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Introduction

Metallocenes of group 4 metals have been known as catalysts for homogeneous olefin polymerization since the early works by Natta¹ and Breslow² in the 1950s. More than 20 years later, the discovery of MAO and then boron-based activators made it possible to dramatically enhance the activity of these catalysts up to a factor of 10 000.^{3,4} Pioneering work by Ewen on the relationship between metallocene symmetry and polymer microstructure pointed out the direction for the design of complexes depending on the desired polypropylene (PP) properties.⁵ In 1985, the first indenyl-based *ansa*-zirconocene was used for isospecific polymerization of propylene by Kaminsky and Brintzinger.⁶ In comparison with the classic Ziegler–Natta catalysts, these early C_2 -symmetric *ansa*-metallocene dichlorides activated with MAO produced isotactic polypropylene (iPP) with relatively low molecular weight (MW) and crystalli-

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Multisubstituted C_2 -symmetric *ansa*-metallocenes bearing nitrogen heterocycles: influence of substituents on catalytic properties in propylene polymerization at higher temperatures[†]

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In this work we systematically studied the effects of modifications of substituents on the performance of the isospecific zirconocene-based catalyst family, $Me_2Si(2-Alk-4-(N-carbazolyl)Ind)ZrX_2$ (X = Cl, Me), wherein the progenitor was shown to be particularly suitable in high-temperature propylene polymerization processes. In order to obtain the required zirconocenes, we developed a novel synthetic pathway to $4-(N-carbazolyl)Ind)ZrX_2$ (X = Cl, Me), which were synthesized *via* Buchwald–Hartwig reaction or electrophilic amination of 4-indenyl Grignard reagents with trimethylsilylmethyl azide. By a number of examples, the anion-promoted *rac*-to-*meso* isomerization method was shown to work reliably well for preparation of *rac*-ZrMe₂-complexes. Certain zirconocenes among the 21 tested in propylene polymerization at 70 and 100 °C under MAO or borate activation outperformed the parent catalyst in molecular weight capability, regio- or stereoselectivity.

nity. Nonetheless, the potential of those systems was recognized by both academia and polyolefin industry, and an extensive effort was aimed at optimizing performance of metallocene-based catalysts for propylene polymerization.⁷ In 1994 Spaleck *et al.* reported that zirconocene *rac*-Me₂Si(2-Me-4-Ph-Ind)₂ZrCl₂ (**I**, Fig. 1) upon activation with MAO produced highly isotactic polypropylene of high MW which was recognized as one of the major achievements in single-site metallocene catalyst design.⁸ The whole family of C_2 -symmetric Me₂Sibridged bis(2-alkyl-4-arylindenyl) metallocenes – which has grown a lot in size and diversity since then – is now often referred to as "Spaleck-type" catalysts. The performance of the Spaleck-type catalysts is known to deteriorate with increasing polymerization temperature. Thus, MW capability, stereo- and regioselectivity drop significantly at temperatures above



Fig. 1 Propylene polymerization precatalysts.

[†]Electronic supplementary information (ESI) available. CCDC 2046384–2046389. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/d1dt00645b

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60 °C.^{7,9–11} Catalyst activity should rise exponentially with reaction temperature, but due to side deactivation processes, monomer diffusion limitations and decrease of monomer concentration (in case of solution polymerization) the productivity *vs.* temperature dependence curve is bell-shaped with a maximum at 60–100 °C. Meanwhile, it is beneficial for industrial processes to conduct polymerization in solution at higher temperatures due to increased throughput, decreased energy needed for devolatilization, and decreased fouling.¹²

Modifications of I by introduction of substituents in the 4-phenyl ring are known to efficiently improve performance of Spaleck-type catalysts in iPP synthesis.^{13,14} It was shown previously that, for example, rac-Me₂Si(2-Me-4-(3,5-tBu₂-Ph) Ind)₂ZrCl₂ forms the catalyst which displays higher stereo- and regioselectivity in comparison with I. In addition, an ethyl group in position 2 of the indenyl moieties can further enhance regiocontrol, and large substituents in position 6 were shown to significantly boost MW capability.¹⁴ Schöbel al. developed rac-Me₂Si(2-Me-4-(3,5-tBu₂-Ph)-7et MeO-Ind)₂HfCl₂ with a record breaking MW capability, regioand stereoselectivity at low polymerization temperatures.¹⁵ These studies prove that modifications of substituents in I can lead to catalysts with advanced performance in terms of activity, MW capability, stereo- and regioselectivities. Recently we reported our results of investigation of 4-(N-azolyl)-substituted metallocenes II-IV (Fig. 1)¹⁶ where we found that catalysts derived from 4-(N-carbazolyl)-substituted zirconocenes, II or MII, demonstrated high stereoselectivity in combination with decent molecular weight capability in propylene polymerization at 100 °C.

Soon after that, a further investigation of catalytic performance of variously substituted in different positions Spalecktype metallocenes in propylene polymerization at high temperature¹¹ confirmed that zirconocene **II** had the best combination of stereo- and regioselectivity resulting in the highest melting point of iPP produced at 100 °C among the series of 21 catalysts. Although higher MW capability was demonstrated by four metallocenes with 6-*t*Bu groups in the indenyls, including the Resconi/Nifant'ev catalyst^{17,18} bearing also MeO-groups in position 5, none of them was close to **II** in the crystallinity of the obtained iPP (*i.e.* its high melting point ($T_{\rm m}$)). This being said, analogues of **II** modified with additional substituents and their polymerization behavior have not been studied yet.

Inspired by the results of systematic studies showing the impact of structural modifications of Spaleck type catalysts on their propylene polymerization performance conducted by some of us in collaboration with Prof. V. Busico group,^{11,13,14} we decided to investigate whether the same and even more diverse manipulations with the ligand substitution on **II** might have similar effects in the 4-(*N*-azolyl)-substituted family of metallocenes, which could lead to new and better performing catalysts for iPP production, particularly at high polymerization temperatures. Thus, we aimed to synthesize a variety of *rac*-Me₂Si(2-Alk-4-(*N*-carbazolyl)Ind)₂ZrX₂ complexes (X = Cl, Me), optionally further substituted in positions 5, 6, and 7 of

the indenyls, and conduct propylene polymerization experiments at 70 and 100 °C using MAO or $[HMe_2NPh][B(C_6F_5)_4]$ (AB) as activators. In addition, we prepared a few 4-(*N*-azolyl) indenyl metallocenes where the *N*-azolyl substituents were different from *N*-carbazolyl to test whether the latter moiety is crucial for the applicability of the respective catalysts at high polymerization temperatures.

