Synthetic Explorations Towards Sterically Crowded 1,2,3-Substituted Bis(indenyl)zirconium(IV) Dichlorides

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The systematic synthesis of 1,3-dialkyl-substituted 2-silylindenes and their suitability as zirconocene ligands is discussed. Unexpected reactivities rendered a number of substitution patterns unfeasible, especially for alkyl groups other than methyl in 2-(trimethylsilyl)indene derivatives, and essentially for all derivatives of 2-(dimethylsilyl)indene. The syntheses of *rac*/*meso*-bis[1-methyl-2-(trimethylsilyl)indenyl]zirconium(IV) dichloride (**12**) and bis[1,3-dimethyl-2-(trimethylsilyl)indenyl]zirconium(IV) dichloride (**13b**) are described. The solid-state structure of the latter displays strong deformations within the ligand framework and an unusually large $Cp_{centroid}$-Zr–$Cp_{centroid}$ angle. Both, **12**/MAO and **13b**/MAO, displayed ethene and ethene-co-1-hexene polymerization activity. Curiously, **13b**/MAO shows an extraordinary monomer selectivity, which can be rationalized by means of DFT calculations on the active site.

Introduction

The field of metallocene-catalyzed olefin polymerization has achieved significant improvements on polymer properties. The ligand−tacticity relationship is well understood and, apart from tailor-made stereocontrol, co-monomer incorporation and block length have been emphasized as keys to innovative materials.[1] The detailed polymerization mechanism with all its variations is complicated and the choice of appropriate polymerization conditions to favor one monomer over the other still requires vast and tedious sets of experiments. An outline of the extensive efforts made within this area can be found in the various review articles.[2]

Previous work from our laboratory addressed unbridged zirconocene dichloride with silyl substituents in the 1 or 2 position.[3] Reports on trisubstituted indenyl ligands, i.e. substituents in the 1, 2, and 3 positions, are still quite uncommon. It may be expected that steric congestion in such complexes is significant and that overall polymerization activity may be negatively influenced. In this study, we wish to present our results on a systematic study of 1,3-dialkyl-2-silyl-trisubstituted indene ligands for the synthesis of zirconocene dichlorides.

Results and Discussion

Ligand Syntheses

The introduction of alkyl groups in the 1 and 3 position of 2-silylindenes should be feasible in a straight forward manner by simple double alkylation of indenyllithium salts. Deprotonation of 2-(dimethylsilyl)indene (**1a**, 2-DMS-Ind) and 2-(trimethylsilyl)indene (**1b**, 2-TMS-Ind) was achieved by *n*-butyllithium in pentane at room temperature or –90 °C, respectively. In spite of the nonpolar solvent, deprotonation at lower temperatures provided hydride substitution products for **1a**, as observed by Kira et al.[4] Alternatively deprotonation can be achieved with potassium hydride at room temperature.

Methylation of the lithium salt of **1a** with methyl iodide at –40 °C in diethyl ether yielded exclusively 3-Me-2-DMS-Ind (**2a**), while 1-Me-2-TMS-Ind (**2b**) was obtained likewise from 2-TMS-Ind. Repetition of the deprotonation−methylation sequence afforded a 1:4 mixture of the 1,1-dimethyl and 1,3-dimethyl isomers for both, **3a** and **3b**. Deprotonation and washing with pentane provided pure lithium salts of the 1,3-dimethyl-2-silylindenes **3a** and **3b** (Scheme 1). **3a** exhibits diastereotopic methyl resonances of the silyl group in a 1:1 ratio due to the presence of the chiral C(1) atom.

In order to determine whether bulkier alkyl substituents could be placed in the 1,3 positions, studies on the introduction of the *i*Pr group were conducted on **1b**, as the TMS

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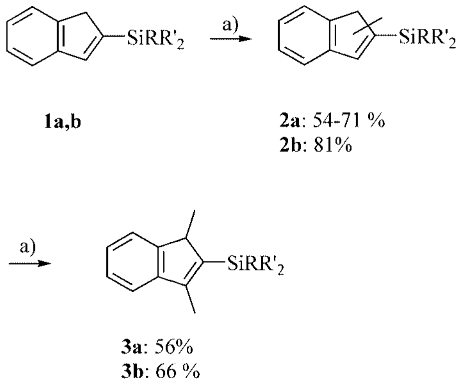
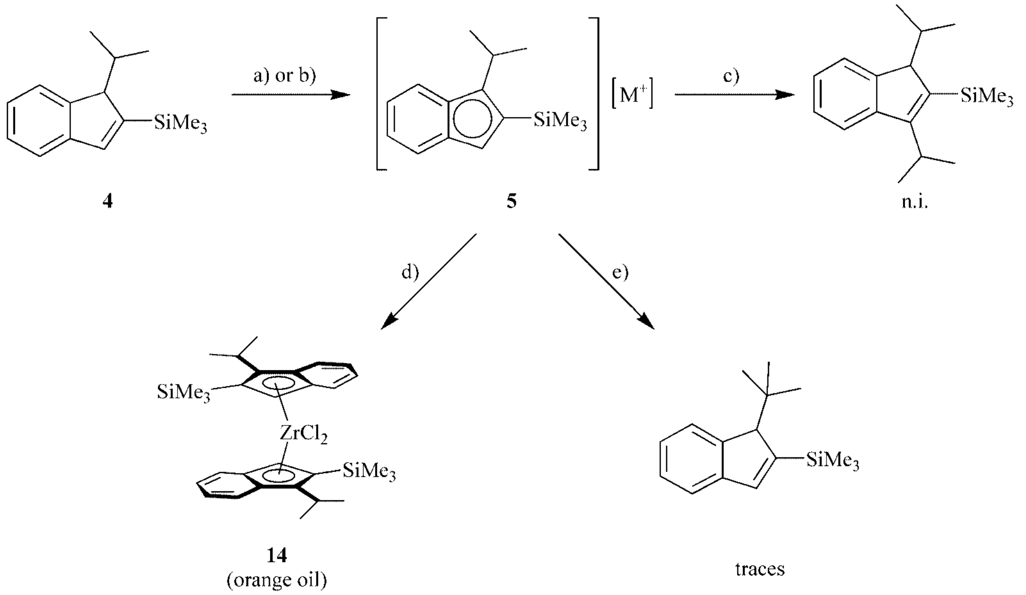


Scheme 1. General route towards 1,3-dialkyl-2-silylindenes. a) *n*BuLi, pentane, room temperature; MeI, diethyl ether, –40 °C. **a:** R = H, R′ = Me. **b:** R = R′ = Me. Yields are reported for the purified lithium salts of **3a** and **3b**, whereas spectroscopic data were obtained on the free ligands.

moiety is less prone to substitution reactions in the presence of lithium organyls. A brief summary of the results is given in Scheme 2. Following the procedure for methylation, exposure of the lithium salt of **1b** to isopropyl iodide sufficed to obtain the 1-*i*Pr isomer **4** in good yield. The proton and carbon NMR spectra of **4** reveal diastereotopic resonances for the *i*Pr methyl groups, and curiously the expected singlet for the trimethylsilyl (TMS) moiety displays two resonance maxima. We interpret these to arise from steric interaction of the *i*Pr and TMS groups. In addition, two different C(1) resonances are found. Deprotonation of **4** with *n*-butyllithium, however, leads to soluble lithium salts, which in a direct second alkylation with isopropyl iodide without prior isolation resulted in a mixture of four isomers, i.e. the mono-alkylated 1 and 3 isomers (3:1 parts) and the dialkylated 1,3 and 1,1 isomers (2:0.1 parts). The slight excess of *n*-butyllithium used in the reaction could be traced by detection of 2-methylhexane (0.3 parts). Deprotonation of **4** with potassium hydride in refluxing THF failed to provide a well-defined, insoluble potassium salt (K[**5**]). Due to the solubility of these salts, washing with pentane was accompanied by a loss of material.

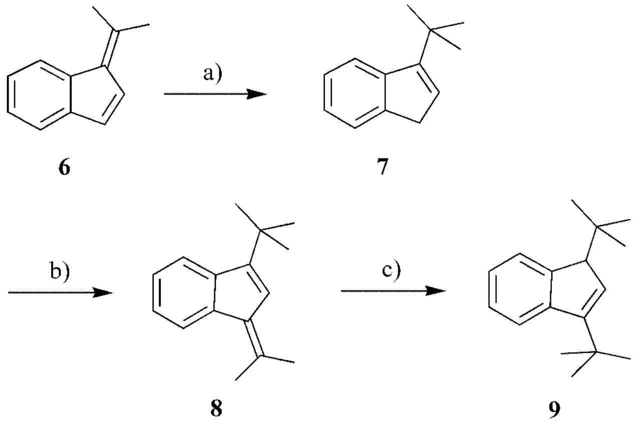
A compelling explanation for these solubilities can be derived from a quenching experiment of Li[**5**] with methyl iodide in THF. GC/MS analysis of the reaction products revealed ten major products, of which one could be identified as 1-*t*Bu-2-TMS-Ind. Apparently Li[**5**] equilibrates between its indenyllithium and alkyllithium derivative, i.e. the lithium migrates from the Cp moiety of the indenyl through the *i*Pr group resulting in a covalent lithium carbon bond. Although satisfactory ^{1}H and ^{13}C NMR spectroscopic data were obtained, K[**5**] appears to be an inhomogeneous, poorly described compound, partially soluble in hydrocarbons. We suspect cation migration is still possible, despite the significantly bigger potassium cation.

Introduction of a *t*Bu group into 2-TMS-Ind may not be expected to be easy. Even in the case of indenyllithium, alkylation with *t*Bu bromide or iodide succeeds only in moderate yields.[5] Aiming for a possibly more demanding, but still more efficient route, we investigated a literature procedure for the synthesis of *t*Bu groups from 6,6-dimethyl(benzo)fulvenes.[6] 6,6-Dimethylbenzofulvene (**6**) is readily available in a one-pot reaction from indene, pyrrolidine and acetone in methanol,[7] and methyllithium is known to react smoothly in a 1,4-addition in diethyl ether to 1-*t*Bu-indenyllithium in a 80% yield. Acidic work-up and distillation afforded 3-*tert*-butylindene (**7**) in a 58% yield. Application of typical activators like TMEDA and $BF_3 \cdot Et_2O$ does not improve the yield, but running the reaction in pentane in the presence of 10 wt.-% $AlCl_3$ offers the advantage of quantitative conversion, though acidic work-up is required prior to further reactions.



