

A counterintuitive, yet efficient synthesis of bis(indenyl)zirconium dihalides

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Abstract

The use of bisindenyl zirconium dimethyl in the synthesis of the corresponding dihalides is described. The synthesis of $\text{Ind}_2\text{ZrCl}_2$ has been carried out, cleanly and quantitatively, by chlorination of $\text{Ind}_2\text{ZrMe}_2$ (**2**) with a variety of inorganic chlorides, including BCl_3 , SCl_2 in either toluene or methylene chloride, and HCl in Et_2O . The latter method is the preferred one, since it produces methane as the only byproduct, and the formed $\text{Ind}_2\text{ZrCl}_2$ precipitates quantitatively from the Et_2O solvent: a simple filtration then gives the analytically pure product in quantitative yield. $\text{Ind}_2\text{ZrBr}_2$ and Ind_2ZrI_2 are obtained by reacting **2** with Br_2 and I_2 , respectively. The ‘inverse’ synthesis of metallocene dichlorides by chlorination of their dimethyl ‘derivatives’ has advantages compared to the classic method: first, $\text{Ind}_2\text{ZrCl}_2$ is obtained in higher yield (90–96%); second, it is easier to purify (at the dimethyl stage) and is obtained free from LiCl . Five bisindenyl zirconium complexes with different sigma ligands have been investigated in solution propylene polymerizations: it is found that the σ -ligands have no relevant influence on the catalyst activity, nor on the polymer properties.

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1. Introduction

We recently described the ‘direct’ synthesis of Group 4 dimethylmetallocenes by means of the one-pot reaction between the π -ligand, a twofold excess of MeLi , and MtCl_4 [1]. This simple synthetic method allows to obtain the dimethyl metallocenes in a simple, rapid and inexpensive way, leading to final yields and purities which are in most cases higher than the ones obtainable with the classic two-step route, that is first the synthesis of the metallocene dichloride (two equivalents of the π -ligand + two equivalents of MeLi , and then one equivalent of MtCl_4) followed by its methylation with two equivalents MeLi (Scheme 1) [2].

Using this synthetic method, $\text{Ind}_2\text{MtMe}_2$ (**1**, $\text{Mt} = \text{Ti}$; **2**, $\text{Mt} = \text{Zr}$, **3**, $\text{Mt} = \text{Hf}$) are the simplest Group 4 metallocenes to make. Yields (typically 70–90%) depend mostly on the purity of the starting reagents and on the exact stoichiometry, and are similar for the three metals (Table 1).

We describe here the efficient, ‘inverse’ synthesis of bisindenyl zirconium dihalides from **2** and their evaluation in propylene solution polymerization in comparison with analogue complexes bearing different σ -ligands.

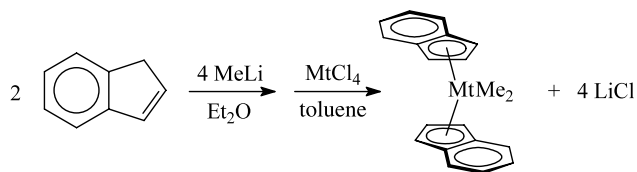
2. Results and discussion

The availability of the dimethyl metallocene complexes prompted us to test their conversion into the corresponding dihalo complexes. This reaction has been attempted before, by using PbCl_2 , and shown to be slow and leading to partial decomposition [3]. Also in our hands, the reaction of PbCl_2 with $\text{Ind}_2\text{ZrMe}_2$ is very slow, and leads to decomposition with partial formation

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Scheme 1.

Table 1
Synthesis of bis(indenyl)dimethyl metalocenes

Entry No.	Complex	Yield (%) ^a
1	Ind ₂ TiMe ₂	79
2	Ind ₂ ZrMe ₂	85
3	Ind ₂ HfMe ₂	74

^a From Ref. [1d]. Isolated yields based on the metal, all reactions at room temperature, using titrated MeLi.

of Ind₂ZrClMe, in several solvents (toluene, CH₂Cl₂, ethers). The synthesis of Ind₂ZrClMe from Ind₂ZrCl₂ and KF–AlMe₃ in hot heptane with a yield of 71% has been reported in a patent [4].

We have investigated other potential halogenating agents, and the available results are collected in Table 2. The chlorination of Ind₂MtMe₂ to Ind₂MtCl₂ was first investigated with Me₃SiCl and SiCl₄. Me₃SiCl gave no reaction with Ind₂ZrMe₂ and Ind₂HfMe₂ (only trace amounts of the monomethyl derivative was observed). In the case of Ind₂TiMe₂, excess SiCl₄ gave quantitative (by ¹H-NMR) conversion to Ind₂TiClMe. Reacting Ind₂ZrMe₂ with two equivalents CuCl, Ind₂ZrClMe is formed. Excess CuCl (five equivalents) is needed to bring the reaction to complete conversion to Ind₂ZrCl₂. More efficient chlorinating agents are BCl₃ (one equivalent in CH₂Cl₂), SCl₂ (two equivalents) or HCl in Et₂O

Table 2
Synthesis of metallocene dihalides

Starting complex	Halogenating agent (equivalents)	Solvent (halog. step)	Product	Yield ^a (%)	T ^b (°C)
Ind ₂ TiMe ₂ ^c	SiCl ₄ (2+2)	Toluene	Ind ₂ TiClMe	100 ^d	23/23–50
Ind ₂ ZrMe ₂ ^c	FeCl ₃ (1)	CH ₂ Cl ₂	Ind ₂ ZrClMe	95 ^d	40
Ind ₂ ZrMe ₂ ^c	CuCl (2.3)	CH ₂ Cl ₂	Ind ₂ ZrClMe	n.d.	23
Ind ₂ ZrMe ₂ ^c	CuCl (5)	CH ₂ Cl ₂	Ind ₂ ZrCl ₂	90	23
Ind ₂ ZrMe ₂ ^c	CuBr (5)	CH ₂ Cl ₂	Ind ₂ ZrBrMe+?	n.d.	23
Ind ₂ ZrMe ₂ ^c	BCl ₃ (1)	CH ₂ Cl ₂	Ind ₂ ZrCl ₂	96	0–23
Ind ₂ ZrMe ₂ ^c	BCl ₃ (1)	CH ₂ Cl ₂	Ind ₂ ZrCl ₂	96	23
Ind ₂ ZrMe ₂ ^c	SCl ₂ (1.3)	CH ₂ Cl ₂	Ind ₂ ZrCl ₂	100	23
Ind ₂ ZrMe ₂ ^c	NEt ₃ HCl (2+3)	CH ₂ Cl ₂	Ind ₂ ZrClMe+dec.	n.d.	23–40
Ind ₂ ZrMe ₂ ^c	HCl (2)	Et ₂ O	Ind ₂ ZrCl ₂	96	23
Ind ₂ ZrMe ₂ ^c	Br ₂ (2)	CH ₂ Cl ₂	Ind ₂ ZrBr ₂	50	23
Ind ₂ ZrMe ₂ ^c	I ₂ (2)	Toluene	Ind ₂ ZrI ₂	100	23
Ind ₂ ZrMe ₂ ^c	I ₂ (2)	CH ₂ Cl ₂	Ind ₂ ZrI ₂	96	23

^a Isolated yields based on the metal.