Results and discussion

Syntheses of the zirconocenes

In our previous paper, we described a simple procedure for installation of carbazolyl group in indenes based on Buchwald–Hartwig reaction of 4/7-bromo-2-methylindene¹⁹ (1) and *N*-carbazolyllithium with Pd(OAc)₂/*t*BuMePhos as a catalyst.¹⁶ The described procedure worked well for syntheses of indenes 7–14 and gave the (*N*-carbazolyl)-substituted indenes in 38–80% yields (Scheme 1).

In the next set of analogues of **II**, we aimed to replace the *N*-carbazolyl with other *N*-azolyl moieties with similar steric properties – 2,5-dimethyl-*N*-pyrrolyl and 2-R-*N*-indolyl (R = Me, Ph) which are substituted versions of **IV** and **III**, respectively. Unfortunately, our attempts to synthesize the corresponding *N*-azolyl-substituted indenes *via* cross-couplings of 4/7-bromo-2-methyl-1*H*-indene and 2,5-dimethylpyrrole or 2-methylindole were unsuccessful leading to side products.¹⁶ Ivchenko *et. al.* described their own attempt to synthesize 2-methyl-4-(2,5-dimethyl-*N*-pyrrolyl)-indene by Friedel–Crafts cyclization of chloroanhydride of 3-(2-(2,5-dimethyl-*N*-pyrrolyl)phenyl)-2-methylpropanoic acid, which resulted in isomerization of 2,5-dimethyl-*N*-pyrrolyl fragment to 2,4-dimethyl-*N*-pyrrolyl.²⁰

Therefore, we opted for a synthetic route based on latestage construction of the pyrrole core *via* well-known Paal-Knorr reaction of 4/7-amino-2-methylindene (**15**) with preassembled indene skeleton. Besides that, there are examples of the synthesis of 2-substituted 1-arylindoles from the corresponding anilines *via* transition metal-catalyzed reactions.²¹⁻²⁴ The previously published synthetic pathway to **15** is too labor-



Scheme 1 Syntheses of (*N*-carbazolyl)indenes *via* Buchwald–Hartwig cross-couplings.

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and time-consuming,²⁵ so we developed our own method for the synthesis of **15** from **1**. First, we tried to apply well-developed Buchwald–Hartwig reaction with various ammonia equivalents.^{26–29} The only effective one was benzophenone imine²⁹ which allowed us to obtain indene **15** in 56% yield (Scheme 2). Analogously, indenes **18–20** were synthesized in 42–58% yields (Scheme 2).

Another method we chose for synthesis of substituted 4/7-aminoindenes was based on electrophilic amination. Trimethylsilylmethyl azide (TMSMA) is known to be used for preparation of aromatic primary amines from sterically hindered aryllithium and aryl Grignard reagents.³⁰ Amine 15 was synthesized *via* reaction of TMSMA with Grignard reagent prepared from 1 by the common method of "entrainment" with 1,2-dibromoethane. Subsequent quenching with water gave the desired product 15 in 51% yield (Scheme 3). Analogously, indenes 18–20 and 22 were synthesized in similar or better yields (Scheme 3) in comparison with the Buchwald–Hartwig procedure (Scheme 2) without the use of transition metals. Notably, more sterically hindered bromoindenes gave higher yields.

As it was expected, **15** readily reacted with 2,5-hexanedione in the presence of 10 mol% of iodine³¹ giving the required (2,5-dimethyl-*N*-pyrrolyl)-substituted indene **23** in 53% yield (Scheme 4, method A). An alternative procedure with $\text{ZrOCl}_2(\text{H}_2\text{O})_8^{32}$ as a catalyst gave 70% yield and was also used for synthesis of *tert*-butyl substituted indene **24** from **18** (Scheme 4, method B). The technique developed by Ackermann²² appeared to be the most effective among those we tested for assembly of the (2-R-*N*-indolyl) core *via* derivatization of **15** giving indenes **25** (R = Me) and **26** (R = Ph) in 76 and 78% yields respectively (Scheme 5).

In 2003 Nozaki and co-workers described a route to multisubstituted carbazoles via palladium-catalyzed double *N*-arylation of primary amines with 2,2'-dihalobiphenvls.^{33,34} Having primary amine 15 in hand, we synthesized several 4/7-(N-carbazolyl)indenes, where the carbazolyl moieties were symmetrically substituted at positions 2, 7, or 3, 6, or 2, 3, 6, 7. In this way, indenes 27-30 were obtained from 15 in 58-65% vields (Scheme 6). Moreover, this method made it possible to synthesize sterically encumbered 4/7-(N-carbazolyl)indenes 31-34 (Scheme 6) containing substituents in ortho-position to the (N-carbazolyl) moiety, which we previously failed to obtain via Buchwald–Hartwig amination of the corresponding 4/7-bromoindenes. Summarizing the above, 4/7-aminoindenes proved to be very convenient starting materials for various (N-azolyl)indenes, where N-azolyl is optionally substituted N-pyrrolyl, N-indolyl or N-carbazolyl.

Me₂Si-bridged bis(indenyl) proligands L1–L22 were prepared from indenes 7–14, 23–34 in good yields by two methods using either CuCN³⁵ or *N*-methylimidazole³⁶ as catalysts for nucleophilic substitution at silicon (Scheme 7, methods A, B; see ESI for details†). The proligands were subsequently dilithiated with *n*BuLi in ether and reacted with $ZrCl_4(THF)_2$ to prepare the corresponding zirconocene dichlor-



Scheme 2 Synthesis of aminoindenes via cross-coupling



Scheme 3 Syntheses of aminoindenes via electrophilic amination.



Scheme 4 Synthesis of 2,5-dimethyl-(N-pyrrolyl)indenes.



Scheme 5 Syntheses of 4-(2-R-N-indolyl)indenes.



Scheme 6 Syntheses of (*N*-carbazolyl)indenes *via* double arylation of aminoindenes.

