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Synthesis, structure, and ethene polymerisation catalysis of 1- or 2-silyl substituted bis[indenyl]zirconium(IV) dichlorides

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The systematic syntheses of 1- and 2-substituted silylindenes, with a wide variety of substitution patterns on the silyl moiety, and their corresponding zirconocene dichlorides are presented. The *rac*- and *meso*-diastereomers of the 1-substituted zirconocene dichlorides can in most cases be separated. Instable zirconocenes were observed for certain substitution patterns. Two of the obtained zirconocene dichlorides, bis[2-(dimethylsilyl)indenyl]zirconium dichloride (**4a**) and bis[2-(trimethylsilyl)indenyl]zirconium dichloride (**4b**), were characterised by single crystal X-ray diffraction. On the basis of DFT results, the two compounds are geometrically similar, *i.e.* the additional methyl group on the silyl moiety only affects the conformational energy profile. Differences in their catalyst performance in the homopolymerisation studies with ethane are thus attributed to conformational control. For the remaining complexes, sterically less demanding silyl groups seem to be favoured with respect to the catalyst performance. All the 2-isomers have lower polymerisation activities than the unsubstituted bis[indenyl]zirconium dichloride/MAO system. Curiously, the *rac*-bis[1-(dimethylphenylsilyl)indenyl]zirconium dichloride/MAO system is found to be the most active catalyst in ethene homopolymerisations.

Introduction

Since the first reports on metallocenes as highly active polymerisation catalysts in combination with methylalumoxane (MAO) some 20 years ago,[1] metallocene design and synthesis have evolved rapidly.[2] The first breakthrough in tailoring polymer tacticity was achieved by the exploitation of chiral *ansa*-metallocenes to produce iso- and later syndiotactic polypropene.[3,4] Sterically demanding and industrially relevant ligand structures have been discovered and successfully employed for commercial processes.[5] All these developments find their roots in the steric and electronic properties of the Cp-based ligands forming the basis of the myriad of metallocene single-site olefin polymerisation catalysts known today. Though *ansa*-metallocenes have received much attention after the discovery of their high degree of stereocontrol, the recent example by Waymouth and coworkers of the unbridged bis[2-(phenyl)indenyl]zirconium dichloride awakened new interest in the ability of rotationally flexible metallocenes to produce elastomeric polypropene (ePP).[6] Recent work by Busico *et al.* provides strong indications that the mechanism of polymerisation is not due to *rac*/*meso*-interconversion of the metallocene ligand framework, as originally suggested, but actually proceeds *via rac*/*rac** interconversion and ascribes the elastomeric properties to isolated stereoerrors.[7] This feature is also attributed to stereoblock PP, which is known to be produced by unbridged metallocenes, as published earlier by Kaminsky and Buschermöhle.[8]

Primarily since the publication of Waymouth's complex, there have been directed explorations of the relationships between catalyst activity, polymer properties and the substituents at the 1- and 2-position of an indenyl ring for unbridged metallocenes. In contrast to Waymouth's complex, related 1- and 1,3-(di)phenylindenyl complexes failed to polymerise propene at all, although they were efficient ethene polymerisation catalysts.[9] As for functionalisation of the 2-position, siloxy,[10] amino,[11] hetaryl,[12] and alkyl and alkenyl[13] substituents have been investigated. Additionally, the syntheses and ethene and propene polymerisations of a systematic series of bis[2-(alkyl)indenyl]zirconium dichloride compounds (alkyl = Me, *iso*-Pr, *n*-Bu, Bn, Cy) were recently reported.[14]

We are interested in the extent to which ligand-based steric bulk affects the subsequent catalyst performance and control over polymer properties. One intriguing route which we surmised could easily provide a large degree of steric and electronic variation is the utilisation of silyl substituted indenyl ligands. While silyl groups have been used as a bridging substituent in the 1-position of an indenyl ligand in *ansa*-metallocenes,[15] very little has been reported on the catalytic behaviour of unbridged indenyl complexes containing silicon directly bonded to the ligand. The synthesis of *rac*- and *meso*-(1-dimethylsilylindenyl)zirconium dichloride was briefly described in a review,[16] while the syntheses of 1- and 2-substituted bis[(trimethylsilyl)indenyl]zirconium dichlorides were only recently reported in the open literature.[17] Hence, we have prepared a series of silyl substituted indenyl zirconium dichloride complexes. As the catalyst properties should strongly depend on the steric environment around the cationic zirconium atom, the silyl substitution patterns presented here systematically increase the bulkiness of the silyl moiety. While our primary interest is in complexes containing the 2-substituted silylindenes, the paucity of corresponding 1-substituted analogues prompted the inclusion of these complexes in our synthetic approach. In particular, ready purification of the *rac* and *meso* stereoisomers of the 1-substituted complexes is described. The crystal structures of two 2-silylindene complexes, bis[2-(dimethylsilyl)indenyl]zirconium

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Table 1 Summary of silyl group substitution pattern, prepared ligands and complexes and their acronyms

