meso-Me$_2$Si(1-indenyl)$_2$ZrCl$_2$/methylalumoxane catalyzed polymerization of the ethylene to ethyl-branched polyethylene

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Abstract

The *meso* ansa zirconocene with dimethylsilyl bridge, activated by methylalumoxane, catalyses the ethylene polymerization, producing ethyl-branched polyethylene. With respect to the polymers obtained with the previously investigated *meso* zirconocenes, we have found higher branching amount and lower molecular weight. The rapid β-H transfer from the growing chain to the coordinated monomer could account for both these features of the polymer. The investigation on the structural parameters of the complex, through X-ray diffraction analysis, and on the electrophilicity of the cationic center, through NMR experiments, suggests, as a possible rationalization of this behavior, the obstruction in the inward site.
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1. Introduction

The aim of obtaining branched polyethylene by ethylene homopolymerization is pursued through a variety of catalytic strategies, by using either late transition metals [1] or group 4 metals with suitable coordination frame [2–10]. A few of the uncountable ansa metallocenes with diastereotopic sites, tested as catalyst precursors for ethylene polymerization, show some capability to produce ethyl-branched polyethylene [5–11]. Such a feature of the polymer chains possibly arises from the chain growing isomerization through β-H transfer to the incoming monomer followed by insertion of the unsaturated chain end into the metal–ethyl bond. This H transfer should occur with *meso* ansa zirconocene catalyst because, when the growing chain sits between the two six-membered rings, the insertion reaction should have not an easy path, according to the theoretical studies of Guerra et al. [12] on propene polymerization. As a consequence should increase the probability of the H transfer with respect that of the insertion.

We have recently reported [7] an attempt to organize the available information on catalyst features into a frame that could allow rationalizing the different ability of *meso* ansa metallocenes to give branched polyethylene. The main conclusion was that for *meso*-indenyl group 4 metallocenes branching was observed only in the case of zirconium derivatives ligated by unsubstituted indenyl ligands.

Among the *meso* ansa zirconocenes, the investigation on those connected by the dimethylsilyl bridge has been, until now, neglected. This short linker was successfully employed in C$_2$ symmetric precursors for ethylene and propene polymerization catalysts [13,14] and it is generally accepted that it improves the ansa zirconocene performance in some respects, and in particular in the increase of the molecular weight of the produced polymers.

In the light of this observation we have carried out the synthesis, isolation and structural characterization of *meso*-dimethylsilylbis(1-indenyl)ZrCl$_2$ and tested its capability to give, when activated by methylalumoxane, the branched polyethylene.

2. Results and discussion

2.1. Synthesis of meso-Me$_2$Si(1-indenyl)$_2$ZrCl$_2$

This complex is a byproduct in the preparation of the racemic mixture. Its synthesis has been performed through the reaction of ZrCl$_4$ with the tin triethylderivative of the dimethylsilylbis(1-indenyl) ligand [15–17]. A 7% yield was obtained of the *meso* product, purified by crystallization and characterized by ^{1}H NMR (see Section 4).

2.2. Synthesis of meso-Me$_2$Si(1-indenyl)$_2$Zr(CH$_3$)$_2$

The dimethylated complex was obtained through reaction of the *meso*-Me$_2$Si(1-indenyl)$_2$ZrCl$_2$ with CH$_3$Li in diethylether at low temperature and purified by crystallization (see Section 4).

2.3. Molecular structure of meso-Me$_2$Si(1-indenyl)$_2$ZrCl$_2$

The X-ray molecular structure of the complex is shown in Fig. 1. As it can be seen, the molecule takes a con-

Fig. 1. X-ray molecular structure of the complex. Thermal ellipsoids are drawn at 30% probability level. Selected bond lenghts (Å) and angles (°): Zr–Cl1 2.454(2), Zr–Cl2 2.408(3), Zr–C1A 2.481(4), Zr–C1B 2.483(4), Zr–C2A 2.468(4), Zr–C2B 2.473(4), Zr–C3A 2.562(4), Zr–C3B 2.573(4), Zr–C4A 2.656(4), Zr–C4B 2.651(4), Zr–C5A 2.586(4), Zr–C5B 2.583(4), Si–C10 1.852(5), Si–C11 1.846(5), Si–C1A 1.877(4), Si–C1B 1.880(4), Cl1–Zr–Cl2 94.3(1), C10–Si–C11 11.4(2), C1A–Si–C1B 94.8(2), Cp–Zr–Cp′ 126.2(1)°.

formation having symmetry (non-crystallographic) almost C_s. Bond lengths between the metal and carbon atoms of the coordinated pentatomic rings range between 2.481(4) and 2.656(4) Å and are quite comparable with literature data on similar complexes [7,18]. This holds also for the distances between the metal and the baricentre (X$_A$ and X$_B$) of the five-membered rings (Zr–X$_A$ = 2.243 Å, Zr–X$_B$ = 2.246 Å) and also for the bond angle X$_A$–Zr–X$_B$ (126.6°).