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Scheme 7 Synthesis of proligands and zirconocenes. ^a Method A: (1) 2.05 equiv. *n*BuLi, Et₂O; (2) 0.1 equiv. CuCN, 0.5 equiv. Me₂SiCl₂, THF. Method B: (1) 2.05 equiv. *n*BuLi, Et₂O; (2) 0.01 equiv. *n*-methylimidazole, 0.5 equiv. Me₂SiCl₂, Et₂O; or, for L3, L4: (1) 1.0 equiv. *n*BuLi, Et₂O; (2) 0.01 equiv. *N*-methylimidazole, 0.5 equiv. Me₂SiCl₂, Et₂O; or, for L3, L4: (1) 1.0 equiv. *n*BuLi, Et₂O; (2) 0.01 equiv. *N*-methylimidazole, 0.5 equiv. Me₂SiCl₂, Et₂O; or, for L3, L4: (1) 1.0 equiv. *n*BuLi, Et₂O; (2) 0.01 equiv. *N*-methylimidazole, 1.0 equiv. 2-Me-4-(*N*-carbazolyl)indenyl-SiMe₂Cl, Et₂O. ^b Method C (for M5, M6, M8, M12): 10 equiv., MeMgBr, Et₂O-PhMe, 100 °C. Method D (for M7, M9–M11, M13): (1) 10 equiv., MeMgBr, Et₂O-PhMe, 100 °C. (2) 0.05 equiv. LiCl, THF, 50 °C. ^c R₆ = H, except for C22. ^d rac/meso = 1/1, not tested. ^e 95% rac.

ides C1–C22 (Scheme 7). Crystallization afforded C1–C4, C6, C11, C12, C16, C18–C20, and C22 as pure *rac*-zirconocenes, and C15, C17, and C21 in low yields (0.9-4%) as mixtures of ~95% *rac* and ~5% of *meso*-isomers. Unfortunately, in some cases we were unable to isolate the required *rac*-complexes even after extensive recrystallizations.

There are a number of examples of racemoselective syntheses of *ansa*-metallocenes in the literature with utilization of special zirconium reagents³⁷⁻⁴⁰ instead of $\text{ZrCl}_4(\text{THF})_2$, or proligand modification.^{41,42} In the former case, additional steps are often required to convert the products of racemoselective reactions to the target metallocene dichlorides. Also, some success was achieved in photoinduced *meso*-to-*rac* isomerization of bridged zirconocenes.⁴³⁻⁴⁵ Drawbacks of the method are instability of the complexes under the isomerization conditions⁴² and dependence of the achievable photostationary *rac/meso* ratios on the ligand substitution resulting in *rac/meso* ratios of <1 in some cases.⁴⁴

In 1999 R. Lin from Albemarle found that *rac/meso* ratio of silicon-bridged zirconocene dichlorides could be adjusted by heating *rac/meso* mixtures with LiCl in DME or THF.⁴⁶ Later, the reversible substitution of cyclopentadienyl ligand by Cl^- anion in zirconocenes was studied by Buck *et al.*⁴⁷ The rate of the anion-promoted *meso*-to-*rac* isomerization depends on the solubility of the starting *rac/meso* mixture in THF, which is very low for the zirconocene dichlorides we had obtained. For this reason, complexes **C5–C13** were converted to more soluble

dimethyl complexes by treatment with excess of MeMgBr in suspension in toluene-ether at 100 °C (Scheme 7, methods C and D). After work up, the yields of the pure rac/meso mixtures of the dimethyl complexes M5-M13 were almost quantitative. Unfortunately, under these conditions, rac/meso mixtures of indolyl-substituted complexes M14 and M15 were formed together with unidentified and inseparable impurities. Dimethyl complexes M6 and M12 were prepared from pure racisomers of C6 and C12 respectively, so no isomerization was needed. Racemic forms of M5 and M8 were successfully isolated from mixtures of methylated rac- and meso-complexes by crystallization (Scheme 7, C). Mixtures of rac/meso-complexes M7, M9-M11 and M13 obtained after methylation were treated with LiCl in THF at 50 °C (Scheme 7, D) which expectedly resulted in the desired enrichment of the rac-isomers, all of which were successfully isolated after subsequent recrystallizations (see ESI for details[†]). Thus, we demonstrated that the method of meso-to-rac isomerization of dimethyl zirconocenes with LiCl previously developed for preparation of MII (Fig. 1)¹⁶ is reliable and can be used for synthesis of racemic dimethyl metallocenes when solubility of the corresponding dichlorides is an issue.

Thus, we successfully synthesized 21 novel racemic *ansa*-zirconocenes, which can be combined in four main groups according to the nature and positions of the varied substituents: (1) 2-alkyl substitution on the indenyls, (2) substituents on 4-(*N*-carbazolyl), (3) substituents in positions 5, 6, 7 of the indenyls, (4) other *N*-heteroaryls instead of carbazolyl (Scheme 7). Single crystals suitable for X-ray structure determination were obtained for *rac*-zirconocenes C16, C22, M6, M7, M10 and M12 by recrystallization from toluene/hexane mixture at -30 °C (Fig. 2, Fig. S1 and Tables S3–S8 in ESI†). Important angles of the complexes are given in Table 1, which includes structural parameters for both halves of each complex, because the structures are not perfectly C_2 -symmetric due to incorporation of solvent molecules and/or crystal lattice effects.

In all of the complexes, the zirconium atoms coordination polyhedron exhibits a pseudotetrahedral geometry. Bond lengths, Zr-Cl in C16 and C22 and Zr-CH₃ in M6, M7, M10 and M12, are in narrow ranges, 2.410-2.421 Å and 2.238-2.266 Å respectively, as well as the distances between the zirconium atoms and centroids of cyclopentadienyls (2.251-2.266 Å) and angles Cp-Zr-Cp', which seem to be weakly dependent on the ligand structure (Table 1). While in complexes M6, M7, M10, M12 with substituted carbazolyl moieties, the dihedral angles between the planes of carbazolyl and indenyl fall in the range 48.15-55.33° (larger angle 68.22° in M7 is caused by cocrystallized toluene molecule), in C16 they are much larger (68.65/77.80°). Apparently, the 5-methyl groups on the indenyls increase the dihedral angle more significantly than the substituents in the carbazolyl moieties. The analogous dihedral angles between the planes of 2,5-dimethyl-



Fig. 2 ORTEP style representation of zirconocene M6 with ellipsoids drawn at 50% probability level. Hydrogen atoms are omitted for clarity.

