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Ansa-zirconocenes bearing 5-NR_2-6-alkyl-4-hydrocarbyl-2-methylindenyl moieties: Synthesis, structure, stereoselective polymerization of propylene

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ABSTRACT

A series of C_2–symmetric $SiMe_2$-bridged *bis*-indenyl zirconium complexes containing 2-methyl-4-aryl/isopropyl-5-amino/pyrrolyl-6-alkylindenyl fragments have been synthesized and unambiguously characterized. These complexes activated by MAO demonstrated high catalytic activity in homo- and heterogeneous polymerization of propylene outperforming the traditional Spaleck system. The degree of electronic interaction of aminogroup in pos. 5 with indenyl ring system was tested via computational investigations, and notable influence of aminogroup on electronic structure of the complexes is witnessed by C (indenyl)–N bond order and a sum of NAC of the $ZrCl_2$ fragment.

1. Introduction

Polyolefins such as polyethylene (PE) and polypropylene (PP) remain the major industrial bulk polymers with more than 150 M ton of annual production [1]. In terms of applications, isotactic PP (iPP) is one of the most versatile polyolefin materials and enjoys a volume growth rate estimated at above 5% for the next 5 years [2]. Although heterogeneous Ziegler-Natta catalysts are still the workhorse of commercial iPP production [3], metallocene and other single-site catalysts enable the production of polypropylenes endowed with molecular properties different from Ziegler-Natta iPP [4]. Metallocenes activated by organoaluminium compounds have been known to polymerize alkenes since the early works of Natta [5a] and Breslow [5b] in the 1950's. But it is the introduction of MAO as an activator [6] that made this type of complexes especially interesting for polyolefin production. Chiral metallocenes suitable for stereoselective polymerization of propylene were introduced by Brintzinger's group in 1979 [7a]. Using these complexes, Ewen et al. formulated the symmetry rules according to which the racemic form of C_2-symmetric *ansa*-metallocenes yields isotactic polypropylene [7b]. The first isoselective molecular catalysts with commercially viable performance in propylene polymerization were introduced by Spaleck et al. [8] and have structure **I** (Fig. 1), where R^1 = Ph, R^2 = H (***rac*-I-Ph**) or R^1 = 1-naphthyl, R^2 = H (***rac*-I-Naph**). Since then, many optimizations of the metallocene structures have been made, the majority of which were variations of hydrocarbyl substituents in the bridged ligand [4a,9]. Besides that, most of the industrial polymerization processes imply heterogeneous catalysts [10], and immobilization of single-site catalysts is an important separate problem [11,12].

Abbreviations: Cp(c), centroid of the cyclopentadienyl ring of the indenyl ligand; HOMO, highest occupied molecular orbital; SPhos, 2-dicyclohexylphosphino-2′,6′-dimethoxybiphenyl.

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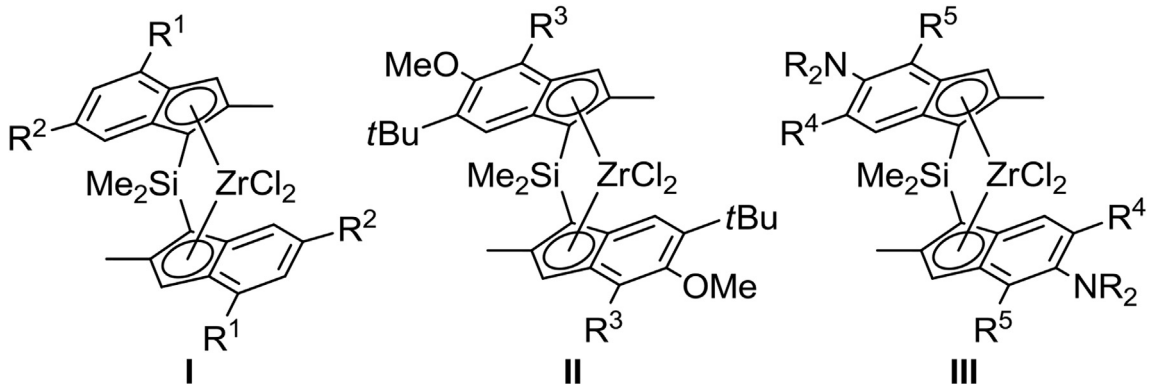


Fig. 1. Types of *ansa*-metallocene precatalysts for stereoselective polymerization of propylene.

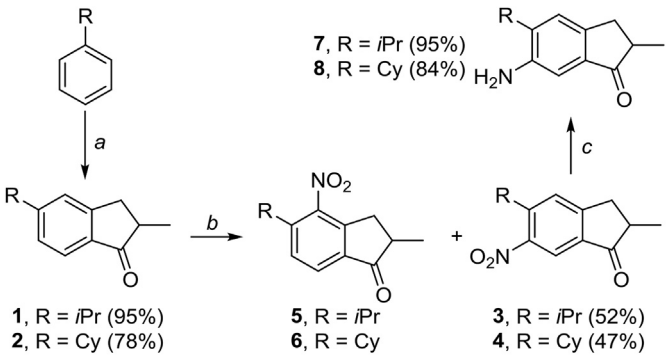
In 2007 Resconi and Nifant'ev reported the synthesis of *ansa*-metallocenes with structure **II** (Fig. 1) [13]. The complex of this type in which $R^3 = Ph$ (***rac*-II-Ph**), upon activation with MAO, exhibited significantly improved catalytic activity and molecular weight capability in polymerization of propylene compared to the complex ***rac*-I-Ph**. A significant drawback of this catalyst is a reduced regioselectivity, that notably decreases the melting point of the resultant iPP [13d,e]. Thus, the complex ***rac*-II-Ph** heterogenized via an emulsion system developed at Borealis [12] produced polypropylene with $T_m < 150\,^{\circ}C$. Linnolahti et al. [14] based on the combined computational and experimental study of complexes of type **I** (Fig. 1) revealed that *tert*-butyl group (R^2) at position 6 of indenyl fragment can induce reduction of regioselectivity. At the same time, as proposed by Nifant'ev et al., such bulky substituent situated *ortho* to a methoxy group is crucial for preventing the coordination of the organoaluminium cocatalyst components to the oxygen of the methoxy group, reducing the electron donating effect of the latter into the aromatic ring system of complexes of type **II** that can undermine their catalytic performance [15].