The dihedral angle between the average planes of the two indenyl ligands, which are planar within 0.02 Å, is 64.9(1)° and is, again, comparable with literature data [7] of the ethylene-bridged analogous (62.3°). A structural feature of the complex worth of being noticed is that Si atom is significantly out of the plane of the two indenyl ligands (Si–C1A–C2A–C3A = −159.3(3)°, Si–C1B–C2B–C3B = 159.2(3)°) without significant distortions of the tetrahedral bonding geometry around Si. This feature seems a consequence of Si atom being directly bonded to the two coordinated indenyl ligands: the optimum coordination geometry of the ligands is maintained, as we have seen above, at cost of some deformation of bonding geometry between Si and the indenyl ligands. Actually, this points to a significant structural difference between this complex and related complexes in which the two indenyl ligands are connected through an ethylene bridge [7,18]. In fact, in the case of the ethylene bridge, some conformational freedom for (small) rotations of the indenyl groups around the M–X$_A$, M–X$_B$ directions is present. These rotations are allowed, to some extent, since they only imply variations of the torsion angle around the ethylene bridge, and this is true, in particular, if the two indenyl groups rotate in opposite directions; this fact is witnessed by the crystal structures of complexes of this type [7,18] in which the conformation found corresponds to a staggered placement of the two indenyl ligands (ca. 10°) with respect to each other; furthermore, also in the solid state, some disorder of the indenyl ligands related to this type of movement is found [7,18]. In the case of the dimethylsilyl bridge, on the other hand, no rotation of the indenyl ligands from the eclipsed arrangement is allowed, because it would require deformation of bond distances and valence angles around Si atom, and in fact we have not found any trace of it in the crystal structure analysis (both at low temperature and at room temperature). So, we can safely state that complexes with the ethylene bridge have some conformational flexibility, which is absent in the present complex.

2.4. NMR experiments

^{1}H NMR spectrum of *meso*-dimethylsilylbis(1-indenyl) zirconium dimethyl recorded in benzene-d_6 at room temperature shows for the diastereotopic Zr–Me's the typical pattern of a *meso* structure complex. In the methyl region there are two quite distinct signals, the upfield peak

Table 1

Complex	B-CH_3 chemical shift (δ)	Ref.
meso-Me$_2$Si(1indenyl)$_2$Zr(CH$_3$)$^+$ B(C$_6$F$_5$)$_3$CH$_3$$^-$	0.74	This work
meso-C$_2$H$_4$-(1-indenyl)$_2$Zr(CH$_3$)$^+$B(C$_6$F$_5$)$_3$CH$_3$$^-$	0.41	[7]

(δ −2.18 ppm) can be assigned to the methyl in the *inward* site, because the shielding resulting from the aromatic ring current, while the methyl in the *outward* site flips at δ 0.14 ppm.

For the formation, in a NMR tube, of the species *meso*-Me$_2$Si(1-indenyl)$_2$Zr(CH$_3$)$^+$B(C$_6$F$_5$)$_3$CH$_3$$^-$, 1 equivalent of solid B(C$_6$F$_5$)$_3$ was added to a benzene-d_6 solution of 10 mg of the dimethyl complex. The ^{1}H NMR spectrum (C$_6$D$_6$, 25 °C, 300 MHz) of the reaction product shows the following resonances: δ 7.30 (d, 2H), δ 6.79 (t, 2H), δ 6.69 (t, 2H), δ 6.55 (m, 2H), δ 6.40 (d, 2H), δ 5.54 (d, 2H), δ 0.74 (broad, B*Me*$^-$), δ 0.36 (s, Si*Me*), δ 0.27 (s, Si*Me*), δ −1.81 (s, Zr*Me*$^+$).