^b T is the reaction temperature of the halogenation step.

^c Reaction carried out on isolated Ind₂ZrMe₂.

^d By ¹H-NMR analysis.

^e Reaction carried out on the crude product between indene, MeLi, and ZrCl₄, after filtration and drying.

(two equivalents), which are sufficient to give 90–100% conversion to Ind₂ZrCl₂. The reaction with HCl, carried out in Et₂O in which the dichloride is insoluble, is quantitative and allows for a very simple product separation: a simple filtration gives spectroscopically and analytically pure Ind₂ZrCl₂. NEt₃HCl did not prove a good chlorinating agent.

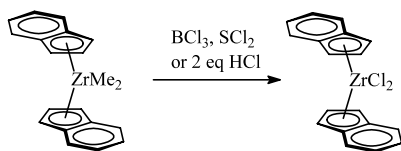
One equivalent FeCl₃ (Et₂O, 40 °C, 2 h) gave a very clean and almost quantitative conversion of Ind₂ZrMe₂ to the monochloro derivative Ind₂ZrClMe.

CuBr gave mostly the monomethyl derivative in combination with minor amounts of an as yet unidentified species. Ind₂ZrBr₂ and Ind₂ZrI₂ are obtained by reacting **2** with Br₂ and I₂, respectively.

The synthesis of Ind₂ZrCl₂ can be carried out quite conveniently starting directly from indene and four equivalents MeLi, without isolating the intermediate Ind₂ZrMe₂, in 90–96% isolated yield of a spectroscopically pure product.

The conventional synthesis of Ind₂ZrCl₂ (reaction of the lithium salt of indene with ZrCl₄) was performed for comparison: Ind₂ZrCl₂ was obtained in very high purity but in only 37% isolated yield in THF and 67% in Et₂O–pentane. The product has a low solubility even in CH₂Cl₂, and requires a tedious procedure for removing LiCl. The best literature result reported for the preparation of Ind₂ZrCl₂ gives a yield of 58% [5].

Although counterintuitive and requiring the sacrifice of two equivalents MeLi, at least for the present case the ‘inverse’ synthesis of the metallocene dichloride by chlorination of its dimethyl ‘derivative’ has some distinct advantages: first, Ind₂ZrCl₂ is obtained in higher yield (90–100%) compared to the classic method; second, it is easier to purify and is obtained free from LiCl, since LiCl can be efficiently removed by filtration



Scheme 2.

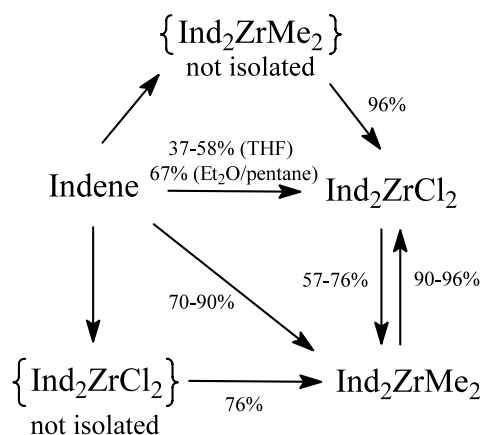
from the more soluble dimethyl complex, then the latter is chlorinated with a reagent such as BCl_3 , SCl_2 or HCl , that give volatile byproducts (Scheme 2).

In Scheme 3, all reported yields for the synthesis of $\text{Ind}_2\text{ZrCl}_2$ and $\text{Ind}_2\text{ZrMe}_2$, and their interconversion, are compared (for details of each method, see Section 3).

The proton NMR resonances of the complexes are listed in Table 3, showing the good correlation between the polarizability of the σ -ligand and the proton chemical shifts.

The availability of a series of bisindenylzirconium complexes carrying different sigma ligands prompted us to study their use as MAO-activated complexes in propylene polymerization, with the aim to verify whether the change of the sigma ligands would induce any changes in catalyst performance. Propylene polymerizations were carried out in toluene solution with the five metallocenes $\text{Ind}_2\text{ZrCl}_2$, $\text{Ind}_2\text{ZrMe}_2$, $\text{Ind}_2\text{ZrBr}_2$, Ind_2ZrI_2 , $\text{Ind}_2\text{Zr}(\text{OC}_6\text{F}_5)_2$, [1d] with MAO as the cocatalyst. The results are reported in Table 4. All catalysts produce low molecular weight, atactic polypropylenes, as expected from a fluxional, achiral complex [6]. End groups include a large predominance of vinylidenes, formed via primary β -H elimination, and only a minor contribution from 2-butenyl end groups due to secondary β -H elimination [7]. Differences of polymer average degree of polymerization, distribution of end groups and tacticity, between the five catalysts, are negligible.

From these results it is clear that, at least for solution propylene polymerizations, the σ -substituent does not have a significant influence on the polymer molecular weight, tacticity, or end group structure.



Scheme 3.

Table 3
Chemical shifts (δ , CD_2Cl_2 , rt) of Ind_2ZrX_2 complexes

X =	CH_3	Cl	Br	I
Cp-H(1,3)	6.13	6.23	6.28	6.42
Cp-H(2)	6.01	6.55	6.57	6.64
Aromatics	7.09–7.19 7.41–7.50	7.28–7.37 7.60–7.69	7.30–7.38 7.63–7.70	7.30–7.40 7.66–7.75

