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Cooperative effects in binuclear zirconocenes: their synthesis and use as catalyst in propene polymerization

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Abstract

The mono- and bis-cyclopentadienyl compounds 1-(Cp")-4-(CH_3)C_6H_4 (**1**) and 1, 4-(Cp")$_2C_6H_4$ (**2**) (Cp" = 3,4-dimethylcyclopenta-1,3-diene-1-yl) have been synthesized. The reactions of the lithium salts of **1** and **2** with $CpZrCl_3 \cdot$dme (dme = dimethoxyethane) and Cp^*ZrCl_3($Cp^* = C_5(CH_3)_5$) yielded the mono- and bi-nuclear bridged zirconocenes 1-(Cp"ZrCpCl_2)-4-(CH_3)C_6H_4 (**3**), 1,4-(Cp"ZrCpCl_2)$_2C_6H_4$ (**4**) and 1,4-(Cp"ZrCp*Cl_2)$_2C_6H_4$ (**5**). When activated with methylaluminoxane (MAO), the mono- and bi-nuclear zirconocenes **3** and **4** catalyse the polymerization of propene. The influence of the catalyst composition on the polymerization kinetics and molecular weight is discussed.

1. Introduction

Metallocenes activated with methylaluminoxane (MAO) are well known, highly active homogeneous Ziegler–Natta catalysts that produce polyolefins with controlled stereoregularity and narrow molecular weight distribution [1].

The objective of the present research was to prepare binuclear metallocenes in order to examine the role of cooperative effects between the two metal centres. This can be achieved by linking monocyclopentadienyl metal halides with a ligand containing two cyclopentadienyl units, resulting in sandwich complexes [2,3]. Cooperative effects become more likely when this ligand, in addition to holding the metal sites in close proximity, also allows electronic interaction via a conjugated unsaturated system.

In the current model for metallocene catalyzed olefin polymerization, the MAO-activator alkylates the metallocene complexes and scavenges the counterion to produce cationic metallocenes [4]. Then the olefin monomer is inserted into the transition metal alkyl bond until the polymer chain is terminated, *e.g.* by β-hydride elimination. Kinetic investigations by Fischer and Mülhaupt [5,6] indicate that a series of dynamic equilibria between active cationic and dormant neutral complexes, involving the MAO activator and the absolute concentration of the transition metal, influence the productivity of the system. Molecular weight control, governed by the ratio of the rate constants for propagation and β-hydride elimination, is affected by the Lewis basicity of the metallocene ligands [11,12]. Therefore, reversible catalyst deactivation as well as the molecular weight control should be influenced by the type of the cyclopentadienyl ligands.

We report here the synthesis and polymerization behaviour of a new type of binuclear metallocene, which is compared with the corresponding mononuclear complex.

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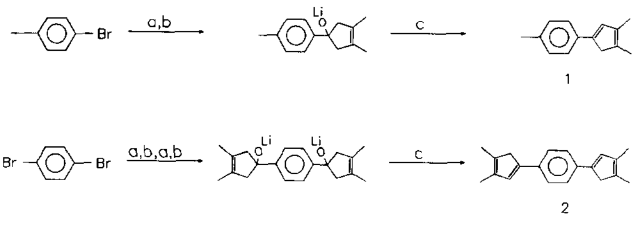


