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ARTICLE

Asymmetric *ansa*-Zirconocenes Containing a 2-Methyl-4aryltetrahydroindacene Fragment: Synthesis, Structure, and Catalytic Activity in Propylene Polymerization and Copolymerization

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Supporting Information

ABSTRACT: A set of asymmetric bis-indenyl zirconium SiMe₂bridged *ansa*-complexes, containing 2-isopropyl-4-arylindenyl and 2-methyl-4-aryltetrahydroindacenyl fragments, have been synthesized. These complexes demonstrate better catalytic activity, stereoselectivty, and polymer molecular weight capability in propylene homo- and copolymerization in comparison to analogues without a tetrahydroindacenyl fragment.



■ INTRODUCTION

Today, after more than 25 years of studies on finding effective single-site catalysts for propylene isotactic polymerization, researchers are more and more often addressing the processes of obtaining saturated hydrocarbon copolymers of different composition and origin.

These compounds, which combine elasticity, impact resistance, and strength, could potentially be used for substitution of polyvinyl chloride and polydiene polymers and copolymers. Ethylene—propylene copolymers containing relatively long (more than 10 subunits) isotactic polypropylene fragments with ethylene insets as well as heterophasic copolymers with rubber fractions of more uniform composition seem to be of particular industrial interest.¹ Obviously, only group 4 *ansa*metallocenes or similar sterically rigid single-site metal complexes that can catalyze isotactic polypropylene formation (i.e., that have C_1 or C_2 symmetry) would catalyze the formation of copolymers of this type.²

Unlike Ziegler–Natta classical heterogeneous catalysts, the comparative activity of different structural type zirconocenes in reactions with ethylene and propylene is widely variable. Zirconocene dichloride, the simplest specimen of the class, catalyzes ethylene polymerization in the presence of MAO, though it

appears to be much less active in propylene polymerization. On the other hand, dimethylsilylenebis(2-methyl-4-phenylindenyl)dichlorozirconium (1) (Scheme 1), an effective propylene polymerization catalyst,³ is less productive for ethylene.⁴ So, we can regard type 1 *ansa*-complexes as prototypes for the creation of effective stereoregular ethylene—propylene copolymerization catalysts.

The use of type 1 zirconocenes for the preparation of high molecular weight, low ethylene content copolymers has been described.⁵ However, preparation of higher ethylene content copolymers has been limited due to transfer to ethylene termination reaction associated with this type of *ansa*-metallocene structure.^{2a,5} One of us⁶ showed that the replacement of one methyl group in position 2 of the indenyl ring by an isopropyl substituent in bis(2-methyl-4-arylindenyl) complexes (structure 2, Scheme 1) would lead to a noticeable change of these complexes' catalytic properties, compared to type 1 symmetric complexes. In particular, homopolymers with increased regioselectivity and polymer melting points were observed, and adding ethylene to the catalytic system based on complex 2 does not result in a significant decrease of the polymer molecular

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weight,^{6b,7} although the catalytic activity of **2** decreases slightly. Also, type **2** metallocenes could be supported on silica without significant deactivation.

Zirconocenes' catalytic activity can also be stimulated by the addition of electron-donor substituents to the indenyl fragments of the corresponding ligands, which would increase stability of alkylzirconocene cationic intermediates and the concentration of catalytic centers. Applying these substitutions to *ansa*-complexes' lateral positions adjacent to the pendent phenyl group can also provide subtle changes to ligand sterics at the monomer co-ordination site. Methyl substituents at these positions have been described for type **2**, type **1**, and similar heterocyclic-containing *ansa*-complexes with increases in catalyst stereoselectivity and polymer molecular weight capability being reported. ^{6b,8,9} Recent theoretical and experimental research^{10,11} suggest that derivatives of 1,5,6,7-tetrahydro-*s*-indacene might be used as perspective indenyl-type electron-donor ligands, which resulted in target structural type **3** (Scheme 1).

RESULTS AND DISCUSSION

In an effort to address the role of the electron-donor indenyltype unit, we prepared a number of substituted tetrahydroindacenes and type 3 zirconocenes therefrom and tested their



Scheme 3

catalytic activity in propylene polymerization and ethylene-propylene copolymerization.

Preparation of Indenes. The commonly used effective method of 2-methyl-4-arylindene synthesis starts from 2-methyl-4-haloindanone and includes a Suzuki coupling reaction and reduction of 2-methyl-4-arylindanone to the corresponding indanol with subsequent dehydration.¹² The key intermediate in the preparation of the target tetrahydroindacenes is 2-methyl-3,5,6,7-tetrahydro-*s*-indacen-1(2H)-one (4).

There are quite a few common methods for substituted indanone synthesis, the most simple of which is arene acylation by halogencarbonic or unsaturated carbonic acids derivatives followed by Nazarov cyclization of the intermediate aryl vinyl ketones. This reaction proceeds nonselectively for alkyl- and 1,2-dyalkylbenzols.⁶ Indane, to the contrary, usually produces a specific isomer, compound 4.¹³ 2-Bromo-2-methylpropionyl bromide (catalyst 2.2–2.5 equiv of AlCl₃, CH₂Cl₂) was used as the acylation agent. Methacryloyl chloride can also be used in this reaction, but the accompanying polymeric byproduct adversely affects the synthesis and purification of the product. The bromating reaction with compound 4 was shown to be possible in the same reaction mixture with no significant decrease in yield of the resulting 4-bromohexahydroindacenone 5 yield, so there is no need for the isolation and purification of 4 and its analogues.

Suzuki coupling reactions with 5 gave 4-arylhexahydroindacenones 6-8, and their further reduction and dehydration resulted in aryltetrahydroindacenes 9-11 (Scheme 2).

Reacting compound 4 with two equivalents of Br_2 produced dibromoderivative 12, the arylation of which by the Suzuki method with subsequent reduction/dehydration resulted in diaryltetrahydroindacene 14 (Scheme 3).

