# **ORGANOMETALLICS**

# Novel Effective Racemoselective Method for the Synthesis of ansa-Zirconocenes and Its Use for the Preparation of C<sub>2</sub>-Symmetric Complexes Based on 2-Methyl-4-aryltetrahydro(s)indacene as Catalysts for Isotactic Propylene Polymerization and Ethylene– Propylene Copolymerization

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**Supporting Information** 

**ABSTRACT:** A general and effective method for the racemoselective synthesis of bis-indenyl-type *ansa*-zirconocenes was proposed and successfully applied for the synthesis of several  $C_2$ -symmetric *ansa*-zirconocenes based on 2-methyl-4-aryltetrahydro-*s*-indacene. This new racemoselective method relies on ZrCl<sub>3</sub>NH-*tert*-Bu as a key reagent. The formation of racemic products was confirmed by NMR studies and single-crystal X-ray diffraction. The novel complexes are potent catalysts for isotactic propylene polymerization and ethylene—propylene copolymerization.



# INTRODUCTION

Racemic forms of group 4 metal *ansa*-complexes are traditionally considered a promising class of metallocene catalysts for isotactic propylene polymerization.<sup>1</sup> High activity was demonstrated in the early 1990s by compounds of general formula  $1;^2$  their modifications included the so-called "heterocenes" (2)<sup>3</sup> and pseudoracemic  $C_1$ -symmetric complexes (3) containing bulky substituents in position 2 of one indenyl ring<sup>4</sup> (Scheme 1).

The development of high-performance heterogeneous catalysts for isotactic propylene polymerization (titanium-magnesium catalysts in the presence of internal and external donors<sup>5</sup>) at the end of the 20th century somewhat reduced interest in the use of metallocenes for this purpose; therefore, researchers are now focused on the prospects of using metallocenes specifically as catalysts for copolymerization.

One trend in the design of catalysts based on bis-indenyl *ansa*-zirconocenes is the introduction of electron-donating structural moieties to the molecule. This alteration stabilizes the catalytically active alkylzirconocene cations, thus increasing their effective concentration in the catalytic system.<sup>6</sup> It is also significant that this structural modification increases the degree of separation between the LZrR<sup>+</sup> [anion]<sup>-</sup> ion pair, thus

facilitating the alkene insertion during polymerization.<sup>7</sup> Both alkyl groups and substituents containing a heteroatom are suitable as electron-donating moieties; although in the latter case, the catalyst may be deactivated through side reactions with organoaluminum cocatalysts.<sup>6</sup> Tetrahydro(*s*)indacenes contain additional alkyl groups and should, therefore, be considered as promising donor ligands.<sup>8</sup> The ability of a  $(CH_2)_3$  moiety to effectively stabilize alkylzirconocene cationic intermediates was indeed demonstrated in our previous publication.<sup>8c</sup> We also demonstrated that the pseudoracemic complexes of structural type **4**, containing one tetrahydroindacene fragment, surpass the bis-indenyl analogues of type **3** in all characteristics.<sup>9</sup>

In this work, we aimed to replace both indenyl moieties of Spaleck complex 1 with tetrahydroindacene moieties to synthesize complexes of type 5 (Scheme 1). The race-moselective synthesis of these complexes is the primary goal of this study.

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#### Scheme 1



Scheme 2





# RESULTS AND DISCUSSION

Preparation of Tetrahydroindacene Ligands and Attempted Synthesis of Zirconocenes by the Reaction of Dilithium Derivatives with ZrCl<sub>4</sub>. 2-Methyl-4-aryltetrahydroindacenes 6–8 were synthesized using a procedure we proposed previously.<sup>9</sup> Bis-indenyl compounds with a dimethylsilylene bridge were synthesized in nearly quantitative yields by the reaction of lithium derivatives of 6-8 with SiMe<sub>2</sub>Cl<sub>2</sub>, in the presence of catalytic amounts of CuCN<sup>10</sup> (Scheme 2), and were used without further purification.

Initially, we intended to synthesize target complexes 12-14 by slightly modifying the commonly used reaction between dilithium derivatives of ligands 9-11 with  $\text{ZrCl}_4$  or  $\text{ZrCl}_4(\text{THF})_2$ . However, only moderate success was achieved by performing the reaction of dilithium derivatives 9a-11a

# Scheme 3



Figure 2. <sup>1</sup>H NMR spectra of (A) the reaction mixture for the formation of 16, (B) compound 16 isolated by filtration, and (C) the reaction mixture containing 12 after treatment of 16 with Me<sub>3</sub>SiCl and removal of the solvents.

with  ${\rm ZrCl}_4$  in pentane, producing moderate yields of diastereomeric forms with similar solubility that were

contaminated by significant (in the case of 12, more than 50%) amounts of oligomeric and polymeric products of

#### Scheme 4



 $LLi_{2} + ZrCl_{3}(THF)_{2}NH-tert-Bu \xrightarrow{\text{toluene}} LZrCINH-tert-Bu \xrightarrow{\text{Me}_{3}SiCl} LZrCl_{2}$ 