N-pyrrolyl and indenyl fragments in C22 are comparable with those in C16 but much higher than in M6, M7, M10, M12, and IV (32.25/49.76° in the latter¹⁶). Based on the data, we can conclude that modification of IV with 2,5-methyls in N-pyrrolyl giving C22 affects the dihedral angle between heterocycle and indene much more than the replacement of *N*-pyrrolyl in **IV** by N-carbazolyl in II. Thus, the 2,5-dimethyl-N-pyrrolyl moiety appears to be closer in steric properties to mesityl rather than to N-carbazolyl which results in a close proximity of methyl groups in N-pyrrolyl to the metal center.¹³ A likely consequence of this is an anomalously large Cl1-Zr-Cl2 angle⁴⁸ in C22 (103.59° vs. 96.65 in IV^{16}), similar to the mesityl-substituted analogue of I as evidenced by the respective structures calculated with DFT.13 The comparatively large Cl1-Zr-Cl2 angle observed in C16 can also be explained by the larger carbazolyl/indenyl dihedral angle in comparison with the other complexes. Large dihedral angles between the space-demanding heteroaryl substituents and indenyls can also be responsible for larger dihedral angles between the two planes of cyclopentadienyl rings in C16 and C22 (63.28° and 63.25°) in comparison with those in III, IV,¹⁶ M6, M7, M10 and M12 (58.33-59.99°).

Propylene polymerization

The next goal was to find how these modifications of the prototypes **II–IV** translate into propylene polymerization performance, and to see if, and to what extent, the previously observed effects of certain structural changes in zirconocene $I^{11,13,14}$ can manifest themselves in 4-(*N*-carbazolyl) family of catalysts.

For propylene polymerization tests at 70 and 100 °C, the rac-zirconocene dichlorides C1-C4, C6, C10-C12, C15-C22, and dimethyl complexes M6-M8, M12, M13 were activated by MAO (molar ratio Al/Zr = 500/1). Complex MII was used as a reference. As the cationic active species formed from both variants (-ZrCl2 and -ZrMe2) of the precatalysts are believed to have identical structure, which is responsible for the MW capability of a catalyst and microstructure of iPP, the differences of those parameters in pairs of ZrCl₂/ZMe₂-based catalysts with the same ligand were neglected. On the other hand, the activity can be affected, because the dichlorides require additional step of alkylation by MAO to form the active species, whereas the dimethyl complexes are already alkylated. Thus, the lower activity of catalysts formed from the dichlorides in comparison with the reference dimethyl zirconocene MII under MAO activation is uninformative, whereas higher activity of the former can be taken into consideration. Besides

Table 1 Selected solid state structural parameters of C16, C22, M6, M7, M10, M12

	C16	C22	M6	M 7	M10	M12
X1-Zr-X2	99.88 ^{<i>a</i>}	103.59 ^{<i>a</i>}	96.83 ^b	97.46 ^b	98.97 ^b	97.66 ^b
Cp–Cp ^{,c} Hetar-Ind ^c	63.28 68.65/77.80	63.25 68.85/82.05	59.97 55.33/53.56	58.45 48.15/68.22	59.41 51.72/59.33	59.99 49.42/50.04

 a X = Cl. b X = Me. c Dihedral angle.

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that, for the purpose of a more precise comparison, a series of additional experiments with anilinium borate activator AB ([HMe_2NPh][B(C₆F₅)₄], molar ratio AB/Zr = 1.1/1) wereconducted for dimethyl zirconocenes **M5–M10** and **M13** also in comparison with **MII**.

Zirconocenes with various 4-(*N*-heteroaryls) instead of 4-(*N*-carbazolyl), activated by MAO (Table 2). Previously, we demonstrated that 4-(*N*-carbazolyl)-substituted zirconocene **II** outperformed 4-(*N*-pyrrolyl) and 4-(*N*-indolyl) analogues in terms of stereo-, regioregularity and MW of iPP produced.¹⁶ None of those contained a 2,5-disubstituted pyrrole core, which could be an alternative to the *N*-carbazolyl. However, it appeared that replacement of *N*-carbazolyl in **MII** with 2,5-dimethyl-*N*-pyrrolyl in **M13** made the latter a substantially worse catalyst in all respects, starting from the activity which dropped by an order of magnitude. The effect of additional 6-*t*Bu in **C22** on the molecular weight was much more modest than what could be expected based on the same modification of **I**.¹⁴ The large Cl-

Zr–Cl' angle in the crystal structure of C22, discussed above, can be an indirect proof of protrusion of the 2,5-methyls in the pyrrolyl into the equatorial plane of the catalyst (previously mentioned for 4-mesitiyl analogue of I^{13}) thus hindering the approach of the monomer to the metal and leading to poor activity of both M13 and C22. On the other hand, 4-(2-Ph-*N*-indolyl)-substituted C15 could compete with MII quite well being 2-fold more active at 100 °C, slightly less selective and displaying molecular weight capability close to that of the reference at both temperatures.

Zirconocenes with varied substitution in the 4-(*N*-carbazolyl) moieties, activated by MAO (Table 3). Having confirmed that the 4-(*N*-carbazolyl) substituent provides higher selectivities in iPP synthesis than the other heterocyclic analogues tested, we were interested to examine if modification of the carbazolyl itself could improve performance of MII.