Silyl group				Ligand		Zirconocene	
R^1	R^2	R^3	Acronym	1-Isomer	2-Isomer	1-Isomer	2-Isomer
H	Me	Me	DMS	**1a**	**2a**	**3a**	**4a**
Me	Me	Me	TMS	**1b**	**2b**	**3b**	**4b**
Me	Me	Ph	DMPS	**1c**	**2c**	**3c**	**4c**
H	Ph	Ph	DPS	**1d**	**2d**	**3d**	n.i.[a]
Me	Me	^{t}Bu	TBDMS	**1e**[b]	**2e**	**3e**	n.i.
H	H	Ph	PS	–	**2f**	–	n.i.
Me	Ph	Ph	DPMS	**1g**	–	n.i.[c]	–

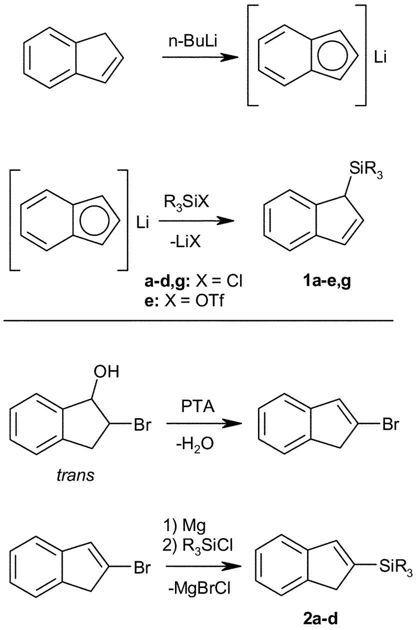
[a] Not isolable. [b] Only the chemically equivalent 3-isomer could be isolated. [c] Could not be isolated pure.

dichloride (**4a**) and bis[2-(trimethylsilyl)indenyl]zirconium dichloride (**4b**), is reported, in addition to a comparison of the ethene polymerisation properties of the 1- and 2-substituted complexes. In some cases steric congestion prevented a successful synthesis or severely affected the polymerisation activity.[18]

Results and discussion

Ligand syntheses

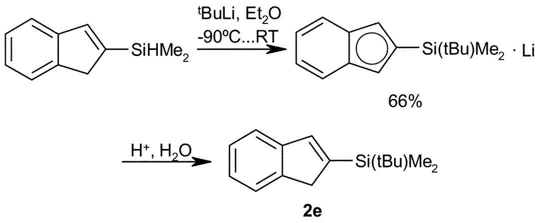
All indene derivatives prepared in this study are summarised in Table 1. The syntheses of the majority of the 1-silylindenes proceed in a straightforward manner in high overall yield and without further purification as shown in Scheme 1. With the exception of 1-(dimethylphenylsilyl)indene (1-DMPS-Ind, **1c**) and 1-(diphenylmethylsilyl)indene (1-DPMS-Ind, **1g**), the 1-substituted ligands are colourless, high-boiling liquids. The synthesis of 1-(*tert*-butyldimethylsilyl)indene (3-TBDMS-Ind, **1e**) yielded the 3-isomer exclusively and could only be obtained from reaction of *tert*-butyldimethylsilyl triflate (TBDMSOTf) with indenyl lithium. Except for 1-(trimethylsilyl)indene (1-TMS-Ind, **1b**) all the 1-substituted silylindenes have diastereotopic substituents on the silyl functionality, as confirmed in the ^{1}H- and ^{13}C NMR spectra.



Scheme 1 Standard synthetic procedure for the preparation of 1- and 2-silyl substituted indene ligand precursors.

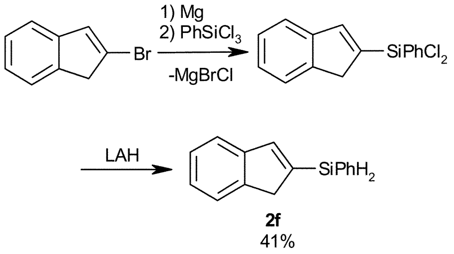
The syntheses of the majority of the 2-silylindenes are also described in Scheme 1 and were based on a literature procedure describing formation of the Grignard reagent of 2-bromoindene and subsequent quenching with the appropriate chlorosilane.[19,20] However, a modification in which the Grignard reagent is added to a 1.1-fold excess of the chlorosilane at room temperature over a couple of hours gave improved yields and easier work-ups, especially for the higher congeners. The analogous Grignard synthesis of 2-(*tert*-butyldimethylsilyl)indene (2-TBDMS-Ind) with TBDMSCl or TBDMSOTf was unsuccessful; only indene and hydrolysis or alcoholysis products were observed upon work-up. Further attempts to prepare 2-TBDMS-Ind *via* indenyl cuprates, 2-indenide lithium from reduction with 4,4′-di-*tert*-butylbiphenyl lithium[21] and higher order cyano cuprates of the lithium silane[22] also were unsuccessful. Analogous attempts to synthesize 2-(diphenylmethylsilyl)indene (2-DPMS-Ind) failed.