Scheme 2. Reactivity of 1-isopropyl-2-(trimethylsilyl)indene (**4**). a) *n*BuLi, pentane; b) potassium hydride, THF; c) 2-Iodopropane, diethyl ether/THF (n.i. = not isolated); d) $ZrCl_4$, THF, –40 °C; e) MeI, THF.

Introduction of a second *t*Bu group by the same means is more complicated (Scheme 3). Formation of the 1-*t*Bu-6,6-dimethylbenzofulvene (**8**) does not occur at room temperature, but with an excess of pyrrolidine and refluxing for several days, nearly quantitative conversion is achieved. Addition of methyllithium to **8**, provides 1,3-di-*t*Bu-indene (**9**), albeit in low yield. It may be reasoned that the *t*Bu group raises the energy of the *exo* double bond by its electron releasing character and thus inhibits nucleophilic attack by methyllithium. Disappointingly, we had to find that the synthesis of 2-TMS-6,6-dibenzofulvene starting from **1b** is not possible with the aforementioned procedure. Alternatively we investigated the reaction of the lithium salt of **1b** with acetone and subsequent dehydration with phosphoric acid or acid anhydrides. The first attempt, which employed phosphoric acid, provided the benzofulvene. Reproduction of this reaction was unsuccessful; we are not primarily interested in ill-defined polymers, but could, however, envision the obtained products to be useful for road building purposes.

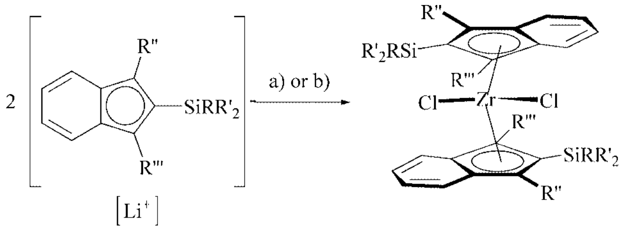


Scheme 3. A selective synthesis of 1,3-di-*t*Bu-indene (**9**). a) MeLi, Et_2O, 0 °C or MeLi, pentane, 5 mol-% $AlCl_3$ / acidic work-up b) Pyrrolidine$_{ex}$, acetone$_{ex}$, MeOH, 48 h reflux; c) MeLi, Et_2O, 6 h reflux.

Zirconocene Syntheses

To facilitate introduction to the coordination sphere of zirconium, **2b**, **3a–b** were all converted into their lithium salts **10**, **11a–b**, respectively, by exposure to stoichiometric amounts of a organyl lithium in pentane. The observed reactivities mirrored those of the starting material **1a–b**. The syntheses of the zirconium complexes were subsequently attempted by a salt metathesis reaction with zirconium tetrachloride, as illustrated in Scheme 4. For disubstituted ligands, *rac* and *meso* diastereomers may be obtained, whereas trisubstituted ligands exclusively provide enantiomers.

rac/*meso*-Bis[1-methyl-2-(trimethylsilyl)indenyl]zirconium(IV) dichloride (**12**) was obtained as a yellow powder in a respectable 55% yield. The *rac* and *meso* diastereomers were detected by ^{1}H NMR at a 1:1 ratio, and isolation or enrichment by crystallization at –40 °C failed. The *rac* and *meso* diastereomers were assigned according to relative chemical shifts, as published elsewhere.[3]



	10	11a	11b	12	13a	13b
R	CH_3	H	CH_3	CH_3	H	CH_3
R'	CH_3	CH_3	CH_3	CH_3	CH_3	CH_3
R''	CH_3	CH_3	CH_3	CH_3	CH_3	CH_3
R'''	H	CH_3	CH_3	H	CH_3	CH_3

Scheme 4. Salt metathesis reaction of the potassium/lithium salts with zirconium tetrachloride to form bis(indenyl)zirconocene dichlorides. a) $ZrCl_4$, Et_2O, 0 °C; b) $ZrCl_4$, THF, –40 °C. When R''' = H, *rac* and *meso* isomers can be formed of which the latter one is omitted for clarity.

Reaction of **11a** with zirconium tetrachloride in diethyl ether at 0 °C provided a yellow oil upon filtration through magnesium sulfate and subsequent solvent removal. Crystallization from diethyl ether was only limitedly successful, and we were not able to obtain an analytically pure sample due to the low yield. NMR spectroscopic data suggest, however, formation of bis[1,3-dimethyl-2-(dimethylsilyl)indenyl]zirconium(IV) dichloride (**13a**). Unreacted **11a** could easily be recovered in good yields. A change of solvent from diethyl ether to THF did not improve the reaction and only decomposition products could be obtained.

Metallation of **11b** in diethyl ether succeeded with formation of a yellow precipitate. The solubility of bis[1,3-dimethyl-2-(trimethylsilyl)indenyl]zirconium dichloride (**13b**) in diethyl ether was too limited to allow work-up in this solvent; toluene proved to be suitable. Orange or yellow powders were obtained in a 44% yield upon recrystallization from diethyl ether solution at –40 °C, depending on the crystallinity of the zirconocene. Single crystals grown from diethyl ether solution are bright orange in color.

As it may be anticipated from the observation of inhomegeneity of K[**5**], an orange oil was obtained as its reaction product with zirconium tetrachloride (Scheme 2). Crystallization was unsuccessful, though crystals would form after a few weeks in the drybox. The ductility of the crystals precluded further isolation.

Crystal Structure

An ORTEP[8] view of **13b** is given in Figure 1; selected bond lengths and angles are listed in Table 1. The coordination sphere of the zirconium atom can be described as a distorted tetrahedron. The two indenyl and chloride ligands are related by C_2 symmetry. The dihedral angle φ, which is defined as Si1–C3–C3*–Si1*, is measured to 165.7°, a nearly perfect *anti*-periplanar conformation of the indenyl ligands. As a consequence, the 1,3-methyl groups on the frontside (C11, C11*) almost ideally intersect the Cl1–Zr1–Cl1* angle, which spans 92.8°. The dihedral angle C11–C4–C4*–C11* is – with only 5.7° distortion – close to a perfect *syn*-periplanar orientation of these methyl groups. In contrast, the methyl groups on the backside (C10, C10*) span a dihedral angle (C10–C2–C2*–C10*) of –57.5° and minimize steric interaction by this strongly *syn*-clinal orientation.

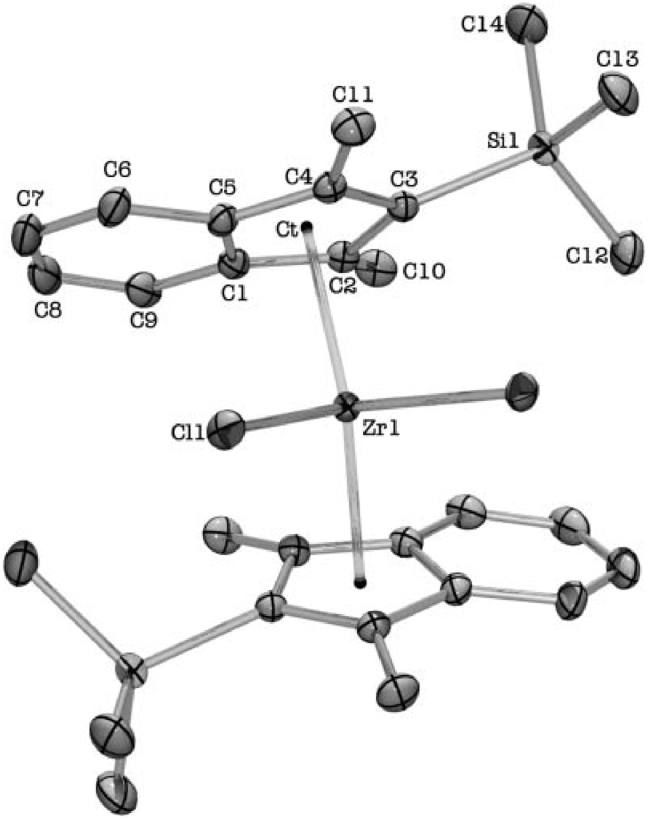


Figure 1. Refined crystallographic structure of bis[1,3-dimethyl-2-(trimethylsilyl)indenyl]zirconium dichloride (**13b**). Hydrogen atoms are omitted for clarity. Thermal ellipsoids are at the 50% probability level.

Table 1. Selected bond lengths [Å] and angles [°] for **13b**.

Bond length/angle [Å / °]	**13b**
Zr1–Cl1	2.4473(3)
Zr1–Ct	2.263
Zr1–C1	2.6188(10)
Zr1–C2	2.5385(10)
Zr1–C3	2.5370(10)
Zr1–C4	2.5320(10)
Zr1–C5	2.6252(9)
Si1–C3	1.8979(10)
Cl1–Zr1–Cl1*	92.843(13)
Ct–Zr1–Ct*	137.40
Ct–C3–Si1	168.84
Ct–C2–C10	167.76
Ct–C4–C11	175.43

The contribution of steric congestion is manifested in the out-of-plane bend angles of the indenyl ligands, which expose a convex surface to the zirconium center. In transversal direction, the frontside methyl groups are bent out of the linear arrangement by 4.6°, whereas the sterically more encumbered methyl groups on the backside are bent out by 12.2° – measured as C11–C4–Ct and C10–C2–Ct, respectively. In longitudinal direction, the curvature climbs from a modest 1.1° within the benzo moiety to 5.2° and 4.2° at the transition from benzo to Cp moiety and within the Cp ring, and finally reaches 19.3° for the transition Cp to silyl moiety. Consequently, the distortion of the tetrahedral symmetry around the zirconium is stronger than usual; the Ct-Zr1–Ct* angle ε measures 137.4°. To the best of our knowledge, this is the largest value ever reported for unbridged bis(indenyl)zirconium dichlorides. The largest values for ε have been reported for *rac*-ferrocenyl-bis(1-indenyl)zirconium dichloride, ferrocenyl-bis[2,3,4,5-tetramethyl-1-Cp]zirconium dichloride[9] and [(1,2,4-tri-(*t*Bu)Cp)(1,2,3,4-tetra-(*i*Pr)Cp)]zirconium dichloride[10] with 129.7, 138.5 and 138.8°, respectively.