Preparation of Bis-indenyl Ligands and Zirconocenes. The most common method of obtaining asymmetric bis-indenyl compounds with a dimethylsilylene bridge is the interaction of lithium and chlorodimethylsilyl derivatives of the corresponding indenes. The bis-indenyl compound (complex 2 "ligand") was obtained previously in high yield by the usage of CuCN as catalyst and ether solvent.⁶ The same method was used for the synthesis of bis-indenyl compounds 15–18 (Scheme 4).

Zirconocene 2 was synthesized by reacting the dilithium derivative of bis-indenyl ligand with $ZrCl_4$ in an ether—toluene solvent system. The pseudo-*rac*-form was isolated by fractional crystallization.⁶

The reaction of dilithium derivatives of **15** and **16** and ZrCl_4 in ether and etheral solvents, toluene, or $\operatorname{CH}_2\operatorname{Cl}_2$ did not result in a high yield of the target zirconocenes. The reactions were accompanied by a large amount of polymeric byproduct, which adversely affected the yield of *ansa*-zirconocenes and separation of diastereometric forms. The reaction of dilithium derivatives **15** and **16** and ZrCl₄ in an inert solvent (pentane) with minimum quantities of ether proved to be a significantly more effective synthesis method. Following these conditions *ansa*-complexes **19** and **20** were finally obtained as a mixture of pseudo-*rac*- and



pseudo-*meso*-forms in \sim 1:1 ratio. This stage of the experiment appeared to be the most difficult due to the fact that type 3 compounds proved to be more soluble than compound 2 despite the approximately similar solubility of their diastereomeric forms: using crystallization methods for diastereomer separation was unsuccessful.

At the same time, **21** and **22** were obtained as a mixture of diastereomers with moderate yield (\sim 70%) by the reaction of **17/18** dilithium derivatives with ZrCl_4 in a \sim 1:1 ether—pentane mixture. Pure pseudo-*racemic* **21** and **22** were separated by crystallization from toluene with moderate to low (22% and 3.5%) yields.

A method for generating pure *rac*-forms of *ansa*-zirconocenes by continuous heating of *rac*-*/meso*-mixtures in dimethoxyethane (or in other etheral solvents) in the presence of lithium or magnesium chlorides was suggested in ref 14. The authors demonstrated that a quantitative conversion of the *meso*-form into the *rac*-form could be obtained under these circumstances for some bis-indenyl complexes. We tried this approach with *rac/ meso*-mixtures of **19** and **20** monitoring the course of the reaction by taking reaction mixture samples and scanning them by ¹H NMR spectroscopy. The results showed prolonged heating of the diastereometric mixtures in DME together with LiCl led to a gradual disappearance of the pseudo-*meso*-form complexes' signals and simultaneous appearance of nonidentified broadened signals although the relative intensity of the pseudo-*rac*-forms did

Scheme 4



Scheme 5

not increase. We can therefore conclude that in the case of nonsymmetric **19** and **20** complexes there is no rearrangement of the pseudo-*meso*-forms into the pseudo-*rac*-forms. However the foremost ones break up and allowed us to isolate the diaster-eometrically pure pseudo-*rac*-**19**/**20**, although with a moderate yield. In contrast, continuous heating of the **21** and **22** *rac*-/*meso*-mixture in dimethoxyethane leads to simultaneous decomposition of diastereomers with final complete dissipation of zirco-nocene signals in the ¹H NMR test. Structural formulas of pseudo-*rac* forms of the obtained complexes are given in Scheme 5.

X-ray Structure Determination of 20. The molecular structure of racemic complex 20 is shown in Figure 1. Selected bond lengths and angles are listed in Table 1. The coordination environment of the Zr atom may be treated as a distorted tetrahedron (assuming that η^5 -C₅ rings occupy one coordination site). The Zr-C distances vary over a wide range, 2.457(5)-2.636(5) Å. The latter is typical for indenyl zirconium complexes^{15,16} and reflects the tendency of Zr atoms to form a η^3 , η^2 linkage with indenvel ligands. As expected, the Zr-C(3) and Zr-C(33) bonds are the shortest since these carbon atoms are linked by a small-scale -SiMe2spacer. Both indenyl ligands are planar within 0.057(4) Å and form a dihedral angle of 64.2(1)°. The Cambridge Structural Database (ver. 5.31, May 2010) contains data for 24 nearly related ansabis(indenyl)zirconocene dichlorides with a -SiMe₂- bridge.¹⁷ The main geometric parameters of molecule 20 are very close to the respective average values retrieved from CSD (see Table 1).

Polymerization Results. Complex **23** synthesized before⁶ was used for comparison.

The results of a series of propylene polymerizations using supported complexes (silica, activation by MAO) in liquid propylene at 65 °C are summarized in Table 2. Propylene polymerizations were done both in the absence and in the presence of hydrogen (0.5 L per 1 L of liquid monomer). As can be seen from the table, there is a wide range of catalytic activity observed and hydrogen has a significant activating effect on all the catalysts.

The obtained data clearly show that substitution of the specific indenyl fragment with the methyl group in the 2 position by tetrahydroindacenyl can sometimes lead to significant increases in catalytic activity and polypropylene molecular mass. The ligand effects on polymer $T_{\rm m}$ are more subtle; however the general trend is higher isoselectivity with complexes incorporating the tetrahydroinacenyl moiety.