3. Experimental

3.1. General procedures and materials

All operations were performed under nitrogen by using conventional Schlenk-line techniques. Solvents were purified by degassing with N_2 and passing over activated (8 h, N_2 purge, 300°C) Al_2O_3 , and stored under nitrogen. MeLi (Acros), TiCl_4 , ZrCl_4 , FeCl_3 , CuBr , PbCl_2 and SiCl_4 (Aldrich), HfCl_4 (Roc-Ric, 99.99% Hf), CuCl (Carlo Erba, RPE-ACS, 95%), and SCl_2 (Riedel de Haen) were used as received. Technical indene (Aldrich) was purified by passing over activated Al_2O_3 . All compounds were analyzed on an AC 200 Bruker spectrometer, by $^1\text{H-NMR}$ (200.13 MHz, CD_2Cl_2 , referenced against the middle peak of residual CH_2Cl_2 at 5.35 ppm, or C_6D_6 , referenced against the peak of residual $\text{C}_6\text{D}_5\text{H}$ at 7.15 ppm) and $^{13}\text{C-NMR}$ (50.323 MHz, Broad Band Decoupling, C_6D_6 , referenced to the central line of C_6D_6 at 128.00 ppm). All NMR solvents were dried over P_4O_{10} or CaH_2 and distilled before use. GC-MS analyses were carried out on a HP 5890—series 2 gas-chromatograph and a HP 5970 mass spectrometer. All dimethyl metal complexes were isolated by extraction with toluene at room temperature, or by continuous extraction with refluxing pentane in a modified Soxhlet apparatus equipped with a glass filter. All reaction yields are based on the metal. Caution: the solid residues after extraction of the reaction mixture might be reactive towards water and alcohols and must be carefully decomposed (e.g. with EtOH) under nitrogen. The metal contents were determined by inductively coupled plasma on an ARL3580 instrument. 1–3 were prepared as previously described [1d].

3.2. $\text{Ind}_2\text{TiClMe}$

0.43 g of $\text{Ind}_2\text{TiMe}_2$ (1.4 mmol) were dissolved in 15 ml of toluene in a 50 ml Schlenk. 0.32 ml of SiCl_4 (99%, 2.79 mmol) were added at room temperature and the solution warmed up to 50°C and stirred for 3 h. $^1\text{H-NMR}$ revealed the formation of a 70:30 mixture of $\text{Ind}_2\text{TiClMe}$ and $\text{Ind}_2\text{TiMe}_2$. To bring the reaction to completion, additional two equivalents of SiCl_4 (0.32 ml) were added, and the red–orange solution stirred for

Table 4
Solution propylene polymerizations

Test	Complex	Yield g	A kg (mmol _{Zr} × h) ⁻¹	\bar{P}_n	Vinylidene %	Int. vinylid. %	Triplet (5,2 ppm)%	cis-2-Butenyl %	mm %	mr %	rr %
1	Ind ₂ ZrMe ₂	1.26	420	340	80.4	4.8	7.6	6.1	25.2	53.1	21.7
1 bis		0.95	320	395	80.7	5.4	8.4	5.4	25.6	52.3	22.1
2	Ind ₂ ZrCl ₂	1.03	340	414	79.0	6.2	8.1	5.4	26.2	51.9	21.9
2 bis		1.22	400	340	83.8	4.1	7.5	4.6			
3	Ind ₂ ZrBr ₂	0.60	200						26.3	50.4	23.3
3 bis		0.64	210	436	75.3	4.3	12.3	6.5			
4	Ind ₂ ZrI ₂	0.79	260	380	80.8	5.2	10.7	3.4			
4 bis		0.71	240						26.8	50.8	22.4
5	Ind ₂ Zr(OC ₆ F ₅) ₂	1.19	400	350	80.4	4.0	7.0	4.5	24.1	52.4	23.5
5 bis		1.34	450	395	78.8	4.3	9.1	6.5			

260 ml reactor, 100 ml toluene, 0.1 mmol TEA, 6 μmol Zr, 3 mmol Al as MAO, 4 bar g propylene, 30 min, 30 °C. End group structures are identified as described in Ref. [7].

3 more hours at 50 °C, then dried, to give a quantitative yield of Ind₂TiClMe (spectroscopically pure by ¹H-NMR) as a brick red powder.

¹H-NMR (C₆D₆, δ, ppm): -0.08 (s, Ti-CH₃, 3H), 5.52 (t, Cp-H(2), 2H, J = 3.33 Hz), 5.80 (ddd, Cp-H(1 or 3), 2H, J = 0.88, 1.96, 3.33 Hz), 5.86 (ddd, Cp-H(3 or 1), 2H, J = 0.88, 1.96, 3.33 Hz), 6.85–7.31 (m, Ar, 8H).

3.3. Ind₂ZrCl₂, 'classical' synthesis in THF

Fourty milliliter of a 1.5 M solution of BuLi in Et₂O (60 mmol) were added dropwise to 7.0 ml of indene (60.0 mmol) in 20 ml of THF, cooled to -78 °C. At the end of the addition, the solution was allowed to warm to room temperature and stirred for 1 h, to give an orange solution. Seven gram of ZrCl₄ (30.0 mmol) were dissolved in 30 ml of THF at -78 °C in a 100 ml flask equipped with reflux condenser (exothermic reaction). The mixture was allowed to reach room temperature with stirring, then refluxed for 30 min, to give a clear, brown solution. To this solution was added the THF solution of indenyllithium at room temperature with stirring, then the resulting suspension was stirred for 2 h. The color turned yellow. The solvents were removed under reduced pressure, the residue slurried in Et₂O and transferred into an extractor, washed with Et₂O until colorless, then extracted with CH₂Cl₂, the extract dried and washed again with Et₂O and then pentane, finally dried to give 4.35 g of yellow, spectroscopically pure (¹H-NMR) Ind₂ZrCl₂. Isolated yield 36.9%.

3.4. Ind₂ZrCl₂, 'classical' synthesis in Et₂O-pentane

9.9 ml of a 1.6 M solution of MeLi in Et₂O (15.8 mmol) were added dropwise to 1.97 g of technical indene (93.3% by GC, 15.8 mmol) in 30 ml of Et₂O. At the end of the addition the mixture was stirred for 40 min at room temperature, then it was added at once to 1.84 g of ZrCl₄ (7.9 mmol) slurried in 30 ml of pentane, then the resulting suspension was stirred for 2 h. The color turned yellow. The product in pentane-Et₂O was transferred into an extractor, filtrated, the filtrate was discarded, the residue dried and extracted at reflux with 80 ml of CH₂Cl₂ for 5 h. The extract was dried to give 2.08 g of lemon yellow Ind₂ZrCl₂, containing 4 mol.% of Ind₂ZrClMe (¹H-NMR). Isolated yield 67%.