Looking at the positive influence of the 5-methoxy substituent in metallocenes of type **II** on their polymerization performance, it seemed reasonable to try introduction of other (potentially) donor atoms instead of oxygen in the metallocene molecule. Nitrogen-based donors are one of the most obvious options, which brings us to the complexes of structure **III**. A significant difference between the donors in **II** and **III** is that two additional substituents R are bonded to the nitrogen atom in **III** rather than one in the case of oxygen (methyl in **II**). Given this, it was reasonable to have less bulky secondary alkyl substituents R^4 in position 6 of the indenyl moieties instead of *tert*-butyl used in **II**. The positive influence of nitrogen-containing substituent(s) in Cp-type ligand of Group 4 single-site catalysts on their polymerization performance is well-documented. One representative example is so-called "heterocenes" which contain a η^5-cyclopentadienyl fragment fused to an electron-rich heterocycle, such as pyrrole [16]. One more well-performing catalyst which was commercialized by Dow Chemical is based on titanium constrained complex containing electron-donating 1-pyrrolidinyl group in the indenyl fragment [17]. At the same time, while 2-methyl-5-methoxy-6-*tert*-butylindanone-1 required for the synthesis of complexes of type **II** can be readily obtained by reaction of 2-*tert*-butylanisole and methacrylic acid under acidic conditions [13c], synthesis of analogous indanones bearing NR_2 substituents requires much more effort. However, apart from application in metallocene synthesis, compounds with 6-aminoindane skeleton might be interesting in terms of biological activity, and development of synthetic approaches to various substituted 6-aminoindanes, -indenes and -indanones can be useful for potential application in medicinal chemistry [18]. Thus, the main purpose of this study was elaboration of reliable pathways to multisubstituted 5-NR_2-indenes and racemic *ansa*-zirconocenes of type **III**. Furthermore, catalytic performance in solution propene polymerization of the catalysts derived from complexes of type **III** has been studied. To better understand the catalytic behaviour of the synthesized metallocenes under the industrially relevant conditions, several complexes were immobilized, and the catalytic performance of the obtained solid catalysts was studied on bench scale.

2. Results and discussion

2.1. Synthesis of 4-aryl-5-NR_2-6-alkyl-2-methyl-1H-indenes

In our opinion, the most practical way to the target indene bearing NR_2 substituent in the desired position starts from nitration of 5-alkyl-2-methylindan-1-ones followed by reduction of the nitro-group. Nitration of indan-1-one by a mixture of potassium nitrate and sulfuric acid, first described in 1923, was found to give a ca. 1:6 mixture of 4- and 6-nitroindan-1-ones [19]. The following reduction of the nitro- [18d-e,19] and ketone-functions [18f] as well as acid-catalyzed elimination of water from the amino-substituted indan-1-ol [18f] were well-documented also. Thus, treatment of both 6-isopropyl- (**1**) and 6-cyclohexyl-substituted substrates (**2**) by a mixture of potassium nitrate and 96% sulfuric acid gave ca. 3:1 (by HPLC) mixtures of 6-/4-nitro-isomers, i.e. **3**, **5** and **4**, **6**, respectively (Scheme 1) [20]. Pure indanone **3** was obtained after crystallization of the crude mixture from isopropyl alcohol, and analytically pure **4** was isolated by flash chromatography on silica



Scheme 1. Synthesis of the substituted 6-aminoindanones 7 and 8 (*a*. $Me_2C(Br)COBr$, $AlCl_3$, CH_2Cl_2; *b*. KNO_3, H_2SO_4; *c*. $SnCl_2$, MeOH).

gel. The nitro-group in **3** and **4** was successfully reduced using tin (II) chloride in methanol to give the respective aminoindanones **7** and **8**.

Both indanones reacted with N-bromosuccinimide in acetonitrile in the presence of ammonium acetate affording 6-amino-7-bromo-5-isopropyl-2-methylindanone-1 (**9**) and 6-amino-7-bromo-5-cyclohexyl-2-methylindanone-1 (**10**), respectively, in high yields (Scheme 2). The Negishi reaction was chosen for arylation of the bromo-substituted indanones **13** and **14** because it tolerates a broad scope of sensitive functional groups [21] including keto-group [21b] and allows coupling of sterically hindered substrates [21f]. First, NH_2 function was alkylated with methyl iodide in DMF in the presence of $NaHCO_3$.

Unfortunately, the obtained indanone **11** was found not to react with *p*-tolylzinc chloride in the presence of $Pd(PtBu_3)_2$ in THF at reflux. There are two possible explanations of the observed reactivity: first, slow oxidative addition of C–Br bond of this sterically hindered aryl bromide to the palladium, and, second, slow reductive elimination of the product due to the increased stability of an intermediate including coordination of palladium with nitrogen and/or oxygen of **11**. Less sterically hindered substrate with fewer heteroatoms in the vicinity of C–Br bond would be a better choice. In fact, indene **13** was found to react with phenylzinc chloride in the presence of $Pd(PtBu_3)_2$ in THF [21f] at reflux giving the required arylation product **15** in 53% yield along with significant amount (19%) of the respective debromination product, i.e. 5-dimethylamino-6-isopropyl-2-methyl-*1H*-indene (Scheme 2). Further on, several 4-aryl-5-dimethylamino-6-alkyl-2-methyl-1*H*-indenes were prepared using the same cross-coupling reaction. Still, the partial debromination (15–30%) of **13** and **14** observed in each case studied was an unavoidable disadvantage of the applied method. The CH-acidity of the indenes under investigation is supposed to be the reason of the observed side debromination reaction.

Presuming that increase of a steric hindrance around C–Br bond due to possible change of Me_2N group with more bulky R_2N group could lead to even lower yields of the desired products, Suzuki-Miyaura cross-coupling was used as an alternative [22]. In this way indene **15** was obtained in 51% yield which is close to the yield of **15** in the above-studied Negishi reaction. However, the debromination was not observed in Suzuki-Miyaura reaction and unreacted **13** was successfully recovered. It was anticipated that the use of a substrate bearing unsubstituted NH_2 group reducing sterical hindrance close to C–Br bond can also accelerate the cross-coupling reaction rate. In order to check this assumption, first, aminoindenes **19** and **20** were prepared as shown in Scheme 3. Further on, 7-aryl-6-amino-substituted indenes **21**–**25** were obtained in high yields and no side debromination was observed. Apparently, it is the lower sterical hindrance in the vicinity to the reaction centre in **19** and **20** compared with **13** and **14** that was the reason of better yields of the arylation products achieved in the former case. Finally, the primary amino group in **21**–**25** was readily modified by several methods as follows: (1) methylation with methyl iodide in the presence of K_2CO_3 in DMF; (2) alkylation with 1,4-dibromobutane or 1,5-dibromopentane in the presence of KI and K_2CO_3 in DMF; and (3) Clauson-Kaas reaction [23] using 2,5-diethoxytetrahydrofurane in the presence of P_4O_{10} in toluene (Scheme 3).