Figure 1. Molecular structure of 20. Displacement ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Angles ((deg) for 20 and Respective Geometric Parameters from CSD Data for ansa-[$(\eta^{s}$ -
Inden-1-yl) ₂ SiMe ₂]ZrCl ₂ Derivatives	

20				CSD data, range (average)			
Zr(1)-Cl(1)	2.4159(16)	Zr(1)-Cl(2)	2.4113(16)	Zr-Cl	2.393-2.454 (2.423)		
$\operatorname{Zr}(1) - \operatorname{Cp}(1)^a$	2.238	$Zr(1) - Cp(2)^*$	2.234	Zr-Cp	2.225-2.272 (2.241)		
Zr(1)-C(3)	2.457(5)	Zr(1) - C(33)	2.471(5)	Zr-C _{Cp}	2.404-2.517 (2.467)		
Zr(1)-C(2)	2.523(5)	Zr(1) - C(32)	2.499(5)		2.441-2.575 (2.493)		
Zr(1)-C(4)	2.521(5)	Zr(1) - C(34)	2.531(5)		2.477-2.592 (2.549)		
Zr(1)-C(1)	2.608(5)	Zr(1) - C(31)	2.578(5)		2.545-2.631 (2.584)		
Zr(1)-C(9)	2.626(5)	Zr(1) - C(42)	2.636(5)		2.604-2.681 (2.644)		
Si(1) - C(3)	1.858(5)	Si(1) - C(33)	1.875(6)	Si-C _{Cp}	1.855-1.905 (1.876)		
C(1) - C(2)	1.405(7)	C(31) - C(32)	1.413(7)	$C_{Cp}-C_{Cp}$	1.367-1.442 (1.406)		
C(2) - C(3)	1.437(7)	C(32)-C(33)	1.424(7)		1.339-1.535 (1.434)		
C(3) - C(4)	1.469(7)	C(33)-C(34)	1.457(7)		1.400-1.516 (1.447)		
C(4) - C(9)	1.428(7)	C(34) - C(42)	1.437(7)		1.288-1.660 (1.439)		
C(9) - C(1)	1.422(7)	C(42) - C(31)	1.419(7)		1.387-1.446 (1.412)		
Cl(1)-Zr(1)-Cl(2)	96.86(5)			Cl-Zr-Cl	94.2-100.1 (97.1)		
Cp(1)-Zr(1)-Cp(2)	127.9			Cp-Zr-Cp	126.3-129.5 (128.2)		
C(3)-Si(1)-C(33)	94.4(2)			C _{Cp} -Si-C _{Cp}	94.1-95.7 (94.9)		
C(23)-Si(1)-C(24)	103.7(3)			Me-Si-Me	100.0-112.1 (108.0)		
C(2) - C(3) - Si(1)	127.2(4)	C(32) - C(33) - Si(1)	127.2(4)	C _{Cp} -C _{Cp} -Si	118.9–129.1 (124.7)		
C(4) - C(3) - Si(1)	124.6(4)	C(34) - C(33) - Si(1)	124.1(4)	C _{Cp} -C _{Cp} -Si	121.9-132.5 (126.7)		
Cp(1) - C(3) - Si(1)	164.5	Cp(2) - C(33) - Si(1)	162.8	Cp-C _{Cp} -Si	158.6–167.7 (163.1)		
$Cp(1)$ and $Cp(2)$ denote the centers of η^5 - C_5 rings (C(1), C(2), C(3), C(4), C(9) and C(31), C(32), C(33), C(34), C(42), respectively).							

Propylene—ethylene copolymerizations were conducted with the same number of complexes. The results of experiments are given in Table 3. Ethylene also has a strong activating effect on the catalysts, and substitution of the indenyl fragment by tetrahydroindacenyl can lead to significant increases in catalytic activity and copolymer molecular mass. The copolymer molecular mass capacity of **20** and **21** is sufficient to make polymerization under ethylene + hydrogen conditions feasible. The obtained data for both homo- and copolmyerizations are presented in Figure 2.

Complex **20** was also tested in propylene homopolymerizations under homogeneous catalyst conditions. Results are given in Table 4.

The relatively high $T_{\rm m}$ of polypropylene with this class of C_1 -symmetric complexes on a supported catalyst was confirmed by 13 C NMR analysis, and microstructures of polypropylene were found to

no.	H_2	act. (kg/g cat h)	act. (kg/mmol Zr h)	melting point (°C)	I.V. b (dL/g)	$M_{ m w}$, $ imes$ 10^{3c}	$M_{\rm w}/M_{\rm n}^{\ c}$
19	_	1.0	63	157.8	4.11	591	3.4
19	+	3.4	213	155.7	2.22	298	3.5
20	_	1.0	63	159.0	3.72	548	2.7
20	+	3.9	244	157.6	1.86	251	2.7
21	_	2.0	125	157.4	4.57	795	2.8
21	+	3.9	244	159.3	1.74	219	2.2
22	_	1.9	119	160.3	2.77	355	2.1
22	+	3.9	244	159.1	2.06	253	1.9
23	_	0.6	38	152.5	2.53	356	2.3
23	+	2.7	169	154.3	1.94	240	2.2
a	11 .	1 .	b	1 17 1 1 1	1: 120.000	11 1	(1C)

Table 2. Catalytic Properties of Supported (silica/MAO, Al/Zr m.r. = 210, 0.016 mmol Zr/g cat) Complexes in Propylene Polymerization^{*a*} (MAO, 65 $^{\circ}$ C, liquid propylene, 1 h)

" Triethylaluminum was used as poison scavenger. " Intrinsic viscosity number, determined in decalin at 135 °C; for details see Experimental Section. ^c M_w and PDI data obtained by GPC.

Table 3. Catalytic Properties of Supported (silica/MAO, Al/Zr m.r. = 210, 0.016 mmol Zr/g cat) Complexes in Propylene–Ethylene Copolymerization^{*a*} (MAO, 65 °C, 3.5 L of liquid propylene, 200 g of ethylene, 32 atm, 1 h)

no.	act. (kg/g cat h)	act. (kg/mmol Zr h)	I.V. ^{b} (dL/g)	$M_{ m w}$, $ imes$ 10^{3c}	$M_{ m w}/M_{ m n}^{\ c}$	melting point (°C)	C2, % ^d
19	3.1	194	4.91	728	3.9	123.5	4.7
20	7.4	463	4.80	909	3.1	123.3	3.8
21	4.2	263	4.95	994	3.7	119.7	4.7
22	4.2	263	4.30	594	2.3	108.1	6.2
23	3.4	213	2.86	433	2.3	125.8	3.2
a Tui atharla	luminum una uradia	maison source on b Interior	i a mia a a citra manala a	" datamainad in da	aslin at 125 °C	for dataila and Ermonimou	ntal Castian

^{*a*} Triethylaluminum was used as poison scavenger. ^{*b*} Intrinsic viscosity number, determined in decalin at 135 °C; for details see Experimental Section. ^{*c*} M_w and PDI data obtained by GPC. ^{*d*} C2 content obtained by FTIR; for details see Experimental Section.

have higher stereo- and regioregularity than those with C_2 -symmetric complexes such as dimethylsilylenebis(2-methyl-4-phenylindenyl) dichlorozirconium (more than 0.80% regiodefects).