3.5. Ind₂ZrMe₂, 'classical' synthesis from Ind₂ZrCl₂

2.38 g (6.1 mmol) of purified Ind₂ZrCl₂ (purified by multiple washing with Et₂O followed by extraction with CH₂Cl₂) were suspended in 60 ml of Et₂O, cooled to -78 °C, and 8 ml of a 1.6 M solution of MeLi in Et₂O (12.8 mmol) added dropwise in 10 min. At the end of the addition, the mixture was allowed to warm to room temperature and stirred for 4 h, to give a light brown

suspension. The suspension was evaporated under reduced pressure to give a brown powder, that was transferred into an extractor, and extracted with pentane at reflux. The extract was brought to dryness under reduced pressure, to give 1.63 g of white, powdery, spectroscopically pure ($^1\text{H-NMR}$) $\text{Ind}_2\text{ZrMe}_2$. Isolated yield 76.4%.

3.6. $\text{Ind}_2\text{ZrMe}_2$, 'direct' synthesis in two-steps

13.4 ml of a 1.4 M solution of MeLi in Et_2O (18.7 mmol) were added dropwise to 2.36 g of technical indene (92% by GC, 18.7 mmol) in 30 ml of Et_2O . At the end of the addition the mixture was stirred for 60 min at room temperature, then it was added at once to 2.18 g of ZrCl_4 (9.35 mmol) slurried in 30 ml of pentane, then the resulting suspension was stirred for 2 h. The color turned yellow. Additional 13 ml of a 1.4 M solution of MeLi in Et_2O (18.2 mmol) were added dropwise and the mixture stirred for 1 h. The product was dried in vacuo, then slurried in 80 ml of pentane and transferred into the extractor, then extracted at reflux for 5 h. The extract was dried to give 2.49 g of light brown, spectroscopically pure (by $^1\text{H-NMR}$) $\text{Ind}_2\text{ZrMe}_2$ powder. Isolated yield 76%.

Heat stability test: an NMR tube containing this $\text{Ind}_2\text{ZrMe}_2$ in C_6D_6 was kept at 70 °C in an oil bath and monitored by $^1\text{H-NMR}$. After 4 h, the product is perfectly stable, no decomposition products could be observed. The same sample proved to be stable also at room temperature for 72 h.

3.7. $\text{Ind}_2\text{ZrCl}_2$ from $\text{Ind}_2\text{ZrMe}_2$ and CuCl in CH_2Cl_2

0.33 g of $\text{Ind}_2\text{ZrMe}_2$ (0.94 mmol) were charged in a 10 ml Schlenk tube, and dissolved in 4 ml of CD_2Cl_2 . 0.485 g of CuCl (95%, 4.65 mmol) were added, and the mixture stirred at room temperature for 6 h, when $^1\text{H-NMR}$ showed the reaction to be complete. Twenty milliliter of CH_2Cl_2 were added and the mixture was filtered over a G4 frit. The yellow–green solution was brought to dryness to give 0.34 g of yellow–green powder (yield 93%) whose $^1\text{H-NMR}$ is identical to that of a true sample of $\text{Ind}_2\text{ZrCl}_2$.

$^1\text{H-NMR}$ (CD_2Cl_2 , δ , ppm): 6.23 (d, H(1–3), 4H, $J = 3.32$ Hz), 6.55 (t, H(2), 2H, $J = 3.32$ Hz), 7.28–7.37 (m, Ar, 4H), 7.60–7.69 (m, Ar, 4H).

3.8. $\text{Ind}_2\text{ZrCl}_2$ from $\text{Ind}_2\text{ZrMe}_2$ and CuCl in toluene

A slurry of CuCl (0.42 g, 4.24 mmol) in 15 ml of toluene was added to a solution of $\text{Ind}_2\text{ZrMe}_2$ (0.71 g, 2.02 mmol) in 15 ml of toluene. The suspension turned immediately from brown to black. After 24 h stirring, $^1\text{H-NMR}$ analysis showed the presence of a mixture of $\text{Ind}_2\text{ZrCl}_2$ and $\text{Ind}_2\text{ZrClMe}$ in the ratio 89/11. The

reaction mixture was then heated at 40 °C for 3 h, but $^1\text{H-NMR}$ analysis showed no reaction progress. Even adding five equivalents of CuCl (0.64 g, 6.46 mmol) and heating for 3 h no progress was observed by $^1\text{H-NMR}$ analysis.

3.9. $\text{Ind}_2\text{ZrCl}_2$ from $\text{Ind}_2\text{ZrMe}_2$ and CuCl in CH_2Cl_2

A slurry of CuCl (0.20 g, 2.02 mmol) in 6 ml of CH_2Cl_2 was added to a solution of $\text{Ind}_2\text{ZrMe}_2$ (0.69 g, 1.96 mmol) in 15 ml of CH_2Cl_2 . After 40 min the suspension turned from orange to black and $^1\text{H-NMR}$ analysis showed the presence of $\text{Ind}_2\text{ZrClMe}$. A second equivalent of CuCl (0.21 g, 2.12 mmol) was then added with 4 ml of CH_2Cl_2 . After 2 h stirring $^1\text{H-NMR}$ analysis showed the presence of a mixture of $\text{Ind}_2\text{ZrCl}_2$ and $\text{Ind}_2\text{ZrClMe}$ in the ratio 63/37. One additional equivalent of CuCl (0.19 g, 1.92 mmol) was added to the reaction mixture. Gas evolution was observed. After 18 h stirring at room temperature $^1\text{H-NMR}$ analysis showed the presence of $\text{Ind}_2\text{ZrCl}_2$ and some free indene.

3.10. $\text{Ind}_2\text{ZrCl}_2$ from $\text{Ind}_2\text{ZrMe}_2$ prepared in situ and CuCl in CH_2Cl_2

2.5 g of indene (92 wt.% by GC, 19.8 mmol) were dissolved in 30 ml of Et_2O in a 250 ml Schlenk tube. 24.8 ml of MeLi 1.6 M in Et_2O (39.7 mmol) were added with stirring at room temperature (exothermic reaction). After stirring for 40 min, a yellow–orange solution was obtained, to which was added a suspension of 2.3 g of ZrCl_4 (9.9 mmol) in 40 ml of pentane (exothermic reaction, the mixture turned dark brown). The mixture was stirred at room temperature for 2 h, then concentrated under reduced pressure to give a black powder, which was slurried in 50 ml of CH_2Cl_2 , and added of 4.9 g of CuCl (47 mmol). The resulting mixture was stirred for 3 h at room temperature, then filtered and extracted with the same CH_2Cl_2 for 4 h on a continuous extractor (the product precipitated in part as a yellow solid during extraction), the extract concentrated under reduced pressure to give a dark brown powder, which was then slurried in 50 ml of pentane, filtered, the filtrate discarded, and the residue brought to dryness under vacuum to give 3.5 g (90% yield based on Zr) of spectroscopically pure $\text{Ind}_2\text{ZrCl}_2$.