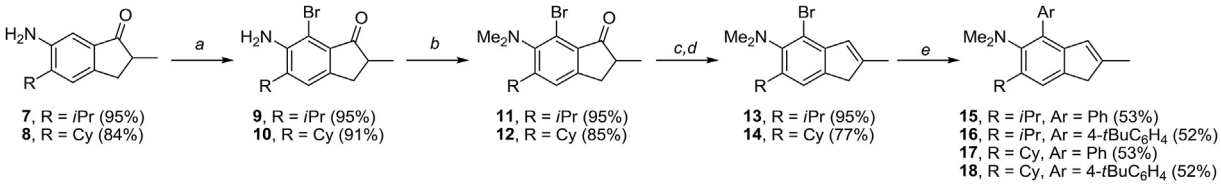
The developed procedure which utilizes 7-bromo-6-aminoindenes as a starting point for the successive arylation and functionalization of amino group allowed us to synthesize 9 indenes with various aryl and tertiary amine groups in a maximum divergent way.

2.2. Synthesis of 5,7-diisopropyl-6-R_2N-2-methyl-1H-indenes

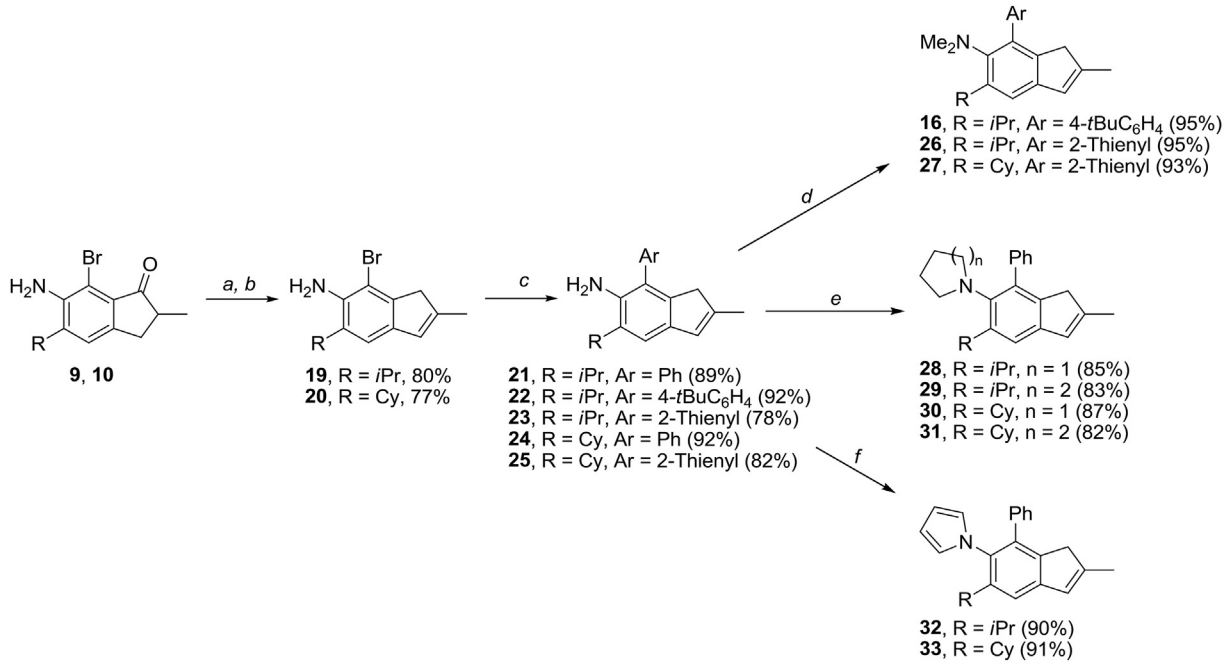
The most readily available di-*ortho*-substituted aniline with an appropriate sterical hindrance around the amino group - 2,6-diisopropylaniline – was chosen as a starting material. The first attempt to obtain 5-amino-4,6-diisopropyl-2-methylindanone-1 via acylation of mesyl-protected 2,6-diisopropylaniline with α-bromoisobutyryl bromide followed by Nazarov cyclization in presence of $AlCl_3$ failed, since one isopropyl group was cleaved under the conditions used. Another option to obtain an indanone precursor was intramolecular acylation of *N*-protected 3-(4-aminophenyl)propionic acid [24]. This method was broadly used for preparation of various indanones (see e.g. ref [25]). Synthesis of the substituted 3-arylpropionc acid started from Pd-catalyzed Heck reaction between the mesyl-protected 4-bromo-2,6-diisopropylaniline **34** [26] and methacrylic acid (Scheme 4). Water appeared to be a good medium for "ligandless" Pd-catalyzed Heck coupling of these polar substrates, and the product **35** was obtained in high yield. The following reduction of the double carbon-carbon bond in **35** to give **36** was successfully carried out using nickel boride in THF [27]. Interestingly that attempts to carry out similar reduction by formic acid [28] or molecular hydrogen in the presence of palladium (0) on charcoal [29] were not successful. Further on, **36** was converted to the respective acid chloride followed by Friedel-Crafts cyclization and deprotection of NH_2 function to give indanone **37**. This 6-aminoindanone-1 was then *N*-methylated, and the obtained product **38** was converted into indene **39** using a standard protocol. Aiming to synthesize indenes bearing various NR_2 substituents, we decided to first prepare 5-amino-4,6-diisopropyl-2-methyl-1*H*-indene (**40**) suitable for subsequent functionalization of the NH_2 group (Scheme 4). This NH_2 group was modified in three different ways giving pyrrolidinyl-, piperidinyl-, and N-pyrrolyl-substituted indanones **41**, **42**, and **43**, respectively, in high yields.

2.3. Synthesis of the bridged ligands and ansa-zirconocenes

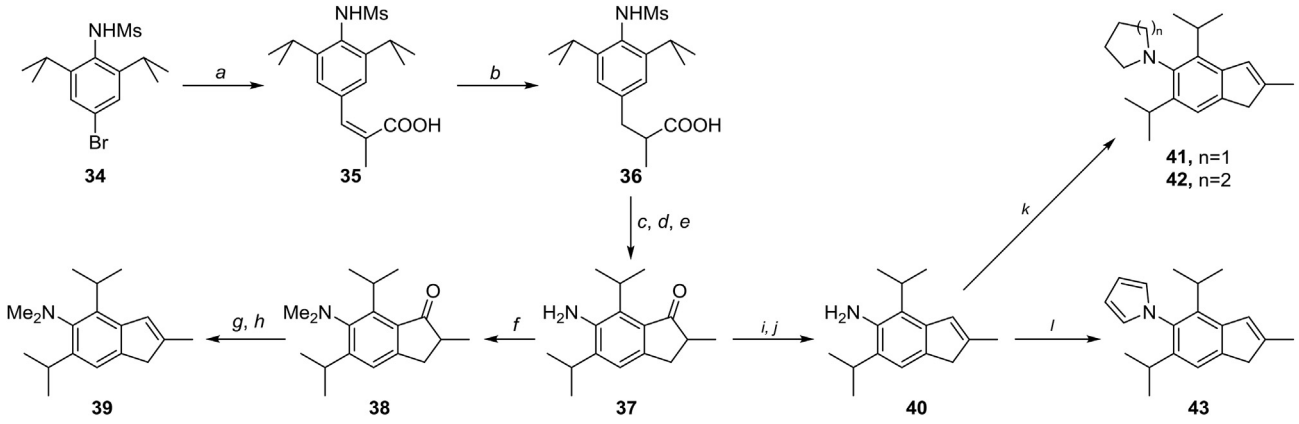
The dimethylsilylene bridged ligands **44**–**57** were prepared as mixtures of two diastereomers stating from lithium salts of the corresponding indenes and 0.5 equiv. of dichlorodimethylsilane in ether followed by chromatographic purification of the crude products (Table 1). Further on, each bridged ligand was metalated



Scheme 2. Synthesis of indan-1-ones 11, 12 and indenes 15–18 (*a*. NBS, NH_4OAc, MeCN; *b*. MeI, $NaHCO_3$, DMF; *c*. $NaBH_4$, MeOH-THF; *d*. TsOH, toluene, 110 °C; *e*. ArZnCl, $Pd(PtBu_3)_2$, THF).