These results could be explained by C_1 -symmetric structural features and two different coordination sites: one is the site with 2-methyl (or generally a primary alkyl) and is sterically more open; the other site has 2-isopropyl (or generally an alphabranched alkyl such as a secondary alkyl) and is sterically more hindered. Each site has different features in propylene polymerizations, and both stereo- and regioselectivity of propylene polymerization at insertion into the more sterically hindered site ("2-isopropyl site"), in which the polymer chain sits in the open site ("2-methyl site"), are expected to be higher than those at the insertion into the 2-methyl site. Back skip of the polymer chain¹⁸ from the 2-isopropyl site to the 2-methyl site increases the chance of propylene insertion into the 2-isopropyl site (Figure 4).

In the copolymerization of propylene with ethylene we suppose that the 2-isopropyl group makes it relatively difficult to transfer to ethylene following a propylene 2,1-insertion and reduces the chance of termination reaction with ethylene and increases the molecular weight of ethylene—propylene copolymer.¹⁹ Recent computational studies on ethylene and alpha-olefin copolymerization with metallocenes lend support to the idea that termination by transfer to ethylene following a propylene 2,1-regioerror can be a primary pathway for reducing polymer molecular weight.²⁰

CONCLUSIONS

The C_1 -symmetric single-site catalysts presented in this study provide access to propylene-rich EP copolymers over a broad range of polymer molecular weights and crystallinity. Metallocene catalysts' high hydrogen response for molecular weight control and the ability to produce copolymers of more uniform composition than multisite catalysts is of particular interest for this type application. Introduction of the 5,6-substituions into the specific position on the indene moiety with a pendent aryl group results in further increases in activity, molecular weight capability (both homo and EP copolymer), and isoselectivity. Of the compounds synthesized, complex **20** appears to be a distinct leader and provides some new opportunities for two-stage impact copolymerization where both a stiff homopolymer matrix and high molecular weight EP rubber fraction are needed. A relatively simple Si/MAO preparation was used to screen catalysts in this study; however the characteristics of the support/activator can influence metallocene performance, and more research is needed in this area.

EXPERIMENTAL SECTION

General Considerations. All operations were performed under argon by using standard Schlenk technique or under vacuum using sealed glass "equipped-with-everything" systems. Indane, 2-bromo-2methylpropionyl bromide, AlCl₃, and BuLi (1.6 or 2.5 M solution in hexanes) (Aldrich) and MAO solution in toluene (Albemarle) were used as purchased. Sylopol 948 (Grace-Davison) was calcined at 600 °C before use. SiMe₂Cl₂ (Aldrich) was refluxed over Al and distilled before use. Toluene, ether, THF, and dimethoxyethane (DME) were dried over Na/benzophenone. CH₂Cl₂ was refluxed and distilled over CaH₂. Pentane was distilled over Na/K alloy. 2-Isopropyl-7-phenyl-1*H*-indene, the corresponding bridged ligand, and zirconocene 23 were prepared in



Figure 2. Polymerization test results for 19-22 and bis-indenyl complex 23.

Table 4. Catalytic Properties of Non-Supported 20 in Propylene Polymerization^{*a*} (0.02 g of metallocene, MAO, Al/Zr m.r. = 28 700, 65 °C, 300 g of liquid propylene, 25 min)

H_2	act. (kg/mmol Zr hour)	melting point (°C)	$I.V.^{b} (dL/g)$	$M_{ m w}$, $ imes$ 10^{3c}	$M_{ m n}$, $ imes$ 10^{3c}	${ m M}_z$, $ imes$ 10 3c	$M_{\rm w}/M_{\rm n}^{\ c}$
_	570	165.6	4.70	1060	357	2353	3.0
+	2800	167.9	2.12	305	140	585	2.2
^{<i>a</i>} Triisobu	tylaluminum (4.0 mmol) w	as used as poison scaver	nger; for details se	e Experimental Se	ction. ^b Intrinsic v	iscosity number, c	letermined in

decalin at 135 °C; for details see Experimental Section. $^{c}M_{\rm w}$ and PDI data obtained by GPC.

accordance with published procedures.⁵ NMR spectra were recorded on a Varian XR-400 spectrometer (400 MHz). Mass spectra were measured using a Hewlett-Packard series 6890 instrument that was equipped with a series 5973 mass analyzer (El, 70 eV).

2-Methyl-3,5,6,7-tetrahydro-s-indacen-1(2H)-one (**4**). Anhydrous AlCl₃ (50.7 g, 377 mmol) was slowly added at 0 °C to a mixture of indane (19.3 g, 163 mmol) and 2-bromo-2-methylpropionyl bromide (38.3 g, 167 mmol) in 500 mL of methylene chloride over a period of 30 min. The reaction mixture became dark red. The suspension was stirred at room temperature for 17 h and then poured into 200 g of crushed ice and 100 mL of concentrated HCl. The organic phase was separated, the water phase was extracted by CH_2Cl_2 (3 × 50 mL), and the combined organic phase was washed subsequently with 100 mL of saturated sodium hydrogen carbonate solution and with 200 mL of water, dried over anhydrous sodium sulfate, and filtered. Removal of the solvent under reduced pressure gave 31 g of compound 4 as a reddish-brown oil. According to GC-MS, the content of 4 in the oil was >90%.