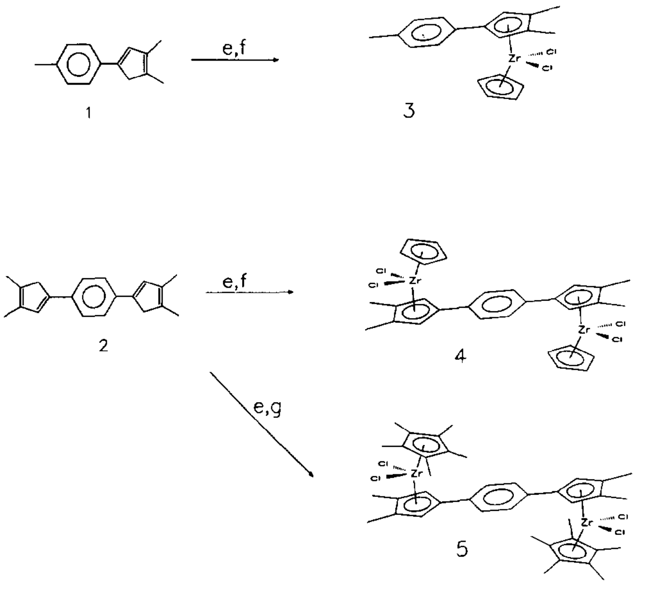
a. + n-BuLi , b. + 3,4-dimethylcyclopentenone , c. + H_3O^+

Scheme 1.

2. Results and discussion

The bis-Cp ligand, 1,4-$(Cp'')_2C_6H_4$ (**2**) (Cp'' = 3,4-dimethylcyclopenta-1,3-diene-1-yl) provides a suitable backbone for our purposes. In the corresponding mono-Cp ligand 1-(Cp'')-4-$(CH_3)C_6H_4$ (**1**), one Cp''group has been formally replaced by a methyl-group (Scheme 1).

Reaction of ^{n}BuLi with the ligands **1** and **2** generated solutions of the corresponding mono- and di-lithio salts, to which $CpZrCl_3 \cdot$ dme or Cp^*ZrCl_3 was added. After prolonged heating under reflux in toluene, the yellow, airstable zirconocenes **3**, **4** and **5** were isolated (Scheme 2). Both of the binuclear complexes **4** and **5** have a low solubility in common solvents.



e. + n-BuLi , f. + $CpZrCl_3$*dme , g. + Cp^* $ZrCl_3$

Scheme 2.

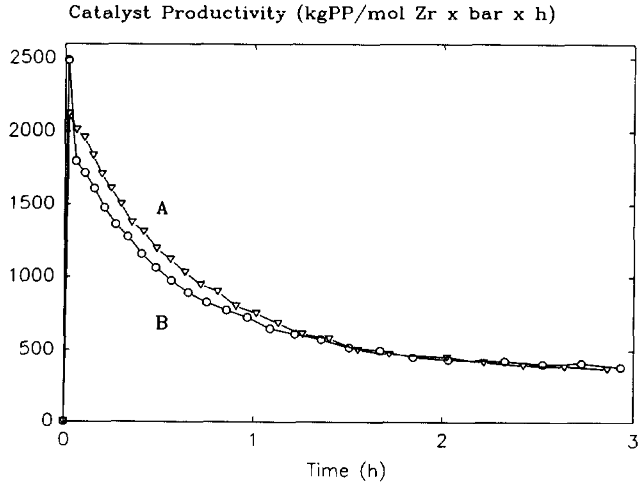


Fig. 1. Catalyst productivity as a function of polymerization time for the binuclear (A) and the mononuclear (B) zirconocene, **4** and **3**, respectively (40°C, 2 bar, [Zr] = 10^{-5} mol/l, molar ratio Al/Zr = 5000).

The mono- and bi-nuclear zirconocenes **3** and **4** were activated with MAO at Al/Zr molar ratios of 2500 and 5000 and Zr concentration of 10^{-5} mol/l in toluene and used as catalysts for propene polymerization at 40°C and 2 bar total pressure. As observed previously in the case of the Cp_2ZrCl_2/MAO model system [5,6], the catalyst is activated almost instantaneously upon contact between the MAO-activator and the zirconocene. Figure 1 shows the rapid decrease in the initial polymerization rate a few minutes after initiation. The rapid initial decay is similar to that for the MAO-activated mononuclear (**3**) and binuclear (**4**) zirconocenes. We conclude that combining two zirconium sites in a binuclear zirconocene does not have a significant influence on the deactivation behaviour.