Scheme 3. Synthesis of the target indenes via cross-coupling chemistry starting from NH_2-substituted indenes 19 and 20 (*a*. $NaBH_4$, THF-MeOH; *b*. TsOH, toluene, 110 °C; *c*. $ArB(OH)_2$, K_3PO_4, $Pd_2(dba)_3$, SPhos, toluene; *d*. MeI, K_2CO_3, DMF; *e*. $Br(CH_2)_{n+3}Br$, KI, K_2CO_3, DMF; *f*. 2,5-diethoxytetrahydrofurane, P_4O_{10}, toluene).



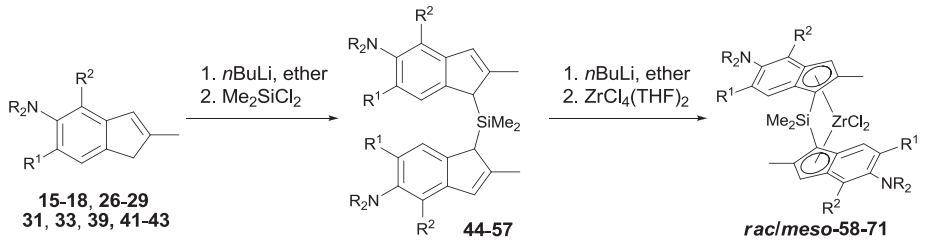
Scheme 4. Synthesis of diisopropyl-substituted indenes 39–43 (a. methacrylic acid, Na_2CO_3, $PdCl_2$, H_2O, 90%; b. $NaBH_4$, $NiCl_2$, MeOH-THF, 71%; c. $SOCl_2$; d. $AlCl_3$, CH_2Cl_2; e. H_2SO_4, 60% for three steps; f. MeI, K_2CO_3, DMF, 94%; g. $NaBH_4$, MeOH-THF; h. TsOH, toluene, 110 °C, 78% for two steps; i. $NaBH_4$, THF-MeOH; j. TsOH, toluene, 110 °C, 85% for two steps; k. $Br(CH_2)_{3+n}Br$, KI, K_2CO_3, DMF, 41: 81%, 42: 87%; l. 2,5-diethoxytetrahydrofurane, P_4O_{10}, toluene, 90%).

with 2 equivs. of *n*-butyllithium, and the obtained di-lithium salt was reacted with 1 equiv. of $ZrCl_4(THF)_2$. The following work-up procedures including crystallizations of the crude mixtures of *rac*- and *meso*-zirconocenes from suitable solvents (see *Supplementary Information* (*SI*) for the details) gave analytically pure *rac*-complexes: ***rac*-58**–**68**, ***rac*-70**, and ***rac*-71** (Table 1), polymerization performance of which was then studied. The only exception was synthesis of complex bearing 4,6-diisopropyl-5-(1-pyrrolidinyl)-2-methylindenyls which was obtained as a ca. 1 to 1 mixture of ***rac*/*meso*-69**. Unfortunately, in the latter case, isolation of pure *rac*-zirconocene was not carried out because of the very small amount of isolated mixture. The complexes ***rac*/*meso*-69** and ***rac*-70** (Table 1, entries 12 and 13) were isolated in very poor because of the low content of *rac*-isomers in the mixtures obtained in the reactions.

2.4. X-ray diffraction study of *rac*-64 and *meso*-68

Single crystals of ***rac*-64** and ***meso*-68** suitable for X-ray crystal structure analysis were successfully obtained during separation of the crude *rac*/*meso*-mixtures. The molecular structures of these compounds as established by X-ray crystallography are shown in Figs. 2 and 3, respectively. The general geometry and bonding of these complexes are quite similar to those of other analogous *ansa*-zirconocenes reported in the literature [8,9b-d,13c,27,30]. In these complexes the Zr atom adopts a distorted-pseudotetrahedral coordination. The Zr–Cl and Zr-Cp(c) distances, as well as the Cp(c)–Zr-Cp(c) and Cl–Zr–Cl angles, are comparable to those observed for the previously studied dimethylsilylene-bridged zirconocene derivatives [8,9b-d,13c,27,30]. Interestingly, the value of the Cp(c)–Zr-Cp(c) angle in the dimethylsilylene-bridged zirconocenes

Table 1
Syntheses of the *ansa*-zirconocenes of type III.



Entry	Indene	R^1	R^2	R_2N	Ligand, yield	Zirconocene, yield
1	**15**	*i*Pr	Ph	Me_2N	**44**, 42%	***rac*-58**, 27%
2	**16**	*i*Pr	4-*t*BuC_6H_4	Me_2N	**45**, 41%	***rac*-59**, 28%
3	**17**	Cy	Ph	Me_2N	**46**, 37%	***rac*-60**, 3%
4	**18**	Cy	4-*t*BuC_6H_4	Me_2N	**47**, 37%	***rac*-61**, 22%
5	**26**	*i*Pr	2-thienyl	Me_2N	**48**, 39%	***rac*-62**, 24%
6	**27**	Cy	2-thienyl	Me_2N	**49,** 44%	***rac*-63**, 43%
7	**28**	*i*Pr	Ph	1-pyrrolidinyl	**50**, 40%	***rac*-64**, 26%
8	**29**	*i*Pr	Ph	1-piperidyl	**51**, 76%	***rac*-65**, 17%
9	**31**	Cy	Ph	1-piperidyl	**52**, 42%	***rac*-66**, 23%
10	**33**	Cy	Ph	1-pyrrolyl	**53**, 40%	***rac*-67**, 21%
11	**39**	*i*Pr	*i*Pr	Me_2N	**54**, 70%	***rac*-68**, 42%
12	**41**	*i*Pr	*i*Pr	1-pyrrolidinyl	**55**, 30%	***rac*/*meso*-69** (~1:1), 2%
13	**42**	*i*Pr	*i*Pr	1-piperidyl	**56**, 70%	***rac*-70**, 4%
14	**43**	*i*Pr	*i*Pr	1-pyrrolyl	**57**, 39%	***rac*-71**, 24%