These NMR evidences suggest the abstraction of the methyl group in the outward site with formation of the anionic group CH$_3$B(C$_6$F$_5$)$_3$$^-$ evidenced by the broad signal at δ 0.74. Actually the sharp signal at δ −1.81 can be assigned to the remaining Zr−Me and its upfield value suggests the inward arrangement. According to Brintzinger and coworkers [19] it is possible to correlate the chemical shift of the methyl on the borate to the distance between the fragments of the ionic pair, shorter is this distance higher is the resonance field. The difference of the chemical shift of the corresponding methyl in complexes with similar structure can be interpreted as reflecting the electrophilicity of the metallic center. In Table 1 such a comparison is reported, by putting together the literature chemical shift of the ethylene-bridged *meso* complex, having similar bite angle (Cp–Zr–Cp′ = 126.2°, as reported in Ref. [12] versus 126.6°, see figure). The higher value for the silyl-bridged complex is indicative of its minor electron-deficiency.

2.5. Ethylene polymerisation

We have performed a series of ethylene polymerizations by using the title complex activated by methylalumoxane and the results are reported in Table 2. The polymerization products have been analyzed through ^{13}C NMR and calorimetry (DSC). The latter characterization indicates melting points ranging between 105 and 110 °C, typical of branched polyethylene. Actually, upon inspection of the ^{13}C NMR spectra one can argue the presence of ethyl branches (signals at 11.2, 26.6, 27.2, 30.3, 33.8, and 39.5 ppm) and evaluate, from the areas of the peaks, around 3.5% their amount, as ratio of the tertiary carbons to the ethylene units.

The polyethylenes obtained at different polymerization temperature and, consequently, at different monomer concentration show no relevant change in the number of branching as well as in the melting temperature. This result is in accordance with what was observed in the presence of *meso* Et(Ind)$_2$ZrCl$_2$/MAO. Actually we reported [5] that, with that catalyst, neither the monomer concentration nor the polymerization temperature affects the branches amount. From a kinetic point of view this fact should indicate that the frequency of β-H transfer from the growing chain to the incoming monomer parallels the frequency of the monomer insertion into the metal carbon bond.

In the same table are also reported, for comparison purpose, the features of the polyethylene's obtained with the previously described *meso*-zirconocene based system with similar bite angle. The catalyst of the present study shows a greater capability to give branching and the corresponding polymers have lower molecular weights. This latter feature is a further consequence of the high frequency of the β-H transfer. These experimental findings are in contrast with the known behavior of the corresponding C$_2$ symmetric zirconocenes in the ethylene polymerization. Actually the comparison between the ethylene-bridged and the Me$_2$Si-bridged *rac*-zirconocenes, reported by Resconi and coworkers [20], shows the production of higher molecular weight polyethylene with the latter, as an effect of minor β-H transfer. On the other hand this same *rac* catalyst produces, at very high temperature, polyethylene

Table 2
Results of the ethylene polymerizations

Catalyst[a]	T (°C)	% Branches	T_m (°C)	M_n	Ref.
meso-Me$_2$Si(1-indenyl)$_2$ZrCl$_2$	−20	3.4	105	2650[b]	This work
	0	3.1	109	6000[b]	This work
	25	3.8	109	3000[b]	This work
	50	3.3	110	11700[b]	This work
meso Et(1-indenyl)$_2$ZrCl$_2$	−20	1.8	121	42000[c]	1
	0	1.6	122	50000[c]	1
	25	1.3	123	48000[c]	1
	50	1.1	121	49000[c]	Unpublished results

[a] Polymerizations carried out at 1 atm of ethylene pressure.

[b] Determined through NMR, from the relative intensity of the chain end signals and that of the inner carbons.

[c] Determined through GPC.

with different kind of branches [10] possibly through different mechanism.

3. Conclusion

The *meso* ansa zirconocene with dimethylsylil bridge produces, when activated by MAO, highly branched polyethylene with low molecular weight. The comparison between the *meso* ethylene-bridged and the *meso*-Me$_2$Si-bridged *bis*(1-indenyl) zirconium dichloride, that have similar bite angle, indicates higher β-H transfer rate for the silyl-bridged complex. This result seems in contrast with the behavior of the C$_2$ symmetric complexes, because the silyl-bridged *rac*-zirconocenes produce polymers with higher molecular weight than the ethylene-bridged ones do.