In contrast to catalyst deactivation, molecular weight control is affected by change in the type of zirconocene. As apparent from the data in Table 1, the

TABLE 1. Propene polymerization [a]

Zirconocene	Al/Zr molar ratio	Productivity [b]	M_n [c] ^{1}H NMR (g/mol)	M_n [d] GPC (g/mol)	M_w/M_n [d]
Binuclear (**4**)	2500	260	1600	2200	2.6
	5000	340	1200	1900	2.6
Mononuclear (**3**)	2500	300	2000	3400	2.9
	5000	360	2400	3500	2.9

[a] 40°C, 2 bar, [Zr] = 10^{-5} mol/l. [b] Productivity after 3 h measured as kg PP/(mol Zr bar h) using the propene partial pressure of 1.922 bar. [c] Determined by end-group analysis by 300 MHz ^{1}H NMR spectroscopy in $CDCl_3$. [d] Determined by size exclusion chromatography (GPC) in $CHCl_3$ at 25°C using polystyrene standards.

molecular weights of oligopropenes obtained with MAO-activated mononuclear zirconocene **3** are markedly higher than those of oligopropenes obtained with the corresponding binuclear zirconocene **4**. Moreover, while in the case of the mononuclear zirconocenes the molecular weights slightly increase with increasing Al/Zr molar ratio, the opposite effect is found for the binuclear zirconocenes, *i.e.* higher Al/Zr molar ratios adversely affect the molecular weights. In both cases, however, the polydispersitivities (M_w/M_n), as measured by size exclusion chromatography, remain narrow.

The observed effects on deactivation and molecular weight control can be explained on the basis of electronic effects and cooperative interactions of the two adjacent zirconium centres in **4**. These two metal centres are electronically coupled through the phenylene bridge. This is important because cationic intermediates are believed to form the active centres in the MAO-promoted polymerization of propylene. The assumed equilibria between active cationic centres and dormant neutral centres make it probable that, for **4**, only one of the zirconocenes is active at a given time. From the viewpoint of the active cationic centre in **4** and **3**, we expect the neutral $Cp''ZrCl_2Cp$-substituent on the phenylene bridge in **4** to have approximately the same electron donating effect as the CH_3-group in **3**. This similarity of the active sites in **3** and **4** explains their similar activity and deactivation behaviour. However, the lower molecular weight of the polypropylene produced by the binuclear complex, **4**, compared with that from the mononuclear zirconocene, **3**, implies a higher rate constant for the β-hydride elimination in **4**. As the active centre is similar for **3** and **4**, we assume that this higher rate constant for the β-hydride elimination in **4** is the result of the different electronic environments of the neutral dormant sites. The electron withdrawing effect of the cationic zirconium centre in **4**, relative to the effect of the methyl group in **3**, reduces the electron density on the cyclopentadienyl ligand at the adjacent dormant neutral zirconium site. The reduced electron density at this dormant neutral zirconium site results in a higher rate for the β-hydride elimination [11,12].

As the Al/Zr molar ratio is raised, the active cationic zirconium site concentration increases in the case of mono- as well as bi-nuclear zirconocenes, thus accounting for increased catalyst productivities. The higher concentration of cationic zirconocenes, relative to that of the dormant zirconocenes, accounts for higher molecular weights of the polypropylenes produced by mononuclear zirconocenes, because there are fewer dormant neutral zirconocenes that favour chain termination by β-hydride elimination. In the case of the binuclear zirconocenes containing active cationic and dormant neutral sites, an increasing proportion of cationic sites results in a lower electron density in, and Lewis basicity of, the cyclopentadienyl ligand system, thus facilitating β-hydride elimination. Therefore, although the productivity increases, polypropylene molecular weight is reduced.

In conclusion, binuclear metallocenes represent a new type of homogeneous Ziegler–Natta catalyst containing two catalytically active or dormant sites in one metallocene complex.

3. Experimental details

Experimental details concerning the polymerization have been given elsewhere [5].