Kira and co-workers recently reported on hydride-substitution of hydridosilanes with nucleophilic bases, yielding hydrocarbon soluble silanes.[23] Inspired by these results, we investigated the reaction of *tert*-butyllithium on 2-(dimethylsilyl)indene (**2a**) in THF and diethyl ether. In both solvents, a mixture of 80% 2-(dimethylsilyl)indenyl lithium and 20% 2-TBDMS-Ind (**2e**) was obtained upon addition of one equivalent of the alkyllithium. Reaction with two equivalents readily provided the lithium salt of **2e** in a respectable 66% yield (Scheme 2). The synthesis of 2-DPMS-Ind *via* 2-DPS-Ind by this means was not attempted.



Scheme 2 Synthesis of 2-(*tert*-butyldimethylsilyl)indene.

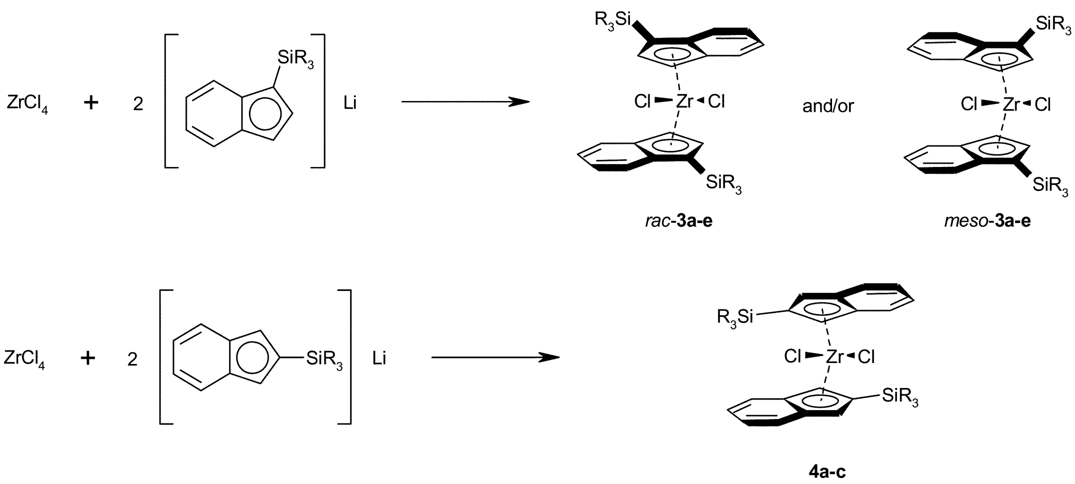
Synthesis of 2-(phenylsilyl)indene (2-PS-Ind, **2f**) proceeded by sequential modification of the silyl moiety as chlorophenylsilane is not readily available. Reaction of 2-(indenide)magnesium bromide with an excess of phenyltrichlorosilane and subsequent reduction with lithium aluminium hydride afforded the desired ligand in moderate yields (Scheme 3).



Scheme 3 Synthesis of 2-(phenylsilyl)indene.

Zirconium complexes

After conversion of the ligand precursors into the corresponding lithium salts *via* deprotonation with *n*-butyllithium, a



Scheme 4 Salt metathesis reaction of indenyl lithium salts with zirconium tetrachloride leading to bis[indenyl]zirconium dichlorides.

salt metathesis reaction introduced the ligands into the coordination sphere of zirconium, as shown in Scheme 4, and provided yellow to orange solids. For compounds with the 1-substituted silylindenes, the yields are moderate, not exceeding 45%. This could be due to C–H activation processes within the silyl moiety as recently described by Choukroun *et al.*,[24] followed by further decomposition reactions. The syntheses of the 1-substituted complexes generally provided a mixture of *rac*- and *meso*-diastereomers. Interestingly, our route to bis[1-TMS-Ind]zirconium dichloride (**3b**) in diethyl ether provided exclusively the *meso*-diastereomer. This assignment was determined by the addition of 2 equivalents of methyl lithium to **3b** to give bis[1-TMS-Ind]dimethylzirconium (**5a**), which exhibited two different methyl signals of equal intensity. The exclusive synthesis of the *meso*-diastereomer contrasts that observed by Deck and co-workers, who isolated only *rac* with THF as reaction solvent, whereas Coville and co-workers obtained a 1 : 1 mixture by using toluene.[17] It appears that the simple change in solvent is in large part responsible for the subsequent change in stereochemistry. A shift in the *rac*/*meso* ratio with solvent change has been observed previously, although this is for an *ansa*-metallocene.[11*b*] While spectroscopic evidence for the formation of bis[1-DPMS-Ind]zirconium dichloride was obtained, isolation of a pure compound was unsuccessful.