4-Bromo-2-methyl-3,5,6,7-tetrahydro-s-indacen-1(2H)-one (5). 4 (31 g, 162 mmol) was added to a suspension of anhydrous AlCl₃ (50 g, 370 mmol) in 200 mL of chloroform while stirring vigorously at 0 °C. After stirring for one hour, a solution of bromine (8 mL, 160 mmol) in 20 mL of chloroform was added dropwise at 0 °C, and the mixture was then stirred overnight. The reaction mixture was poured into 500 g of an ice/water mixture. The organic phase was separated off, washed with 5% aqueous NaHCO3 and water, and then dried over magnesium sulfate. Filtration and removal of the solvent under reduced pressure gave 50 g of a red oil. The mixture was separated by column chromatography on silica gel using methylene chloride as eluent. This gave 18.7 g (44% yield) of compound 5 (yellow oil). Found, %: C, 58.96; H, 4.99; O, 6.01. Calcd for $C_{13}H_{13}BrO$, %: C, 58.89; H, 4.94; O, 6.03. ¹H NMR (CDCl₃, 20 °C): δ 1.32 (d, 1H), 2.15 (t, 2H), 2.59 (dd, 1H), 2.74 (m, 1H), 2.98 (m, 4H), 3.28 (dd, 1H), 7.48 (s, 1H). $^{13}\mathrm{C}$ NMR (CDCl₃, 20 °C): δ 16.2, 25.6, 33.2, 34.3, 35.5 42.3, 117.8, 118.7, 137.1, 145.8, 151.8, 152.4, 208.2.



Figure 3. ¹³C NMR spectrum (methyl region) of polypropylene in Table 2. Upper: Run 20/+ in Table 2 (*mrrm* = 0.21%; 2,1 = 0.29%; 1,3 = 0.06%). Lower: Run 22/- in Table 2 (*mrrm*: undetectable; 2,1 = 0.20%; 1,3 = 0.20%).



Figure 4. Supposed propylene polymerization mechanism.

4-Phenyl-2-methyl-3,5,6,7-tetrahydro-s-indacen-1(2H)-one (6). 5 (10 g, 37.7 mmol), phenylboronic acid (5.5 g, 45.3 mmol), Na₂CO₃ (8.8 g,, 80 mmol), 80 mL of ethylene glycol, and 12 mL of water were placed under a protective argon atmosphere and heated to 80 °C. While stirring vigorously freshly prepared catalyst solution of 20 mg of Pd(OAc)₂, 260 mg of 3,3',3"-phoshinidynetris(benzenesulfonic acid)trisodium salt (TPPTS) in 4 mL of water was added, and the reaction mixture was refluxed for 3 h. After cooling to room temperature, 40 mL of water was added, and the ethylene glycol phase was extracted with toluene (3 \times 80 mL). The combined organic phases were washed by 2 \times 100 mL of aqueous NaCl and dried over Na2SO4. Removal of solvents gave 9.6 g of brown oil, which was gradually crystallized (97%, GC-MS). Found, %: C, 87.0; H, 7.00; O, 6.00. Calcd for C₁₉H₁₈O, %: C, 86.99; H, 6.92; O, 6.10. ¹H NMR (CDCl₃, 20 °C): δ 1.26 (d, 3H), 2.08 (m, 2H), 2.52 (dd, 1H), 2.68 (m, 1H), 2.81 (m, 2H), 3.00 (t, 2H), 3.17 (dd, 1H), 7.31 (d, 2H), 7.39(dd, 1H), 7.45 (d, 2H), 7.61 (s, 1H).

4-(4-tert-Butylphenyl)-2-methyl-3,5,6,7-tetrahydro-s-indacen-1(2H)-one (**7**). Pd(OAc)₂ (0.3 g, 3 mol %) and triphenylphosphine (0.7 g, 6 mol %) were added to a well-stirred mixture of **5** (12 g, 45 mmol), 4-tert-butylphenylboronic acid (11.2 g, 63 mmol), and Na₂CO₃ (13.4 g, 126 mmol) in 170 mL of DME/56 mL of water. The reaction mixture was refluxed for 6 h, poured into water, and extracted with methylene chloride (5 × 100 mL). The combined organic phases were washed with water and dried over MgSO₄. After removal of the solvent, the crude product was chromatographed on silica gel (hexane/CHCl₃ from 4:1 to 1:1). This gave 10 g (70% yield) of compound 7 as a viscous oil. Found, %: C, 86.83; H, 8.35; O, 4.64. Calcd for C_{2.3}H₂₆O, %: C, 86.75; H, 8.23; O, 5.02. ¹H NMR (CDCl₃, 20 °C): δ 1.26 (d, *J* = 7.2 Hz, 3H), 1.38 (s, 9H), 2.07 (m, 2H), 2.56 (m, 1H), 2.69 (m, 1H), 2.84 (dd, 2H), 2.99 (dd, 2H), 3.21 (m, 1H), 7.40 (d, *J* = 8.2 Hz, 2H), 7.46 (d, *J*=8.3 Hz, 2H), 7.59 (s, 1H).

4-(2,5-Dimethylphenyl)-2-methyl-3,5,6,7-tetrahydro-s-indcen-1(2H)-one (**8**). Obtained by the method used for 7. Found, %: C, 86.80; H, 7.68; O, 5.52. Calcd for $C_{21}H_{22}O$, %: C, 86.85; H, 7.64; O, 5.51. Yield: 77% (yellow oil). EIMS: m/z (%) 290 (M⁺, 100), 269 (92), 247 (43), 226 (31), 203 (22), 165 (8).