3.1. Polymer characterization

^1H NMR spectra were recorded at 300 MHz for $CDCl_3$ solutions with tetramethylsilane as internal reference on a Bruker ARX300 spectrometer. The molecular weights of the polypropylenes were determined by end-group analysis based on the signal of the vinylidene endgroup (4.7 ppm) resulting from β-hydride elimination. Size exclusion chromatography was performed at 25°C with polypropylene solutions in $CHCl_3$ and polystyrene standards.

3.2. Synthesis of the metallocenes

All reactions were carried out under dry nitrogen in carefully dried solvents. NMR spectra: Bruker AC 200 F, ^1H NMR (200 MHz), ^{13}C NMR (50 MHz). Spectra were recorded at 300 K in $CDCl_3$ and referenced to residual $CHCl_3$ (7.26 ppm) or $CDCl_3$ (77.00 ppm). Elemental analyses were performed at the Mikroanalytisches Laboratorium der Chemischen Laboratorien der Universität Freiburg. Starting materials were commercially available or were prepared by published procedures namely 3,4-dimethylcyclopent-2-enone [8], $CpZrCl_3 \cdot dme$ [9], Cp^*ZrCl_3 [10]. The procedure previously described for $1,4-C_6H_4(Cp'')_2$ [7] was modified.

3.3. $1-(Cp'')-4-(CH_3)-C_6H_4$ (1)

To a stirred solution of *p*-bromotoluene (455 mg, 5 mmol) in 25 ml of THF at 0°C was added ^nBuLi (2 ml, 2.5 M in hexane) followed 10 min later by 3,4-dimethylcyclopent-2-enone (550 mg, 5 mmol). The mixture was stirred at room temperature for 1 h and then quenched with 25 ml of aqueous NH_4Cl and 25 ml of Et_2O. The organic layer was separated, the aqueous layer was extracted with 25 ml of Et_2O, *p*-toluenesulfonic acid (0.25 g) was added to the combined organic phases, and stirring was continued for 30 min. The organic layer was extracted with water, separated, dried over

$MgSO_4$, and filtered, and the solvent evaporated. The residue was recrystallized from methanol and sublimed to yield 350 mg (38% yield) of a white powder. The product decomposes at room temperature and had to be stored at −30°C. Anal. Found: C, 91.34; H, 8.70. $C_{14}H_{16}$ (184.28) calc.: C, 91.25; H, 8.75%. ^1H NMR: δ 1.90 (s, 3H, Cp"CH_3); 1.98 (s, 3H, Cp"CH_3); 2.33 (s, 3H, ArCH_3); 3.25 (s, 2H, CH_2); 6.61 (s, 1H, CH); 7.08, 7.12, 7.33, 7.37 (AA'BB', 4H, ArH). ^{13}C NMR: δ 12.61 (Cp"CH_3); 13.40 (Cp"CH_3); 21.12 (ArCH_3); 45.29 (CH_2); 124.45 (CH); 129.19 (CH); 130.80 (CH); 133.72, 135.25, 135.47, 135.65, 142.53 (C).

3.4. 1,4-(Cp")$_2C_6H_4$ (2)

To an ice-cooled, stirred solution of 1,4-dibromobenzene (11.8 g, 50 mmol) in 100 ml of Et_2O was added ^nBuLi (20 ml, 2.5 M in hexane). After 10 min 3,4-dimethylcyclopent-2-enone (5.45 g, 50 mmol) was added dropwise. The solution was allowed to stand at room temperature and stirred for 60 min. ^nBuLi (20 ml, 2.5 M in hexane) was added, followed after 30 min by 3,4-dimethylcyclopent-2-enone (5.45 g, 50 mmol). After 60 min, 20% HCl (50 ml) were added slowly and the mixture stirred for a further 60 min. The yellow precipitate formed was filtered off, washed with aqueous $NaHCO_3$, dried *in vacuo*, and extracted with refluxing $CHCl_3$ (50 ml) in a Soxhlet apparatus. The $CHCl_3$ extract was kept at +4°C overnight. The precipitate was filtered off, washed with $CHCl_3$ (10 ml), and dried *in vacuo* to give 4.3 g (33% yield) of a yellow powder.