Figure 3. Scope and limitations of the  $ZrCl_3(THF)_2NH$ -tert-Bu based approach for the syntheses of bis-indenyl ansa-zirconocenes for different bisindenyl ligands L. Isolated yields of the corresponding  $LZrCl_2$  chlorides and the selectivity of racemic amide formation are given.

unknown structure. In diethyl ether, toluene, or  $CH_2Cl_2$ , these impurities became the major reaction products. The method we used previously<sup>9</sup> to isolate *rac*-zirconocenes, based on controlled destruction of the *meso* forms by heating isomer mixtures in DME in the presence of LiCl, allowed the isolation of *rac*-14 with moderate purity (<95%) and relatively low yield (29%) (Scheme 2). In contrast, for compounds 12 and 13, decomposition of the *rac* and *meso* forms occurred at similar rates.

Search for a Racemoselective Method for the Synthesis of 12–14. To deeply assess properties of complexes 12–14 and further on establish an accurate properties– structure relationship, it is mandatory to use an effective and reliable racemoselective synthesis. Among recently published racemoselective syntheses, three have attracted our attention: (i) transmetalation of racemic distannylated or disilylated derivatives,<sup>11</sup> (ii) the reactions of LLi<sub>2</sub> with the bis-phenolates Z r Cl<sub>2</sub> (O A r)<sub>2</sub>,<sup>12</sup> or (iii) cyclic a mid e ZrCl<sub>2</sub>(PhNCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NPh).<sup>13</sup> The two latter-mentioned methods apply the "pro-racemic" zirconium complexes LZrCl<sub>2</sub>, whose geometry is complementary to the ligand orientation in the *rac* form of metallocene (Figure 1). Besides, one of us<sup>14</sup> also reported that the reaction of LLi<sub>2</sub> with the ZrCl<sub>3</sub>(THF)<sub>2</sub>NH-*tert*-Bu complex **15** formed in situ gave



Figure 4. Crystal structures of 12 (a) and 16 (b). Displacement ellipsoids are shown at 50% probability. Hydrogen atoms are omitted for clarity.

diastereomeric mixtures of the amide complexes LZrClNH-*tert*-Bu in which racemic forms predominated (Figure 1).

We carried out experiments using lithium derivative **9a** and both  $ZrCl_2(3,5,3',5-tetra-$ *tert*-butyl-2,2'-biphenolate) and $<math>ZrCl_2(PhNCH_2CH_2CH_2NPh)$ , but were not successful because polymeric byproducts were formed in both cases. However, the experiment carried out with lithium derivative **9a** and  $ZrCl_3(THF)_2NH$ -*tert*-Bu **15** (Scheme 3) yields the corresponding diastereomeric mixture and side products; the mixture contained approximately 70–80% of the racemic amide complex **16** (NMR data), the *meso* form of **16**, the dichloride **12**, and a noticeable amount of unidentified polymeric impurities. Treatment of this mixture with MeSO<sub>2</sub>Cl, followed by removal of the solvents and recrystallization of the residue from a  $CH_2Cl_2$ -hexane mixture, produced the target complex **12** with a moderate yield (~30%), but with a high purity.

Although this racemoselective method proved successful in preparing complex 12, the moderate yield prompted us to continue experimenting to optimize this method.

Optimization of the Method for the Synthesis of the C<sub>2</sub>-Symmetric Tetrahydroindacene Complexes Using ZrCl<sub>3</sub>(THF)<sub>2</sub>NH-tert-Bu. Amine Variation. We studied the reaction of dilithium derivative 9a with several ZrCl<sub>3</sub>(THF)<sub>2</sub>NRR' amides obtained in situ. We found that satisfactory yields and selectivities were obtained only by using sterically hindered primary amines, namely, 1-adamantanamine (yield 50%, racemoselectivity > 10), 2,6-diisopropylaniline (yield ~ 70%, racemoselectivity of ~12), and *tert*-butylamine. The latter compound produced the best product (yield > 70%, selectivity > 15), making it the reagent of choice for this reaction. The use of less hindered or secondary amines sharply decreases the yield of the target product. It is also worth mentioning that the racemic tert-butylamido derivative 16 readily crystallizes and has convenient solubility; therefore, it can be easily separated from the reaction mixture (LiCl) and then purified by a single recrystallization step.

Conversion of Amide Complexes to Racemic Dichlorides. To convert amide 16 to dichloride 12, we first used MeSO<sub>2</sub>Cl according to a previously described procedure.<sup>14</sup> Presumably, the moderate yield of the target product 12 may be caused by excessive reactivity of MeSO<sub>2</sub>Cl, causing side reactions involving the amide complex 16. Because we had a sufficient amount of amide complex 16 of adequate purity, we studied its reaction with various RCl "chlorinating agents". The reactions were carried out at room temperature using 2-fold excesses of RCl (the concentration of 16 was ~0.2 M). Dichloride 12 was isolated by removal of the solvent, crystallization of the residue in pentane, and then filtration. Treatment of 16 with MeSO<sub>2</sub>Cl affords dichloride 12 in 60% yield contaminated with the sulfonamide MeSO<sub>2</sub>NH-*tert*-Bu and polymeric byproduct. The use of acyl chlorides (CH<sub>3</sub>COCl, CICOCOCl) resulted in complete and fast decomposition of the *ansa*-complexes.