The two diastereomers were usually separated by fractional crystallisation at −40 °C except for bis[1-DMS-Ind]zirconium dichloride (**3a**) and bis[1-TBDMS-Ind]zirconium dichloride (**3e**), for which only one pure diastereomer could be isolated. The ^{1}H NMR chemical shifts of the protons in the 2- and 3-positions of the indenyl ligands of verified diastereomers of **3b** were used to assign the different stereoisomers of all complexes except **3e**. The *meso*-stereoisomers generally show more downfield chemical shifts for 2-H and upfield shifts for 3-H, as compared to *rac*, as previously reported by Coville and co-workers[17] This rule fails to describe the diastereomers of **3e** correctly and the correct stereoisomer was established by chloride/methyl exchange to yield bis[1-TBDMS-Ind]dimethylzirconium (**5e**). Corresponding to the NMR spectra for the ligands, **3a**,**c**–**e** also show diastereotopic groups on the silyl substituent.

In contrast to the low yields for the 1-substituted complexes, the yields for the 2-substituted silylindenyl zirconium complexes are significantly higher, between 60 and 75%. A solvent effect on the yield of **4b** is observed, as a 32% yield in toluene is reported by Coville and co-workers,[17] whereas 75% of **4b** is obtained from diethyl ether. The room-temperature NMR spectra of these complexes are much simpler than for the 1-substituted isomers. This spectral simplicity of the complexes bearing prochiral silyl groups is not explicitly due to C_{2v} ligand symmetry, but is also likely influenced by the *rac*/*rac** exchange of the diastereotopic probes as proposed by Busico.[7]

Surprisingly, and in contrast to the 1-substituted isomer, a zirconium complex containing the 2-DPS-Ind (**2d**) ligand could not be obtained. Deprotonation of **2d** with *n*-butyllithium gave only low yields of a brownish-white solid, and reaction of this solid with zirconium tetrachloride resulted only in black decomposition products. Deprotonation of **2d** with potassium hydride gave moderate yields of a green salt whose ^{1}H NMR spectrum is consistent with the formation of potassium 2-(diphenylsilyl)indenylide, while sodium hydride failed to deprotonate the silylindene. A compelling explanation for this unexpected reactivity is competitive deprotonation between the acidic indenyl proton and the silane proton in **2d**. Recently, the pK_a of triphenylsilane was determined to be approximately 35,[25] and it can be argued that the pK_a of the silane proton of **2d** has roughly the same value.[26] On the other hand, reaction of the potassium salt with methyl iodide gave ^{1}H- and ^{13}C NMR signals corresponding to a new methyl indene moiety, indirectly indicating indene deprotonation. This result is supported by the fragmentation pattern of low-resolution GC/MS analysis. The failure of the *n*-butyllithium reaction could be therefore due to hydride substitution.[23] Further studies which we are currently carrying out in our laboratory suggest that the decomposition pathway of the *trans*-metallation of the potassium salt proceeds *via* a *mono*-[2-DPS-Ind]zirconium trichloride species.[27]

Zirconium complexes could also not be obtained with either **2e** or **2f**. For **2f**, the isolation of a salt proved to be difficult, and the yield for the deprotonation with *n*-butyllithium was low though it afforded a white precipitate. Addition of this solid to zirconium tetrachloride resulted in immediate decomposition and was not pursued further. For **2e**, the reaction mixture in THF turned from yellow to black around −40 °C and further studies imply that the decomposition pathway is somewhat different from that for **2d** and **2f**.

Structural characterisation

Structure of 4a. An ORTEP[28] view of **4a** is shown in Fig. 1; selected bond distances and angles are listed in Table 2. The geometry around the zirconium centre is a distorted tetrahedron; internal C_2 symmetry relates the two indenyl and chloride ligands. The DMS groups very nearly bisect the benzo moiety of the other indenyl ligand, leaving the Cl atoms relatively exposed. The DMS group is slightly deflected out of the Cp-plane of the indenyl ligand and away from the zirconium centre, as evidenced by the Ct–C4–Si (Ct = centroid of C1–C5) angles of 175.2 and 172.3°. The dihedral angle φ (Si1a–C4a–C4b–Si1b) is measured to 177.2°.

Structure of 4b. Fig. 2 shows the ORTEP view of **4b**; selected bond distances and angles are listed in Table 2. The co-

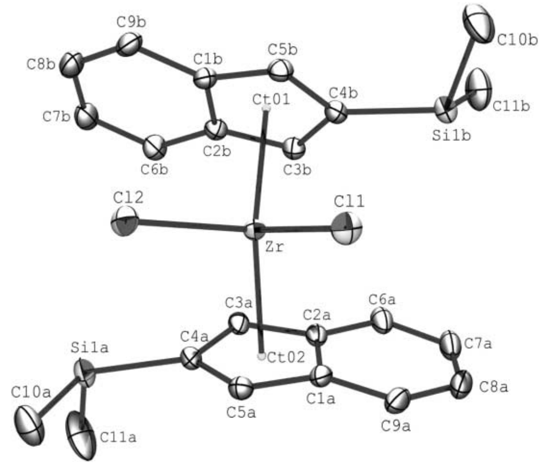


Fig. 1 Refined crystallographic structure of bis[2-(dimethylsilyl)-indenyl]zirconium dichloride (**4a**). Hydrogens are omitted for clarity. Thermal ellipsoids at 50% probability level.