6-Methyl-4-phenyl-1,2,3,5-tetrahydro-s-indacene (9). A mixture of 6 (6.4 g, 24.4 mmol) and NaBH₄ (2.10 g, 55 mmol) in 40 mL of toluene was heated to 50 °C, 7 mL of methanol was added slowly, and the reaction mixture was stirred at 50 °C for 3 h. After cooling to room temperature 12 mL of water and 40 mL of 1 M HCl were added, and the mixture was stirred for 30 min. After phase separation the water phase was extracted with toluene. The organic phase was evaporated, and the residue was taken up in 100 mL of toluene and mixed with 100 mg of ptoluenesulfonic acid. Water was distilled off from this reaction mixture by refluxing for 1 h with a water separator until the reaction was complete. The reaction mixture was washed once with 100 mL of NaHCO3 aqueous solution and dried over MgSO4. After removal of the solvent, the residue was dried in vacuo and purified by column chromatography (200 g of silica gel, heptane/Et₂O, 9:1). Yield: 5.1 g (85%). Found, %: C, 92.56; H, 7.44. Calcd for C₁₉H₁₈, %: C, 92.64; H, 7.36. ¹H NMR (CDCl₃, 20 °C): δ 2.04 (t, 2H), 2.08 (s, 3H), 2.77 (t, 2H), 2.97 (t, 2H), 3.15 (s, 2H), 6.47 (s, 1H), 7.13 (s, 1H), 7.35-7.48 (m, 5H).

4-(4-tert-Butylphenyl)-6-methyl-1,2,3,5-tetrahydro-s-indacene (**10**). A solution of 7 (9.9 g, 31 mmol) in Et₂O (30 mL) was added dropwise at 0 °C to a solution of LiAlH₄ (0.6 g, 16 mmol) in Et₂O (I00 mL). The

reaction mixture was allowed to warm to room temperature and stirred for 1 h. A 50 mL amount of 5% hydrochloric acid was added. Benzene (200 mL) was added, and the organic phase was separated, washed by water, dried over MgSO₄, filtered, and concentrated to a residual volume of ~150 mL. *p*-Toluenesulfonic acid (0.5 g) was added, and the mixture was refluxed for 1 h with a water separator until the reaction was complete. The solution was cooled to room temperature, washed with 5% aqueous NaHCO₃, and dried over MgSO₄. Evaporation of the solvent gave pure **10** in quantitative yield. Found, %: C, 91.30; H, 8.70. Calcd for C₂₃H₂₆, %: C, 91.34; H, 8.66. ¹H NMR (CDCl₃, 20 °C): δ 1.36 (s, 9H), 2.02 (m, 2H), 2.06 (s, 3H), 2.78, 2.84 (dd, 2H), 2.95 (dd, 2H), 3.17, 3.29 (s, 2H), 6.43–6.45 (m, 1H), 7.10 (s, 1H), 7.30 (d, *J* = 8.2 Hz, 2H), 7.41 (d, *J* = 8.2 Hz, 2H).

4-(2,5-Dimethylphenyl)-6-methyl-1,2,3,5-tetrahydro-s-indacene (11). Ketone 8 (24.0 g, 80.6 mmol) was dissolved in 300 mL of methyl-tert-butyl ether and treated with 46 mL of an ethereal solution of LiAIH4 (1 M, 46 mmol) at 0 °C. After stirring at room temperature for 2 h, 20 mL of a 2 M HCl solution was added cautiously. The organic phase was separated, and the water phase was extracted two times with methyl-tert-butyl ether. The combined organic fractions were dried (MgSO₄) and evaporated. The resulting oil was dissolved in toluene (200 mL), p-toluenesulfonic acid (0.5 g) was added, and the mixture was stirred at reflux for 1 h. After cooling, the reaction mixture was washed subsequently by a saturated aqueous solution of NaHCO3 and brine and dried (MgSO4). Evaporation of solvent gave 20.4 g of the product (92% yield). Found, %: C, 91.87; H, 8.13. Calcd for C₂₁H₂₂, %: C, 91.92; H, 8.08. ¹H NMR (CDCl₃, 20 °C): δ 2.0 (s, 3H), 2.1 (s, 3H), 2.0–2.2 (m, 2H), 2.3 (s, 3H), 2.4–2.7 (m, 2H), 2.8–3.1 (m, 3H), 6.5 (s, 1H), 6.9 (s, 1H), 7.0–7.3 (m, 3H). EIMS: *m*/*z* (%) 274 (M⁺, 100), 258 (43), 231 (29), 215 (25), 189 (8), 169 (9), 152 (8).

4,8-Dibromo-2-methyl-3,5,6,7-tetrahydro-s-indacen-1(2H)-one (12). A suspension of AlCl₃ (73.2 g, 542 mmol) in CHCl₃ (290 mL) was treated by a solution of 4 (45 g, 240 mmol) in CHCl₃ (150 mL) at 0 °C under vigorous stirring. After 1 h, the mixture was treated dropwisely with Br2 (24 mL, 480 mmol) in CHCl₃ (50 mL) within 10 min at 0 °C, the cooling bath was removed, and the solution was stirred overnight. The reaction mixture was poured into ice water and extracted with CH2Cl2. The combined organic phase was washed with aqueous NaHCO₃ and water, dried over MgSO₄, and evaporated to dryness under vacuum to give 93 g of a dark oil, which was gradually crystallized. This crude product was suspended in 100 mL of *n*-heptane, stirred for 1 h at room temperature, and filtered. A brown solid was obtained (52 g), and it was determined by GC-MS to contain almost 100% of the target compound (yield: 63%). The filtrate was concentrated, and the same procedure was repeated to get 10 g of the solid (total yield 62 g, 75%). Found, %: C, 45.48; H, 3.56; O, 4.70. Calcd for C13H12Br2O, %: C, 45.38; H, 3.52; O, 4.65. ¹H NMR (CDCl₃, 20 °C): δ 1.31 (d, 3H), 2.16 (pent., 2H), 2.53 (dd, 1H), 2.75 (m, 1H), 3.07 (m, 4H), 3.22 (dd, 1H). ¹³C NMR (CDCl₃, 20 °C): δ 16.5, 23.3, 34.7, 34.9, 35.8, 43.3, 115.5, 118.1, 133.9, 147.1, 152.7, 154.6, 205.5.