Benzyl chloride was a satisfactory reagent, yet the obtained complex 12 contained a noticeable (approximately 10%) amount of polymer impurities. Better results were obtained using chlorosilanes. Use of SiCl<sub>4</sub> in benzene or SiMe<sub>2</sub>Cl<sub>2</sub> in CH<sub>2</sub>Cl<sub>2</sub> produced compound 12 in yields better than 70%; moreover, the content of polymeric byproduct was not significant. The best chlorinating agent proved to be Me<sub>3</sub>SiCl in CH<sub>2</sub>Cl<sub>2</sub>. The reaction of 16 with Me<sub>3</sub>SiCl was barely contaminated by side products (Figure 2), and complex 12 was isolated in 80% yield (total yield from 9 is 55%) after a single recrystallization. Using this optimized method, racemic complexes 13 and 14 were subsequently prepared (Scheme 4), and intermediate amides 17 and 18, respectively, were isolated. Note that the final yields of the pure racemic products 12–14 after recrystallization were higher than 50% in all cases.

Scope and Limitations of This Racemoselective Method Based on ZrCl<sub>3</sub>(THF)<sub>2</sub>NH-tert-Bu. We applied this newly optimized racemoselective method to the preparation of several SiMe<sub>2</sub>-bridged bis-indenyl *ansa*-complexes. The experimental results are presented in Figure 3.

As shown in Figure 3, this approach can be successful and allows for the easy preparation of several racemic *ansa*-metallocenes. The best results were clearly observed for tetrahydroindacene complexes 5 (Figure 3, in green) and 2-methylindenyl- and 2-methylbenzindenyl-based complexes. *ansa*-Zirconocene of type 4 (Figure 3, in green) was also successfully prepared, albeit in low yield (the ready solubility of the amide complex makes its isolation very difficult and reduces the overall yield). Type 2 "heterocenes", as well as  $C_1$ -symmetric complexes of type 3 (Figure 3, in brown), can also

# Table 1. Selected Bond Lengths (Å) and Angles (deg) for 12 and 16

$12^a$				16	
molecule A		molecule B			
Zr(1)-Cl(11)	2.4205(7)	Zr(2)-Cl(21)	2.4199(7)	Zr(1)-N(1)	2.036(3)
Zr(1)-Cl(12)	2.4213(7)	Zr(2)-Cl(22)	2.4287(7)	Zr(1)-Cl(1)	2.4503(10)
Zr(1)-C(11)	2.448(3)	Zr(2) - C(51)	2.449(3)	Zr(1) - C(11)	2.478(4)
Zr(1)-C(31)	2.475(2)	Zr(2) - C(71)	2.483(2)	Zr(1) - C(32)	2.529(4)
Zr(1)-C(32)	2.506(2)	Zr(2) - C(72)	2.497(2)	Zr(1) - C(31)	2.538(4)
Zr(1) - C(12)	2.509(2)	Zr(2) - C(52)	2.516(3)	Zr(1) - C(12)	2.542(4)
Zr(1)-C(22)	2.525(3)	Zr(2) - C(62)	2.516(2)	Zr(1) - C(33)	2.568(4)
Zr(1)-C(33)	2.562(2)	Zr(2) - C(73)	2.551(2)	Zr(1)-C(22)	2.586(4)
Zr(1)-C(42)	2.563(2)	Zr(2) - C(82)	2.563(2)	Zr(1) - C(42)	2.619(4)
Zr(1) - C(13)	2.600(2)	Zr(2) - C(53)	2.590(2)	Zr(1) - C(13)	2.656(4)
Zr(1) - C(14)	2.632(2)	Zr(2) - C(54)	2.617(2)	Zr(1) - C(34)	2.665(4)
Zr(1)-C(34)	2.633(2)	Zr(2) - C(74)	2.630(2)	Zr(1) - C(14)	2.724(4)
Si(1)-C(30)	1.861(3)	Si(2)-C(70)	1.856(3)	Si(1) - C(30)	1.865(4)
Si(1) - C(50)	1.867(3)	Si(2)-C(90)	1.865(3)	Si(1) - C(50)	1.867(4)
Si(1) - C(11)	1.878(2)	Si(2)-C(51)	1.872(3)	Si(1) - C(31)	1.873(4)
Si(1)-C(31)	1.881(3)	Si(2)-C(71)	1.886(3)	Si(1) - C(11)	1.874(4)
				N(1)-C(1)	1.484(5)
$Cp(11)-Zr(1)-Cp(12)^{b}$	129.6	Cp(21)-Zr(1)-Cp(22)	128.8	Cp(1)-Zr(1)-Cp(2)	126.7
Cl(11)-Zr(1)-Cl(12)	100.06(2)	Cl(21)-Zr(2)-Cl(22)	98.02(3)	N(1)-Zr(1)-Cl(1)	101.53(10)
C(30)-Si(1)-C(50)	105.94(14)	C(70)-Si(2)-C(90)	105.45(14)	C(30) - Si(1) - C(50)	105.5(2)
C(30)-Si(1)-C(11)	112.62(12)	C(70)-Si(2)-C(51)	113.29(12)	C(30)-Si(1)-C(31)	114.65(19)
C(50)-Si(1)-C(11)	113.08(12)	C(90)-Si(2)-C(51)	112.41(13)	C(50) - Si(1) - C(31)	114.08(19)
C(30)-Si(1)-C(31)	115.31(13)	C(70)-Si(2)-C(71)	114.91(13)	C(30)-Si(1)-C(11)	113.40(19)
C(50)-Si(1)-C(31)	114.19(12)	C(90)-Si(2)-C(71)	115.44(13)	C(50)-Si(1)-C(11)	112.76(19)
C(11)-Si(1)-C(31)	95.82(11)	C(51)-Si(2)-C(71)	95.50(11)	C(31)-Si(1)-C(11)	96.68(17)
				C(1)-N(1)-Zr(1)	147.7(3)