Polymerization Characteristics and DF Calculations

In order to establish a rough estimate on the properties of **12** and **13b** as polymerization catalyst precursors in ethene homopolymerizations with MAO as cocatalyst, isobar and isothermal experiments were run at two different catalyst concentrations. Reference experiments were carried out with bis(indenyl)zirconium dichloride/MAO (**RefH**) and bis[2-(trimethylsilyl)indenyl]zirconium dichloride/MAO (**RefTMS**) at concentrations of $c(\mathrm{Zr}) = 1.0\cdot10^{-7}$ mol/L and $c(\mathrm{Zr}) = 1.0\cdot10^{-6}$ mol/L at Al/Zr ratios of 10000 and 1000, respectively. For **12**/MAO and **13b**/MAO, these conditions were not sufficient for detectable polymerization activity. Rather, **12**/MAO and **13b**/MAO required higher catalyst and MAO concentrations in order to show sufficient activity. A rough comparison of the catalyst's activities and the molecular weights obtained is given in Table 2.

The results for the homopolymerizations suggest a decrease in activity with increasing degree of substitution of the catalysts' ligand framework. We ascribe the significantly lower activities for high catalyst concentrations of **RefH**/MAO and **RefTMS**/MAO to diffusion control in the course of polymerization. The high amount of polymer produced increases the viscosity and hence reduces ethene up-take and agitation of the reaction mixture. Considering the polymer molecular masses, only **12**/MAO displays a notably different value compared to the other catalysts. The higher polydispersity index (PDI) obtained from **12**/MAO may be explained by the presence of the *rac* and *meso* isomer as active sites. The PDI's relative proximity to the value of 2 suggests their polymerization characteristics to be fairly alike.

The comonomer response of the different catalysts cannot be described by a simple consideration of steric congestion. Whereas the unsubstituted **RefH**/MAO displays a positive comonomer response, **RefTMS**/MAO and **12**/MAO suffer from strong deactivation by 80 to 90% relative to the

Table 2. Polymerization activities of **12**/MAO and **13b**/MAO in ethene and ethene-*co*-1-hexene polymerizations. $c(\mathrm{Zr}) = 1.0 \cdot 10^{-7}$ mol·L^{-1} and $c(\mathrm{Zr}) = 1.0 \cdot 10^{-6}$ mol·L^{-1} at 30 °C in toluene; $c(\mathrm{E}) = 0.14$ mol·L^{-1}.

Catalyst	$c(\mathrm{Zr})$ [mol·L^{-1}]	Activity/ [kg·mol$_{\mathrm{Zr}}^{-1}$·mol$_{\mathrm{E}}^{-1}$·h^{-1}]	Al/Zr	M_w [Kg·mol^{-1}]	PDI
HDPE–X_H = 0.0					
RefH	$1.0 \cdot 10^{-6}$	272000 ± 3500	1000	770	2.7
RefH	$1.0 \cdot 10^{-7}$	1560000 ± 160 000	10000	820	2.0
RefTMS	$1.0 \cdot 10^{-6}$	327000 ± 52000	1000	625	2.6
RefTMS	$1.0 \cdot 10^{-7}$	817000 ± 1400	10000	785	2.6
12	$2.0 \cdot 10^{-7}$	165000 ± 22000	10000	450	3.5
13b	$1.0 \cdot 10^{-6}$	135000 ± 21000	4000	790	2.6
LLDPE–X_H = 0.6					
RefH	$1.0 \cdot 10^{-6}$	376000 ± 14000	1000	189	3.0
RefTMS	$1.0 \cdot 10^{-6}$	53,700 ± 1700	1000	45	16
12	$2.0 \cdot 10^{-5}$	15900 ± 8800	2000	195	31[a]
13b	$1.0 \cdot 10^{-6}$	176000	2000	428	2.2

[a] Trimodal distribution observed, $M_n = 6.2$.

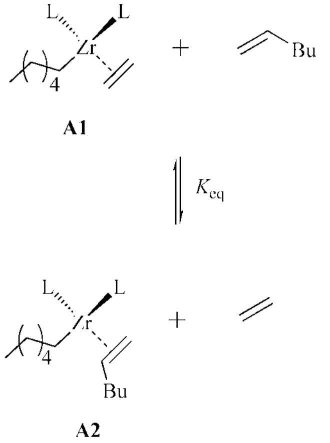
homopolymerization. In contrast, **13b**/MAO displays virtually no response to the comonomer and polymerises with roughly the same rate as before.

The fairly low activity of **13b**/MAO prompts the question of whether or not the catalyst precursor is sufficiently activated by the MAO available during the polymerization. To assess the dependence of **13b**/MAO on the Al/Zr ratio, a series of experiments was run at constant zirconium, ethene, and 1-hexene concentrations, while varying the Al/Zr ratio from approximately 1000 to 19000. The data obtained are listed in Table 3. We suggest that the catalyst activity does not strongly depend on the concentration of MAO or the Al/Zr ratio, though the data point to a slight increase in activity.

Table 3. Polymerization activities of **13b** in ethene-*co*-1-hexene polymerizations as a function of the Al/Zr ratio. $c(\mathrm{Zr}) = 1.0 \cdot 10^{-6}$ mol·L^{-1}, $c(\mathrm{E}) = 0.14$ mol·L^{-1}, $X_H = 0.5$ at 30 °C in toluene.

Activity [kg·mol$_{\mathrm{Zr}}^{-1}$·mol$_{\mathrm{E}}^{-1}$·h^{-1}]	Al/Zr
6000	950
18600	1900
26100	2800
45400	5700
44000	9500
33000	14200
79100	18900

Another issue of interest is the neutral to positive comonomer response of **13b**/MAO, which does not fit into the trend set by **RefTMS**/MAO and **12**/MAO. A ^{13}C NMR analysis of the copolymer obtained from **13b**/MAO was conducted according to the signal assignments published by Randall[11] and revealed a signal pattern typical for LLDPE polymers. The comonomer content was determined to 0.3 mol-% 1-hexene, which is essentially the detection limit. Assuming that the statistical distribution of the comonomer in the polymer chain is proportional to the equilibrium constant K_{eq} that would describe the population of the active site models **A1** and **A2**, as depicted in Scheme 5, it is possible to calculate the Gibbs energy [Equation (1)] for the enchainment of 1-hexene relative to ethene.



Scheme 5. Simplified representation of the active site with a polymer chain (*n*-hexyl) attached: **A1** with an ethene and **A2** with a 1-hexene ligand. For clarity, the 1,3-dimethyl-2-TMS-indenyl ligands are abbreviated as "L" and charges are omitted.

$$\Delta_r G = -RT\ln(K_{eq}) \quad (1)$$

$$K_{eq} = \frac{x_E x_H}{X_E X_H} \quad (2)$$

At 303.15 K with X_E and $X_H = 0.5$, and $x_E = 0.997$ and $x_H = 0.003$, we obtain $\Delta_r G = 11$ kJ/mol and estimate the lower and upper limit to 10 and 14 kcal/mol, respectively. This value includes the reaction entropy, which could in general be obtained from an Arrhenius plot. A set of experiments was designed to investigate the dependence of the equilibrium constant K_{eq} on the temperature, as suggested by the van't Hoff equation. The results summarized in Table 4 indicate that there is no detectable relation between the polymerization temperature and catalyst activity or comonomer incorporation. The activity varies unsystematically, and the 1-hexene incorporation is constant. An experimental estimate of the reaction entropy is therefore not available.

Table 4. Polymerization activities of **13b** in ethene-*co*-1-hexene polymerizations as a function of the reaction temperature. The error indicates the experimental standard deviation; $c(\mathrm{Zr}) = 1.0{\cdot}10^{-6}$ mol·L^{-1}, $c(\mathrm{E}) = 0.14$ mol·L^{-1}, $X_{\mathrm{H}} = 0.5$ at Al/Zr = 4000 in toluene.

T/°C	Activity [kg·mol$_{\mathrm{Zr}}^{-1}$·mol$_{\mathrm{E}}^{-1}$·h^{-1}]	M_{w} [Kg·mol^{-1}]	PDI	x_{H}
20	24400 ± 3100	494	11	0.003
30	18900 ± 1900	533	20	0.003
40	29600 ± 2200	391	15	0.003
48	44400 ± 1800	273	2.6	0.003
60	29800 ± 2000	172	6.9	0.003

In order to validate the quality of our estimate of the reaction Gibbs energy, we conducted DF calculations on an active site of **13b** which features a *n*-hexyl ligand and one ethene or 1-hexene unit. For the ethene complex, a pronounced α-agostic interaction of the polymer chain and the zirconium center was found, stretching the C–H bond length to 1.13 Å. The ethene ligand shows slight rehybridization through a HCH bond angle of 116.4° and is symmetrically coordinated at the typical Zr···C distances of 2.72 Å (C1) and 2.85 Å (C2). The 1-hexene complex displays evidence of steric strain already on visual inspection, as the *Z*-side of the 1-hexene ligand is tilted away from the zirconium center by a 16.5° deviation from the perfect orthogonal side-on coordination. This is due to intrusion of the butyl substituent into the space occupied by the methyl groups in the 1 and 3 positions of the indenyl ligands. Consequently, the Zr-olefin distance is increased to 2.78 Å (C1) and 3.32 Å (C2). An α-agostic interaction is not detectable, and there is an insignificant lengthening of the Zr−carbon bond to the polymer chain by 0.03 Å.

