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The effect of substituents in bis(cyclopentadienyl)zirconium dichloride complexes on catalytic properties with $Al(i\text{-}Bu)_3/CPh_3B(C_6F_5)_4$ as activator in ethylene polymerization*)

Summary — A series of zirconocenes $(RCp)_2ZrCl_2$ (R = H, Me, *i*-Pr, *n*-Bu, *i*-Bu, Me_3Si, *cyclo*-C_6H_{11}) and a "constrained geometry catalyst" $Me_2SiCp^*N(t\text{-}Bu)ZrCl_2$ ($Cp^* = C_5(CH_3)_4$), activated with $Al(i\text{-}Bu)_3/CPh_3B(C_6F_5)_4$, were studied in relation to catalytic properties in ethylene polymerization. With varying substituents, the complexes gave polymer yields diminishing in the following descending order: Me > *i*-Pr > *n*-Bu > *i*-Bu > Me_3Si > *cyclo*-C_6H_{11}. The logarithm of initial polymerization rate (eqn. 3) was found to be directly related to the superposition of inductive and steric constants of the substituents in the ternary systems (Fig. 3, Table 2). The *M* of the PE produced with the aid of ternary catalytic systems was higher than that of PE produced with the corresponding complexes using methylaluminoxane (MAO) as cocatalyst. Polymerization kinetics data allow to suggest the $Al(i\text{-}Bu)_3$ to have been incorporated into the active center as a heteronuclear bridged complex.

Key words: polymerization of ethylene, catalyst systems, zirconocenes, polymerization kinetics, catalyst activity.

Metallocene dichloride complexes of transition metals with polymethylalumoxane (MAO) are well known as catalysts (1) highly effective in the polymerization of olefins. Recent investigations [1—3] have shown the active complexes to be preparable *in situ* by making zirconocene dichloride react with a trialkylaluminum and then with tetrakis(pentafluorophenyl)borate (2).

$$(LCp)_2ZrCl_2 + MAO \longrightarrow (LCp)_2Zr^+Me...ClMAO^- \quad (1)$$

$$\begin{aligned}&(LCp)_2ZrCl_2 + Al(i-Bu)_3 + CPh_3(C_6F_5)_4 \rightarrow \\ &\rightarrow (LCp)_2Zr^+(i-Bu)...B^-(C_6F_5)_4\end{aligned} \quad (2)$$

However, only scarce data are available on the composition of the active species in such ternary systems. AlR_3 is often considered to pre-alkylate the dichloride complex and to act as a scavenger. Bochmann *et al.* [4] have suggested that AlR_3 (R = Me, Et) forms heterobinuclear complexes in an equilibrium reaction. Thus, the complexes do not participate directly in chain propagation, but they influence the catalytic activity.

This study is undertaken (*i*) to establish the effect of substituents in the cyclopentadienyl ligands (L) on the catalytic performance and on the properties of the polymers formed in ethylene polymerization over ternary catalytic systems (metallocene dichloride/TIBA/$CPh_3B(C_6F_5)_4$; (*ii*) to determine differences in the catalytic performance of the ternary catalytic systems and of the corresponding zirconocenes activated with MAO; (*iii*) to examine the role of TIBA in the formation of active species in the ternary catalytic systems.

EXPERIMENTAL

Polymerization

Each measurement was carried out in an inert gas atmosphere. A 100-mL glass pressure reactor, containing a magnetic bar, was evacuated, flushed several times, and filled with 20 mL of purified toluene. Argon was replaced by the monomer, TIBA was added and 5—10 minutes later a zirconocene dichloride complex was injected. The mixture was stirred 5 min at room temperature, cooled or warmed to a desired temperature, and saturated with the monomer; finally, $CPh_3B(C_6F_5)_4$ dissolved in toluene was added to start polymerization. The polymeri-

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zation mixture was quenched with acidic 1% ethanol, the polymer was filtered, washed with ethanol, and dried at 60°C to constant weight. Melting and crystallization curves were recorded on a DSM-3 system. Molecular weight was determined *via* intrinsic viscosity measurements.