<sup>a</sup>Two independent molecules. <sup>b</sup>Cp denotes the center of the  $\eta^{5}$ -C<sub>5</sub> ring.

be prepared using this method, but again with low overall yields and selectivities. Surprisingly, the method is not selective for type 1 metallocenes (Figure 3, in black), viz. the Spaleck complexes. We believe the observed high selectivity is due to dissociation of one cyclopentadiene, rotation of the resulting cyclopentadienyl anion, and its subsequent coordination to the zirconium atom. The primary amine may donate its lone pair electrons into one orbital of the zirconium atom, triggering the isomerization process.

Molecular Structure of 12 and 16. The molecular structure of racemic dichloride complex 12 is shown in Figure 4a. Crystal 12 contains two crystallographically independent molecules with very similar geometric parameters (Table 1). The coordination environment of the Zr atoms may be described as a distorted tetrahedron (assuming that  $\eta^5$ -C<sub>5</sub> rings occupy one coordination site). The Zr-C distances vary in a wide range from 2.448(3) to 2.633(2) Å. The latter is typical for indenyl zirconium complexes<sup>15</sup> and reflects the tendency of Zr atoms to form  $\eta^3$ ,  $\eta^2$  linkages with indenvel ligands. The Zr– C(n1) (n = 1, 3, 5, 7) bonds are the shortest because these carbon atoms are linked by a small-scale -SiMe<sub>2</sub> spacer. The indenyl ligands are planar within 0.028(2) Å and form dihedral angles of  $59.20(6)^{\circ}$  and  $58.56(6)^{\circ}$ . The principal geometric parameters of molecule 12 are very similar to the respective average values for closely related bis-(indenyl)zirconocenedichlorides as retrieved from the CSD.<sup>16</sup>

Complex 16 comprises the same *ansa*-bis(indenyl) ligand as compound 12 (Figure 4b). The primary geometric features of the metal core in 16 are similar to those in 12 (Table 1). The only difference is that one chlorine ligand (12) is substituted by a Me<sub>3</sub>C-NH- group (16). The large C-N-Zr angle (147.7°)

is indicative of the strong  $p\pi$ - $d\pi$  interaction between nitrogen and zirconium atoms.

**Catalytic Activity of 14.** The catalytic activity of supported complex 14, the most available one, was estimated using classical polymerization conditions (see the Experimental Section).<sup>17</sup>

Propylene Homopolymerization. The experiments were carried out at 65 °C in a 10 L reactor, charged with propylene and  $Et_3Al$  as a scavenger and allowed to react for 1 h. As shown in Table 2, catalyst 14 showed excellent performance (85 kg/

Table 2. Catalytic Properties of Supported Complex 14 (Silica Gel/MAO, Al/Zr = 21, 0.020 mmol Zr/g of cat) for the Propylene Polymerization (MAO, 65 °C, Liquid Propylene, 1 h) in the Presence of  $H_2$ 

no.	catalyst (mg)	$H_2$ (NL)	act. (kg/mmol Zr $\cdot$ h)	I.V. $(dL/g)$
1	62.6	7	196.9	1.3
2	78.9	5	251.5	2.3
3	80.9	2.5	113.3	3.7
4	81.9	1.2	47.7	4.4

(mmol × *h*). The polymer had a  $M_w$  of 1 200 000 ( $M_w/M_n$  = 3.9, mp 153.4 °C) and produced polypropylene with a very high xylene-insoluble fraction with approximately 99.4% yield.