3.11. $\text{Ind}_2\text{ZrCl}_2$ from $\text{Ind}_2\text{ZrMe}_2$ and BCl_3 in CH_2Cl_2

0.25 g of $\text{Ind}_2\text{ZrMe}_2$ (0.71 mmol) were dissolved in 10 ml of CH_2Cl_2 in a 25 ml Schlenk tube, and 0.71 ml of BCl_3 1 M in heptane (0.71 mmol) were added, a yellow precipitate started to form, and the slurry was stirred at room temperature for 1 h, when $^1\text{H-NMR}$ showed the conversion to $\text{Ind}_2\text{ZrCl}_2$ to be quantitative. The yellow suspension was brought to dryness to give 0.27 g of

yellow, powdery, spectroscopically pure $\text{Ind}_2\text{ZrCl}_2$ (yield 97%). Its $^1\text{H-NMR}$ is identical to that of a true sample of $\text{Ind}_2\text{ZrCl}_2$.

3.12. $\text{Ind}_2\text{ZrCl}_2$ from $\text{Ind}_2\text{ZrMe}_2$ prepared in situ and BCl_3 in CH_2Cl_2

2.5 g of indene (92 wt.% by GC, 19.8 mmol) were dissolved in 30 ml of Et_2O in a 250 ml Schlenk tube. 24.8 ml of MeLi 1.6 M in Et_2O (39.7 mmol) were added with stirring at room temperature (exothermic reaction). After stirring for 40 min, a yellow–orange solution was obtained, to which was added a suspension of 2.3 g of ZrCl_4 (9.9 mmol) in 40 ml of pentane (exothermic reaction, the mixture turned dark brown). The mixture was stirred at room temperature for 2 h, then concentrated under reduced pressure to give a black powder, which was slurried in 50 ml of CH_2Cl_2 , cooled to 0°C , and added of 9.9 ml of BCl_3 1 M in heptane (9.9 mmol). During the addition, the mixture turned from dark grey to dark green. This was allowed to warm to room temperature and stirred for 30 min at room temperature (complete conversion to the dichloride observed by $^1\text{H-NMR}$ at this time), then filtered and extracted with the same CH_2Cl_2 for 8 h on a continuous extractor (the product precipitated in part as a yellow solid during extraction), the extract concentrated under reduced pressure to give a yellow powder, 3.74 g (96% yield based on Zr) of spectroscopically pure $\text{Ind}_2\text{ZrCl}_2$.

Anal. Calc. for $\text{C}_{18}\text{H}_{14}\text{Cl}_2\text{Zr}$: C, 55.09; H, 3.6; Cl, 18.07; Zr, 23.24. Found: C, 54.9; H, 3.5; Cl, 18.5.

3.13. $\text{Ind}_2\text{ZrCl}_2$ from $\text{Ind}_2\text{ZrMe}_2$ and BCl_3 in hexane

0.172 g of $\text{Ind}_2\text{ZrMe}_2$ (0.49 mmol) were slurried in 5 ml of hexane in a 10 ml Schlenk tube, and 0.49 ml of BCl_3 1 M in heptane (0.49 mmol) were added at room temperature, and the mixture stirred for 2 h, to give a 45:55 mixture of $\text{Ind}_2\text{ZrCl}_2$ and $\text{Ind}_2\text{ZrClMe}$ ($^1\text{H-NMR}$); additional 0.3 ml of BCl_3 1 M in heptane (0.3 mmol) was added and stirred for additional 2 h. At this point the reaction was complete and the product $\text{Ind}_2\text{ZrCl}_2$ was found spectroscopically pure by $^1\text{H-NMR}$.

3.14. $\text{Ind}_2\text{ZrCl}_2$ from $\text{Ind}_2\text{ZrMe}_2$ prepared in situ and BCl_3 in hexane

24.0 ml of MeLi 1.4 M in Et_2O (33.5 mmol) were added with stirring at room temperature (slightly exothermic reaction) to 2.08 g of indene (93.3 wt.% by GC, 16.7 mmol) in 60 ml of hexane in a 250 ml Schlenk tube. After stirring for 1 h, a cloudy yellow–orange solution was obtained, to which was added 1.95 g of ZrCl_4 (8.36 mmol) as a solid (slightly exothermic reaction, the mixture turned dark brown). The mixture

was stirred at room temperature for 2 h, then concentrated under reduced pressure to remove about 30 ml of solvent, the slurry was transferred into the extractor and extracted at reflux for 3 h (bath temperature 95°C): the extracted slurry turned black, although $^1\text{H-NMR}$ showed the presence of pure $\text{Ind}_2\text{ZrMe}_2$ only.

8.36 ml of BCl_3 1 M in heptane (8.36 mmol) were added. The mixture was stirred for 30 min at room temperature, then brought to dryness under reduced pressure, to give 2.55 g of a 1:1 mixture of $\text{Ind}_2\text{ZrCl}_2$ and $\text{Ind}_2\text{ZrClMe}$ ($^1\text{H-NMR}$), the solid was slurried in 20 ml of heptane and additional 5.0 ml of BCl_3 1 M in heptane (5.0 mmol) were added, and the mixture stirred overnight. At this point, $^1\text{H-NMR}$ shows complete conversion to the dichloride, but also a relevant amount of decomposition to unidentified organic byproducts.

3.15. $\text{Ind}_2\text{ZrCl}_2$ from $\text{Ind}_2\text{ZrMe}_2$ and FeCl_3 in CH_2Cl_2

380 mg of $\text{Ind}_2\text{ZrMe}_2$ (1.08 mmol) were dissolved in 5 ml of CH_2Cl_2 in a 10 ml Schlenk tube. 175 mg of anhydrous FeCl_3 (99.9%, 1.08 mmol) were added at room temperature (immediate darkening to black), and then the mixture is heated at 40°C for 6 h. After 3 h $^1\text{H-NMR}$ showed the presence of a 98:2 mixture of $\text{Ind}_2\text{ZrClMe}$ and residual $\text{Ind}_2\text{ZrMe}_2$, traces of the dichloride, and free from decomposition products. After another 3 h the dimethyl species was absent, while the dichloride was increased to 30 mol.% of the total. Traces of indene were also present. This method appears to be the most selective towards $\text{Ind}_2\text{ZrClMe}$.