The relative energies of both olefin complexes, compared to the energies of the uncoordinated olefins, is a measure of their populations in the equilibrium during the polymerization process (Scheme 5). Since both olefins were present in equal amounts, stoichiometric corrections are not required. For the *rac*-like conformer of the active site the energy difference calculates to 8 kJ/mol, whereas the *meso*-like conformer is somewhat less stable with 13 kJ/mol. A meaningful comparison of product equilibria with stability of starting materials usually requires the knowledge of activation enthaplies. All attempts to calculate the activation enthalpies for the insertion process failed since the optimization of the transition state exclusively led to geometries where the olefin ligands would rotate along the zirconium−olefin bond and result in non-planar geometries. Although we have been able to calculate nonplanar transition states for other systems, the calculations would not converge in the case of **A1** or **A2**. The polydispersity index of 2.2 for the copolymerization suggests that only one active site needs to be considered.

Conclusions

The herein investigated syntheses of sterically demanding 1,2,3-substituted indenyl ligands on the basis of 2-silylindenes are unexpectedly difficult. Apart from hydride substitution problems, which may arise for the DMS moiety, substituents larger than a methyl group are surprisingly prone to hydrogen shift reactions of the deprotonated ligands. This side reaction affects the yield and applicability of the indenyl salts significantly. Introduction of an alkyl moiety without hydrogen shift capability like *t*Bu was precluded by steric strain in the synthesis of a suitable precursor. Further, the DMS-substituted ligand would not afford the desired zirconocene complex. As we have seen in earlier work, the presence of hydrogen on the silyl groups in 2 position does not seem to be favored for the zirconocene synthesis.[3]

In contrast, the syntheses of bis[1-methyl-2-TMS-indenyl]zirconium(IV) dichloride (**12**) and bis[1,3-dimethyl-2-TMS-indenyl]zirconium(IV) dichloride (**13b**) were achieved without undue difficulty, although the separation of the *rac* and *meso* diastereomers of **12** failed. The (basic) polymerization studies presented herein suggest that the activity in ethene polymerizations decreases with an increasing degree of substitution. In contrast to the very moderate activities, the molecular weights are less effected and this may be rationalized by the reduction in available space at the active site. Chain termination by chain transfer requires a β-agostic structure *and* the association of a monomer unit. Chain transfer to MAO requires an intimate interaction with the very same. Both processes are likely to be suppressed by a bulky ligand framework. This effect is even more pronounced for **13b**, which does not show the expected increase in activity with increasing Al/Zr ratio. Such an effect is often observed and poorly understood.

The virtual inertness of **13b** towards 1-hexene as a monomer is an interesting feature, which is to the best of our knowledge unprecedented. The unsuccessful attempts to find the transition state for this process support our idea that the selectivity is governed by steric factors. Nevertheless an interesting agreement between experiment and theory has been found: The calculated energy difference of 8 to 13 kJ/mol for the olefin complexes falls into the same range as the Gibbs energy of 11 kJ/mol, as derived from Boltzmann statistics on the 1-hexene incorporation into the polymer chain. This may indicate that the insertion of the monomer units may be controlled by a single activation barrier, despite our inability to calculate any suitable transition state. Systems like **13b**, employed in a catalyst mixture, are industrially desirable as they show a monomer selectivity which could be used to produce long chain branches in a copolymerization with 1-hexene. The catalyst activity is, however, traded for this selectivity.

Experimental Section

General: Unless otherwise indicated, all procedures were conducted using Schlenk techniques under argon. All solvents were dried from sodium with benzophenone or anthracene (diethyl ether, THF, and toluene) or lithium aluminium hydride (pentane) and distilled prior to use. Acetone (Merck) was dried with anhydrous magnesium sulfate for three days and distilled under argon. When used as a filter agent, magnesium sulfate (Merck) was dried at 140 °C for at least two days prior to use. Iodomethane (Fluka) was dried with calcium hydride (Merck, used as received) and distilled under argon. 2-Iodo-propane (Fluka) and methanol p.a. (Merck) were used as received. Aluminum trichloride (resubl. grade, Aldrich Chemicals), pyrrolidine (Fluka), magnesium turnings (Merck and Aldrich Chemicals), *n*-butyllithium (Aldrich Chemicals or Merck), methyllithium (Aldrich Chemicals), *tert*-butyllithium (Aldrich Chemicals), boron trifluoride diethyl etherate (Aldrich Chemicals) and zirconium tetrachloride (Strem, 99.95%+, sublimed grade) were used as received. Column chromatography was conducted on silica gel 60 (0.040–0.063 mm) provided by Merck. Methylalumoxane (MAO) was purchased at Crompton Bergkamen, Germany, as a 10% toluene solution. Prior to use, the MAO solution was filtered through a D4-frit and volatiles removed in vacuo yielding a white solid. Polymerization grade ethene was provided by Borealis Stathelle, Norway. 1-Hexene (Aldrich) was purified before copolymerization by drying over potassium/benzophenone and subsequent distillation in an argon atmosphere. ^{1}H- and ^{13}C NMR spectra acquired with a Varian Gemini 300 MHz instrument were referenced to the residual solvent peaks. Low resolution MS was conducted with a Hewlett–Packard 5973 MSD, coupled with a Hewlett–Packard 6890 GC unit. GC columns used were HP-5, I.D. 0.32 mm, 0.250 µm, 30 m and DB-17, I.D. 0.25 mm, 0.250 µm, 30 m, both manufactured by J&W Scientific. GPC characterizations of the HDPE samples were conducted with a Waters 150CVplus instrument, operating with two HMW 6E and one HMW7, or three HT6E styragel columns (Waters) at 140 °C with trichlorobenzene as elution solvent and a dRI & viscosity detector. Alternatively, weight and number average molecular weights and polydispersity indices were measured at 140 °C with a Waters Alliance 2000 size exclusion chromatography (SEC) instrument equipped with Waters HT3, HT4, HT5 and HT6 columns. 1,2,4-Trichlorobenzene was used as solvent at a flow rate of 1.0 $\mathrm{cm^3 \cdot min^{-1}}$. The columns were universally calibrated with narrow molecular weight polystyrene standards. Well-characterized lithium salts which resulted in isolable Zr complexes were not subjected to EA.

2-(Dimethylsilyl)indene (1a) and 2-(Trimethylsilyl)indene (1b): These compounds were prepared according to a published literature procedure.[3]

2-(Dimethylsilyl)-3-methylindene (2a). Potassium Hydride Route: Potassium hydride (432 mg, 10.8 mmol) was dissolved in THF (40 mL) and cooled to –90 °C. 2-(Dimethylsilyl)indene (1.88 g, 10.8 mmol) dissolved in THF (8 mL) was injected into the cold potassium hydride/THF suspension and the reaction mixture was warmed to room temperature while being stirred overnight. Substitution of THF by 20 mL diethyl ether and filtration through a cannula resulted in a clear, yellow-green solution of the 2-(dimethylsilyl)indenylpotassium complex. In a second Schlenk flask equipped with a pressurized addition funnel, methyl iodide (2.0 mL, 32.4 mmol) and diethyl ether (20 mL) were cooled to –40 °C before the potassium complex was added dropwise under isothermal conditions over a period of 30 minutes. The reaction was stirred overnight and warmed to room temperature, to yield a copious white precipitate. Filtration to remove insolubles and acidic quenching was followed by extraction with water (2 × 20 mL). Drying over magnesium sulfate and removal of solvent afforded the product (1.29 g, 6.9 mmol, 64%) at 85% purity. The isomer distribution was 4% 3 isomer, 81% 1 isomer, 8% un- and 7% disubstituted.

***n*-Butyllithium Route:** 2-(Dimethylsilyl)indene (2.04 g, 11.7 mmol) and pentane (50 mL) were placed in a Schlenk flask. *n*-Butyllithium (6.4 mL, 10.3 mmol) was slowly added via syringe. The solution was stirred overnight with waterbath cooling to yield a white precipitate. By filtration with a cannula, washing with pentane (2 × 20 mL) and drying under high vacuum a white powder (1.85 g, 10.3 mmol) was obtained. The 2-(dimethylsilyl)indenyllithium salt was dissolved in 30 mL diethyl ether and placed in an addition funnel mounted on a Schlenk flask charged with methyl iodide (2.9 mL, 46.8 mmol) in diethyl ether (30 mL). Drop-wise addition provided a yellow solution, which was stirred overnight prior to acidic work-up (20 mL 0.1 mol/L hydrochloric acid) in diethyl ether. Phase separation, washing of the organic layer with deionized water followed by drying over magnesium sulfate and removal of solvent at 70 mbar/40 °C afforded a pale yellow liquid (1.56 g, 8.3 mmol, 71%). Impurities were not detectable by GC/MS analysis. ^{1}H NMR (300 MHz, [D$_6$]benzene, 25 °C): δ = 0.19 [d, ^3J = 3.9 Hz, 6 H, SiH(CH_3)$_2$], 2.15 [t, ^5J = 2.1 Hz, 3 H, C(3)-Me], 3.14 [q, ^5J = 2.4 Hz, 2 H, C(1)-H], 4.69 [hept, ^3J = 3.9 Hz, 1 H, SiH(CH$_3$)$_2$], 7.17–7.25 [m, 1 H, C(5)-H], 7.25–7.27 [m, 2 H, C(6,7)-H], 7.32–7.37 [m, 1 H, C(4)-H] ppm. ^{13}C{^{1}H} NMR (75 MHz, [D$_6$]benzene, 25 °C): δ = –3.1 [2 C, SiH(CH$_3$)$_2$], 13.8 [1 C, C(3)-Me], 42.6 (1 C, C-1), 119.7 (1 C, C-4), 124.0 (1 C, C-7), 125.6 (1 C, C-6), 126.8 (1 C, C-5), 137.2 (1 C, C-3), 147.1 (1 C, C-2), 147.9 (1 C, C-7a), 150.4 (1 C, C-3a) ppm. GC/MS (70 eV): *m*/*z* (%) = 188 (100) [M$^+$], 173 (74) [M$^+$ − CH$_3$], 145 (41) [$C_9H_9Si^+$], 128 (75) [$C_{10}H_8^+$], 115 (15) [$C_9H_7^+$], 73 (10) [$Si(CH_3)_3^+$], 59 (78) [$SiH(CH_3)_2^+$].