As given in Table 2, catalyst 14 showed a good H<sub>2</sub> response. In the presence of slight amounts of hydrogen, it efficiently (activity of >100 kg/(mmol  $\times h$ )) catalyzed the polymerization of propylene while maintaining the polymer's molecular mass at a reasonable level. Copolymerization of Ethylene and Propylene. A comparative polymerization test of 14 and previously synthesized<sup>4</sup> complex 17 (Scheme 5) was carried out as a two-stage



experiment. Propylene was first polymerized in the presence of hydrogen (30 atm, 70  $^{\circ}$ C); then, a 1:3 ethylene and propylene mixture was copolymerized (21 atm, 60  $^{\circ}$ C). The experimental results and important characteristics of the obtained polymer are summarized in Table 3.

Table 3. Catalytic Properties of Supported Complexes 14 and 17 (Silica Gel/MAO, Al/Zr = 210, 0.040 mmol Zr/g of cat) in the Two-Stage Polymerization Process: (a) Propylene and (b) Ethylene–Propylene Copolymerization

catalyst	act. (kg/ mmol Zr · h), stage a	act. (kg/ mmol Zr · h), stage b	C2 <sub>EPR</sub> (% wt)	xylene soluble fraction (%)	xylene soluble fraction I.V. (dL/ g)	xylene soluble fraction mp (°C)
14	110.0	160	26.3	70.7	2.55	153.2
17	62.5	57.5	21.0	65.9	0.71	152.0

This work has proven that the introduction of electrondonating groups, such as  $(CH_2)_3$ , onto the ligand backbone leads to better catalysts. Complex 17 (Scheme 5) was the worst catalyst for propylene polymerization and ethylene-propylene copolymerization. Complex 14 efficiently catalyzes the ethylene-propylene polymerization to produce a high-mass polymer. Hence, complex 14 was used to elucidate the effect of the ethylene-to-propylene ratio on the catalytic activity and the properties of the resulting copolymer. This goal was accomplished by performing a series of experiments in which initial prepolymerization of pure propylene was carried out for 5 min and was then followed by ethylene-propylene copolymerization. The ethylene-propylene copolymer was separated by dissolution in xylene, the yield was determined, and the product was analyzed. The results are summarized in Table 4.

These obtained data suggest that the molecular mass of the ethylene–propylene copolymer obtained with catalyst **14** is not significantly dependent on the ethylene-to-propylene ratio in the mixture.

The polymerization experiments confirmed our assumption concerning the efficiency of using an electron-donating tetrahydroindacene moiety in the design of highly active metallocene catalysts. The complexes in this study are more

Table 4. Catalytic Properties of Supported Complex 14
(Silica Gel/MAO, 0.020 mmol Zr/g of cat) in Ethylene-
Propylene Copolymerization (21 atm, 60 $^{\circ}$ C) <sup><i>a</i></sup>

no.	catalyst (mg)	Al/ Zr	C3 (g) charge	C2 (% wt) charge	act. (kg/ mmol Zr · h)	C2 (% wt)	I.V. (dL/ g)
1	67.0	285	703	45	65.6	43.6	3.7
2	67.0	285	703	30	61.1	32.0	3.8
3	73.1	285	699	73	15.3	57.0	3.7
4	79.2	262	700	30	36.3	21.8	3.7
5	60.9	262	698	61	26.7	49.0	3.7
6	54.8	262	697	21	34.4	15.3	3.3
7	54.8	262	698	13	14.3	8.5	3.8
<sup>*</sup> The data refer to the xylene-soluble fraction.							

active for propylene polymerization than their indenyl analogues and are suitable catalysts for the preparation of high-mass ethylene–propylene copolymers with an arbitrary monomer ratio.

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We have herein reported a new powerful and straightforward racemoselective synthesis of *ansa*-metallocenes based on a ZrCl<sub>3</sub>NH<sup>t</sup>Bu organometallic species. This synthetic method proved to be most efficient when applied to 2-methyl-4-aryltetrahydroindacenes. These compounds are promising catalysts for alkene copolymerization due to their high activity, lack of selectivity in the ethylene—propylene monomer pair, and the minor effect of the monomer ratio on the copolymer mass. These catalytic characteristics are an improvement over other metallocene catalysts for polymerization, making them an attractive option as the foundation for the development of general-purpose, new-generation industrial metallocene catalysts.