2-Methyl-4,8-phenyl-3,5,6,7-tetrahydro-s-indacen-1(2H)-one (**13**). Obtained by the method used for 7. Yield: 97%. Found, %: C, 88.73; H, 6.58; O, 4.69. Calcd for $C_{25}H_{22}O$, %: C, 88.72; H, 6.55; O, 4.73. ¹H NMR (CDCl₃, 20 °C): δ 1.22 (d, 3H), 2.02 (pent., 2H), 2.53 (dd, 1H), 2.64 (m, 1H), 2.86 (m, 4H), 3.18 (dd, 1H), 7.34–7.50 (m, 10H). ¹³C NMR (CDCl₃, 20 °C): δ 16.4, 25.8, 32.0, 33.1, 33.8, 43.1, 127.3, 127.5, 127.6, 127.8, 127.9, 128.4, 128.6, 128.9, 129.0, 129.1, 132.0, 135.5, 136.0, 137.3, 138.3, 143.8, 150.2, 151.6.

6-Methyl-4,8-diphenyl-1,2,3,5-tetrahydro-s-indacene (**14**). Obtained by the method used for **9**. Yield: 94%. Found, %: C, 93.18; H, 6.82. Calcd for C₂₅H₂₂, %: C, 93.12; H, 6.88. ¹H NMR (CDCl₃, 20 °C): δ 2.00 (t, 2H), 2.04 (s, 3H), 2.84 (t, 2H), 2.90 (t, 2H), 3.24 (s, 2H), 6.44 (s, 1H), 7.35 (m, 2H), 2.44 (m, 8H). ¹³C NMR (CDCl₃, 20 °C): δ 145.7, 143.0, 141.1, 140.6, 140.3, 139.9, 138.5, 133.5, 129.7, 129.5, 128.9, 128.2, 128.1, 126.8, 126.6, 126.3, 42.5, 32.8, 32.5, 31.9, 31.5, 26.1, 16.8.

[4-(4-tert-Butylphenyl)-2-isopropyl-1H-inden-1-yl](dimethyl)(2-methyl-4-phenyl-1,5,6,7-tetrahydro-s-indacen-1-yl)silane (15). n-BuLi (2.5 M) in *n*-hexane (18.7 mL, 45 mmol) was added at -70 °C to a solution of 9 (10.0 g, 40.6 mmol) in Et₂O (400 mL). The solution was slowly warmed to room temperature and stirred for 3 h. The mixture was cooled to -70 °C, and CuCN (135 mg, 1.5 mmol) and [4-(4-tert-butylphenyl)-2isopropyl-1H-inden-1-yl](chloro)dimethylsilane (14 g, 42.8 mmol) were added. The mixture was warmed to room temperature and stirred for 5 h. The resulting back slurry was passed through silica and evaporated to give 23.6 g of crude product, which was purified by column chromatography (1200 g of silica gel, heptane/CH₂Cl₂, 5:l). Yield: 17.8 g (74%). Found, %: C, 87.38; H, 8.33. Calcd for $C_{46}H_{52}Si$, %: C, 87.28; H, 8.28. ¹H NMR $(CDCl_3, 20 \ ^{\circ}C): \delta -0.23, -0.16 \ (s, 6H), 1.10 \ (m, 3H), 1.25 \ (m, 3H),$ 1.39, 1.40 (s, 9H), 2.05 (m, 2H), 2.21 (s, 3H), 2.71 (sept, 1H), 2.86-2.96 (m, 4H), 3.65, 3.69, 3.90, 3.97 (s, 2H), 6.49, 6.53 (s, 1H), 6.81, 6.83 (s, 1H), 7.17–7.51 (m, 13H). MS (direct): $M^+ = 592 (C_{43}H_{48}Si)$.

 μ -Dimethylsilylene[η^5 -4-(4-*tert*-butylphenyl)-2-isopropyl-1*H*-inden-1-yl](η^{5} -2-methyl-4-phenyl-1,5,6,7-tetrahydro-s-indacen-1-yl)dichlorozirconium(IV) (19). BuLi (2.5 M) in hexanes (14 mL, 35 mmol) was added at -40 °C to a solution of 15 (10.4 g, 17.5 mmol) in 150 mL of diethyl ether. After the addition was complete, the mixture was allowed to warm to room temperature and stirred for 3 h. Solvents were removed under reduced pressure, pentane (200 mL) was added, the mixture was cooled to -60 °C, and ZrCl₄ (4.1 g, 17.5 mmol) was added with stirring. After 1 h of stirring at -60 °C, Et₂O (5 mL) was added, and the mixture was gradually warmed to room temperature and stirred overnight. The orange precipitate was then separated off on a G3 frit and washed with 50 mL of n-pentane. The orange residue on the frit was dried under vacuum to give 11 g of crude complex (pseudo-rac/ pseudo-meso = 1:1, yield: 80%). This mixture was then refluxed in 150 mL of DME within 16 h. The resulting solution was separated by decantation and evaporated, and the residue was recrystallized from toluene/hexane, giving 3.8 g of pure pseudo-rac-form. Yield: 29% (orange crystalline powder). Found, %: C, 69.42; H, 6.38. Calcd for C46H50Cl2SiZr, %: C, 69.66; H, 6.35. ¹H NMR (CDCl₃, 20 °C): δ 1.07 (d, 3H), 1.10 (d, 3H), 1.32 (s, 6H), 1.37 (s, 9H), 2.00 (m, 2H), 2.20 (s, 3H), 2.82, 2.96 (m, 4H), 3.35 (sept., 1H), 6.65 (s, 1H), 7.01 (s, 1H), 7.06 (dd, 1H), 7.31 (t, 1H), 7.35 (d, 1H), 7.38 (s, 1H), 7.41 (t, 2H), 7.46 (d, 2H), 7.54 (broad, 2H), 7.62 (d, 1H), 7.64 (d, 2H). MS (direct): $M^+ = 750 (C_{43}H_{46}C1_2SiZr)$.