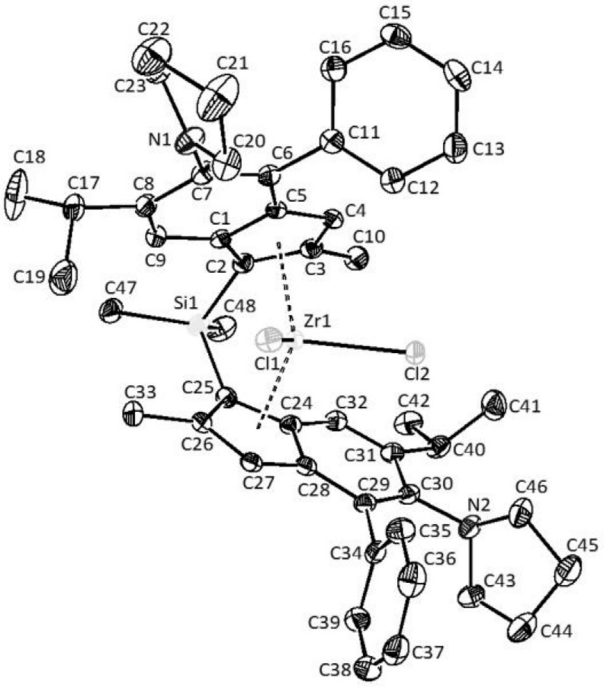


Fig. 2. Molecular structure of ***rac*-64** with the non-hydrogen atom labeling scheme. Thermal ellipsoids correspond to 50% probability. Selected bond lengths (Å): Zr (1)–Cl (1) 2.4057 (5), Zr (1)–Cl (2) 2.4220 (5), Zr (1)-Cp(c) 2.239, Zr (1)-Cp(c)' 2.244, Si(1)–C (2) 1.879 (2), Si(1)–C (25) 1.873 (2); selected bond angles (deg): Cl (1)-Zr (1)-Cl (2) 98.194 (18), C (2)-Si(1)-C (2) 95.87 (8), Cl (1)-Zr (1)-Cp(c) 105.76, Cl (1)-Zr (1)-Cp(c)' 107.21, Cl (2)-Zr (1)-Cp(c) 106.12, Cl (2)-Zr (1)-Cp(c)' 106.51, Cp(c)-Zr (1)-Cp(c)' 128.90, C (7)–N (1) 1.420 (3), C (30)–N (2) 1.429 (3).

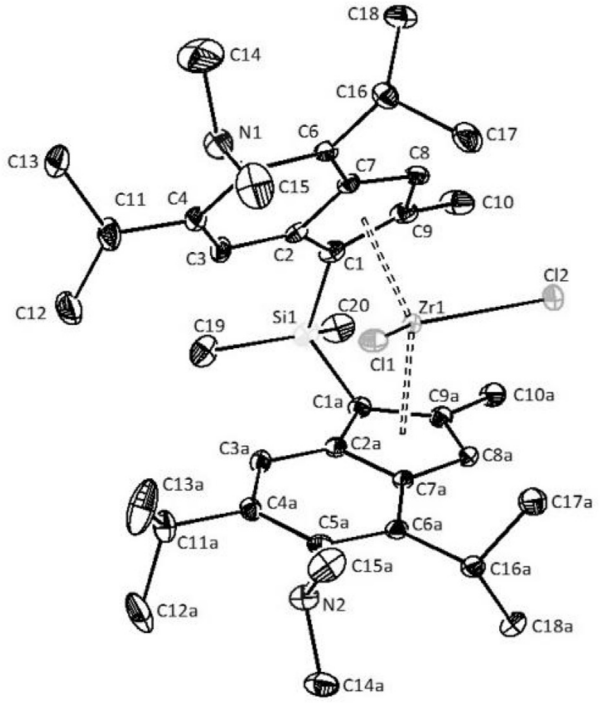


Fig. 3. Molecular structure of ***meso*-68** with the non-hydrogen atom labeling scheme. The displaced atoms are omitted for the sake of clarity. Thermal ellipsoids correspond to 50% probability. Selected bond lengths (Å): Zr (1)–Cl (1) 2.4063 (5), Zr (1)–Cl (2) 2.4438 (5), Zr (1)-Cp(c) 2.249, Zr (1)-Cp(c)' 2.245, Si(1)–C (1) 1.8774 (19), Si(1)-C (1A) 1.8692 (18); selected bond angles (deg): Cl (1)-Zr (1)-Cl (2) 100.807 (18), C (1)-Si(1)-C (1A) 96.10 (8), Cl (1)-Zr (1)-Cp(c) 106.44, Cl (1)-Zr (1)-Cp(c)' 105.12, Cl (2)-Zr (1)-Cp(c) 105.47, Cl (2)-Zr (1)-Cp(c)' 106.54, Cp(c)-Zr (1)-Cp(c)' 129.12, C (5)–N (1) 1.435 (2), C (5A)-N (2) 1.435 (2).

practically does not depend on the bulk of the substituents at Cp ligands and symmetry of the compound (the range of values is 128.90–129.12°). Structure of ***meso*-68** is similar to the other known *meso*-isomers with two coordination sites which are non-equivalent (see Zr–Cl distances, Fig. 3), one of them being sterically hindered by the C6-rings of the indenyl moieties from the top and the bottom, whereas the other is essentially unencumbered.

The pyrrolidine rings in ***rac*-64** and dimethylamino groups in ***meso*-68** are essentially rotated relative to the indenyl units. This twist can be described by the dihedral angles between the planes