#### EXPERIMENTAL SECTION

General Considerations. All experiments were performed under argon using standard Schlenk techniques or under vacuum using sealed glass "equipped-with-everything" systems. Indane, 2-bromo-2methylpropionyl bromide, AlCl<sub>3</sub> and BuLi (1.6 or 2.5 M solution in hexanes) (Aldrich), and MAO solution in toluene (Albemarle) were used as purchased. SiMe<sub>2</sub>Cl<sub>2</sub> and Me<sub>3</sub>SiCl (Aldrich) were refluxed over Al and distilled before use. Toluene, ether, and THF were dried over Na/benzophenone and distilled before use. Dichloromethane was refluxed and distilled over CaH2. Pentane was distilled over Na/K alloy. Dimethylbis(2-methyl-1H-inden-1-yl)silane,<sup>18</sup> dimethylbis(2methyl-4,5-benzoinden-1-yl)silane,<sup>2</sup> [4-(4-*tert*-butylphenyl)-2-isopropyl-1H-inden-1-yl](dimethyl)(2-methyl-4-(4-tert-butylphenyl)-1,5,6,7tetrahydro-s-indacen-1-yl)silane,<sup>9</sup> dimethyl(2,5-dimethyl-3-(2-methylphenyl)-1,6-dihydro-1-thiapentalen-6-yl)silane,<sup>3</sup> [4-(4-tert-butylphenyl)-2-isopropyl-1*H*-inden-1-yl](dimethyl)(2-methyl-4-(4-*tert*-butyl-phenyl)-1*H*-inden-1-yl)silane,<sup>19</sup> dimethylbis(2-methyl-4-phenyl-1*H*inden-1-yl)silane,<sup>2</sup> dimethylbis(2-methyl-4-(4-tert-butylphenyl)-1Hinden-1-yl)silane and the corresponding zirconocene 17,<sup>4</sup> dimethylbis-(2-isopropyl-4-(4-*tert*-butylphenyl)-1*H*-inden-1-yl)silane,<sup>20</sup> were prepared according to published procedures. Tetrahydroindacenes 6 and 8 were prepared by the method described in our recent paper.<sup>9</sup> NMR spectra were recorded on a Varian XR-400 spectrometer (400 MHz). Elemental analysis was performed on a PerkinElmer Series II CHNS/ O Analyzer 2400.

**2-Methyl-4-(4-methylphenyl))-1,5,6,7-tetrahydro-s-indacene** (7). This product was obtained in a yield of 76% by the method used in the synthesis of 6.<sup>9</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>, 20 °C)  $\delta$ : 2.12 (m, 2H), 2.16 (s, 3H), 2.48 (s, 3H), 2.87 (t, 2H), 3.05 (t, 2H), 3.24 (broad s, 2H), 6.55 (s, 1H), 7.19 (s, 1H), 7.30 (2H) and 7.36 (2H) {AA'BB',  ${}^{3}J_{AB} =$  8.0 Hz}. Found, %: C, 92.19; H, 10.81. Calculated for  $C_{20}H_{20}$ , %: C, 92.26; H, 7.74.

Dimethylbis(2-methyl-4-phenyl-1,5,6,7-tetrahydro-s-indacen-1-yl)silane (9). A solution of 6 (16.76 g, 68 mmol) in Et<sub>2</sub>O (200 mL) was cooled to -40 °C, and n-BuLi in hexane (1.6 M, 43.4 mL, 69.4 mmol) was added. The mixture was allowed to warm to room temperature, stirred for 2 h, and cooled to -60 °C, and then CuCN (183 mg, 2.04 mmol) was added. After 15 min, SiMe<sub>2</sub>Cl<sub>2</sub> (4.1 mL, 34 mmol) was also added. The resulting mixture was allowed to warm to room temperature and stirred for 16 h. Hexane (400 mL) and H<sub>2</sub>O (10 mL) were added, and the organic phase was separated, dried over MgSO<sub>4</sub>, then passed through silica gel and evaporated. The residue was dried in vacuo and used without purification. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 20 °C) δ: -0.05 (bs, 6H, Si-CH<sub>3</sub>), 2.18 (m), 2.90-3.11 (m) {12H, -CH<sub>2</sub>-}, 2.28 (s), 2.34 (s) {6H, C-CH<sub>3</sub>}, 3.87 (s), 3.90 (s) {2H, >CH-}, 6.68 (bs, 2H, -CH=), 7.47 (m, 4H), 7.56 (m, 6H), {Ph}. Found, %: C, 87.65; H, 7.44. Calculated for C40H40Si, %: C, 87.54; H, 7.35

**Dimethylbis(2-methyl-4-(4-methylphenyl))-1,5,6,7-tetrahydro-s-indacen-1-yl)silane (10).** This was synthesized using the method described for 9. The product was used without purification. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 20 °C)  $\delta$ : -0.10 (s), -0.09 (s, double intensity), -0.08 (s) {Si-CH<sub>3</sub>}, 2.25 (s, 3H), 2.32 (s, 3H), 2.52 (s, 6H) {C-CH<sub>3</sub>}, 2.16 (m), 2.92–3.06 (m) {12H, -CH<sub>2</sub>-}, 3.84 (s), 3.87 (s) {2H, >CH-}, 6.66 (broad, 2H, -CH=), 7.36 (m, 4H), 7.43 (m, 4H), 7.45 (bs, 2H) {C<sub>At</sub>-H}. Found, %: C, 87.49; H, 7.80. Calculated for C<sub>42</sub>H<sub>44</sub>Si, %: C, 87.40; H, 7.69.