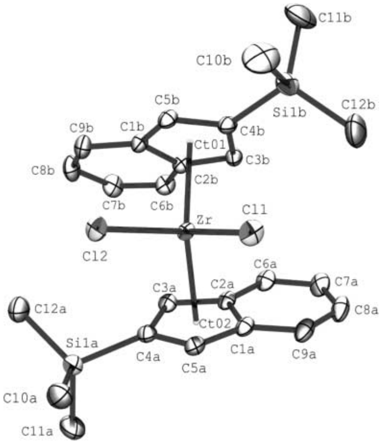


Fig. 2 Refined crystallographic structure of bis[2-(trimethylsilyl)-indenyl]zirconium dichloride (**4b**). Hydrogens are omitted for clarity. Thermal ellipsoids at 50% probability level.

ordination sphere of the zirconium atom resembles, as in **4a**, a distorted tetrahedron, while the geometry is C_2 symmetric. Again the silyl moieties are bent out of the Cp-plane by up to 10.8°. In contrast to **4a**, the TMS groups have two methyl groups pointing inwards to the opposite ligand, to minimize steric intrusion of the TMS group into the inter-ligand space. The chlorides intersect the very same two methyl groups of the TMS moieties. The dihedral angle φ spans 120.9° and deviates significantly from a *rac*-like, antiperiplanar conformer as seen in **4a**. The Ct01–Zr–Ct02 angles ε of both compounds, **4a** and **4b**, are basically identical, measuring 129.8 and 129.9°.

The bond distances between the carbon atoms of the Cp ring and the zirconium atom for **4a** and **4b** are comparable to those reported for bis[indenyl]zirconium dichloride (**6**).[29] The carbon atoms C(3a) and C(3b) of **4a**, those carbon atoms *furthest* from chloride, are the closest to the zirconium atom, at 2.488(1) and 2.456(1) Å, as compared to 2.48 and 2.47 Å for the unsubstituted system. The respective bond distances for **4b** are identical within 0.02 Å. Zirconium chloride distances range around the expected 2.44 Å. The chloride–zirconium–chloride angle of **4a** is close to the one observed for **6**, *i.e.* 95.57(1)° and 94.7° respectively, while **4b** exhibits a much smaller angle of 92.57(2)°. The aromatic character of the annelated benzo ring is not very pronounced as the carbon–carbon bond lengths alternate between 1.43 and 1.37 Å, and display rather the behaviour of conjugated double bonds. This coincides with a bent benzo-moiety in **4a** and **4b**, in contrast to a planar and hence more aromatic benzo-moiety in **6**. Interestingly, the angle ε reported for bis[indenyl]zirconium dichloride is only 1.5° smaller than for **4a** and **4b**, but the conformers differ considerably. While **4a** and **4b** crystallise in antiperiplanar and anticlinal conformations, a synclinal conformer is observed for the unsubstituted complex.

The different solid state structures, particularly the different dihedral angles, suggest the influence of crystal packing effects. Quantum chemical calculations were carried out in an attempt to shed further light on this question. The initial geometry optimizations constrained the dihedral angle φ to the experimental values. As shown in Table 3, the computed gas-phase energy for **4a** changes by only 0.6 kcal mol^{-1} upon changing φ from 177 to 121°, suggesting the actual conformer arises from packing effects. The additional methyl group on the silyl moiety in **4b**, however, changes the situation, as the energy for the antiperiplanar gas phase conformer is 3.7 kcal^{-1} mol less stable than the observed anticlinal solid state structure. Relaxation of the geometrical constraints and reoptimisation of the geometry reveals that the anticlinal and antiperiplanar conformers of **4a** represent local and almost degenerate energy minima.[30] For **4b**, however, optimisations starting from the antiperiplanar conformer converge to the anticlinal one. The angles ε are equal to within 2° for all computed geometries for both species. Coordinate drive calculations, in which φ was stepped from 177 to -7° in 10° increments, revealed another, lower lying minimum for **4b**, while it did not indicate any new minima for **4a**. The failure of the coordinate drive calculation to find the global minimum is due to another crucial degree of freedom that remains unrestrained in order to keep the computational effort on a reasonable scale: The dihedral angle ϕ spanned by Cl1–Zr–C4a–Si1a is floating free and the calculation does not necessarily take the lowest energy path on the two-dimensional φ–ϕ-surface. Details on this problem will be reported elsewhere. The calculated energies reported for the crystal structures are considerably higher than those obtained from unconstrained geometry optimisations, even though the positions of the hydrogen atoms were allowed to relax in the former calculations. The resulting difference may be assigned to the error in measurement and crystal packing forces.