defined by C (6)–C (7)–C (8) and C (20)–N (1)–C (23), C (29)–C (30)–C (31) and C (43)–N (2)–C (46) for ***rac*-64** as well as C (4)-C (5)-C (6) and C (14)-N (1)-C (15), C (4A)-C (5A)-C (6A) and C (14A)-N (2)-C (15A) for ***meso*-68**. For ***rac*-64** these values equal 68.67/84.95° whereas for ***meso*-68** they are 89.85/88.48°, respectively. This conformation should sufficiently weaken the conjugation between the nitrogen lone pair and the indenyl fragment that particularly attributed for ***meso*-68** for which Me_2N substituents are almost perpendicular to the respective indenyls. The proposed low degree of conjugation is witnessed by elongated C (indene)–N bond lengths (1.420/1.429 Å for ***rac*-64** and 1.435/1.435 Å for *meso*-**68**) compared with the mean value for the effectively conjugated C(Ar)–N bond in N-arylpyrrolydines (1.356–1.373 Å) having no bulky *ortho*-substituents [31]. Actually, in the solid state, there is strong correlation between the entire sets of C (indene)–N bond lengths and the respective dihedral angles (between the planes of the indenyl and NC_2 fragments). Furthermore, nitrogen atoms in these two complexes are slightly pyramidized, and the sum of the bond angles around them are equal to 357.5/347.6° for ***rac*-64** and 348.5/347.4° for ***meso*-68**, indicating sp^3-hybridized nitrogen in each case. An analogous situation was observed in crystal structures of *rac*-$Me_2Si(2\text{-}Me_2N\text{-indenyl})_2ZrCl_2$ [32a] and *rac*-$(2\text{-}Me_2N\text{-EBI})_2ZrCl_2$ [32b] bearing bulky Me_2Si bridging group in *ortho*-position to nitrogen. In these structures, the nitrogen atoms were found to be pyramidized and C (indene)–N bond lengths are 1.40 (2) and 1.406 (6) Å, respectively. Perhaps, the repulsion between the closely situated bridge and the amino group forces the latter to twist. Interestingly, in unbridged complexes without bulky substituents around the amino group (but with *ortho*-situated cyclopentadienyl ring), such as $[4,7\text{-}(Me_2N)_2\text{-indenyl}]_2ZrCl_2$ and $[4,7\text{-}(Me_2N)_2\text{-indenyl}]CpZrCl_2$, nitrogen atoms are pyramidized too, and C (indene)–N bond lengths were found to be 1.417/1.422 and 1.411/1.421 Å, respectively [33]. The situation is different for unbridged complexes with an aminogroup bonded with cyclopentadienyl ring not having substituents in the neighbouring position to nitrogen, such as $(2\text{-}Me_2N\text{-indenyl})_2ZrCl_2$ [32], $[2\text{-(N-morpholinyl)indenyl}]_2ZrCl_2$ [34a] and $Me_2Si(1,2,3,4,5,6,7,8\text{-octahydrofluoren-9-yl})(3\text{-pyrrolydinyl-indenyl})ZrCl_2$ [34b]. In these cases, nitrogen is almost planar, and C (indene)–N bond lengths are equal to 1.354 (7) [32], 1.349/1.381 [34a] and 1.351 Å [34b], We believe that steric interations of the methylene or methyl groups (next to the nitrogen atom) with 4-phenyl and 6-isopropyl groups are presumably responsible for the observed pyrrolidinine and dimethylamine conformations in the complexes.

Interestingly, in complexes of type **II** significant twist of the methoxy group out of indenyl plane and elongation of C (indenyl)–O bond length were observed also, but the authors studied these complexes still suggested conjugation of oxygen lone pair with π-electrons of indenyl fragment of the cationic species derived from **II** [13c,35]. The potential differences in the nature of the bonding in NR_2-substituted complexes of type **III** and RO-substituted complexes of type **II** may be due to the presence of single lone pair of electrons in the corresponding nitrogen atoms, while the oxygen atoms have two lone pairs. Thus, even if the RO fragment in the former complexes would lie in a plane that is perpendicular to the plane of the indenyl fragment, the lone pair of oxygen atom would still have the opportunity to effectively overlap with the π-system of the indenyl fragment. In type **III** complexes, similar interaction would be forbidden for the NR_2 group in its conformation when the lone pair lies in the plane of the indenyl fragment. This is the case of ***meso*-68** for which the angles between the planes of C6-ring and NMe_2 moiety are 87.87/89.29° which means that the two lone pairs lie almost exactly in the planes of the respective C6-rings. This extreme situation is not observed in ***rac*-64** structure, in which, according to the X-Ray data, the corresponding dihedral angle is 21.33/5.05°, and analogously to the oxygen-containing complexes, one can speak of more or less effective donation of a lone pair of the heteroatom to π-system of the indenyl.

2.5. DFT study of *rac*-64, *rac*-68 and related complexes

To get a more detailed picture of possible differences in bonding of heteroatomic fragments, DFT calculation was performed for ***rac*-64**, ***rac*-68** and *rac*-$Me_2Si(2\text{-Me-4-}(4\text{-}t\text{Bu}C_6H_4)\text{-5-MeO-6-}t\text{Bu-indenyl})_2ZrCl_2$ (***rac*-II-*t*BuPh**) (see *Supplementary material* for details). It appeared that the main geometrical parameters of the molecules determined experimentally (X-Ray) and via calculations (DFT) are very close for both ***rac*-64** and ***rac*-II-*t*BuPh**. Calculations confirm the presence of shortened carbon (indene)-heteroatom bonds, indicating donation of lone pair of the nitrogen atom in ***rac*-64** and oxygen in ***rac*-II-*t*BuPh** to π-system of the indenyl fragment. The presence of overlapping is also demonstrated by the characteristic form of HOMO of the studied molecules. This is also in accordance with the calculated values of the carbon (indene)-heteroatom bond orders in these molecules, i.e. 1.139 and 1.125, respectively.

It would be incorrect to compare geometric parameters of the coordination polyhedra of the zirconium atom in ***meso*-68** (X-Ray) and ***rac*-68** (DFT) structures, since they belong to different isomers. Nevertheless, the experimentally determined and calculated geometries of the Me_2N-indenyl fragments in these complexes are pretty close taking into account influence of the packing forces on conformation of the substituents in the solid state structure. At the same time, it should be noted that the N–C (indenyl) bonds in ***meso*-68** (X-Ray) and ***rac*-68** (DFT) are elongated compared to similar bonds in ***rac*-64** complex. This indicates a significantly poorer conjugation of the lone pair on the nitrogen atom with the π-system of indenyl in ***rac/meso*-68**. The DFT calculation gives a value for the bond order of N–C (indenyl) in ***rac*-68** equal to 1.066 which is significantly lower than that of ***rac*-64** complex.

Additional evidences of the poor conjugation in ***rac*-68** (compared to ***rac*-64**, where the overlapping is essential) are calculated values of a sum of net atomic charges (NAC) of $ZrCl_2$ fragment in ***rac*-64**, ***rac*-68** and similar complexes that do not contain substituents in pos. 5 of indenyls (Table S5, *Supplementary material*). After excluding NR_2 substituents from ***rac*-64** (as well as OMe substituents from ***rac*-II-*t*BuPh**) the calculated value of a sum of NAC of the $ZrCl_2$ fragment increases significantly. A similar manipulation with ***rac*-68** is accompanied by a slight change in the value of a sum of NAC of the $ZrCl_2$ fragment, indicating the weak π-donor properties of the NMe_2 fragments in this compound (π-donation is almost completely compensated by electron withdrawing effect of the electronegative nitrogen atom). The lack of effective interaction is also indicated by the shape of HOMO-orbitals of ***rac*-68**. Origin of this phenomenon (when NMe_2 does not exhibit electron donation properties in certain steric surrounding) could be attributed to the twisted conformation of NR_2 with respect to indene, which does not allow for the overlapping of the orbitals of lone nitrogen pair with the π-orbital of indenyl. In turn, the observed specific rigid conformation of the NMe_2 substituent in pos. 5 of each indenyl in ***rac*-68** is explained by steric repulsion from the neighbouring isopropyl groups in pos. 4 and 6.

