : Zr was increased from 100 to 400, the catalytic activity increased by ~2 times and simultaneously the molecular mass of the polymer significantly increased (Fig. 4). Some decrease in the molecular mass was observed at Al : Zr = 500. Similar effects of activity growth (by ~2.6 times) and the bell-shaped dependence of the molecular mass on the concentration of $\mathrm{AlBu^i_3}$ have been observed previously[23] for ethylene polymerization in the catalytic system $\mathrm{Cp_2ZrCl_2{-}B(C_6F_5)_3{-}AlBu^i_3}$ and for propene polymerization[24] in the catalytic system *rac*-$\mathrm{Me_2SiInd_2ZrCl_2{-}AlBu^i_3{-}CPh_3B(C_6F_5)_4}$ (an increase in the activity by ~2 times and an increase in the molecular mass from 56000 to 64000 along with an increase in the Al : Zr ratio from 250 to 500). However, examination of the ^{13}C NMR spectra of the polypropylene samples has shown[24] that $\mathrm{AlBu^i_3}$, unlike $\mathrm{AlEt_3}$, does not participate in the chain transfer reactions. In the latter case, an increase in the concentration of $\mathrm{AlEt_3}$ results in a sharp decrease in the catalytic activity and the molecular mass of the polymer. Similar dependences of the catalytic activity and molecular masses on the concentration of $\mathrm{AlR_3}$ (R = Me, Et) have been found[11] for the catalytic system $\mathrm{Cp_2ZrMe_2{-}CPh_3B(C_6F_5)_4}$. The authors[11] supposed that the chain

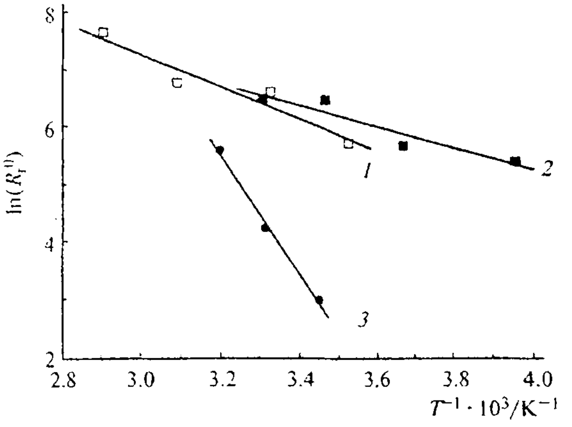


Fig. 3. The Arrhenius plot for the initial consumption rates (R_r^0) of ethylene by the catalytic systems: $\mathrm{Pr^iCp_2ZrCl_2{-}MAO}$ (*1*), $\mathrm{Pr^iCp_2ZrCl_2{-}AlBu^i_3{-}CPh_3B(C_6F_5)_4}$ (*2*), (*cyclo*-$\mathrm{C_6H_{11})Cp_2ZrCl_2{-}AlBu^i_3{-}CPh_3B(C_6F_5)_4}$ (*3*).

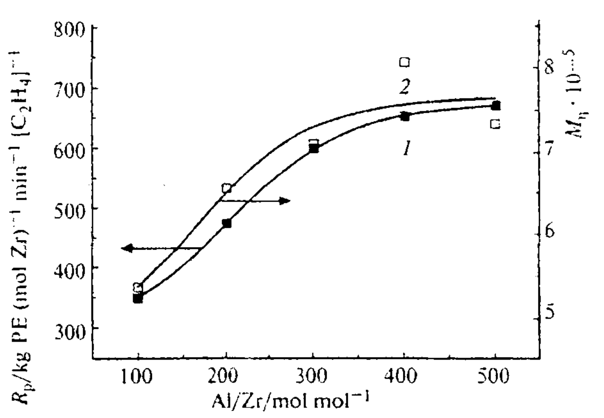


Fig. 4. Dependences the initial polymerization rate (*1*) and of the molecular mass of the polyethylene samples (*2*) on the Al : Zr ratio for the catalytic system $\mathrm{Pr^iCp_2ZrCl_2{-}AlBu^i_3{-}CPh_3B(C_6F_5)_4}$.