3.16. $\text{Ind}_2\text{ZrCl}_2$ from $\text{Ind}_2\text{ZrMe}_2$ and NEt_3HCl

157 mg of $\text{Ind}_2\text{ZrMe}_2$ (0.45 mmol) were dissolved in 15 ml of CH_2Cl_2 in a 25 ml Schlenk tube. 125 mg of NEt_3HCl (98%, 0.9 mmol) were added at room temperature and after 10 min stirring the salt was completely dissolved. After 30 min $^1\text{H-NMR}$ showed the presence of a 60:40 mixture of starting dimethyl and $\text{Ind}_2\text{ZrClMe}$, also containing some free indene. After 1 h at 40°C , only traces of the starting material were observed, and the product was mainly $\text{Ind}_2\text{ZrClMe}$ and indene (26 mol.%). Adding three equivalents excess NEt_3HCl and heating at 40°C for 2 h only increased the amount of indene.

$^1\text{H-NMR}$ (CD_2Cl_2 , δ , ppm): -0.59 (s, Zr-CH_3 , 3H), $6.1-6.3$ (m, Cp-H , 6H), $7.2-7.3$ (m, Ar, 4H), $7.4-7.6$ (m, Ar, 4H).

3.17. $\text{Ind}_2\text{ZrCl}_2$ from $\text{Ind}_2\text{ZrMe}_2$ and HCl in Et_2O

300 mg of $\text{Ind}_2\text{ZrMe}_2$ (0.85 mmol) were dissolved in 20 ml of Et_2O in a 50 ml Schlenk tube. 0.85 ml of a 2 M solution of HCl in Et_2O (1.71 mmol) were added at room temperature. Gas evolution (CH_4) was observed,

together with instantaneous formation of a yellow precipitate. After 2 h stirring $^1\text{H-NMR}$ showed the presence of a 80:20 mixture of $\text{Ind}_2\text{ZrCl}_2$ and $\text{Ind}_2\text{ZrClMe}$, free from decomposition products. Stirring for additional 5 h did not change the composition, while adding additional 0.1 ml of HCl in Et_2O (0.2 mmol) brought the reaction to completion. Removing the solvent under reduced pressure gave 320 mg of pure $\text{Ind}_2\text{ZrCl}_2$, yield 96%. This experiment shows that the reaction between $\text{Ind}_2\text{ZrMe}_2$ and HCl is fast and quantitative, without decomposition. The lack of complete conversion in the first addition indicates that the concentration of HCl in Et_2O is approximate.

3.18. $\text{Ind}_2\text{ZrCl}_2$ from *in situ* prepared $\text{Ind}_2\text{ZrMe}_2$ and HCl in Et_2O –toluene

A 1.66 M MeLi solution in Et_2O (17.4 ml, 28.9 mmol) was added over a period of about 5 min at room temperature under nitrogen atmosphere to a solution of indene (93.4% by GC-MS, 1.76 g, 14.2 mmol) in 20 ml of Et_2O in a 100 ml Schlenk flask. During the addition exothermicity and gas evolution were observed. So the obtained yellow–orange solution was stirred for 30 min at room temperature and then was added to a slurry of ZrCl_4 (1.68 g, 7.21 mmol) in 40 ml of toluene in a 250 ml Schlenk flask (exothermic reaction). The brown reaction mixture was stirred for 80 min at room temperature and then filtered on a G4 frit. Other 10 ml of toluene were used to transfer completely the final suspension into the frit. The dark brown filtrate was treated at room temperature with a 1.87 M HCl solution in Et_2O (7.7 ml, 14.4 mmol): during the addition exothermicity and gas evolution were observed. The resulting lemon yellow suspension was stirred for 60 min at room temperature, evaporated to dryness under reduced pressure to give 2.57 g of a salmon colored powder as product. The latter was then washed with 20 ml of Et_2O to give 2.46 g of a yellow powder (86.9% metal-based yield), which was characterized by $^1\text{H-NMR}$ as spectroscopically pure $\text{Ind}_2\text{ZrCl}_2$.

Anal. Calc. for $\text{C}_{18}\text{H}_{14}\text{Cl}_2\text{Zr}$: C, 55.09; H, 3.60; Cl, 18.07; Zr, 23.24. Found: C, 53.8; H, 3.8.

$^1\text{H-NMR}$ (CD_2Cl_2 , δ , ppm): 6.23 (d, 4H, Cp–H(1,3), $J = 3.32$ Hz); 6.55 (t, 2H, Cp–H(2), $J = 3.32$ Hz); 7.28–7.37 (m, 4H, Ar); 7.60–7.69 (m, 4H, Ar).

3.19. $\text{Ind}_2\text{ZrCl}_2$ from $\text{Ind}_2\text{ZrMe}_2$ and HCl in *i*Pr $_2\text{O}$ –toluene

A 2.1 M solution of HCl in Et_2O (titrated against KOH, 12.2 ml, 25.6 mmol) was added to a solution of $\text{Ind}_2\text{ZrMe}_2$ (3.92 g, 11.1 mmol) in 60 ml of toluene and 60 ml of diisopropylether, in a 250 ml Schlenk flask. The yellow suspension obtained was stirred at room temperature for 2 h and then evaporated to dryness under

reduced pressure to give a yellow powder which was characterized by $^1\text{H-NMR}$ as a mixture of $\text{Ind}_2\text{ZrCl}_2$ and $\text{Ind}_2\text{ZrClMe}$ in the ratio 93/7. The powder was then treated with 25 ml of ether, 25 ml of toluene and 1 ml of the HCl solution previously used (2.1 mmol). After 2 h stirring the yellow suspension was evaporated to dryness under reduced pressure to give 4.38 g of a yellow powder (100% metal-based yield), which was characterized by $^1\text{H-NMR}$ as spectroscopically pure $\text{Ind}_2\text{ZrCl}_2$.

3.20. $\text{Ind}_2\text{ZrCl}_2$ from $\text{Ind}_2\text{ZrMe}_2$ and PbCl_2 in toluene

A slurry of 2.53 g of PbCl_2 (9.10 mmol) in 15 ml of toluene was added to a solution of $\text{Ind}_2\text{ZrMe}_2$ (1.25 g, 3.56 mmol) in 35 ml of toluene, in a 100 ml Schlenk flask. The dark orange suspension obtained was stirred 38 h at room temperature and 10 h at 40–45 °C, during which time formation of a black powder was observed. The suspension was then filtered on a G4 frit and the filtrate was evaporated to dryness under reduced pressure to give 1.1 g of a dark yellow powder, which was shown by $^1\text{H-NMR}$ to contain a mixture of $\text{Ind}_2\text{ZrClMe}$ and $\text{Ind}_2\text{ZrCl}_2$ in the ratio 90/10.

0.63 g of this mixture were treated with 30 ml of toluene and 1.2 g of PbCl_2 (4.31 mmol). The suspension obtained was stirred for 30 h at room temperature and 12 h at 40 °C. $^1\text{H-NMR}$ analysis showed some progress of the reaction to $\text{Ind}_2\text{ZrCl}_2$ but also decomposition of the product to indene.