Preparation of the Catalysts. A 0.206 mmol sample of corresponding zirconocene dichloride was added at room temperature to 43.3 mmol of MAO (30% toluene solution). The resulting solution was allowed to stand overnight at room temperature and was subsequently diluted with 10.9 mL of toluene. The diluted solution was carefully added to 10 g of silica (Sylopol 948 (Grace-Davison), calcined at 600 °C). After 10 min, the catalyst suspension was evaporated and dried *in vacuo*.

Polymerizations. Propylene homopolymerizations with supported catalysts were carried out in a 10 L reactor charged with 3.5 kg of liquid propene. The reactor was made inert by means of nitrogen before being charged. Eight milliliters of a 20% strength by weight solution of triethylaluminum in Exxsol (from Witco) was introduced into the reactor, and the mixture was stirred at 30 °C for 15 min. If hydrogen was added, its concentration was set to 0.5 standard liters per liter of liquid propylene. A suspension of the respective catalyst in 20 mL of Exxsol was introduced into the reactor. The reactor temperature was increased to 65 °C and maintained at this temperature for 60 min. Copolymerizations were carried out in a 10 L reactor charged with 3.5 kg of liquid propylene. A 20% by weight solution of triethylaluminum in Exxsol (from Witco) was introduced into the reactor, and the mixture was stirred at 30 °C for 15 min. A suspension of the respective catalyst in 20 mL of Exxsol was introduced into the reactor. Ethylene was introduced into the reactor (total of 160 g). The reactor temperature was increased to 65 °C and maintained at this temperature for 60 min.

The pressure in the reactor was maintained at 32 bar by continuous addition of ethylene using a mass flow meter on closed loop control (about 47 g of further ethylene introduced). The polymerizations were stopped by venting the reactor. The polymers were dried overnight under reduced pressure before being analyzed. Propylene homopolymerizations with homogeneous catalysts were conducted in a one-liter stainlesssteel Büchi reactor equipped with an oil-circulating temperature control bath. The reactor was swept with dry nitrogen at 110 °C for 1 h prior to polymerization. At 25 °C 2-4 mL of a 1.0 M toluene solution of triisobutylaluminum was added followed by 250 g of liquid propylene. Stirring was initiated, and the reactor was heated to the polymerization temperatures. Hydrogen was added (if required) at this stage. A toluene solution of the zirconocene was reacted with a toluene solution of MAO for 10 min, and polymerization was initiated by charging the catalyst solution to the reactor with 50 g of liquid propylene under pressure. The polymerization was stopped by venting and cooling the reactor.

Polymer Analysis. Determination of the Melting Point. The melting point, $T_{\rm m}$, was determined by means of a DSC measurement in accordance with IS0 Standard 3146 in a first heating phase at a heating rate of 20 °C per minute to 200 °C, a dynamic crystallization at a cooling rate of 20 °C per minute down to 25 °C, and a second heating phase at a heating rate of 20 °C per minute back to 200 °C. The melting point was then the temperature at which the curve of enthalpy versus temperature measured in the second heating phase displayed a maximum.

Gel Permeation Chromatography. Gel permeation chromatography (GPC) was carried out at 145 °C in 1,2,4-trichlorobenzene using a Waters 150C GPC apparatus. The evaluation of the data was carried out using the software Win-GPC from HS-Entwicklungsgesellschaft fur wissenschaftliche Hard- and Software mbH, Ober-Hilbersheim. The columns were calibrated by means of polystyrene standards having molar masses ranging from 100 to 10^7 g/mol. The mass average molar mass (M_w) and number average molar mass (M_n) of the polymers were determined. The Q value is the ratio of mass average molar mass (M_w) to number average molar mass (M_n).

Determination of the Intrinsic Viscosity Number (I.V.). The intrinsic viscosity number was determined in an Ubbelohde viscometer PVS 1 fitted with an S 5 measuring head (both from Lauda) in decalin at 135 °C. To prepare the sample, 20 mg of polymer was dissolved in 20 mL of decalin at 135 °C for 2 h. Then 15 mL of the solution was placed in the viscometer, and the instrument carried out a minimum of three running-out time measurements until a consistent result had been obtained. The I.V. was calculated from the running-out times by means of the relationship I.V. = $(t/t_o - 1) \times 1/c$, where t = mean of the running-out time of the solution, t_o = mean of the running-out time of the solvent, and c = concentration of the solution in g/mL.

Microstructure Analysis of Polyproypylene by ¹³C *NMR*. ¹³C *NMR* spectra of PP were acquired on a DPX-400 spectrometer operating at 100.61 MHz in the Fourier transform mode at 120 °C. The peak of the *mmmm* pentad carbon were used as internal reference at 21.8 and 29.9 ppm, respectively. The samples were dissolved in 1,1,2,2-tetrachloroethane- d_2 at 120 °C with a 8 wt %/v concentration in a 5 mm tube. Each spectrum was acquired with a 90° pulse, 12 s of delay between pulses, and CPD (WALTZ 16) to remove ${}^{1}\text{H} - {}^{13}\text{C}$ coupling. About 2500 transients were stored in 32K data points using a spectral window of 6000 Hz. The assignments of PP spectra were made according to ref 21. The content of 2,1 [E] and 3,1 [H] errors was obtained as follows: [E] = 100 (E9/S[CH₂]), [H] = 100 (0.5 H2/S[CH₂]), where E9 is the peak at 42.14 ppm, H2 is the peak at 30.82 ppm, and S[CH₂] is the sum of all CH₂ groups.

Determination of Ethylene Content in Copolymers. Ethylene content was measured by analyzing pressed thin films of the polymers by FTIR. The FTIR was calibrated with copolymer standards having an ethylene content ranging from 1 to 6 mol % as determined by 13 C NMR.

ASSOCIATED CONTENT

Supporting Information. Experimental details for preparation of similar bridged ligands and zirconocenes, crystal data and processing parameters for complex **20**, and CIF file giving X-ray crystal structural data. This material is available free of charge via the Internet at http://pubs.acs.org.

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