Polymerisation results

In order to establish a rough estimate on the properties of the herein presented zirconocene dichlorides as polymerisation catalyst precursors in ethene homopolymerisations with MAO as cocatalyst, isobar and isothermal experiments were run at two different catalyst concentrations. Experiments were conducted for 30 min at 30 °C and 1.2 bar (0.14 mol L^{-1}) ethene at 1.0×10^{-6} and 1.0×10^{-7} mol L^{-1} zirconium. Fig. 3 summarises the measured activities. For comparison **6**/MAO was utilized as an internal reference, since polymerisation activities tend to vary with the experimental procedures and setup. All systems

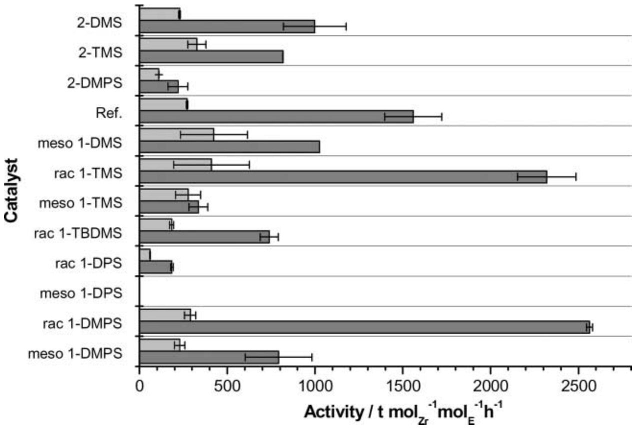


Fig. 3 Polymerisation activities of the zirconocene dichlorides/MAO in ethene homopolymerisations. The error bars indicate the experimental standard deviation; c(Zr) = 1.0×10^{-7} mol L^{-1}, Al/Zr = 10000 (light grey); c(Zr) = 1.0×10^{-6} mol^{-1} L, Al/Zr = 1000 (dark grey).

Table 2 Selected bond distances (Å) and angles (°) for **4a** and **4b**

	4a	**4b**
Zr–Cl1	2.4487(3)	2.4310(4)
Zr–Cl2	2.4421(3)	2.4397(4)
Zr–Ct01	2.231	2.224
Zr–Ct02	2.231	2.228
Zr–C1a	2.6036(10)	2.5745(15)
Zr–C2a	2.5880(10)	2.5577(14)
Zr–C3a	2.4880(10)	2.4796(15)
Zr–C4a	2.5153(10)	2.5375(16)
Zr–C5a	2.5119(11)	2.5180(16)
Si1a–C4a	1.8818(11)	1.8811(17)
Si1b–C4b	1.8889(11)	1.8762(16)
Cl2–Zr–Cl1	95.572(11)	92.567(17)
Ct02–Zr–Cl1	106.9	104.2
Ct01–Zr–Cl1	107.4	109.5
Ct02–Zr–Cl2	107.2	109.6
Ct01–Zr–Cl2	104.8	104.9
Ct01–Zr–Ct02	129.8	129.9

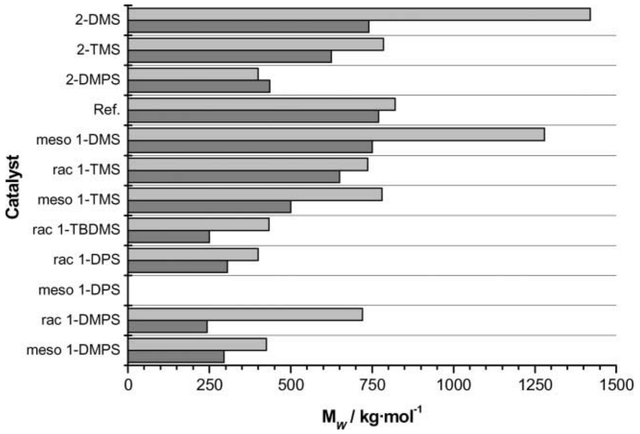


Fig. 4 Molecular weights of HDPE samples as determined by high-temperature GPC; c(Zr) = 1.0 × 10^{-7} mol L^{-1}, Al/Zr = 10000 (light grey); c(Zr) = 1.0 × 10^{-6} mol L^{-1}, Al/Zr = 1000 (dark grey).

displayed virtually instantaneous maximum activity and rapid deactivation within the first 3 min of the polymerisation experiment. The remaining consumption of ethene was low and differences can hardly be granted relevance. Since the activities of all complexes at the 1.0 × 10^{-7} M Zr concentration are low and nearly equal within experimental error, only the high catalyst concentration results will be compared.

Among the 2-isomers, there is a clear inverse correlation between the size of the silyl moiety and the activity, with the smallest DMS system **4a** giving the highest activity. All 2-isomers perform poorer than the unsubstituted reference system. However, **4b**/MAO is 80 to 160 times more active in our hands than recently reported by Coville and co-workers.[17] The picture is less clear for the 1-isomers. The data suggest higher activities for the *rac*-diastereomers than for the corresponding *meso*-diastereomers. For the available data, there is a general decrease in activity with the steric bulk of the ligand. The exceptions are the DMPS systems, and, surprisingly, *rac*-**3c** is overall the most active one. Since the PDI of polymers obtained from this catalyst are relatively narrow (Table 4), this effect could be ascribed to a limited number of accessible and possibly more active conformers than for the other catalyst systems. In addition, counterion contact should be strongly reduced due to steric bulk. However, the more congested *rac* and *meso* isomers of the DPS system display only little or no polymerisation activity. Both *rac*-**3b** and *rac*-**3c** are more active than the unsubstituted reference system.