RESULTS AND DISCUSSION

A series of zirconocenes $(RCp)_2ZrCl_2$ (R = H, Me, *i*-Pr, *n*-Bu, *i*-Bu, Me_3Si, *cyclo*-C_6H_{11}) and a "constrained geometry catalyst" $Me_2SiCp^*N(t\text{-}Bu)ZrCl_2$ ($Cp^* = C_5(CH_3)_4$) activated with $Al(i\text{-}Bu)_3/CPh_3B(C_6F_5)_4$ were studied as catalysts in ethylene polymerization with triisobutylaluminum (TIBA) and tetrakis(pentafluorophenyl)borate used as a combined cocatalyst (Table 1). The catalytic systems activated with MAO were considerably more active than the ternary systems. The unsubstituted complex showed a moderate activity (Fig. 1, curve 1). The complexes with alkyl substituents (Fig. 2) gave rise to a high initial, and later a low, polymerization rate. All the other complexes showed a lower polymerization activity but their catalytic behavior was stable (Fig. 1, curves 2, 3).

T a b l e 1. Initial polymerization rate and molecular weight of polyethylenes prepared*) by using ternary catalytic systems with $Al(i\text{-}Bu)_3/CPh_3B(C_6F_5)_4$ and binary catalytic systems with MAO

Catalytic system	R_{p0}, kg PE/ (mol Zr · min · $[C_2H_4]$)	M_n
$(MeCp)_2ZrCl_2$ ternary	780	397 000
binary**)	3030	346 000
$(i\text{-}PrCp)_2ZrCl_2$ ternary	663	519 000
binary	2600	291 000
$(n\text{-}BuCp)_2ZrCl_2$ ternary	651	665 000
binary	830	323 000
$(i\text{-}BuCp)_2ZrCl_2$ ternary	189	398 000
binary	780	273 000
Cp_2ZrCl_2 ternary	160	380 000
binary	2270	214 000
$(Me_3SiCp)_2ZrCl_2$ ternary	107	828 000
binary	1290	655 000
(*cyclo*-$C_6H_{11}Cp)_2ZrCl_2$ ternary	21	193 000
binary	990	197 000
$Me_2SiCp^*N(t\text{-}Bu)ZrCl_2$ ternary	46	2 000 000
binary***)	—	635 000
$Me_2SiCp^*N(t\text{-}Bu)ZrCl_2$ ternary (70°C)	51	1 820 000
$Me_2SiCp^*N(t\text{-}Bu)ZrCl_2$ ternary (90°C)		
binary (80°C)***)	705	127 000
	—	360 000

*) Polymerization conditions by the systems: ternary (toluene, [Zr] = 3.0 · 10^{-5} mol/L, Al/Zr = 500, 1.1 atm, 20 °C); binary (toluene, [Zr] = 1 · 10^{-5} mol/L, Al/Zr = 2000, 0.54 atm, 30°C). **) Results with MAO published elsewhere [5]. ***) See [11].

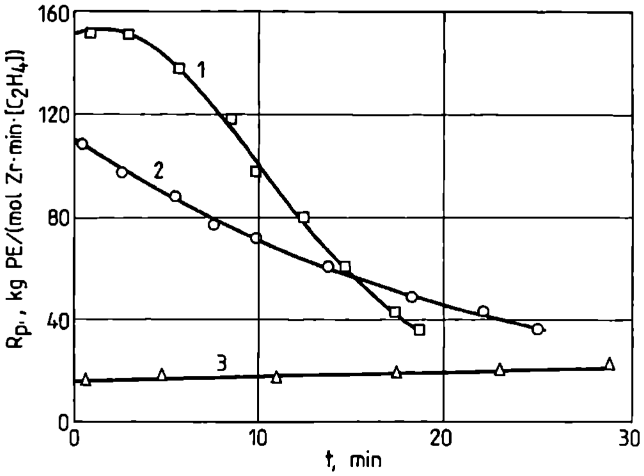


Fig. 1. Ethylene consumption rate vs. time plots for the complexes: 1 — Cp_2ZrCl_2; 2 — $(Me_3SiCp)_2ZrCl_2$; 3 — (cyclo-$C_6H_{11}Cp)_2ZrCl_2$. Polymerization conditions: toluene, [Zr] = 3 · 10^{-5} mol/L, Al/Zr = 500, B/Zr = 1.1 atm, 20°C