Minor structural modifications of zirconocene, particularly in distant regions of the ligand, should accordingly have a

Pre-cat.	4-(<i>N</i> -azolyl) (R ₆)	<i>T</i> _p , °C	A^b	<i>M</i> _w , kDa	D^{c}	<i>T</i> _m , °C	mmmm, %	Regioerrors ^d	
								[2,1]	[3,1]
MII	Reference	70	158	575	2.1	159.1	98.5	22	7
		100	109	309	1.9	156.8	97.7	18	12
M13	2,5-Me ₂ -pyrrolyl (H)	70	8	496	1.6	153.9	98.0	13	24
		100	10	96	1.8	150.7	_	_	_
C22	$2,5-Me_2$ -pyrrolyl (6-tBu)	70	3	672	2.0	150.0	91.1	29	67
	, 210 5 ()	100	11	129	1.9	147.8	_		
C15	2-Ph-indolyl (H)	70	198	597	2.5	156.4	97.5	26	10
	5 ()	100	198	286	1.8	154.3	96.8	26	19

^{*a*} Polymerization conditions: 0.04 µmol precat. (0.06 µmol for C22), 500 eq. MAO, 4.1 mL toluene, 1.0 mL propylene, reactor quenched at 8 psig pressure loss or at a maximum time limit of 30 minutes. ^{*b*} Activity in $kg_{PP}/(mmol_{Zr} h)$. ^{*c*} M_w/M_n . ^{*d*} Number per 10⁴ monomer units.

Table 3 Propylene polymerization using zirconocenes C6, M6–M8, C10–C12, M12 activated by MAO^a

		T _p , ℃	A^b	<i>M</i> _w , kDa			mmmm, %	Regioerrors ^d	
Pre- cat.	Substitution in 4-(N-carbazolyl)				D^{c}	$T_{\rm m}$, °C		[2,1]	[3,1]
MII	Reference	70	158	575	2.1	159.1	98.5	22	7
		100	109	309	1.9	156.8	97.7	18	12
C6	$4,5-(CH_2CH_2)$	70	197	358	2.4	157.2	96.0	28	7
	, (,	100	104	196	1.6	154.6	96.0	27	19
M6	$4,5-(CH_2CH_2)$	70	252	296	2.3	157.1	97.7	27	9
	, (,	100	120	171	1.8	154.1	93.2	26	12
M7	3.6-Me ₂	70	174	442	2.0	156.8	98.4	28	8
	, 2	100	79	260	2.0	154.1	97.6	25	16
M8	2,7-Me ₂	70	163	557	2.1	159.2	96.7	25	7
	, 2	100	92	352	1.8	155.2	98.4	25	10
C10	2,3;6,7-Bis(CH ₂) ₃	70	104	602	2.2	158.0	96.9	28	4
	,,,, (2)0	100	102	240	2.0	154.1	97.5	24	13
C11	3,6- <i>t</i> Bu ₂	70	20	1006	1.5	159.2	_	_	_
	, _	100	22	304	1.4	155.1	_	_	_
C12	$2.7 - tBu_2$	70	39	674	1.6	156.9	97.5	35	2
	, _	100	7	293	1.6	152.2	97.7	32	14
M12	$2.7 - tBu_2$	70	117	505	1.7	157.6	98.3	35	3
	, 2	100	6	268	1.7	153.3	97.7	38	14

^{*a*} Polymerization conditions: 0.04 µmol precat. (0.025 µmol for C11), 500 eq. MAO, 4.1 mL toluene, 1.0 mL propylene, reactor quenched at 8 psig pressure loss or at a maximum time limit of 30 minutes. ^{*b*} Activity in kg_{PP} (mmol_{2r} h)⁻¹. ^{*c*} M_w/M_n . ^{*d*} Number per 10⁴ monomer units.

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subtle influence on the performance of the respective catalyst. Indeed, this was observed for the complexes containing small methyl or $-CH_2-$ groups in positions 2–7 of the carbazolyl moiety. One would not expect that in some cases (*e.g.* C6, M6, M7, and C10) those presumably innocent modifications had albeit predictably small but negative effect on the stereo- and regioselectivity of the catalysts which produced iPP with slightly larger number of errors and consequently lower $T_{\rm m}$ (by 1–3 °C ν s. that for MII at both polymerization temperatures). M7 also gave iPP with lower $M_{\rm w}$ at 70 °C than the reference.

Lower selectivity and molecular weight capability of C6/M6, however, is perfectly explained by the slightly different geometry of the 4,5-(CH₂CH₂)-substituted carbazolyl in comparison with the unsubstituted one, caused by the subtending effect of the $-CH_2CH_2-$ group. The contraction of the two benzene rings makes such angles as N2–C40–C41 (Fig. 2 (M6), Fig. S2†) in the carbazolyl fragment larger (133.91–134.19° in M6 and 129.84–130.33° in M7) thus decreasing steric hindrance near the catalytic site and disencumbering rotation of the carbazolyl about the C(Ind)–N bond. This is remarkable evidence of the virtually optimal geometry of *N*-carbazolyl as an aromatic substituent in position 4 of bis(indenyl) *ansa*-zirconocene isospecific propylene polymerization catalysts.

Nevertheless, 2,7-Me₂-*N*-carbazolyl-substituted **M8** appeared to be comparable with **MII** in selectivity and was able to produce iPP with somewhat higher M_w at 100 °C than the reference catalyst. The larger 3,6-*t*Bu₂ groups on the carbazolyl gave **C11** a ~1.5-fold advantage over the reference catalyst in the molecular weight capability at 70 °C, which however vanished at 100 °C. When the positions 2 and 7 in carbazolyl are occupied by two *t*Bu groups in **C12/M12**, the regioselectivity appears to be lower than that of **MII** and **M8**. Besides that, under MAO activation, a severe drop in activity at 100 °C *vs*. 70 °C was observed for both catalysts in this pair, and particularly for **M12**, for which there was a 20-fold decrease. Zirconocenes with varied substitution in positions 5, 6, and 7 of indenyls, activated by MAO (Table 4). Most of the zirconocenes in this group contain structural changes which effects on polymerization performance have been thoroughly studied recently for Spaleck-type catalysts.^{11,13,14} To our surprise, in some cases, those effects were not reproduced for the 4-(*N*-carbazolyl) catalysts.

For example, the increase of MW capability caused by additional 6-tBu groups was observed for six 6-tBu/6-H pairs of catalysts in propylene polymerization at 60 °C with an average ~2-fold difference,¹¹ and for five pairs at 100 °C with a ~2-4 fold difference.¹⁴ This effect was accompanied with higher or nearly the same stereoselectivity and lower regioselectivity that resulted in lower $T_{\rm m}$ of the obtained iPP. However, modification of II with 6-tBu groups giving zirconocene C18 did not result in an increase of MW capability of the latter, whereas the numbers of stereoerrors became higher for polymerization at 100 °C, and regioselectivity was lower at both temperatures. Furthermore, unlike the rest of the catalysts in Table 4, C18 was tested in isohexane under conditions identical to those used for II in our previous report.¹⁶ Thus, a more direct comparison with the latter results reveals that C18 produced iPP with lower $M_{\rm w}$ than II (617 kDa for C18, and 1073 kDa for II¹⁶) at 70 °C. At 100 °C II, MII, and C18 gave iPP of similar Mw, with C18 being considerably less stereo- and regioselective.