1-Methyl-2-(trimethylsilyl)indene (2b): The methylation of **1b** was conducted in a similar manner to **2a**. To a Schlenk flask charged with 2-(trimethylsilyl)indene (3.00 g, 15.0 mmol) dissolved in pentane (40 mL) at room temperature, *n*-butyllithium (19.0 mL, 49.0 mmol) was added through a septum and stirred vigorously. The reaction mixture was stirred overnight and warmed to room temperature to yield a clear, yellow solution. Upon addition of diethyl ether (2.0 mL) and stirring for another ten minutes, the formation of copious precipitate was observed. Solvent volume reduction to approximately 60% and subsequent filtration through a D4-frit provided a white solid, which was washed twice with pentane (10 mL) and dried under vacuum for 1 h. A second Schlenk flask equipped with an addition funnel and charged with methyl iodide (3.0 mL, 48.5 mmol) in diethyl ether (20 mL) was cooled to –40 °C. The lithium salt was dissolved in diethyl ether (30 mL), transferred to the addition funnel of the second Schlenk flask and dropwise added to the methyl iodide solution at –40 °C. After stirring overnight, the reaction was quenched with hydrochloric acid (20 mL, 0.1 mol/L). The organic layer was washed twice with water (20 mL) and dried with magnesium sulfate. Removal of solvent afforded the product (2.45 g, 12.1 mmol, 81%) with a purity of 99%, as determined by GC/MS. ^{1}H NMR (300 MHz, [D$_6$]benzene, 25 °C): δ = 0.24 [s, 9 H, Si(CH_3)$_3$], 1.30 [d, ^3J = 7.4 Hz, 3 H, C(1)-CH$_3$], 3.48 [dq, ^3J = 7.4, ^5J = 1.6 Hz, 1 H, C(1)-H], 6.90 [d, ^5J = 1.6 Hz, 1 H, C(3)-H], 7.28–7.35 [m, 2 H, C(5,6)-H], 7.37–7.43 [m, 2 H, C(4,7)-H] ppm. ^{13}C{^{1}H} NMR (75 MHz, [D$_6$]benzene, 25 °C): δ = –0.2 [3 C, Si(CH$_3$)$_3$], 17.4 [1 C, C(1)-Me], 49.7 (1 C, C-1), 121.6 (1 C, C-4), 123.2 (1 C, C-7), 125.8 (1 C, C-6), 127.1 (1 C, C-5), 140.9 (1 C, C-3), 145.0 (1 C, C-2), 153.1 (1 C, C-7a), 154.8 (1 C, C-3a) ppm. GC/MS (70 eV): *m*/*z* (%) = 202 (28) [M$^+$], 187 (11) [M$^+$ − CH$_3$], 159 (5) [M$^+$ − C_3H_7], 145 (6) [M$^+$ − C_4H_9], 128 (14) [M$^+$ − TMS], 115 (4) [$C_9H_7^+$], 73 (100) [TMS$^+$], 59 (7) [$SiH(CH_3)_2^+$].

1,3-Dimethyl-2-(dimethylsilyl)indene (3a): The synthesis was carried out in a fashion similar to **2a**. 2-(Dimethylsilyl)-1-methylindene (2.68 g, 14.3 mmol), *n*-butyllithium (8.8 mL, 14.1 mmol) and methyl iodide (3.5 mL, 57.2 mmol) were employed to obtain a yellow liquid (2.65 g). Column chromatography with pentane on silica provided a colorless liquid (1.61 g, 8.0 mmol, 57%), containing both the product (70%) and its 1,1 isomer (30%). No further purification was attempted. ^{1}H NMR (300 MHz, $[D_6]$benzene, 25 °C): δ = 0.24 [d, ^{3}J = 3.9 Hz, 3 H, $SiH(CH_3)_2$], 0.25 [d, ^{3}J = 3.9 Hz, 3 H, $SiH(CH_3)_2$], 1.21 [d, ^{3}J = 7.5 Hz, 3 H, C(1)-CH_3], 2.12 [d, ^{5}J = 1.8 Hz, 3 H, C(3)-CH_3], 3.36 [dq, $^{5}J_d$ = 2.1, $^{3}J_q$ = 7.5 Hz, 1 H, C(1)-H], 4.68 [m, ^{3}J = 3.9 Hz, 1 H, $SiH(CH_3)_2$], 7.17–7.24 [m, 2 H, C(5,6)-H], 7.24–7.31 [m, 2 H, C(4,7)-H] ppm. $^{13}C\{^{1}H\}$ NMR (75 MHz, $[D_6]$benzene, 25 °C): δ = –2.4 [2 C, $SiH(CH_3)_3$], 17.6 [1 C, C(1)-Me], 25.8 [1 C, C(3)-Me], 49.3 (1 C, C-1), 119.7 (1 C, C-4), 122.9 (1 C, C-7), 126.0 (1 C, C-6), 127.0 (1 C, C-5), 143.5 (1 C, C-3), 146.5 (1 C, C-2), 149.4 (1 C, C-7a), 152.7 (1 C, C-3a) ppm. GC/MS (70 eV): m/z (%) = 202 (50) [M^+], 187 (33) [$M^+ - CH_3$], 159 (19) [$C_{10}H_{11}Si^+$], 142 (100) [$C_{11}H_{10}{}^+$], 128 (42) [$C_{10}H_8{}^+$], 115 (17) [$C_9H_7{}^+$], 73 (25) [$Si(CH_3)_3{}^+$], 59 (66) [$SiH(CH_3)_2{}^+$].

1,3-Dimethyl-2-(trimethylsilyl)indene (3b): Prior to the addition of *n*-butyllithium (15.0 mL, 37.5 mmol), **2b** (2.45 g, 12.1 mmol) in pentane (30 mL) was placed in a Schlenk flask and cooled to –90 °C. The solution was stirred overnight and warmed to room temperature, affording a suspension with a white precipitate after addition of diethyl ether (1 mL). Reduction of the solvent volume to approximately 60% was followed by a filtration through a D4-frit and washing of the precipitate with pentane (3 × 10 mL). While the white precipitate was dried in vacuo, a second Schlenk flask was equipped with an addition funnel and methyl iodide (2.25 mL, 36.3 mmol) in diethyl ether (20 mL) and cooled to –40 °C. The lithium salt was dissolved in diethyl ether (30 mL) and THF (10 mL), transferred to the addition funnel and dropwise added to the solution at –40 °C. Stirring overnight and acidic work-up provided a pale yellow crude product (2.21 g, 10.2 mmol). Its composition was determined to be ca. 20% of the 1,1 and 80% the desired 1,3 isomer. No further separation of the isomers was attempted. The spectroscopic data was derived from the hydrolysis of the pure 1,3-dimethyl-2-(trimethylsilyl)indenyllithium. ^{1}H NMR (300 MHz, $[D_6]$benzene, 25 °C): δ = 0.24 [s, 9 H, $Si(CH_3)_3$], 1.20 [d, ^{3}J = 7.4 Hz, 3 H, C(1)-CH_3], 2.08 [d, ^{5}J = 2.0 Hz, 3 H, C(3)-CH_3], 3.48 [qq, ^{5}J = 2.0, ^{3}J = 7.4 Hz, 1 H, C(1)-H], 7.19–7.25 [m, 2 H, C(5,6)-H], 7.25–7.31 [m, 2 H, C(4,7)-H] ppm. $^{13}C\{^{1}H\}$ NMR (75 MHz, $[D_6]$benzene, 25 °C): δ = 0.9 [3 C, $Si(CH_3)_3$], 18.2 [1 C, C(1)-Me], 26.0 [1 C, C(3)-Me], 49.4 (1 C, C-1), 119.6 (1 C, C-4), 122.9 (1 C, C-7), 125.9 (1 C, C-6), 127.0 (1 C, C-5), 146.0 (1 C, C-3), 146.8 (1 C, C-2), 148.3 (1 C, C-7a), 152.8 (1 C, C-3a) ppm. GC/MS (70 eV): m/z (%) = 216 (29) [M^+], 201 (12) [$M^+ - CH_3$], 141 (11) [$M^+ -$ TMS], 128 (11) [$M^+ - Si(CH_3)_4$], 115 (6) [$C_9H_7{}^+$], 73 (100) [TMS^+], 59 (6) [$SiH(CH_3)_2{}^+$].

1-Isopropyl-2-(trimethylsilyl)indene (4): The synthesis was carried out according to the procedure for **2b**. 2-(Trimethylsilyl)indenyllithium (870 mg, 4.5 mmol) and 2-iodopropane (0.5 mL, 5.0 mmol) were reacted to provide a yellow oil (770 mg, 3.3 mmol, 74%). ^{1}H NMR (300 MHz, $[D_6]$benzene, 25 °C): δ = 0.202 [s, 4.5 H, $Si(CH_3)_3$], 0.204 [s, 4.5 H, $Si(CH_3)_3$], 0.48 [d, ^{3}J = 6.6 Hz, 3 H, C(1′)-H], 1.21 [d, ^{3}J = 7.4 Hz, 3 H, C(3′)-H], 2.40 [dqq, ^{3}J = 3.0, ^{3}J = 6.9 Hz, 1 H, C(2′)-H], 3.52 [dd, ^{4}J = 2.4, ^{3}J = 2.7 Hz, 1 H, C(1)-H], 6.99 [d, ^{4}J = 1.8 Hz, 1 H, C(3)-H], 7.11 [ddd, ^{4}J = 1.2, ^{3}J = 7.2, ^{3}J = 7.2 Hz, 1 H, C(5)-H], 7.22 [ddm, J = 0.6, ^{3}J = 7.2, ^{3}J = 7.2 Hz, 1 H, C(6)-H], 7.30 [dm, J = 0.6, ^{3}J = 7.5 Hz, 1 H, C(4)-H], 7.45 [d, ^{3}J = 7.5 Hz, 1 H, C(7)-H] ppm. $^{13}C\{^{1}H\}$ NMR (75 MHz, $[D_6]$benzene, 25 °C): δ = –0.2, –0.1 [3 C, $Si(CH_3)_3$], 16.4 (1 C, C-1′), 22.9 (1 C, C-2′), 30.3 (1 C, C-3′), 61.3, 61.4 (1 C, C-1), 121.7 (1 C, C-4), 124.9 (1 C, C-7), 125.4 (1 C, C-6), 127.3 (1 C, C-5), 142.3, 142.4 (1 C, C-3), 146.8 (1 C, C-2), 149.2 (1 C, C-7a), 152.9 (1 C, C-3a). GC/MS (70 eV): m/z (%) = 230 (23) [M^+], 215 (4) [$M^+ - CH_3$], 172 (6) [$C_{11}H_{12}Si^+$], 156 (16) [$C_{12}H_{12}{}^+$], 141 (7) [$C_{11}H_9{}^+$], 128 (6) [$C_{10}H_8{}^+$], 115 (5) [$C_9H_7{}^+$], 73 (100) [$C_3H_9Si^+$], 59 (7) [$C_2H_7Si^+$].