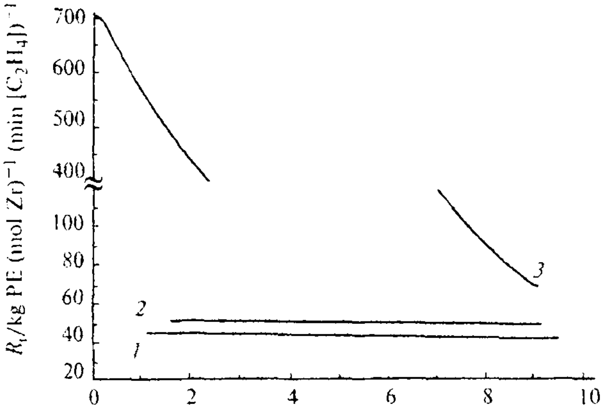


Fig. 5. The kinetics of ethylene polymerization in the presence of the catalytic system $Me_2SiCp^*NBu^tZrCl_2$—$AlBu^i_3$—$CPh_3B(C_6F_5)_4$ at *T* of reaction (°C): 30 (*1*); 70 (*2*); 90 (*3*) (for the rest of the reaction conditions see Table 1, runs *21—23*).

transfer to an organoaluminum compound and the equilibrium formation of bridged heterometallic complexes, which are inactive in polymerization, through the reaction between L_2Zr^+Me and AlR_3 can explain the effects mentioned. The above data suggest that the role of $AlBu^i_3$ consists in not only alkylation of zirconium dichloride complex followed by the formation of the cationic complex under the action of perfluorophenyl borate but also in the formation of the active site, most probably, in the form of bridged (alkyl or alkyl halide) Zr—R—Al cationic complexes.

The activity of the ternary catalytic systems and the molecular mass of the polymer formed are interrelated: the most active complexes produce polyethylene samples with the least molecular masses. Thus, high-molecular PE (~2000000 g mol^{-1}; see Table 1, runs *21* and *22*) is formed upon polymerization in the presence of the least active complex Cp^*NBu^t combined with $AlBu^i_3$—$CPh_3B(C_6F_5)_4$. When MAO was used as a cocatalyst, this complex produced PE with a molecular mass of 212000 in similar conditions.[31] The molecular mass of PE obtained in the presence of the zirconium complex with the Me_3Si ligand that is the next in the activity sequence of the complexes studied is equal to 828000 g mol^{-1} (run *16*), other conditions being the same, and the molecular mass of the PE obtained in the presence of the more active Pr^iCp is equal to 734000 g mol^{-1} (run *2*). As a whole, the molecular masses of PE samples formed in the ternary catalytic systems are substantially higher than those of polymers obtained in the presence of similar complexes activated by MAO. According to the DSC data, the samples of PE prepared without MAO have higher degrees of crystallinity (65—70%). These facts give evidence of the difference in the active sites in the catalytic systems under comparison. One can suggest that the reactivity of the metal—carbon bond in the active site formed in the ternary catalytic system determines not only the insertion rate of an olefin but also the rate of chain transfer.

The results of experiments with the ternary catalytic system containing the complex with a "constrained geometry" $Me_2SiCp^*NBu^tZrCl_2$—$AlBu^i_3$—$CPh_3B(C_6F_5)_4$ also reveal the possible formation of active sites of various types, depending on the reaction conditions and zirconocene nature, when the catalyst was activated by $AlBu^i_3$. The basic NBu^t group is directly bound to the active site that is more electron-deficient as compared to the derivatives of $(RCp)_2ZrCl_2$ and more open sterically. The effect of the steric constituent is increased by the negative inductive effect, resulting in low initial rates of ethylene polymerization and high molecular masses of PE obtained in the presence of this complex activated by $AlBu^i_3$—$CPh_3B(C_6F_5)_4$. Ethylene is consumed at temperatures of 30 and 70 °C with a low constant rate (Fig. 5). An increase in the temperature from 70 to 90 °C resulted unexpectedly in a 14-fold increase in the initial rate followed by exponential decay of polymerization. The molecular mass of PE obtained at the reaction temperature of 90 °C is 14 times lower than that of PE obtained at 70 °C (see Table 1, runs *22* and *23*). Such a sharp change in the catalytic performance of the system and the molecular mass of PE because of an increase in temperature can be due to the formation of complexes of other types in the presence of $AlBu^i_3$. One can assume that the dialkylation stage and the formation of the bridged heteronuclear complex without the electron-acceptor chloride ligand precede the formation of the active cationic complex in the presence of borate at high temperature.

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