Similarly, it was previously shown that substitution of I with 5-Me on indenyls (referred to as "hard lock") limits the range of possible values of the indenyl/4-aryl dihedral angle improving stereoselectivity and MW capability at the expense of lower regioselectivity.¹⁴ In contrast with those findings, 5-Me-substituted **C16** demonstrated reduced stereoselectivity and produced iPP with lower $M_{\rm w}$ and lower $T_{\rm m}$.

On the contrary, C17 bearing smaller 5-CH₂-group that is pulled back being a part of 5-membered cycle, displayed an even slightly better stereoselectivity in comparison with **MII**.

Table 4	Pronvlene n	olymerization	usina zi	irconocenes	C16 - C21	activated by	
	Propyterie p	olymenzation	using zi	rconocenes	CI0-CZI	activated by	Y MAO

Pre-cat.		T _p ℃	A^b	<i>M</i> _w , kDa	D^{c}		mmmm, %	Regioerrors ^d	
	Deviation from MII structure					$T_{\rm m}$, °C		[2,1]	[3,1]
MII	Reference	70	158	575	2.1	159.1	98.5	22	7
		100	109	309	1.9	156.8	97.7	18	12
C16	5-Me	70	52	572	1.8	156.2	94.4	17	0
		100	74	197	1.8	155.1	95.3	18	14
C17	$5,6-(CH_2CMe_2CH_2)$	70	127	534	1.8	158.3	98.6	23	13
C17	, , ,,	100	166	215	1.9	154.9	98.1	16	29
C18 ^e	6-tBu	70	59	617	2.4	154.5	98.6	21	21
Kill Refer C16 5-Me C17 5,6-(0 C18 ^e 6-tBu C19 5-Me C20 7-Me		100	63	311	1.9	152.5	96.1	25	33
C19	5-MeO-6-tBu	70	56	861	1.9	155.6	97.6	31	10
		100	49	493	1.7	153.4	_		—
C20	7-MeO	70	68	369	1.8	158.5	99.0	27	3
		100	77	87	1.9	156.4	97.8	24	14
C21	4-(2,3,6,7-Me ₄ -carbazolyl)-5-MeO-6-tBu	70	11	1290	1.7	151.4	_	_	_
-		100	47	497	1.7	150.8	97.9	58	13

^{*a*} Polymerization conditions: 0.04 µmol precat. (0.08 µmol for C18), 500 eq. MAO, 4.1 mL toluene, 1.0 mL propylene, reactor quenched at 8 psig pressure loss or at a maximum time limit of 30 minutes. ^{*b*} Activity in kg_{PP} (mmol_{Zr} h)⁻¹. ^{*c*} M_w/M_n . ^{*d*} Number per 10⁴ monomer units. ^{*e*} Solvent: 0.5 mL toluene, 3.6 mL isohexane.

The slightly lower $T_{\rm m}$ of the iPP is probably caused by a somewhat larger number of regioerrors. At 100 °C, C17 also appeared to be ~1.5-fold active *vs.* the reference, but produced lower $M_{\rm w}$ iPP even at 70 °C despite the 5,6-dialkyl substitution, whereas both 5- and 6-Me-substituted analogues of I showed an advantage over I in this regard.¹⁴

Rieger's "ultra-rigid" metallocene Me₂Si(2-Me-4-(3,5-tBu₂-Ph)-7-MeO-Ind)ZrCl₂¹⁵ was demonstrated to have a higher stereo- and slightly lower regioselectivity resulting in higher crystallinity of iPP produced at 100 °C in comparison with its 7-unsubstituted analogue, while the M_w was somewhat lower (44 vs. 60 kDa, respectively).¹¹ C20, which is the 7-MeO-substituted II, did not show any improvement over the reference **MII** in selectivity, but the M_w of iPP produced by C20 appeared to be almost 2-fold lower at 70 °C and furthermore 3.5-times lower at 100 °C vs. **MII**.

Meanwhile, the positive effect of Resconi/Nifant'ev 5-MeO-6-tBu indenyl substitution pattern^{17,18} on the MW capability of metallocene catalysts in propylene polymerization appears to be real for the 4-(N-carbazolyl)-substituted family. Thus, at 70 °C, C19 gave iPP with 1.4-fold higher M_w in comparison with MII, and with 1.6-fold higher $M_{\rm w}$ at 100 °C. However, in line with the difference previously observed between I and Resconi/Nifant'ev catalyst,11,14,18 the regioselectivity of C19 is lower in comparison with MII. C21 containing 4-(2,3,6,7-Me₄-N-carbazolyl) moiety in addition to the 5-MeO-6-tBu substitution demonstrated the highest MW capability among the newly prepared zirconocenes outperforming C20 at 70 °C. This advantage of C21 over C19 disappeared in polymerization at 100 °C with both catalysts producing iPP with almost identical M_w. Crystallinity of iPP produced by C21 was lower than in the case of C19. Interestingly, C21 was the only catalyst in the study where activity at 100 °C was significantly higher (~4-fold) than at 70 °C.

Zirconocenes with varied substitution in position 2 of indenyls, activated by MAO (Table 5). Isopropyl groups in position 2 of indenyls in C1 dramatically deteriorate catalytic performance in comparison with **MII**. Although no regioerrors were found, stereoselectivity and MW capability dropped so significantly, that only low melting and low MW polymers were formed at both temperatures in the case of C1. Exactly the same effect was observed previously for Spaleck metallocenes.¹⁴ Substitution of one isopropyl group with methyl significantly enhanced performance of C3 in comparison with C1. There is substantially less discrepancy in the performance indicators between C3 and MII than between C3 and C1, that can be explained by chain back skip between the "2-methyl" and "2-isopropyl" sites.⁴⁹ Nevertheless, C3 was still a much worse catalyst than MII. Replacement of 2-methyls in MII with 2-isobutyls in C2 gave almost the same catalyst performance with a bit different distribution of errors, similar MW capability and slightly lower T_m for iPP produced at 100 °C which probably originates from a somewhat higher number of regioerrors. However, at 70 °C, the unsymmetrically 2-Me/ 2-*n*Bu substituted C4 was able to produce iPP with the same $T_{\rm m}$ and 1.7-fold higher $M_{\rm w}$ in comparison with MII. At 100 °C the MW capability of C4 became similar to that of MII, whereas the stereo- and regioselectivities were slightly lower, resulting in a lower iPP $T_{\rm m}$ by 2 °C νs . MII.