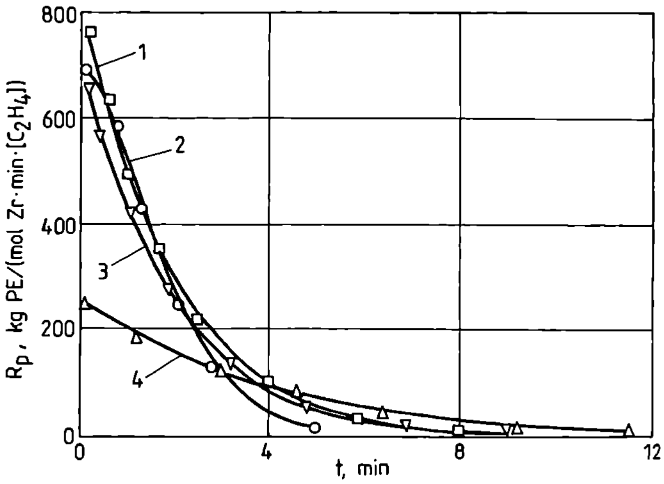


Fig. 2. Ethylene consumption rate vs. time plots for the complexes: 1 — $(MeCp)_2ZrCl_2$, 2 — $(i\text{-}PrCp)_2ZrCl_2$, 3 — $(n\text{-}BuCp)_2ZrCl_2$, 4 — $(i\text{-}BuCp)_2ZrCl_2$

The specific productivity of the complexes was found to decrease in the descending order: MeCp > *i*-PrCp > *n*-BuCp > *i*-BuCp > Me_3SiCp > CyCp. This sequence matches the series of activities achieved by activation with MAO [5]. The logarithm of the initial polymerization rate was found to be directly related to the combined effect of inductive (σ*) and steric (E_s^0) constants [6, 7] of substituents in the ternary systems (Fig. 3, Table 2):

$$\ln\left(\frac{R_0^{CpR}}{R_0^{Cp}}\right) = \rho\sigma^* + \delta E_s^0 \qquad (\rho = -4.23, \delta = 1.18) \qquad (3)$$

This correlation can be used to predict the catalytic behavior.

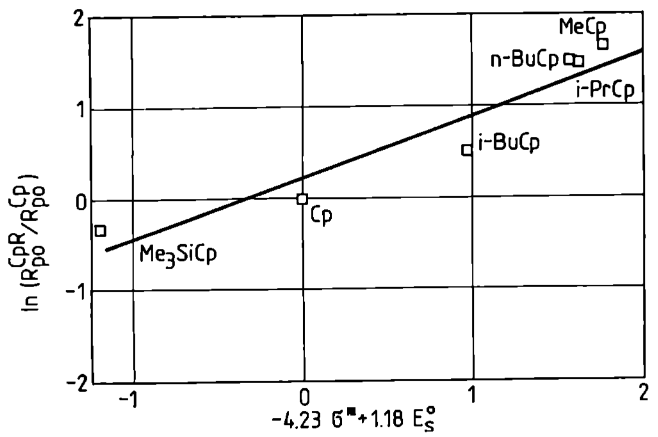


Fig. 3. The logarithm of initial polymerization rate vs. combined effect of inductive and steric factors of substituents of zirconocene dichloride with $Al(i\text{-}Bu)_3/CPh_3B(C_6F_5)_4$

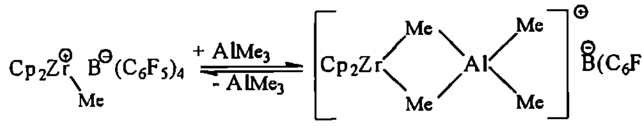
T a b l e 2. **Electronic (σ*) and steric (E_s^0) factors of substituents**