2.6. Homogenous polymerization of propylene

Performance of the obtained *rac*-zirconocenes activated by MAO (Al/Zr = 500) was first studied in polymerization of propylene under homogeneous conditions in toluene at 70 °C [36]. These small scale experiments, including those conducted in the presence of molecular hydrogen, were performed in 8 ml glass vials using

Table 2
Propylene polymerization in toluene solution.[a]

Entry	Cat.[a]	p (H_2)[b], mbar	Activity[c]	T_m[d], °C	M_w[e], kDa	PDI[e]
1	**58**	0	84	-	1103	1.4
2	**58**	5.17	94	149.7	1026	1.4
3	**58**	10.34	71	149.1	398	1.4
4	**60**	0	185	148.5	912	1.3
5	**60**	10.34	353	147.8	322	1.6
6	**61**	5.17	107	151.2	950	1.4
7	**61**	10.34	266	151.9	425	1.3
8	**63**	0	74	145.1	84	1.5
9	**63**	10.34	535	144.4	28	1.4
10	**64**	0	146	149.8	884	1.6
11	**64**	5.17	161	-	718	1.6
12	**64**	10.34	132	149.1	460	1.5
13	**65**	0	41	146.6	717	1.8
14	**65**	5.17	90	-	409	1.9
15	**65**	10.34	135	147.8	256	1.7
16	**66**	0	151	146.7	690	1.5
17	**66**	5.17	425	145.5	253	1.5
18	**66**	10.34	522	-	242	1.5
19	**67**	0	20	147.9	1431	1.7
20	**67**	10.34	26	148.5	383	1.5
21	**68**	5.17	79	155.5	21	1.7
22	**I-Ph**	0	44	-	915	1.5
23	**I-Ph**	5.17	63	157.1	1000	1.5
24	**I-Ph**	10.34	244	158.8	403	1.5

[a] Polymerization conditions: 0.006–0.010 μmol precatalyst, 500 equivs of MAO, 3.0 ml propylene, 2.0 ml toluene, 70 °C. Reactor quenched at a time limit of 10 min.
[b] Hydrogen was added as H_2/N_2 mixture 0.5%/99.5%, press, partial pressure is given.
[c] Activity: kg (PP)·mmol (Zr)$^{-1}$·h^{-1}.
[d] Determined via differential scanning calorimetry.
[e] Determined using rapid gel permeation chromatography in 1,2,4-$C_6H_3Cl_3$ at 135 °C versus polystyrene standards.

Symyx high-throughput setup described elsewhere [37] (for full experimental details see *Supplementary material*). The obtained data are collected in Table 2. The well-known Spaleck's complex *rac*-Me_2Si(2-Me-4-Ph-Ind)$_2ZrCl_2$ (***rac*-I-Ph**) [8] activated by MAO (i.e. catalyst **I-Ph**) was chosen as a reference system.

In the absence of hydrogen, most of the tested catalysts exhibited comparable or higher activities (41–185 kg (PP)·mmol (Zr)$^{-1}$·h^{-1}) than **I-Ph**. Upon activation with MAO ***rac*-60** showed a 4.2-fold increase in activity versus the reference Spaleck's system (entry 4 *vs.* entry 22, Table 2). The catalyst **67** bearing aromatic N-pyrrolyl group in pos. 5 demonstrated the lowest activity in the tested series (entry 19) which can result from a lower stability of the pyrrolyl substituted metallocene under the used conditions. Regarding the influence of the substituent R^1 (Fig. 1) on the catalyst performance, the cyclohexyl group is more promising in terms of activity than the isopropyl group (**58** *vs.* **60**, or **65** *vs.* **66**), probably, since the former seems to better protect nitrogen from possible coordination with MAO. On the other hand, the substitution pattern in pos. 5 (*i*Pr *vs.* Cy) does not influence much on M_w and T_m (Table 2) of the produced PP. Additionally, the influence of structure of NR_2 moiety on activity could be elucidated from comparison of the catalysts within two groups (1) **58**, **64** and **65**; and (2) **60**, **66** and **67**. As it can be seen from the results, the best choice of NR_2 in the case of the first group of complexes was 1-pyrrolidinyl (**64**), though, in the second case, it was NMe_2 (**60**). Thus, the activity of the catalysts drops in the following order: 1-pyrrolidinyl > NMe_2 > 1-piperidinyl > 1-pyrrolyl (if all other structure parameters are almost the same). Interestingly that the molecular weight capability trends are very similar, and M_w of PP decreased in the same order. This is not the case for T_m of the formed PPs which are comparable for the complexes bearing 4-Ph or 4-(4-*t*BuC_6H_4) and 5-(1-pyrrolidinyl) or 5-NMe_2 but noticeably lower for 5-(1-piperidinyl) substituted catalysts **65** and **66**. It should be noted that the reference catalyst **I-Ph** gave PP with higher T_m (~159 °C) than other catalysts under investigation (~144–150 °C). The higher T_m of PP means the fewer total number of stereo- and/or regiodefects in the polymer [38,39]. According to ^{13}C NMR of PP obtained with the system ***rac*-66**/MAO (Fig. S3, *Supplementary material*) the polymer is highly isotactic with [mmmm] > 99% ([mrrm] < 0.2%). On the other hand, the measured amount of [1,2]-regioerrors is 1.0 mol % ([1,3]-regioerrors were not found) which is significantly higher than that in iPP obtained with **I-Ph** [40].

For the most catalysts studied, the activity significantly increased with addition of 5.17 or 10.34 mbar of hydrogen along with a sharp drop in the molecular weight of PP. This is, actually, a common phenomenon for catalytic propylene polymerization using single-site catalysis [41]. However, for **58** and **64**, the activity only slightly increased (at 5.17 mbar H_2) or even slightly decreased (at 10.34 mbar H_2) at simultaneous drop of M_w of the formed PP (entries 1–3 and 10–12 respectively, Table 2) that is quite unusual for *ansa*-metallocene catalysts [41d]. As it was postulated in the literature, the enhancement of catalytic activity in the presence of hydrogen is related with reactivation of the dormant sites originated from 2,1-insertions of propylene into Zr^+-Polymer bond [41].

It is known that insertion of sterically demanding substituents such as *tert*-butyl in pos. 6 of the indenyls was found to decrease regioselectivity of the catalyst and lead to an increase of 2,1-regioerrors [13c,14]. In the case of catalytic system based on precatalysts of type **III** (Fig. 1), the more sterically demanding substituents are at pos. 5 and 6 of the precatalyst the lower T_m of the resulting polymer (compare *i*Pr vs. Cy: entries 1–2 *vs.* 4–5 and 13–15 *vs.* 16–18; compare NMe_2 and $N(CH_2)_4$ *vs.* $N(CH_2)_5$: entries 1–3 and 10–11 *vs.* 13–15, Table 2). Apparently, the cyclohexyl or isopropyl groups at pos. 6 in combination with disubstituted

Table 3
Propylene polymerization of supported catalysts.[a].