Selected dimethyl zirconocenes, activated by AB (Table 6). Activation of dimethyl complexes with AB allows for a more precise comparison of the respective catalysts including also evaluation of their activity. In this way, zirconocene M5 with *n*-butyl groups in position 2 of indenyls, M6–M10, M12 containing variously substituted carbazolyl moieties, and the reference zirconocene MII were tested in propylene polymerization at 70 and 100 °C.

These experiments confirmed the lower stereo- and regioselectivities and MW capability of M6 and M12 in comparison with the reference. This being said, these two catalysts appeared to be the most active in the series, with M12 exceeding 5.5 times the activity of MII at 70 °C and 3.7 times at 100 °C. The behavior of M7–M10 with alkyl-substituted carbazolyl moieties represents an interesting trend. First, M9 with tetramethyl-substituted carbazolyl appeared to generate slightly more stereo- and regioerrors than both M7 and M8 bearing 3,6-Me₂-*N*-carbazolyl and 2,7-Me₂-*N*-carbazolyl respectively, and M10 where positions 2,3 and 6,7 in the carbazolyl

Table 5 Pro	able 5 Propylene polymerization using zirconocenes C1–C4 activated by MAO ^a										
Pre- cat.		T _p , ℃					mmmm, %	Regioerrors ^d			
	R_2, R_2'		A^b	<i>M</i> _w , kDa	D^{c}	$T_{\rm m}$, °C		[2,1]	[3,1]		
MII	Me	70	158	575	2.1	159.1	98.5	22	7		
		100	109	309	1.9	156.8	97.7	18	12		
C1 ^e	iPr	70	3	47	1.5	137.7	85.4	0	0		
		100	3	11	1.4	105.3	66.3	5	10		
C2	iBu	70	71	602	1.6	158.6	98.4	28	6		
		100	55	251	1.6	155.8	97.7	19	18		
C3	Me, iPr	70	17	207	1.6	155.4	96.0	10	23		
		100	9	52	1.9	147.1	_	_	_		
C4	Me, <i>n</i> Bu	70	37	957	1.6	159.5	97.9	23	3		
		100	18	297	1.6	154.9	96.8	19	14		

^{*a*} Polymerization conditions: 0.04 µmol precat. (0.08 µmol for C1), 500 eq. MAO, 4.1 mL toluene, 1.0 mL propylene, reactor quenched at 8 psig pressure loss or at a maximum time limit of 30 minutes. ^{*b*} Activity in kg_{PP} (mmol_{Zr} h)⁻¹. ^{*c*} M_w/M_n . ^{*d*} Number per 10⁴ monomer units. ^{*e*} Solvent: 0.5 mL toluene, 3.6 mL isohexane.

Table 6 Propylene polymerization using zirconocenes M5–M10, and M12 activated with AB^a

Pre- cat.		$T_{\rm p}$, °C	A^b	<i>M</i> _w , kDa		<i>T</i> _m , °C	mmmm, %	Regioerrors ^d		
	Deviation from MII				D^{c}			[2,1]	[3,1]	
MII	Reference	70	130	815	2.3	162.1	98.8	16	5	
		100	212	222	1.8	155.4	97.3	14	13	
M5	2- <i>n</i> Bu	70	77	867	1.8	161.1	98.5	15	3	
		100	94	220	1.8	156.7	96.4	8	12	
M6	4,5-(CH ₂) ₃ - carbazolyl	70	452	366	3.2	156.1	97.1	14	11	
		100	559	131	2.3	154.2	95.6	11	20	
M7	3,6-Me ₂ -carbazolyl	70	104	830	1.9	159.6	99.1	19	5	
	· _ ·	100	133	219	1.9	156.1	97.5	15	14	
M8	2,7-Me ₂ -carbazolyl	70	113	956	2.3	159.3	98.6	21	4	
	· _ ·	100	189	312	1.8	156.0	98.2	16	13	
M9	2,3,6,7-Me ₄ -carbazolyl	70	193	674	2.6	157.3	98.1	23	8	
	• • • •	100	294	205	2.1	154.5	97.4	19	16	
M10	2,3;6,7-bis-(CH ₂) ₃ -carb.	70	87	962	2.0	159.1	98.9	23	4	
		100	185	278	1.9	157.1	97.9	17	14	
M12	2,7- <i>t</i> Bu ₂ -carbazolyl	70	717	284	3.7	154.3	98.5	20	17	
	v	100	789	150	2.4	154.9	97.8	16	24	

^{*a*} Polymerization conditions: 0.025 µmol precat., 1.1 equiv. [HMe₂NPh][B(C₆F₅)₄], 0.5 µmol Al(*n*-octyl)₃, 0.2 mL toluene, 3.9 mL isohexane, 1 mL propylene; reactor quenched at 8 psig pressure loss or at a maximum time limit of 30 minutes. ^{*b*} Activity in kg_{PP} (mmol_{Zr} h)⁻¹. ^{*c*} M_w/M_n . ^{*d*} Number per 10⁴ monomer units.

are occupied with smaller CH₂-groups included in 5-membered rings which further reduce their steric effect. In other words, the four methyl groups in **M9** is already "too much", whereas 3,6-Me₂ (**M7**), 2,7-Me₂ (**M8**), and 2,3,6,7-bis(CH₂)₃ (**M10**) is just enough. The latter two modifications of the carbazolyl also gave catalysts with better stereoselectivities at 100 °C than **MII**, the same (**M8**) or even slightly higher (**M10**) $T_{\rm m}$ and 1.3–1.4-fold higher $M_{\rm w}$ of iPP produced.