In principle the greater readiness to the hydrogen transfer could be ascribed either to higher electrofilicity of the metal or to geometric factors. The NMR study allows to disregard the hypothesis of the higher electrophilicity for the cation generated from the Si-bridged complex as the cause of its more frequent H transfer. So possibly, the driving force for this phenomenon should be the different geometry of the complexes. Due to the monoatomic bridge, the indenyl moieties are eclipsed, whereas the ethylene bridge allows the rapid interconversion between two staggered conformations [18]. As a consequence, with the present catalyst there is less room in the inward site and the growing chain, when sits between the two six-members aromatic rings, should be more strictly compelled into the conformation suitable to transfer the β-hydrogen to the incoming monomer. This secondary reaction is responsible for the branching formation as well as of the low molecular weight in the produced polyethylenes.

4. Experimental part

All manipulations involving air-sensitive reagents and materials were carried out under nitrogen or argon atmosphere using Schlenk or dry box techniques. Solvents were dried over Na-diphenylketyl (toluene, light petroleum ether, heptane, THF), over LiAlH$_4$ (diethyl ether), over CaH$_2$ (dichloromethane) and distilled before the use. Deuterated solvents were dried by distillation over CaH$_2$ and stored over activated molecular sieves (4 Å). MAO was purchased from Witco as a 10 wt.% solution in toluene, before use the volatile components were removed in vacuum to yield a powdery solid. Polymerization grade ethylene was purchased from SON and further purified by bubbling through a 5 mol% xylene solution of Al^{i}Bu$_3$.

4.1. Synthesis of Me$_2$Si(1-indenyl)$_2$ZrCl$_2$

To a solution of 60.0 g (208 mmol) of di(1*H*-inden-1-yl)(dimethyl)silane in 1000 cm^3 of diethyl ether 166 ml of

2.5 M ^{n}BuLi in hexanes (416 mmol) was added drop wise for 30 min at vigorous stirring at −40 °C. The resulted mixture was stirred for 3 h at ambient temperature, then, cooled to −40 °C, and 69.4 ml (100 g, 416 mmol) of Et$_3$SnCl was added. This mixture was stirred for 5 h at ambient temperature and, then, evaporated to dryness. To the residue 100 ml of toluene was added, and the resulted solution was evaporated to dryness to remove ether traces. To the residue 750 ml of toluene was added. Then, the mixture was cooled to −50 °C, and 48.5 g (208 mmol) of ZrCl$_4$ was added. The resulted mixture was stirred for 48 h at room temperature, 3 h at reflux, and, then, filtered through glass frit (G4). This procedure gave orange precipitate and red solution. To this filtrate 300 ml of hexanes was added. Crystals precipitated at −30 °C from the obtained solution were collected, washed by 3 × 30 ml of hexanes, and dried in vacuum. Yield 6.28 g (7%) of red crystals of pure *meso*-complex. Anal. calc. for C$_{20}$H$_{18}$Cl$_2$SiZr: C, 53.55; H, 4.04. Found: C, 53.39; H, 3.95. ^{1}H NMR (CDCl$_3$): δ 7.55 (m, 2H), 7.53 (m, 2H), 7.21 (m, 2H), 6.96 (dd, J = 3.3 Hz, J = 0.8 Hz, 2H), 6.93 (m, 2H), 6.13 (d, J = 3.3 Hz), 1.37 (s, 3H), 0.97 (s, 3H). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ 135.97, 128.89, 128.53, 127.61, 127.25, 127.15, 120.99, 120.83, 92.24, 0.15, −1.80. Next, the orange precipitate was washed by 2 × 50 ml of dimethoxyethane and dried in vacuum. This procedure gave 39.7 g (43%) of orange solid of pure *rac*-complex. Anal. found: C, 53.67; H, 4.11. ^{1}H NMR (CD$_2$Cl$_2$): δ 7.54 (m, 2H), 7.50 (m, 2H), 7.32 (m, 2H), 7.05 (m, 2H), 6.85 (dd, J = 3.2 Hz, J = 1.0 Hz, 2H), 6.09 (d, J = 3.2 Hz, 2H), 1.10 (s, 6H).

4.2. Synthesis of meso-Me$_2$Si(1-indenyl)$_2$Zr(CH$_3$)$_2$

An amount of 1 g (2.31 mmol) of *meso*-Me$_2$Si(1-indenyl)$_2$ZrCl$_2$ was suspended in 25 mL of diethyl ether. The reaction mixture was cooled at −78 °C, and 2 equiv. of Et$_2$O solution of CH$_3$Li 1.4 M were added. After 30 min the mixture was slowly warmed to room temperature and stirred for further 4 h. Then the solvent was removed under reduced pressure and the residue extracted with 30 mL of anhydrous toluene. Concentration of the extract followed by cooling to −20 °C gave 0.31 g (yield 50%) of a pure yellow crystalline product, identified by ^{1}H and ^{13}C NMR.