Entry	Complex	Catalyst	Al (%)[b]	Zr (%)[b]	Al/Zr[b]	Activity, kg (PP)·mmol (Zr) $^{-1}$·h^{-1}	MFI, g/10 min
1	***rac*-60**	**Cat-60**	20.10	0.26	261	1159	1.7
2	***rac*-61**	**Cat-61**	22.70	0.29	264	654	1.7
3	***rac*-63**	**Cat-63**	20.80	0.30	234	292	n.d.[d]
4	***rac*-64**	**Cat-64**	27.50	0.29	320	1035	n.d.[d]
5	***rac*-65**	**Cat-65**	22.50	0.33	230	717	n.d.[d]
6	***rac*-66**	**Cat-66**	25.00	0.30	281	1431	2.0
7	***rac*-67**	**Cat-67**	24.40	0.32	258	100	n.d.[d]
8	***rac*-I-Ph**	**Cat-I**	25.50	0.38	227	276	0.6
9	***rac*-II-Ph**[c]	**Cat-II**	23.50	0.32	248	1286	0.3

[a] Polymerization conditions: 11.2–31.1 mg catalyst in 5 ml hexadecafluoro-1,3-dimethylcyclohexane, 200 μl Et_3Al as a scavenger in 5.0 mL pentane, 6 mmol of H_2, 1100 g propylene. Temp. 70 °C. Reactor quenched at a time limit of 30 min.
[b] Determined by inductively coupled plasma elementary analysis (ICP).
[c] Ref. [13b].
[d] Not determined.

aminogroup at pos. 5 of the indenyls are enough to increase content of 2,1-insertions which leads to the increased amount of [1,2]-regioerrors in iPP and dormant sites in catalytic system.

2.7. Slurry polymerization of propylene

Immobilized catalysts for bench scale slurry polymerization were prepared according to the procedure described in example 5 of ref. [12a] using hexadecafluoro-1,3-dimethylcyclohexane as the continuous phase, a mixture of perfluoroalkylethyl acrylate esters having different perfluoroalkyl chain lengths as the surfactant precursor, and the desired *rac*-zirconocene dichloride. The catalyst particles consist of solid mixture of MAO and the selected *rac*-zirconocene (alkylated and cationized by MAO) with Al/Zr ratio equal to 230–320 (Table 3).

The polymerization experiments have been performed in a 5 L reactor in liquid propylene in the presence of molecular hydrogen at 70 °C. The catalyst composition data and polymerization results obtained are collected in Table 3 (for full experimental details, see the *Supplementary material*) [42]. Similarly prepared solid catalysts **Cat-I-Ph** and **Cat-II-Ph** based on ***rac*-I-**Ph [8] and *rac*-Me_2Si(2-Me-4-Ph-5-MeO-6-*t*Bu-Ind)$_2ZrCl_2$ (***rac*-II-Ph**) [13], respectively, were chosen as the reference catalysts. The polymerization data obtained and included in Table 3 mostly describe the activity of the obtained catalysts. Several resultant PP samples were characterized by Melt Flow Index (MFI). In general a lower MFI indicates a higher molecular weight of the polymer. The immobilized indenyls were found to give PP samples with lower molecular weight (resulting in higher MFI values) than both reference catalysts. Considering structure-activity trends for the studied series of the heterogeneous catalysts, one can conclude that they behave similarly to the respective homogeneous catalysts in the presence of 5.17 mbar of H_2. The absolute activities of the immobilized catalysts studied on bench scale were found to be several times higher than activities obtained in small-scale screening experiments performed for the respective homogeneous catalysts. Within the series, the best immobilized catalyst in terms of activity was found to be **Cat-66** based on ***rac*-66** (entry 6, Table 3), and its activity was 5.5 and 1.1 times higher than activity of the reference catalysts **Cat-I-Ph** (entry 8, Table 3) and **Cat-II-Ph** (entry 9, Table 3), respectively. At the same time, the MFI of the polymer obtained with **Cat-66** is significantly higher than that obtained with the reference catalysts. These results clearly indicate that although the introduction of nitrogen as a donor atom instead of oxygen in pos. 5 of the indenyl moieties can give propene polymerization catalysts of comparable or even higher activity, this change lead to the significant drop of molecular weight of the resultant polymer.

3. Conclusions

In the present work, we successfully developed a synthetic approach to different 6-alkyl-4-aryl-2-methyl-5-NR_2-substituted indenes from readily available alkylbenzenes. The synthetic step of introduction of amino group into the indane skeleton was achieved via nitration of 6-alkyl-2-methylindanone-1 followed by reduction with Sn(II) chloride. The key step of installation of the required aryl substituents was performed by Suzuki-Miyaura cross-coupling reaction on the substrate containing primary unprotected amino group. Additionally, synthesis of various 4,6-diisopropyl-2-methyl-5-NR_2-substituted indenes from 2,6-diisopropylaniline was accomplished. Afterwards, we successfully synthesized the respective *ansa*-zirconocenes of this novel family bearing NR_2 groups in pos. 5 of the indenyls. Structures of two complexes – ***rac*-64** and ***meso*-68** – were established by X-ray crystallography. The obtained metallocenes activated by MAO were found to be active and isoselective catalysts of propylene polymerization in toluene solution at 70 °C. The best of the tested catalysts exhibited higher activity in solution than the reference catalyst based on *rac*-Me_2Si(2-Me-4-Ph-Ind)$_2ZrCl_2$. It was shown that complexes with cyclohexyl substituents on pos. 6 of the indenyl moieties are more responsive to addition of hydrogen than their isopropyl substituted analogues which might be an evidence of higher regioselectivity of the latter. ***Rac*-60**, ***rac*-61** and ***rac*-63**–**67** were immobilized, and polymerization performance of the obtained catalysts was studied. The results obtained for heterogenized complex ***rac*-66** clearly demonstrated that introduction of nitrogen instead of oxygen in metallocene can increase activity of the corresponding immobilized propene polymerization catalysts compared to the reference complex *rac*-Me_2Si(2-Me-4-Ph-5-MeO-6-*t*Bu-Ind)$_2ZrCl_2$ immobilized on MAO, but at the expense of iPP molecular weight.

4. Experimental

Full experimental procedures, computational details and experimental data are provided in the *Supplementary material*.

Authors contributions

L.R. supervised the project as the author of the idea, P.S.K., I.A.P., A.N.T. and A.F.A. designed and performed the synthetic experiments, D.V.U., A.Z.V. and V.V.I. directed the synthetic studies and analyzed the data, N.A., T.V., R.V. and P.C. performed and analyzed the polymerization experiments, G.P.G. conducted the computational studies, P.S.K., D.V.U., L.R. and A.Z.V. prepared the manuscript.

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Appendix A. Supplementary data

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