It was shown previously that the 2-ethyl homologue of I displayed better regioselectivity than the latter.¹⁴ In experiments with MAO activation, we did not see any improvements in regioselectivity of the two zirconocenes containing larger primary 2-alkyls in indenyls (2-iBu in C2 and 2-Me/2'-*n*Bu in C4) over MII. However, M5, the 2-*n*-butyl-subtitued homologue of MII, upon activation with AB gave iPP with notably less regioerrors than the reference catalyst. Together with just slightly lower stereoselectivity, this resulted in 1 °C lower T_m of iPP produced at 70 °C and 1 °C higher at 100 °C. At both polymerization temperatures, the M_w of iPP was about the same for M5 and MII. Noteworthy in 2-Me/2-Et pairs of Spaleck complexes, the 2-ethyl-substituted ones produced polymers with lower MW, with the difference being more pronounced at higher temperature.¹¹

Conclusions

In this work, we synthesized a series of analogues of promising zirconocene catalysts for high-temperature propylene polymerization, *rac*-Me₂Si(2-Me-4-(*N*-carbazolyl)Ind)₂ZrX₂ (X = Cl, Me), with various structural modifications on the indenyl and carbazolyl moieties and evaluated their effects on the catalytic performance using activation with MAO or [HMe₂NPh]-[B(C₆F₅)₄]. We applied a novel approach in the synthesis of 4/7(N-carbazolyl)indenes starting from 4/7-haloindenes. Buchwald-Hartwig reaction and electrophilic amination of the Grignard reagents derived from the 4/7-haloindenes afforded 4/7-aminoindenes, which were converted to the various 4/7-(Npyrrolyl)indenes, 4/7-(N-indolyl)indenes and 4/7-(N-carbazolyl) indenes. Some of the sterically hindered 4/7-(N-carbazolyl) indenes were unavailable by other methods. The developed pathway allowed for excellent divergence of the synthetic sequence. In the synthesis of rac-zirconocenes, we extensively applied anion-promoted meso-to-rac isomerization of ZrMe2complexes, which use was previously described only once by ourselves. A total of 22 novel zirconocenes were prepared (for six of which we determined the crystal structures by X-ray diffraction analysis) and 21 of them were tested in propylene polymerizations at 70 and 100 °C in comparison with the reference catalyst, rac-Me₂Si(2-Me-4-(N-carbazolyl)-Ind)₂ZrMe₂ (MII). In some cases, we managed to achieve better molecular weight capability at 100 °C versus the reference at the same level of stereo- and regioselectivity (zirconocenes bearing alkyl-substituted carbazolyl moieties), or at the expense of regioselectivity (5-MeO-6-tBu-indenyl substitution).

Experimental part

Starting compounds 7-bromo-2-methyl-1*H*-indene (1),⁵⁰ 3,6dimethyl-9*H*-carbazole,⁵¹ 3,6-di-*tert*-butyl-9*H*-carbazole,⁵² 8,9dihydro-4*H*-benzo[*def*]carbazole,⁵³ 4-bromo-2-isopropyl-1*H*indene (2),⁵⁴ 7-bromo-2-methyl-5-*tert*-butyl-1*H*-indene (5),⁵⁵ 7-bromo-4-methoxy-2-methyl-1*H*-indene (6),⁵⁶ 4-bromo-2,5dimethyl-1*H*-indene (16),⁵⁰ 7-bromo-5-*tert*-butyl-6-methoxy-2methyl-1*H*-indene (21),⁵⁷ 1-bromo-2-(methylethynyl)benzene,⁵⁸ 1-bromo-2-(phenylethynyl)benzene,⁵⁹ 2,2'-dibromo-4,4'-di-*tert*-butyl-1,1'-biphenyl,⁶⁰ were synthesized as previously described. Syntheses of 4-bromo-2-butyl-1*H*-indene (3), 4-bromo-2-isobutyl-1*H*-indene (4) and 4-bromo-2,2,6-trimethyl-1,2,3,5-tetrahydro-s-indacene (17) was accomplished according to the previously published procedure⁵⁰ for syntheses of various 4-bromoindenes (see ESI†). Syntheses of 2,2'-dibromo-4,4'-dimethylbiphenyl, 2,2'-di-bromo-4,4',5,5'-tetramethylbiphenyl, 6,6'-dibromo-2,2',3,3'-tetrahydro-1*H*,1'*H*-5,5'-biindene and general experimental details are described in ESI.†

Small scale propylene polymerization experiments

Propylene homopolymerizations were performed in a parallel pressure reactor setup with 48 reaction cells (PPR48), fully contained in glovebox under nitrogen. The method was generally described previously.⁶¹ A pre-weighed glass vial (5.0 mL working volume) insert and disposable stirring paddle were fitted to each reaction vessel of the reactor. For experiments with activation by MAO, toluene, a solution of MAO in toluene (500 equiv.), and liquid propylene (1.0 mL) were added via syringe. The reactor was then heated to process temperature (70 °C or 100 °C) while stirring at 800 RPM. A precatalyst solution (in toluene) was then added via syringe to the reactor at process conditions. The total amount of solvent added to the reactor, including that used for MAO and precatalysts solutions was 4.1 ml. For experiments with activation by AB, isohexane (3.8 mL,) and liquid propylene (1.0 mL) were added via syringe, and the reactor was then heated to process temperature (70 °C or 100 °C) while stirring at 800 RPM. Solutions of scavenger ((n-octyl)₃Al in isohexane), AB (1.1. equiv., in toluene), and, finally, precatalyst (in toluene) were then added via syringe to the reactor at process conditions. The total amount of toluene added to the reactor from precatalyst and AB solutions was 0.2 ml. Reactor temperature was monitored and typically maintained within ±1 °C. Polymerizations were halted by addition of approximately 50 psi O_2/Ar (5 mol% O_2) gas mixture to the reactors for approximately 30 seconds. The polymerizations were quenched based on a predetermined pressure loss of approximately 8 psi or for a maximum of 30 minutes polymerization time. Further work-up and analysis of the polymer samples are detailed in the ESI.†

Conflicts of interest

There are no conflicts to declare.

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indenes, if any of positions 4 or 7 in the indanol precursor is substituted. However, at a later step, both isomeric indenes are deprotonated to give the same indenyl anion, so the initial position of the double bond is unimportant.

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