3.21. $\text{Ind}_2\text{ZrCl}_2$ from $\text{Ind}_2\text{ZrMe}_2$ and PbCl_2 in CH_2Cl_2

A solution of $\text{Ind}_2\text{ZrMe}_2$ (0.71 g, 2.02 mmol) in 10 ml of CH_2Cl_2 was added to a suspension of PbCl_2 (1.65 g, 5.93 mmol) in 10 ml of CH_2Cl_2 , in a 100 ml Schlenk flask. The brown suspension formed turned to black in 1 h. After 24 h stirring at room temperature, the suspension was filtered on a G4 frit and the filtrate evaporated to dryness under reduced pressure to give 0.62 g of a yellow powder, which was characterized by $^1\text{H-NMR}$ as a mixture of $\text{Ind}_2\text{ZrClMe}$ and $\text{Ind}_2\text{ZrCl}_2$ in the ratio 91/9. This powder was then treated with 20 ml of CH_2Cl_2 and 1.68 g of PbCl_2 (6.04 mmol), but after 24 h stirring at room temperature no reaction progress was observed by $^1\text{H-NMR}$. The reaction mixture was then heated at 35 °C for 24 h, but decomposition of the product was observed by $^1\text{H-NMR}$.

3.22. $\text{Ind}_2\text{ZrCl}_2$ from $\text{Ind}_2\text{ZrMe}_2$ and SCl_2 in toluene

A solution of SCl_2 (0.17 g, 1.65 mmol) in 5 ml of toluene was added to a suspension of $\text{Ind}_2\text{ZrMe}_2$ (0.50 g, 1.42 mmol) in 12 ml of toluene. During the addition exothermicity was observed and the reaction mixture turned immediately from brown to yellow. After 45 min stirring at room temperature the reaction mixture was

evaporated to dryness under reduced pressure to give 0.51 g (91.4% metal-based yield) of a pale-yellow powder which was characterized by $^1\text{H-NMR}$ as spectroscopically pure $\text{Ind}_2\text{ZrCl}_2$.

3.23. $\text{Ind}_2\text{ZrCl}_2$ from $\text{Ind}_2\text{ZrMe}_2$ and SCl_2 in CH_2Cl_2

A solution of SCl_2 (0.16 g, 1.55 mmol) in 10 ml of CH_2Cl_2 was added to a suspension of $\text{Ind}_2\text{ZrMe}_2$ (0.55 g, 1.56 mmol) in 10 ml of CH_2Cl_2 . During the addition exothermicity was observed and the reaction mixture turned clearer. After 3 h stirring at room temperature the reaction mixture turned reddish and $^1\text{H-NMR}$ analysis showed a mixture of $\text{Ind}_2\text{ZrCl}_2$ and $\text{Ind}_2\text{ZrClIme}$ in the ratio 61/39. Additional 0.055 g of SCl_2 (0.53 mmol) were added to the reaction mixture. After 1 h stirring, the brown suspension was evaporated to dryness under reduced pressure to give 0.61 g (100% metal-based yield) of a clear brown powder. $^1\text{H-NMR}$ analysis showed the presence of $\text{Ind}_2\text{ZrCl}_2$ together with a minor amount of unidentified impurities.

3.24. Reaction of $\text{Ind}_2\text{ZrMe}_2$ with CuBr

A suspension of 0.40 g of CuBr (98%, 2.7 mmol) in 5 ml of CH_2Cl_2 was added to a solution of 0.46 g of $\text{Ind}_2\text{ZrMe}_2$ (1.3 mmol) in 10 ml of CH_2Cl_2 . The black suspension obtained was stirred at room temperature for 4 h. After that time $^1\text{H-NMR}$ analysis showed the presence of $\text{Ind}_2\text{ZrMeBr}$. The solution was then heated at 40 °C for 4 h. $^1\text{H-NMR}$ analysis showed the presence of a mixture of $\text{Ind}_2\text{ZrBr}_2$ and $\text{Ind}_2\text{ZrMeBr}$ in a 1:1 ratio.

$\text{Ind}_2\text{ZrMeBr}$ was characterized by $^1\text{H-NMR}$ (CD_2Cl_2 , δ , ppm): -0.93 (s, 3H, Zr-CH_3), 6.20–6.29 (m, 6H, $\text{Cp-H}(1,2,3)$); 7.21–7.29 (m, 4H, Ar); 7.44–7.64 (m, 4H, Ar).

3.25. $\text{Ind}_2\text{ZrBr}_2$ from $\text{Ind}_2\text{ZrMe}_2$ and Br_2

A solution of 0.59 g of Br_2 (3.69 mmol) in 7 ml of CH_2Cl_2 was added to a solution of 0.65 g of $\text{Ind}_2\text{ZrMe}_2$ (1.85 mmol) in 20 ml of CH_2Cl_2 . The reaction was exothermic, and gas evolution was observed. The light brown suspension obtained was stirred at room temperature for 18 h and then evaporated to dryness under reduced pressure to give 1.11 g of a brick-red powder. To remove the impurities, this powder was taken up in 30 ml of Et_2O and filtered. No product dissolved in Et_2O . The residue was further purified by dissolving in toluene and filtering. The filtrate was evaporated to dryness under reduced pressure to give $\text{Ind}_2\text{ZrBr}_2$, pure by $^1\text{H-NMR}$. Yield 50%.

$^1\text{H-NMR}$ (CD_2Cl_2 , δ , ppm): 6.28 (d, 4H, $\text{Cp-H}(1,3)$, $J = 3.42$ Hz); 6.57 (t, 2H, $\text{Cp-H}(2)$, $J = 3.42$ Hz); 7.30–7.38 (m, 4H, Ar); 7.63–7.70 (m, 4H, Ar).

3.26. Ind_2ZrI_2 from $\text{Ind}_2\text{ZrMe}_2$ and I_2 in CD_2Cl_2

164 mg of $\text{Ind}_2\text{ZrMe}_2$ (0.46 mmol) were dissolved in 2 ml of CD_2Cl_2 in a 10 ml Schlenk tube. 120 mg of I_2 crystals (0.47 mmol) were added at room temperature. The solution was warmed to 40 °C. After 5 min stirring the I_2 was fully solubilized, to give a bright orange solution that was stirred for 6 h at 40 °C. $^1\text{H-NMR}$ analysis shows the presence of $\text{Ind}_2\text{ZrMe}_2$, Ind_2ZrIme and Ind_2ZrI_2 , in the ratio 6:67:27.