The molecular weights of the poly(ethene)s were determined by means of high-temperature GPC and are summarised in Fig. 4 and Table 4. The molecular weights of poly(ethene) samples produced by the 2-isomers decrease with increasing size of the substituent. The same trend is valid for the 1-isomers, and no clear distinction can be made between the *rac* and *meso* diastereomers. According to earlier reports, a substituent in the 2-position may increase the molecular weight with respect to the unsubstituted catalyst **6** for selected examples like phenyl or ethyl moieties.[17] Somehow, a systematic comparison of the influence of the substituent on the molecular weight of homopolymers is lacking or poorly reliable, as the reported figures vary substantially.[16,17] The individual rates of the several termination reactions are usually ascribed to steric but not to electronic effects, and the data presented here for **4a**/MAO and **4b**/MAO allow the same conclusion. Since the DFT calculations show equivalent steric contributions to the Ct–Zr–Ct angles and the ligand framework is electronically indistinguishable, only conformer effects will govern the steric environment of the active site. The influence of the cocatalyst MAO and its residual TMA is still disputed. While an increase in aluminium concentration is generally supposed to increase the termination probability by chain transfer through transmetallation, notably for certain zirconocenes,[31] Charpentier *et al.* did not confirm this observation.[32] Interestingly, we report an increase in the molecular weight for higher Al/Zr ratios, at constant aluminium concentrations. This effect is not necessarily in conflict with the observations by Rytter and Rieger,[31] since the transmetallation process is bimolecular and a decrease in concentration of one of the relevant reactants will reduce the overall probability of the process.

The polydispersity indexes measured for the different catalyst systems are presented in Table 4. Most of the PDIs differ considerably from the expected value of two for a single-site catalyst and imply the presence of more than one active conformational state of the activated catalyst.

Conclusions

The preparative routes described in this paper provide feasible methods to obtain 1- and 2-substituted silylindenes. The corresponding metallocene yields were good for most ligands, but disappointingly, a number of the 2-substituted ligands failed to

Table 3 Dihedral angle φ, angle ε and relative energies E as derived from XRD or DF calculations

	2-DMS (**4a**)			2-TMS (**4b**)		
Geometry	φ/°	ε/°	E/kcal mol^{-1}	φ/°	ε/°	E/kcal mol^{-1}
XRD	177	129.8	5.05	121	129.9	6.54
DF,[a] opt./con.[b]	177	130.7	0.64	177	131.7	4.32
DF, opt./con.	121	130.8	0.03	121	129.8	0.60
DF, opt.	$^{177}173^{c}$	130.6	0.62	$^{177}120$	129.8	0.60
DF, opt.	$^{121}117$	130.1	0.00	$^{121}120$	129.8	0.60
DF, coord. dr.[d]	177	130.7	0.64	103	130.4	0.00

[a] DF calculations used B3LYP functional and 6-31G* basis set. [b] opt. = Geometry optimization; con. = constrained in φ. [c] Superscript gives start value for φ. [d] Coordinate drive of φ from 177° to −3° in steps of 10°, geometry optimization constrained in φ.

Table 4 Molecular weights of HDPE samples as determined by high-temperature GPC for $c(\mathrm{Zr}) = 1 \times 10^{-7}$ mol L^{-1} and $c(\mathrm{Zr}) = 1 \times 10^{-6}$ mol L^{-1}

	Al/Zr = 10000			Al/Zr = 1000		
Catalyst	M_w/kg mol^{-1}	M_n/kg mol^{-1}	PDI	M_w/kg mol^{-1}	M_n/kg mol^{-1}	PDI
2-DMS	1420	486	2.9	625	240	2.6
2-TMS	785	300	2.6	740	299	2.5
2-DMPS	400	100	4.0	435	155	2.8
BisInd	820	409	2.0	770	282	2.7
meso 1-DMS	1280	521	2.5	750	294	2.5
rac 1-TMS	737	372	2.0	650	247	2.6
meso 1-TMS	780	306	2.5	500	166	3.0
rac 1-TBDMS	433	164	2.6	250	82	3.0
rac 1-DPS	400	115	3.5	305	75	4.1
meso 1-DPS	n.a.[a]	n.a.	n.a.	n.a.	n.a.	n.a.
rac 1-DMPS	720	308	2.3	245	101	2.4
meso 1-DMPS	425	153	2.8	295	115	2.5

[a] Not applicable as catalyst, does not exhibit any polymerisation activity.

yield the corresponding metallocene. The separation of the *rac*- and *meso*-diastereomers of the 1-substituted zirconocenes was feasible for most complexes and, in the case of **3b** unexpected diastereomer sensitivity on the reaction solvent was observed. Crystal structures for **4a** and **4b** show different conformers. DF calculations imply that the observed structure of **4a** is due to crystal packing forces, whereas **4b** crystallises in a conformer that resembles a global minimum for the calculated gas phase structure. According to these data, the steric implications of the silyl group on the catalyst geometry are negligible, although conformational dynamics are affected.