**Dimethylbis(2-methyl-4-(4-***tert***-butylphenyl)-1,5,6,7-tetra-hydro-s-indacen-1-yl)silane (11).** This was synthesized using the method described for 9. The product was used without purification. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 20 °C)  $\delta$ : −0.10 (bs, 6H, Si-CH<sub>3</sub>), 1.50 (s, 18H, −C(CH<sub>3</sub>)<sub>3</sub>), 2.14 (m), 2.89–3.12 (m) {12H, −CH<sub>2</sub>−}, 2.27 (s), 2.33 (s) {6H, C−CH<sub>3</sub>}, 3.86 (s), 3.87 (s) {2H, >CH−}, 6.72 (bs, 2H, −CH=), 7.30–7.60 {groups of m, 10H, aryl}. Found, %: C, 87.26; H, 8.64. Calculated for C<sub>48</sub>H<sub>56</sub>Si, %: C, 87.21; H, 8.54.

μ-{Bis-[η<sup>5</sup>-2-methyl-4-phenyl-1,5,6,7-tetrahydro-s-indacen-1-yl]dimethylsilanediyl}dichlorozirconium(IV) (12). Method A (9-Li<sub>2</sub> + ZrCl<sub>4</sub>). Ligand 9 (10.12 g, 18.44 mmol) was dissolved in Et<sub>2</sub>O (80 mL) and cooled to -40 °C, and n-BuLi (1.6 M in hexane, 23.8 mL, 38 mmol) was added. The mixture was allowed to warm to room temperature, stirred for 3 h, and evaporated. The resulting orangeyellow powder was suspended in pentane (150 mL) and cooled to -60 °C, and ZrCl<sub>4</sub> (4.43 g, 19 mmol) was added. After 5 min, Et<sub>2</sub>O (1 mL) was added, and the resulting mixture was allowed to warm to room temperature with stirring, stirred for an additional 16 h, and filtered. The orange-yellow powder was dried, DME (150 mL) and LiCl (0.5 g) were added, and the solution was refluxed with stirring for 6 h. The solvent was then evaporated and the product was crystallized from Et<sub>2</sub>O/hexane, producing a small amount (0.3 g,  $\sim$ 5%) of the meso form. Method B (9-Li<sub>2</sub> + ZrCl<sub>3</sub>(THF)<sub>2</sub>NH-tert-Bu). A solution of n-BuLi in hexane (1.6 M, 15 mL, 24 mmol) was added to a cooled (-20 °C) solution of tert-butylamine (2.4 mL, 22.9 mmol) and THF (1.85 mL, 23 mmol) in toluene (25 mL). The mixture was allowed to warm to room temperature, stirred for 2 h, and transferred into a dropping funnel. The  $ZrCl_4 \times 2THF$  (8.7 g, 23 mmol) was suspended in toluene (20 mL) and cooled to 0 °C, and lithium tert-butyl amide was added within 10 min. This mixture was allowed to warm to room temperature and stirred for 2 h. A second solution with previously prepared 9 (12.53 g, 22.8 mmol) was dissolved in a toluene (40 mL) and THF (3.78 mL, 46.6 mmol) solution and cooled to -40 °C, and then n-BuLi (1.6 M in hexane, 29.1 mL, 46.6 mmol) was added. This second mixture was allowed to warm to room temperature, stirred for 3 h, and cooled to -20 °C, and the mixture containing trichlorozirconium tert-butyl amide was added within 20 min. The resulting orange solution was stirred for 16 h, filtered, and evaporated. Hexane (100 mL) was added, and the precipitate of amide 16 was filtered out and washed with pentane. The precipitate was dissolved in  $CH_2Cl_2$  (50 mL), and the resulting dark red solution was treated with chlorotrimethylsilane (12.7 mL, 100 mmol). The mixture was stirred for 1 h, after which hexane (100 mL) was added, and then most of the

solvent was eliminated under reduced pressure (residual volume approximately 40 mL). The yellow precipitate was filtered out, washed with pentane, and dried in vacuo to yield 8.9 g (55%) of product. Pure (>98%) crystalline product was obtained by recrystallization from pentane–CH<sub>2</sub>Cl<sub>2</sub> (4:1). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 20 °C)  $\delta$ : 1.33 (s, 6H, Si-CH<sub>3</sub>), 1.95–2.05, 2.77–3.05 (group of m,12H, –CH<sub>2</sub>–), 2.26 (s, 6H, C–CH<sub>3</sub>), 6.67 (s, 2H, –CH=), 7.35 (t, 2H), 7.44 (t, 4H), 7.46 (s, 2H), 7.56 (d, 4H) {C<sub>Ar</sub>-H}. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 20 °C)  $\delta$ : 2.8, 18.4, 26.5, 32.0, 33.2 (aliphatic C), 118.2, 121.4, 127.2, 128.2, 129.1 (–CH=), 126.7, 132.2, 132.9, 134.4, 138.5, 143.3, 144.5 (=C<). Found, %: C, 67.64; H, 5.43. Calculated for C<sub>40</sub>H<sub>38</sub>Cl<sub>2</sub>SiZr, %: C, 67.77; H, 5.40.