^{1}H NMR (C$_6$D$_6$, 25 °C, 300 MHz): δ 7.42 (d, 2H), δ 7.14 (d, 2H), δ 6.96 (t, 2H), δ 6.82 (t, 2H), δ 6.70 (m, 2H), δ 5.53 (d, 2H), δ 0.71 (s, SiMe$_{outward}$), δ 0.41(s, SiMe$_{inward}$), δ 0.21 (s, ZrMe$_{outward}$), δ −2.15 (s, ZrMe$_{inward}$).

^{13}C NMR (C$_6$D$_6$, 25 °C, 300 MHz): δ 129.8, δ 129.4, δ 126.2, δ 125.8, δ 125.09, δ 124.8, δ 117.4, δ 112.4, δ 85.1, δ 42.4 (ZrCH$_{3inward}$), δ 29.1 (ZrCH$_{3outward}$), δ −1.63 (SiCH$_{3outward}$), δ −2.39 (SiCH$_{3inward}$).

4.3. X-ray analysis of meso-Me$_2$Si(1-indenyl)$_2$ZrCl$_2$

Crystals were obtained by toluene/hexane at −20 °C. Data collection was performed in flowing N$_2$ at −100 °C on a Bruker-Nonius kappaCCD diffractometer (Mo Kα radiation,

CCD rotation images, thick slices, φ scans + ω scans to fill the asymmetric unit). Cell parameters from least-squares fit [21] of θ angles of 83 reflections are in the range $3.51° \leq \theta \leq 19.97°$. Crystal data: $C_{20}H_{18}Cl_2SiZr$, $M = 448.55$ g/mol, monoclinic, P2$_1$/c, $Z = 4$, red crystal, 0.24 mm × 0.20 mm × 0.10 mm, $a = 11.41(1)$, $b = 11.43(1)$, $c = 14.80(2)$ Å, $\beta = 102.5(1)°$, $V = 1884(3)$ Å^3, $\rho_{calc} = 1.581$ g/cm^3, $\mu = 0.929$ mm^{-1}. Semi empirical absorption correction (SADABS) was applied. 12881 reflections collected ($\pm h$, $\pm k$, $\pm l$), max. $\theta = 27.51°$, 4298 independent reflections ($R_{int} = 0.0711$). Structure solved by direct method (SIR97 package [22]) and refined by the full matrix least-squares method (SHELXL program of SHELX97 package [23]) on F^2 against all independent measured reflections. H atoms coordinates were refined. Two-hundred-and-seventy-three refined parameters, $R = 0.0413$ (on reflections with $I > 2\sigma(I)$) and $R = 0.0745$ on all reflections. Max. and min. residual electron density (e· Å^{-3}): +0.537 and −0.537. All crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC). Deposition number is CCDC 250118. These data can be obtained at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (internat.) +44-1223/336-033; email: deposit@ccdc.cam.ac.uk] free of charge. No relevant difference was found in the room temperature crystal structure of the compound, as compared with the low temperature analysis.

4.4. Calorimetric analysis

The thermal measurements were carried out on a Du Pont 2920 differential scanning calorimeter at heating rate of 10 °C/min on about 10 mg of sample. The instrument was calibrated by the measurement of the melting point of indium.

4.5. Polymerizations

Ethylene polymerizations at atmosphere pressure were carried out in a 100 mL glass flask charged, under nitrogen atmosphere, with 27 mL of freshly prepared MAO solution (15.2 mg/mL), prepared by dissolving solid MAO in toluene. The mixture, magnetically stirred, was thermostated at the desired temperature, the inert gas was replaced with ethylene at 1 atm and then were injected 3 mL of a toluene solution of *meso*-Me$_2$Si(1-indenyl)$_2$ZrCl$_2$ (1 mg/mL). The pressure in the flask was kept constant by feeding with the monomer and after 1 h the reaction mixture was poured into methanol acidified with HCl. The polyethylene was recovered by filtration and dried under vacuum. Its amount ranges between 0.2 g (polymerization at −20 °C) and 1.5 g (at 50 °C).

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