1-Isopropyl-2-(trimethylsilyl)indenyllithium/potassium (5): The preparation of the lithium salt followed a literature procedure.[12] At –90 °C **4** (4.44 g, 19.3 mmol) was reacted with *n*-butyllithium (8.5 mL, 21.3 mmol) in pentane (30 mL). Stirring overnight and warming to room temperature provided an orange solution. A precipitate could be obtained neither by addition of diethyl ether (2 mL) nor by solvent removal. GC/MS analysis after quenching a sample of the reaction with methyl iodide in THF displayed 10 major products, of which 7 could be identified by the fragmentation pattern: (**i**) 1-Methyl-1-isopropyl-2-(trimethylsilyl)indene. GC/MS (70 eV): m/z (%) = 244 (32) [M^+], 229 (5) [$M^+ - CH_3$], 170 (40) [$M^+ -$ TMS], 155 (17) [$C_{12}H_{11}{}^+$], 141 (12) [$C_{11}H_9{}^+$], 128 (7), 115 (6) [$C_9H_7{}^+$], 73 (100) [$C_3H_9Si^+$]; (**ii**) 1-isopropyl-2-(trimethylsilyl)indene (**4**); (**iii**) 3-methyl-1-isopropyl-2-(trimethylsilyl)indene. GC/MS (70 eV): m/z (%) = 244 (22) [M^+], 229 (6) [$M^+ - CH_3$], 201 (12) [$M^+ - C_3H_7$], 185 (6) [$C_{12}H_{14}Si^+$], 170 (25) [$M^+ - C_3H_9Si$], 155 (7) [$C_{12}H_{11}{}^+$], 141 (6) [$C_{11}H_9{}^+$], 128 (6), 73 (100) [$C_3H_9Si^+$], 59 (8) [$C_2H_7Si^+$]; (**iv**) 1,3-diisopropyl-2-(trimethylsilyl)indene; (**v**) 1-methyl-3-isopropyl-2-(trimethylsilyl)indene. GC/MS (70 eV): m/z (%) = 244 (36) [M^+], 229 (8) [$M^+ - CH_3$], 170 (54) [$M^+ -$ TMS], 155 (14) [$C_{12}H_{11}{}^+$], 141 (9) [$C_{11}H_9{}^+$], 128 (7), 115 (5) [$C_9H_7{}^+$], 73 (100) [$C_3H_9Si^+$], 59 (7) [$C_2H_7Si^+$]; (**vi**) 1,1-diisopropyl-2-(trimethylsilyl)indene. GC/MS (70 eV): m/z (%) = 272 (19) [M^+], 257 (5) [$M^+ - CH_3$], 198 (55) [$M^+ -$ TMS], 183 (18) [$C_{14}H_{15}{}^+$], 169 (5) [$C_{13}H_{13}{}^+$], 155 (5) [$C_{12}H_{11}{}^+$], 141 (5) [$C_{11}H_9{}^+$], 73 (100) [$C_3H_9Si^+$], 59 (7) [$C_2H_7Si^+$]; (**vii**) 3-*tert*-butyl-2-(trimethylsilyl)indene. GC/MS (70 eV): m/z (%) = 244 (25) [M^+], 229 (69) [$M^+ - CH_3$], 214 (100) [$M^+ - C_2H_6$], 199 (43) [$M^+ - C_3H_9$], 187 (5) [$M^+ - C_4H_9$], 169 (5) [$C_{13}H_{14}{}^+$], 155 (13) [$C_{12}H_{11}{}^+$], 141 (6) [$C_{11}H_9{}^+$], 128 (7), 115 (7) [$C_9H_7{}^+$], 73 (7) [$C_3H_9Si^+$]. Attempted preparation of the potassium salt: Potassium hydride (568 mg, 13.9 mmol) was added to a solution of **4** (2.9 g, 12.6 mmol) in THF (40 mL) at –90 °C. Quantitative reaction was not achieved before refluxing the suspension for several days. Filtration with a cannula, solvent removal, washing with pentane and drying in vacuo afforded a yellow-brown solid (1.8 g, 6.7 mmol, 53%). ^{1}H NMR (300 MHz, $[D_8]$THF, 25 °C): δ = 0.46 [s, 9 H, $Si(CH_3)_3$], 1.68 [d, ^{3}J = 9.0 Hz, 6 H, C(1′,3′)-H], 3.62 [hept, ^{3}J = 9.0 Hz, 1 H, C(2′)-H], 6.16 [s, 1 H, C(3)-H], 6.47–6.59 [m, 2 H, C(5,6)-H], 7.39 [m, 1 H, C(4)-H], 7.63–7.71 [m, 1 H, C(7)-H] ppm. $^{13}C\{^{1}H\}$ NMR (75 MHz, $[D_8]$THF, 25 °C): δ = 1.9 (3 C), 25.0 (2 C), 32.2, 99.8, 112.5, 112.8, 119.4, 119.8, 121.0, 123.1, 127.6, 132.0 (1 C) ppm.

Attempted Synthesis of 1,3-Diisopropyl-2-(trimethylsilyl)indene: The preparation was attempted by in situ derivatization of Li[**5**] without prior isolation. Following the procedure for the preparation of **3b**, 2-iodopropane (2.1 mL, 21 mmol) was used. After stirring for 6 h and incomplete conversion according to GC/MS analysis, another aliquot of iodopropane was added and reacted overnight. Acidic work-up and GC/MS analysis of the crude product revealed the presence of four components: 1- and 3-isopropyl-2-(trimethylsilyl)-indene, 1,1- and 1,3-diisopropyl-2-(trimethylsilyl)indene. To the crude product dissolved in THF at –40 °C, potassium hydride (791 mg, 19.3 mmol) was added. Stirring overnight afforded a green solution. Solvent removal and extraction with diethyl ether provided a light green precipitate and a dark green filtrate. Washing the light green precipitate with pentane led to partial dissolution of the precipitate. Drying in vacuo provided a light green, pyrophoric powder (3.3 g). We could not isolate a pure fraction of the desired product. GC/MS (70 eV): m/z (%) = 228 (24) [M^+], 257 (7) [$M^+ - CH_3$], 198 (66) [$M^+ -$ TMS], 183 [$C_{14}H_{15}{}^+$], 169 (6) [$C_{13}H_{14}{}^+$], 155

(6) $[C_{12}H_{11}^+]$, 141 (6) $[C_{11}H_9^+]$, 73 (100) $[C_3H_9Si^+]$, 59 (7) $[C_2H_7Si^+]$.

Attempted Synthesis of 1-Isopropylidene-2-(trimethylsilyl)indene: To a Schlenk flask charged with dry acetone (0.1 mL, 1.4 mmol) and $BF_3{\cdot}Et_2O$ (0.1 mL, 789 µmol) in diethyl ether (20 mL), 2-(trimethylsilyl)indenyllithium (100 mg, 824 µmol) was added. Formation of a colorless suspension was achieved within one hour. The solvent was replaced by a mixture of pentane and THF (20 mL, 3 mL), prior to addition of orthophosphoric acid (6 mL, 85%). The organic layer turned yellow while stirring overnight. Acidic work-up, washing with deionized water, drying over magnesium sulfate and drying in vacuo provided a yellow oil (100 mg, 284 µmol, 34%). Product: GC/MS (70 eV): *m/z* (%) = 228 (31) $[M^+]$, 213 (6) $[M^+ - CH_3]$, 197 (13) $[M^+ - C_2H_6]$, 155 (6) $[C_{12}H_{11}^+]$, 141 (7) $[C_{11}H_9^+]$, 128 (5), 115 (6) $[C_9H_7^+]$, 73 (100) $[C_3H_9Si^+]$. Hydrated intermediate: GC/MS (70 eV): *m/z* (%) = 228 (6) $[M^+ - H_2O]$, 201 (14) $[C_{13}H_{17}Si^+]$, 187 (43) $[C_{12}H_{14}Si^+]$, 173 (12) $[C_{11}H_{12}Si^+]$, 157 (6) $[C_{10}H_8Si^+]$, 145 (21) $[C_9H_9Si^+]$, 128 (11), 115 (12) $[C_9H_7^+]$, 73 (100) $[C_3H_9Si^+]$, 58 (15) $[C_3H_7O^+]$.