3.5. 1-(η^5-3,4-$Me_2C_5H_2$-$ZrCpCl_2$)1-14-(Me)-C_6H_4 (3)

A solution of ^nBuLi (0.8 ml, 2.5 M in hexane) was added to a stirred solution of **1** (184 mg, 1 mmol) in 20 ml of toluene. After 30 min, $CpZrCl_3 \cdot$ dme (353 mg, 1 mmol) was added and the mixture refluxed for 24 h. The volatiles were removed *in vacuo* and 5 ml of concentrated hydrochloric acid was added. The yellow solid was filtered off, and sublimed *in vacuo* (130°C, 0.1 Torr). Yield: 75 mg (18%). Anal. Found: C, 54.89; H, 4.73. $C_{19}H_{20}Cl_2Zr$ (410.50) calc.: C, 55.59; H, 4.91%. ^1H NMR: δ 2.17 (s, 6H, Cp"CH_3); 2.39 (s, 3H, ArCH_3); 6.14 (s, 5H, C_5H_5); 6.55 (s, 2H, Cp"H); 7.18, 7.25, 7.39, 7.44 (AA'BB', 4H, ArH). ^{13}C NMR: δ 13.82 (Cp"CH_3); 21.19 (ArCH_3); 113.97, 115.98, 116.53, 122.94, 125.14, 128.66, 129.85, 137.59.

3.6. 1,4-(η^5-3,4-$Me_2C_5H_2$-$ZrCpCl_2$)$_2C_6H_4$ (4)

A solution of ^nBuLi (0.8 ml, 2.5 M in hexane) was added to a stirred suspension of **2** (262 mg, 1 mmol) in 20 ml of toluene. The mixture was heated at 70°C for 30 min then $CpZrCl_3 \cdot$dme (706 mg, 2 mmol) was added at room temperature. The mixture was refluxed for 24 h then filtered through Celite. The filtrate was discarded and the residue extracted repeatedly with boiling $CHCl_3$. The extract was concentrated to *ca.* 10 ml and the yellow product filtered off and dried *in vacuo*. Yield: 400 mg (56%). Anal. Found: C, 49.82; H, 4.11. $C_{30}H_{30}Cl_4Zr_2$ (714.83) calc.: C, 50.41; H, 4.23%. ^1H NMR: δ 2.20 (s, 12H, Cp"CH_3); 6.17 (s, 10H, C_5H_5); 6.63 (s, 4H, Cp"H); 7.60 (s, 4H, ArH).

3.7. 1, 4-(η^5-3,4-$Me_2C_5H_2$-$ZrCp^*Cl_2$)$_2C_6H_4$ (5)

A solution of ^nBuLi (0.8 ml, 2.5 M in hexane) was added at room temperature to a stirred suspension of **2** (262 mg, 1 mmol) in 20 ml of toluene. The mixture was heated at 70°C for 30 min then Cp^*ZrCl_3 (665 mg, 2 mmol) was added at room temperature and refluxing was continued for 48 h. The hot suspension was filtered through Celite and the product crystallized from the filtrate upon cooling to 0°C. The solid was filtered off, washed with pentane, and dried *in vacuo* to produce 360 mg (42% yield) of a yellow powder. Anal. Found: C, 55.71; H, 5.72. $C_{40}H_{50}Cl_4Zr_2$ (855.10) calc.: C, 56.18; H, 5.89%. ^1H NMR: δ 1.84 (2, 12H, Cp"CH_3); 2.10 (s, 30H, Cp^*CH_3); 6.38 (s, 4H, Cp"H); 7.49 (s, 4H, ArH). ^{13}C NMR: δ 12.27 ($Cp(CH_3)_5$); 13.55 ($Cp(CH_3)_2$); 116.30, 121.75, 124.36, 127.49, 127.83, 132.04.

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