Substituent	σ*	E_s^0
Me	-0.49	-0.25
i-Pr	-0.68	-1.10
n-Bu	-0.62	-0.84
i-Bu	-0.62	-1.38
H	0	0
Me$_3$Si	-0.75	-3.70

The molecular weight of the polymers obtained is related to the nature of the substituent in Cp-ring both in ternary and in binary systems, but in a different way (Table 1). The molecular weights of polyethylene generated by ternary catalytic systems are generally higher than those of the polymers prepared by the corresponding complexes with MAO as cocatalyst. Generally, in ternary catalytic systems, the catalytic activity is correlated with the molecular weight of the resulting polyethylene: the higher the activity of the catalyst, the lower the molecular weight (Table 1). Thus, the most active zirconocene with the ring Me-group yields polyethylene endowed with the lowest molecular weight in the series ($\sim 4 \cdot 10^5$). The result is similar to that obtained with the MAO-activated complex. The "constrained geometry" zirconium complex, the least active of all the examined pre-catalysts, generated polyethylene of the highest molecular weight ($\sim 2 \cdot 10^6$); if activated with MAO, about 600 000 (Table 1).

Our data indicate that the active species formed from the pre-catalysts in the binary and the ternary systems should be different. One can find considerable differences between the two systems in chain propagation and chain transfer rates.

TIBA is thus supposed to participate in the formation of active centers. In contrast to $AlEt_3$ and $AlMe_3$, TIBA has been reported not to participate in chain transferring [8—10]. The alkylaluminum has been reported [4] to yield bridged heterometallic complexes (4) that are inactive in polymerization:



(4)

We examined the ternary system with *i*-Pr-substituted biscyclopentadienyl zirconocene dichloride to study its response to the concentration of TIBA. Polymerization is a first-order reaction with respect to the monomer and effectively a 0.4-order reaction with respect to TIBA. As the TIBA concentration was increased, the yield and the molecular weight of PE rose (Fig. 4).

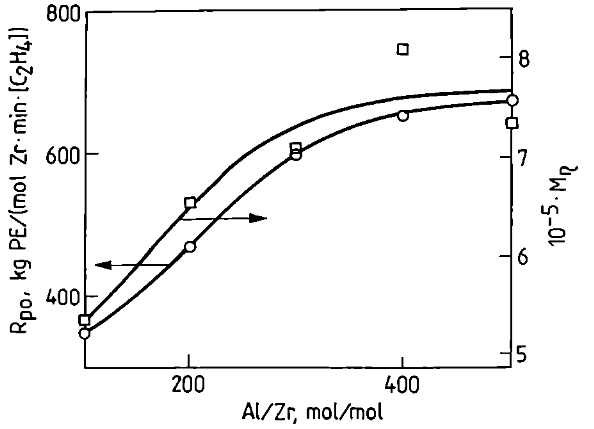
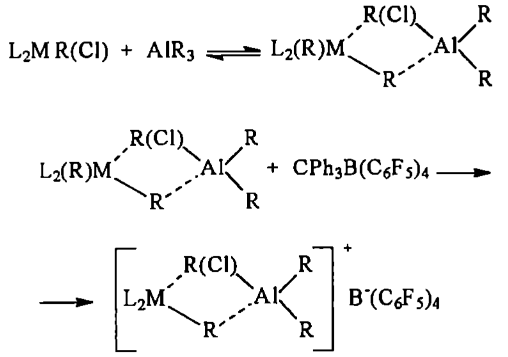


Fig. 4. Molecular weight of PE (right ordinates) and specific productivity (left ordinates) in relation to Al/Zr ratio for the catalytic system $(i\text{-}PrCp)_2ZrCl_2/Al(i\text{-}Bu)_3/CPh_3B(C_6F_5)_4$. Polymerization conditions: toluene, [Zr] = $3 \cdot 10^{-5}$ mol/L, Al/Zr = 500, B/Zr = 1.1 atm, 30°C

Summing up, we conclude that TIBA does not simply operate as an alkylating agent or as an impurity scavenger, but it can be involved in the formation of active centers (possibly in an equilibrium manner) as a heteronuclear alkyl or halide-bridged Zr—Al cationic complex.