6,6-Dimethylbenzofulvene (6): The synthesis followed a literature procedure and does not require Schlenk technique.[7] By stirring indene (5 mL, 42.9 mmol), acetone (3.8 mL, 51.8 mmol) and pyrrolidine (4.3 mL, 51.8 mmol) in methanol (50 mL) for two days and subsequent distillation (0.05Torr), a yellow oil (4.94 g, 31.7 mmol, 74%) was obtained. ^{1}H NMR (300 MHz, [D$_6$]benzene, 25 °C): δ = 1.84 [s, 3 H, C(1′)-CH$_3$], 1.97 [s, 3 H, C(3′)-CH$_3$], 6.72 [s, 2 H, C(2,3)-H], 7.17 [m$_c$, 2 H, C(5,6)-H], 7.28 [m$_c$, 1 H, C(4)-H], 7.64 [m$_c$, 1 H, C(7)-H] ppm. ^{13}C{^{1}H} NMR (75 MHz, [D$_6$]benzene, 25 °C): δ = 22.9 (1 C, C-1′), 24.8 (1 C, C-3′), 121.8 (1 C, C-4), 124.3 (1 C, C-7), 125.4 (1 C, C-6), 126.7 (1 C, C-5), 128.2 (1 C, C-3), 129.2 (1 C, C-2), 136.8 (1 C, C-2′), 137.8 (1 C, C-1), 142.7 (1 C, C-7a), 145.0 (1 C, C-3a) ppm. GC/MS (70 eV): *m/z* (%) = 156 (93) $[M^+]$, 141 (100) $[M^+ - CH_3]$, 128 (21) $[C_{10}H_9^+]$, 115 (36) $[C_9H_7^+]$.

3-*tert*-Butylindene (7): Following a literature procedure,[6] the product was obtained from reacting **6** (1.51 g, 9.7 mmol) with methyllithium (6.9 mL, 9.7 mmol) at 0 °C in diethyl ether (30 mL). Acidic work-up afforded a colorless liquid (740 mg, 4.3 mmol, 44%). As an alternative, the reaction may be run in pentane in the presence of 10 wt.-% freshly resublimated AlCl$_3$ at room temperature. Addition of methyllithium via syringe provided a white precipitate in quantitative yield within one hour. ^{1}H NMR (300 MHz, [D$_6$]benzene, 25 °C): δ = 1.33 (s, 9 H, *t*Bu), 3.02 [d, ^3J = 2.1 Hz, 2 H, C(1)-H], 5.99 [t, ^3J = 2.1 Hz, 1 H, C(2)-H], 7.12 [ddd, ^4J = 1.8, ^3J = 7.2, ^3J = 7.2 Hz, 1 H, C(5)-H], 7.23 [dd, ^3J = 7.8, ^3J = 7.8 Hz, 1 H, C(6)-H], 7.32 [d, ^3J = 7.5 Hz, 1 H, C(4)-H], 7.59 [d, ^3J = 7.8 Hz, 1 H, C(7)-H] ppm. ^{13}C{^{1}H} NMR (75 MHz, [D$_6$]benzene, 25 °C): δ = 29.9 (3 C, *t*Bu), 33.6 (1 C, *t*Bu), 37.7 (1 C, C-1), 122.8 (1 C, C-2), 124.67 (1 C, C-4), 124.72 (1 C, C-7), 126.35 (1 C, C-6), 126.40 (1 C, C-5), 144.6 (1 C, C-7a), 146.4 (1 C, C-7a), 154.0 (1 C, C-3) ppm. GC/MS (70 eV): *m/z* (%) = 172 (78) $[M^+]$, 157 (77) $[M^+ - CH_3]$, 142 (78) $[M^+ - C_2H_6]$, 128 (29) $[C_{10}H_8^+]$, 116 (82) $[C_9H_8^+]$, 57 (100) $[C_4H_9^+]$.

3-*tert*-Butyl-1-(isopropylidene)indene (8). A Schlenk flask equipped with a condenser was charged with **7** (1.54 g, 8.7 mmol), acetone (1.5 mL, 20.5 mmol), pyrrolidine (1.7 mL, 20.5 mmol), and methanol (30 mL) under air. Reflux of the reaction mixture for three days and removal of all volatiles in vacuo provided a red-brown oil. Vacuum distillation provided a yellow liquid boiling at 80 °C$_{0.05\mathrm{Torr}}$ which would solidify at room temperature (1.05 g, 5.0 mmol, 58%). ^{1}H NMR (300 MHz, [D$_6$]benzene, 25 °C): δ = 1.39 (s, 9 H, *t*Bu-H), 1.92 [s, 3 H, C(1′)-CH$_3$], 2.04 [s, 3 H, C(3′)-CH$_3$], 6.60 [s, 1 H, C(2)-H], 7.13–7.24 [m, 2 H, C(5,6)-H], 7.60 [m$_c$, 1 H, C(4)-H], 7.72 [m$_c$, 1 H, C(7)-H] ppm. ^{13}C{^{1}H} NMR (75 MHz, [D$_6$]benzene, 25 °C): δ = 23.0 (1 C, C-1′), 24.9 (1 C, C-3′), 30.2 (3 C, *t*Bu-C), 35.6 (1 C, *t*Bu-C), 122.2 (1 C, C-2′), 122.7 (1 C, C-4), 124.4 (1 C, C-7), 124.9 (1 C, C-6), 126.2 (1 C, C-5), 136.3 (1 C, C-2), 138.9 (1 C, C-7a), 139.9 (1 C, C-3a), 143.6 (1 C, C-1), 151.0 (1 C, C-3) ppm. GC/MS (70 eV): *m/z* (%) = 212 (29) $[M^+]$, 197 (10) $[M^+ - CH_3]$, 182 (5) $[M^+ - C_2H_6]$, 165 (15), 156 (100) $[C_{12}H_{12}^+]$, 141 (50) $[C_{11}H_9^+]$, 128 (13) $[C_{10}H_9^+]$, 115 (17) $[C_9H_7^+]$, 57 (47) $[C_4H_8^+]$.

1,3-Di-(*tert*-butyl)indene (9): The synthesis followed essentially the synthesis of **7**. To an agitated solution of 3-*tert*-butyl-1-(isopropylidene)indene (4.89g, 23.1 mmol) in diethyl ether (30 mL), methyllithium (16.5 mL, 26.4 mmol) was added dropwise at 0 °C. After stirring for 2 h with warming to room temperature, GC/MS analysis of the reaction mixture showed only traces of the product. Addition of more methyllithium (15.0 mL, 24 mmol) and refluxing the reaction for 10 h provided a conversion of 25% (GC/MS). The reaction was poured over a mixture of diluted hydrochloric acid, diethyl ether and crushed ice (300 mL). Adjustment to pH 4 was followed by stirring for 10 minutes and phase separation. The organic layer was washed with deionized water (2×100 mL) and dried with magnesium sulfate prior to solvent evaporation. Column chromatography at silica gel (420 g) afforded a colorless liquid (0.652 g, 2.9 mmol, 12%). ^{1}H NMR (300 MHz, [D$_6$]benzene, 25 °C): δ = 0.94 [s, 9 H, C(1)-*t*Bu], 1.34 [s, 9 H, C(3)-*t*Bu], 3.08 [d, ^3J = 2.4 Hz, 1 H, C(1)-H], 6.16 [d, ^3J = 2.1 Hz, 1 H, C(2)-H], 7.10 [ddd, ^4J = 1.8, ^3J = 7.5, ^3J = 7.5 Hz, 1 H, C(5)-H], 7.21 [ddd, ^4J = 1.2, ^3J = 7.8, ^3J = 7.8 Hz, 1 H, C(6)-H], 7.50 [d, ^3J = 7.2 Hz, 1 H, C(4)-H], 7.54 [d, ^3J = 7.5 Hz, 1 H, C(7)-H] ppm. ^{13}C{^{1}H} NMR (75 MHz, [D$_6$]benzene, 25 °C): δ = 23.5 [1 C, C(1)-*C*(CH$_3$)$_3$], 29.0 [3 C, C(1)-C(*C*H$_3$)$_3$], 30.0 [3 C, C(3)-C(*C*H$_3$)$_3$], 32.6 [1 C, C(3)-*C*(CH$_3$)$_3$], 59.2 (1 C, C-1), 122.8 (1 C, C-4), 124.4 (1 C, C-7), 125.7 (1 C, C-6), 126.6 (1 C, C-5), 130.4 (1 C, C-2), 145.1 (1 C, C-7a), 148.4 (1 C, C-3a), 153.4 (1 C, C-3) ppm. GC/MS (70 eV): *m/z* (%) = 228 (41) $[M^+]$, 172 (43) $[M^+ - C_4H_8]$, 157 (59) $[C_{12}H_{13}^+]$, 141 (31) $[C_{11}H_9^+]$, 128 (11) $[C_{10}H_8^+]$, 116 (37) $[C_9H_8^+]$, 57 (100) $[C_4H_9^+]$.

1-Methyl-2-(trimethylsilyl)indenyllithium (10): The deprotonation was carried out in a similar fashion to **2b**. The lithium salt could be isolated as a white powder in quantitative yield.

1,3-Dimethyl-2-(dimethylsilyl)indenyllithium (11a): The deprotonation of the ligand precursors followed a literature procedure.[12] The indene derivative (1.0 equiv.) and *n*-butyllithium (1.0 equiv.) were placed in a Schlenk flask charged with pentane (30 mL). Stirring at room temperature overnight provided little precipitate. Addition of 1 mL diethyl ether lead to the formation of appreciable amounts of precipitate, but filtration via cannula turned out to be difficult due to the formation of a viscous gel. Washing with pentane (2×30 mL) and subsequent solvent removal under high-vacuum yielded a light yellow powder (1.07 g, 5.1 mmol, 64%). $C_{13}H_{17}LiSi$ (208.30): calcd. C 74.96, H 8.23; found C 74.40, H 8.16. ^{1}H NMR (300 MHz, [D$_8$]THF, 25 °C): δ = 0.51 [d, ^3J = 3.9 Hz, 6 H, SiH(C*H*$_3$)$_2$], 2.65 [s, 6 H, C(1,3)-Me], 4.94 [hept, ^3J = 3.9 Hz, 1 H, Si*H*(CH$_3$)$_2$], 6.58 [m$_{\mathrm{AA'XX'}}$, 2 H, C(5,6)-H], 7.38 [m$_{\mathrm{AA'XX'}}$, 2 H, C(4,7)-H] ppm.