Ind_2ZrIme : $^1\text{H-NMR}$ (CD_2Cl_2 , δ , ppm): -1.47 (s, 3H, Zr-CH_3), 6.09 (t, 2H, Cp-H_2 , $J = 3.52$ Hz), 6.39 (m, 2H, $\text{Cp-H}(1,3)$), 6.54 (m, 2H, $\text{Cp-H}(3,1)$), 7.23–7.28 (m, 4H, Ar), 7.64–7.69 (m, 4H, Ar).

Additional 60 mg of I_2 were added, and the solution stirred at room temperature for 72 h. $^1\text{H-NMR}$ analysis showed $\sim 80\%$ conversion to the target Ind_2ZrI_2 .

Ind_2ZrI_2 : $^1\text{H-NMR}$ (CD_2Cl_2 , δ , ppm): 2.19 (CH_3I , cfr. CH_3I in $\text{CDCl}_3 = 2.16$ ppm); 6.42 (d, $\text{Cp-H}(1,3)$, 4H, $J = 3.33$), 6.64 (t, $\text{Cp-H}(2)$, 2H, $J = 3.33$), 7.30–7.40 (m, Ar, 4H), 7.66–7.75 (m, Ar, 4H). An impurity has $^1\text{H-NMR}$: 1.29 (s), ca. 6.6, ca. 6.8 (Cp-H), 7.9 (m).

3.27. Ind_2ZrI_2 from $\text{Ind}_2\text{ZrMe}_2$ and I_2 in toluene

Crystals of I_2 (0.70 g, 2.76 mmol) were added to a suspension of $\text{Ind}_2\text{ZrMe}_2$ (0.48 g, 1.36 mmol) in 20 ml of toluene. The orange suspension turned to dark purple in a few minutes. After 30 min stirring at room temperature, the suspension was evaporated to dryness under reduced pressure to give 0.83 g (100% yield) of an orange powder, which was characterized by $^1\text{H-NMR}$ as pure Ind_2ZrI_2 .

$^1\text{H-NMR}$ (CD_2Cl_2 , δ , ppm): 6.42 (d, 4H, $\text{Cp-H}(1,3)$, $J = 3.33$ Hz); 6.64 (t, 2H, $\text{Cp-H}(2)$, $J = 3.33$ Hz); 7.30–7.40 (m, 4H, Ar); 7.66–7.75 (m, 4H, Ar).

3.28. Ind_2ZrI_2 from $\text{Ind}_2\text{ZrMe}_2$ and I_2 in CH_2Cl_2

Crystals of I_2 (0.72 g, 2.84 mmol) were added to a suspension of $\text{Ind}_2\text{ZrMe}_2$ (0.50 g, 1.42 mmol) in 20 ml of CH_2Cl_2 . The orange suspension turned to dark purple in few minutes. After 30 min stirring at room temperature, the suspension was evaporated to dryness under reduced pressure to give 0.79 g (96% yield) of an orange powder, which was characterized by $^1\text{H-NMR}$ as pure Ind_2ZrI_2 .

3.29. Polymerization of propylene

The polymerizations were carried out in a 260 ml Büchi glass reactor equipped with a mechanical stirrer, a thermocouple and monomer feeding line. The autoclave was purged with N_2 , filled with 95 ml of toluene containing 0.1 mmol AlEt_3 , warmed at 30 °C and purged with propylene. The catalytic system was prepared in 5 ml of toluene by mixing 6 μmol of the

metallocene and 3 mmol of MAO (Witco, 10% w/v solution in toluene, used as received, $Al_{MAO}-Zr = 500$). This solution was introduced into the reactor after less than 30 s stirring at room temperature, the reactor was closed and the pressure raised to 4 bar g and kept constant by feeding propylene. After 30 min, the polymerization was stopped by degassing the reactor and adding 1.5 ml of methanol. The solution was filtered to remove the catalyst residues, and evaporated to dryness. The low molecular weight, atactic PP produced were dried overnight in a vacuum oven.

3.30. Polymer analysis

The ^{13}C -NMR spectra were acquired at 120 °C on a Bruker DPX-400 spectrometer, operating in the Fourier transform mode at 100.61 MHz. The samples were dissolved in $C_2D_2Cl_4$ with a concentration of 8% w/v. The spectra were acquired with a 90° pulse and 12 s of delay between pulses. About 1500 transients were stored for each spectrum. Proton spectra were acquired with a 45° pulse and 5 s of delay between pulses on the same spectrometer at 120 °C. 256 transients were stored for each spectrum. As references, the residual peak of C_2DHCl_4 in the 1H spectra (5.95 ppm) and the peak of the *mmmm* pentad in the ^{13}C spectra (21.8 ppm) were used.

4. Conclusions

We have found that the ‘inverse’ synthesis of Ind_2ZrCl_2 can be carried out, cleanly and quantitatively, by chlorination of Ind_2ZrMe_2 with excess $CuCl$, one equivalent BCl_3 , SCl_2 , or two equivalents HCl in Et_2O . The latter method is the preferred one, since it produces methane as the only byproduct, and the formed Ind_2ZrCl_2 precipitates quantitatively from the Et_2O solvent: a simple filtration then gives the analytically pure product in quantitative yield.

Although counterintuitive, the synthesis of metallocene dichlorides by chlorination of their dimethyl ‘derivatives’ has some manifest advantages: first, Ind_2ZrCl_2 is obtained in higher yield compared to the classic method; second, it is easier to purify (at the dimethyl stage) and is obtained free from $LiCl$. In summary, while the ‘classic’ route to Ind_2ZrCl_2 gives 37–67% yield of a low solubility product that requires a tedious procedure for removing $LiCl$, the ‘inverse’ synthesis, although requiring the sacrifice of two

equivalents $MeLi$, yields the product in 90–100% isolated yield and with a much easier purification procedure.

This procedure, for the bisindenylmetal halides, appears to be more convenient than that recently reported by Eisch et al. [8].

By reaction of Ind_2ZrMe_2 with one equivalent $FeCl_3$, the monochloro derivative $Ind_2ZrClMe$ is obtained (98% conversion by 1H -NMR), while Ind_2ZrBr_2 and Ind_2ZrI_2 are formed in good yields by reaction with Br_2 and I_2 , respectively.

The availability of complexes with different sigma ligands has prompted us to investigate the influence of the latter on the polymerization performance of the MAO-activated catalysts. We found that, in solution propylene polymerizations, the σ -ligands have no influence on polymer tacticity, molecular weights or end-group structures. A possible influence of the σ -ligands on the rate and extent of catalyst activation would be a further topic for study.

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