The possible presence of the chloride atom in the vicinity to the active center can be confirmed by experiments with a ternary catalytic system involving a "constrained geometry" zirconocene. Negative induction of the substituents and steric accessibility of the Zr-center led to lower initial polymerization rates and a high molecular weight of PE (Table 1). As the temperature was raised from 30 to 90°C, the initial rate abruptly increased (about 14 times). Such an increase in the ethylene consumption rate cannot be attributed to a simple increase in the number of active species. The effect is likely to be due to the formation of other types of active centers. As we assume for ternary systems, the active center carries a chloride ligand in the coordination sphere of the bridged heterobinuclear cation (5)—(7). The action of the halide ligand should decrease the reactivity of the metal-carbon bond and should suppress chain -transferring. The increase in temperature could result in the chloride ligand replaced by the alkyl-group of excess TIBA.

$$L_2MCl_2 + AlR_3 \longrightarrow L_2MR(Cl) \qquad (5)$$



(6)

(7)

So, if labile ligands of only the alkyl type were present in the coordination sphere of the cation, the catalytic activity would increase and the molecular weight would decrease.

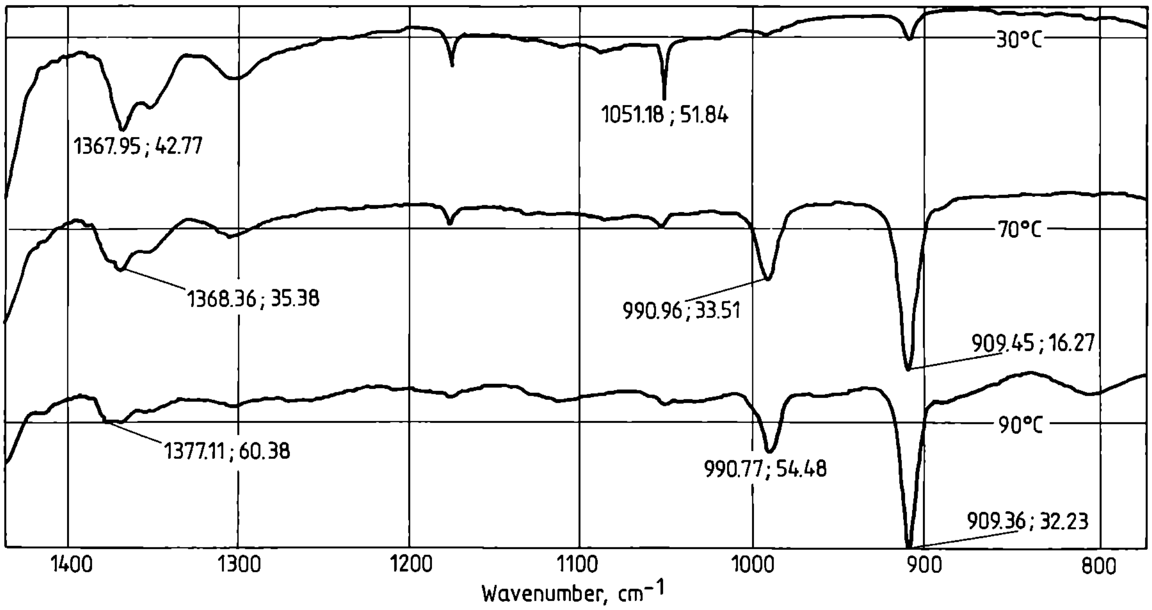


Fig. 5. IR spectra of polyethylenes obtained with the catalytic system $Me_2SiCp^*N(t\text{-}Bu)ZrCl_2/Al(i\text{-}Bu)_3/CPh_3B(C_6F_5)_4$

IR spectra of samples show appreciable changes in polymer chain features (Fig. 5). At 30 and 70°C, the dichloride "constrained geometry" complex yielded unbranched PE (1367—1368 cm^{-1}) containing minor quantities of vinyl end groups (909 and 990 cm^{-1}). The increase in temperature led to appreciably branched PE containing more vinyl end groups.

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