μ-{Bis-[ $η^5$ -2-methyl-4-(4-methylphenyl)-1,5,6,7-tetrahydro-sindacen-1-yl] dimethylsilanediyl}dichlorozirconium(IV) (13). Method B, as described above for the synthesis of 12, was also used to prepare 13 with a yield of 52%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 20 °C) δ: 1.32 (s, 6H, Si-CH<sub>3</sub>), 1.99–2.04, 2.83–3.01 (group of m, 12H, –CH<sub>2</sub>–), 2.23 (s, 6H), 2.40 (s, 6H) {C–CH<sub>3</sub>}, 6.67 (s, 2H, –CH=), 7.24 (d, 4H), 7.43 (s, 2H), 7.45 (d, 4H), {C<sub>Ar</sub>-H}. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 20°°C) δ: 2.7, 18.2, 21.2, 26.4, 31.9, 33.1 (aliphatic C), 117.9, 121.4, 126.6, 128.8, 128.9, 132.1, 132.9, 134.2, 135.5, 136.7, 143.0, 144.4 (=C< and –CH=). Found, %: C, 68.31; H, 5.80. Calculated for C<sub>42</sub>H<sub>42</sub>Cl<sub>2</sub>SiZr, %: C, 68.45; H, 5.74.

 $\mu$ -{Bis-[ $\eta$ <sup>5</sup>-2-methyl-4-(4-*tert*-butylphenyl)-1,5,6,7-tetrahydro-s-indacen-1-yl]dimethylsilanediyl}dichlorozirconium(IV) (14). Method B, as described above for the synthesis of 12, was also used to prepare 14 with a yield of 67%. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 20 °C) δ: 1.30 (s, 6H, Si-CH<sub>3</sub>), 1.34 (s, 18H,  $-C(CH_3)_3$ ), 1.91–2.00, 2.70–2.98 (group of m, 12H,  $-CH_2$ -), 2.19 (s, 6H, C–CH<sub>3</sub>), 6.62 (s, 2H, -CH=), 7.44 (broad, 10H, C<sub>Ar</sub>-H). Found, %: C, 70.01; H, 6.66. Calculated for C<sub>48</sub>H<sub>54</sub>Cl<sub>2</sub>SiZr, %: C, 70.21; H, 6.63.

Synthesis of Zirconocenes Using ZrCl<sub>3</sub>(THF)<sub>2</sub>NH-tert-Bu, Typical Experiment. A solution of *n*-BuLi in hexane (1.6 M, 12.5 mL, 20 mmol) was added to a cooled (-20 °C) solution of tertbutylamine (2.2 mL, 20.5 mmol) and THF (1.65 mL, 20 mmol) in toluene (20 mL). The mixture was allowed to warm to room temperature, stirred for 2 h, and transferred into a dropping funnel. The  $ZrCl_4 \times 2THF$  (7.6 g, 20 mmol) was suspended in toluene (20 mL) and cooled to 0 °C, and lithium tert-butyl amide was added within 10 min. This mixture was allowed to warm to room temperature and stirred for 2 h. The corresponding bis-indenyl ligand was dissolved in a toluene (35 mL) and THF (3.30 mL, 40 mmol) solution and cooled to -40 °C, and then *n*-BuLi (1.6 M in hexane, 25.6 mL, 41 mmol) was added. This second mixture was allowed to warm to room temperature, stirred for 3 h, and cooled to -40 °C, and the mixture containing trichlorozirconium tert-butyl amide was added within 20 min. The resulting solution was stirred for 16 h. The probe from this mixture (ca. 0.2 mL) was evaporated to dryness in vacuo, and CH<sub>2</sub>Cl<sub>2</sub> (0.5 mL) and Me<sub>3</sub>SiCl (0.1 mL) were added. After 1 h, the probe was evaporated, dried, dissolved in CDCl<sub>3</sub>, and analyzed by NMR <sup>1</sup>H spectroscopy; rac-selectivity was determined by comparison of vinyl and/or Me<sub>2</sub>Si signals for rac and meso isomers. The yield of the rac isomer was determined after its isolation by recrystallization.

**X-ray Crystallography.** Experimental intensities were measured on a Bruker SMART APEX II diffractometer (graphite monochromatized Mo K $\alpha$  radiation,  $\lambda = 0.71073$  Å) at 160 K using  $\omega$  scan mode. The structures were solved by direct methods and refined by fullmatrix least-squares on  $F^2$  with anisotropic thermal parameters for all non-hydrogen atoms.<sup>21</sup> All hydrogen atoms were placed in calculated positions and refined using a riding model. The C(38) envelope atom of the five-membered cycle is disordered over two positions with an occupancy ratio of 0.57/0.43.

# ASSOCIATED CONTENT

#### **Supporting Information**

Details of crystal structure determinations, atomic coordinates, isotropic and anisotropic displacement parameters, and bond lengths and angles of complexes **12** and **16**. Experimental details for catalyst preparation, polymerization procedure, and

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polymer analysis. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications no. CCDC-873359 and 873360. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. code +44(1223)336-033; E-mail: deposit@ccdc.cam.ac.uk]. This material is available free of charge via the Internet at http://pubs.acs.org.

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#### Notes

The authors declare no competing financial interest.

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