1,3-Dimethyl-2-(trimethylsilyl)indenyllithium (11b): The deprotonation was carried out in a similar fashion to **2b**, but started at –90 °C. Using an isomer mixture of **3b** (2.21 g, 10.2 mmol, 78% purity) and *n*-butyllithium (12.2 mL, 30.6 mmol) in pentane (30 mL) provided a light green powder (1.58 g, 7.1 mmol, 89%) after filtration through a D4-frit, washing with pentane (2×10 mL) and solvent removal under high vacuum.

***rac*/*meso*-Bis[1-methyl-2-(trimethylsilyl)indenyl]zirconium(IV) Dichloride (12):** To a Schlenk flask equipped with a septum, charged with **10** (714 mg, 3.4 mmol) and zirconium tetrachloride (396 mg, 1.7 mmol) and cooled to 0 °C, diethyl ether (30 mL) was added via syringe. Stirring overnight afforded a suspension of a yellow precipitate. Filtration trough a D4 frit with a layer of magnesium sulfate (3 cm) and washing with diethyl ether until all yellow residue in the Schlenk flask was dissolved, provided a clear, yellow solution. Volume reduction to the formation of precipitate was followed by crystallization at –40 °C. Subsequent crystallizations failed to separate the *rac* and *meso* isomer, which were obtained in a 1:1 ratio (528 mg, 941 µmol, 55%). $C_{26}H_{34}Cl_2Si_2Zr$ (564.86): calcd. C 55.29, H 6.07; found C 55.55, H 6.15. ***rac* Isomer:** ^1H NMR (300 MHz, [D$_6$]benzene, 25 °C): δ = 0.32 [s, 18 H, Si(CH_3)$_3$], 2.29 [s, 6 H, C(1)-CH$_3$], 5.62 [s, 2 H, C(3)-H], 6.84–6.94 [m, 4 H, C(5,6)-H], 7.48–7.56 [m, 2 H, C(4,7)-H] ppm. ***meso* Isomer:** ^1H NMR (300 MHz, [D$_6$]benzene, 25 °C): δ = 0.14 [s, 18 H, Si(CH_3)$_3$], 2.52 [s, 6 H, C(1)-CH$_3$], 5.07 [s, 2 H, C(3)-H], 6.94–7.00 [m, 4 H, C(5,6)-H], 7.10–7.15 [m, 2 H, C(4)-H], 7.25–7.30 [m, 2 H, C(7)-H] ppm. ***rac* and *meso* Isomer:** $^{13}C\{^1H\}$ NMR (75 MHz, [D$_6$]benzene, 25 °C): δ = 0.7 [6 C, Si(CH$_3$)$_3$], 1.1 [6 C, Si(CH$_3$)$_3$], 14.1 [2 C, C(1)-CH$_3$], 14.4 [2 C, C(1)-CH$_3$], 106.8 (2 C, C-3), 109.8 (2 C, C-3), 124.7, 124.8, 125.0, 125.1, 125.2, 125.4, 125.6, 125.9, 126.3, 126.6, 127.6, 128.5, 132.3, 133.0, 135.3, 138.8 ppm.

Attempted Synthesis of Bis[1,3-dimethyl-2-(dimethylsilyl)indenyl]zirconium(IV) Dichloride (13a): In a Schlenk flask, **11a** (185 mg, 889 µmol) and zirconium tetrachloride (104 mg, 446 µmol) were reacted in diethyl ether (30 mL) at 0 °C. The initially brown-yellow suspension turned green-yellow while stirring overnight. A clear yellow solution was obtained by filtration through a layer of magnesium sulfate on a D4 frit and washing of the reaction residue with diethyl ether. Volume reduction to 10 mL and refrigeration to –40 °C provided traces of precipitate. The obtained NMR spectroscopic data suggests the formation of the desired product, but reliable analysis including elemental analysis was precluded by the small amount of precipitate obtained. ^1H NMR (300 MHz, [D$_6$]benzene, 25 °C): δ = 0.24 [d, ^3J = 3.9 Hz, 12 H, SiH(CH_3)$_2$], 2.15 [s, 12 H, C(1,3)-CH$_3$], 4.76 [hept, ^3J = 4.2 Hz, 2 H, SiH(CH$_3$)$_2$], 6.80–7.00 [m, 4 H, C(5,6)-H], 7.15–25 [m, 4 H, C(4,7)-H] ppm.

Bis[1,3-dimethyl-2-(trimethylsilyl)indenyl]zirconium(IV) Dichloride (13b): A Schlenk flask with **11b** (1.00 g, 3.4 mmol) and zirconium tetrachloride (0.52 g, 1.69 mmol) was cooled to 0 °C before diethyl ether (30 mL) was added dropwise. The suspension turned dark yellow and formed a yellow precipitate while stirring overnight. Filtration with a cannula and a D4-frit loaded with magnesium sulfate (3 cm) afforded a dark yellow solution. Extraction of the reaction residue and filter cake with diethyl ether and toluene, followed by recrystallization from the respective solvent afforded four crops of a yellow or orange solid (393 mg, 665 µmol, 44%). Single crystals of X-ray quality were grown from a cold saturated diethyl ether solution at –40 °C. $C_{28}H_{38}Cl_2Si_2Zr$ (592.91): calcd. C 56.72, H 6.46; found C 56.75, H 6.48. ^1H NMR (300 MHz, [D$_6$]benzene, 25 °C): δ = 0.31 [s, 18 H, Si(CH_3)$_3$], 2.13 [s, 12 H, C(1,3)-CH_3], 6.86 [m$_{AA'XX'}$, J_A = 6.5, J_X = 0.8, J = 8.7, J' = 1.0 Hz, 4 H, C(5,6)-H], 7.15–7.19 [m, 4 H, C(4,7)-H] ppm. $^{13}C\{^1H\}$ NMR (75 MHz, [D$_6$]benzene, 25 °C): δ = 2.0 [6 C, Si(CH$_3$)$_3$], 13.8 (4 C, 1,3-CH$_3$), 121.0 (4 C, C-1,3), 124.0 (4 C, C-4,7), 124.8 (4 C, C-5,6), 127.7 (4 C, C-3a,7a), 139.9 (2 C, C-2) ppm.

Attempted Synthesis of *rac*/*meso*-Bis[1-isopropyl-2-(trimethylsilyl)indenyl]zirconium(IV) Dichloride (14): To a Schlenk flask charged with 1-isopropyl-2-(trimethylsilyl)indenylpotassium (**5**) (1.00 g, 3.7 mmol) and zirconium tetrachloride (429 mg, 1.86 mmol), THF (40 mL) was added at –40 °C. Stirring overnight afforded a yellow solution. Solvent change from THF to diethyl ether led to the formation of precipitate. Filtration via cannula and through magnesium sulfate on a D4 frit yielded a brown-yellow oil upon solvent removal. Crystallization occurred after two months of storage in the drybox, though the crystals were too ductile to be isolated. No conclusive NMR spectroscopic data could be obtained for this complex.

Crystal Structure Determination: A yellow platelet with dimensions 0.85 × 0.33 × 0.10 mm was mounted on a glass fiber. Pertinent data for the crystal and solution are collected in Table 5. Reflections were measured with a Siemens SMART 1000 CCD-diffractometer using Mo-K_α radiation. The data collections with SMART[13a] included three sets of exposures with the detector set at 2θ = 26 and crystal-to-detector distance 50 mm. Data integration and cell refinement was carried out by SAINT,[13b] while absorption correction was carried out by SADABS.[13c] SHELXTL[13d] was used for structure solution by direct methods as well as for subsequent full-matrix least-squares refinement on F^2. All atoms except protons were refined anisotropically.
CCDC-253467 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 5. Crystallographic data, collection and refinement parameters for **13b**.

Parameter	**13b**
Formula	$C_{28}H_{38}Cl_2Si_2Zr$
Mass	592.88
System	orthorhombic
Space group	Fdd2
a [Å]	18.2879(8)
b [Å]	38.1327(17)
c [Å]	8.0947(4)
V [Å^3]	5645.0(4)
Z	8
Radiation	Mo-K_α
λ [Å]	0.71073
T [°C]	–168
$D_{calcd.}$ [g/mL]	1.395
μ (mm^{-1})	0.679
$R(F_0)$	1.91[a]
$R_w(F_O{}^2)$	4.75[b]
GOF	1.050

[a] Calculated on 5395 reflecions with $I > 2\sigma(I)$. [b] Calculated on all 5687 reflections.

General Polymerization Procedure: Polymerizations were carried out in 100-mL glass reactors equipped with a cooling/heating mantle, an argon/vacuum connection, magnetic stirrer and a septum. Prior to use, the reactors were evacuated at 90 °C for two hours and flushed three times with argon. At 30 °C, the reactors were charged with 50 mL aliquots of freshly distilled toluene, the appropriate amount of solid MAO and subsequently pressurized to a preset pressure of ethene until no further ethene consumption could be registered by the massflow controllers. Polymerization was initiated by injection of the appropriate volume of a toluene solution of the catalyst precursor. Typically, the catalyst precursor solutions had concentrations of $1.0 \cdot 10^{-3}$ mol/L. The reaction was stopped by addition of methanol (5 mL). Work-up of the polymers included extraction of the toluene suspension with methanol/hydrochloric acid (9:1) to remove inorganic residues. Products were filtered, washed with methanol and dried under high vacuum for two days.

Computational Details: Hybrid DFT calculations were performed with the Gaussian98 package.[14] The B3LYP functional with the 6-31G* basis set was employed for our purposes and proved to be suitable.[15] For Zr, a modified version of the LANL2DZ ECP basis was used.[16] In the original basis set, the 4d shell is described by two contracted functions consisting of three and one primitive Gaussians denoted (31), respectively. To increase flexibility in the d shell we decontracted the set to three functions, consisting of 2, 1, and 1 primitive functions, respectively. For integration, ultrafine grid was employed. All other settings remained default. Due to the high demand for computation time of transition state searches, these were conducted with the Gaussian03 package using the density fitting approximation with auxiliary basis sets as implemented with a pure BP86 functional and a 6-31G* basis set.[17] All calculations were conducted with ultrafine integration grid, while all other parameters remained default.

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