These data further suggest that the differences in the polymerisation activities and molecular weights in the ethene homopolymerisations of **4a**/MAO and **4b**/MAO are predominantly due to the conformational and to lesser degree to sterical variations in the immediate proximity of the zirconium atom. The enchainment rate of the catalysts may be assumed constant if the steady-state-approximation is applicable, time-dependent deactiviation processes need not to be considered, differences in electronic effects for the systems **4a** and **4b** should be negligible, and both complexes feature practically identical cone angles. The turnover rate will therefore be a function of the steric environment around zirconium, which, as discussed above, is manifested in different conformational effects. Activities for the 2-isomers tend to be lower than for the unsubstituted bis[indenyl]zirconium dichloride/MAO, while molecular weights decrease upon sterically more demanding substitution patterns in the 2-position. The polydispersity indexes measured here suggest that we do not have single-site catalyst systems after activation with MAO, but rather different stable conformers of longer life than polymer growth time. Curiously, the most active catalyst system is that of the relatively sterically demanding *rac*-**3c**/MAO.

Further synthetic, polymerisation and modelling studies based on molecular mechanics and DFT techniques are currently being carried out in our group.

Experimental

General comments

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. Indene (Merck) was dried over calcium hydride 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. All chlorosilanes (ACBR GmbH or Aldrich Chemicals) were distilled under argon or vacuum prior to use. Silyl triflates (Aldrich Chemicals) were employed as received. Magnesium turnings (Merck), *n*-butyllithium (Acros, Aldrich or Merck), zirconium tetrachloride (Aldrich or Strem), and methyllithium (Janssen Chemica or Aldrich) 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 filtrated through a D4-frit and volatiles removed *in vacuo* yielding a white solid. Ethene of polymerisation grade was received from Borealis Stathelle, Norway. *rac*-bis[1-(trimethylsilyl)-indenyl]zirconium dichloride was prepared according to a literature procedure.[17] ^{1}H and ^{13}C NMR spectra acquired on a Varian Gemini 300 MHz instrument were referenced to the residual solvent peaks. Determination of the AA'XX' spin system of **4b** was carried out according to a published procedure.[33] Low resolution MS was conducted on 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 characterisations of the HDPE samples were conducted on 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.

2-Bromoindene

The synthesis is a conceptual copy of a literature procedure,[34] which did not work in our hands and contains apparent errors in the amounts of chemicals employed. To a suspension of 32 g (0.15 mol) *trans*-2-bromo-1-indanol in 200 mL toluene in a 250 mL round bottom flask equipped with a Dean–Stark trap, 0.8 g (3 mol%) PTA was added. The reaction mixture turned homogeneous and golden-coloured around 80 °C and was refluxed at 140 °C oil-bath temperature. While refluxing for 6 h, the collected azeotrope was frequently removed from the Dean–Stark trap and the suspension developed a tan colour. The solution was refrigerated over night, filtered and dried over magnesium sulfate. Volume reduction to 100 mL, three extractions with aliquots of 100 mL saturated sodium hydrogen carbonate solution, drying over magnesium sulfate and filtration yielded an organic phase with pH 5. Removal of solvent and three subsequent recrystallisations from 20 mL of methanol at −40 °C yielded 11.7 g (60.0 mmol, 40%) of a white, microcrystalline powder. Alternatively, the crude product can be distilled under high vacuum in approximately the same yield. Unfortunately the distillation leads to decomposition. GC/MS analysis revealed one single peak, which was identified to be the desired product. GC/MS (70 eV): *m*/*z* (%): 194 (21) [M$^+$], 115 (100) [M$^+$ − Br].

1-(Dimethylsilyl)indene/1-DMS-Ind (1a)

The synthesis was based on a literature procedure[35] and utilised indenyl lithium (5.17 g, 42.3 mmol) and chlorodimethylsilane (4.7 mL, 42.3 mmol). The product was 6.86 g of a pale yellow liquid (39.4 mmol, 93%) which was used without further purification. ^{1}H NMR (300 MHz, [D$_6$]benzene, 25 °C): δ −0.27 (d, ^3J = 3.6 Hz, 3 H, $\mathrm{SiH(C}\mathit{H}_3)_2$), −0.17 (d, ^3J = 3.6 Hz, 3 H, $\mathrm{SiH(C}\mathit{H}_3)_2$), 3.35 (d, ^3J = 1.9 Hz, 1 H, 1-H), 4.09 (m, 1 H, $\mathrm{Si}\mathit{H}(\mathrm{CH}_3)_2$), 6.43 (dd, ^3J = 1.9 Hz, ^3J = 5.3 Hz, 1 H, 2-H), 6.84 (dd, ^4J = 1.7 Hz, ^3J = 5.4 Hz, 1 H, 3-H), 7.17–7.23 (m, 2 H, 5,6-H), 7.41–7.44 (m, 2 H, 4,7-H). ^{13}C{^{1}H} NMR (75 MHz, [D$_6$]benzene, 25 °C): δ −6.05 (1 C, $\mathrm{SiH(}\mathit{C}\mathrm{H}_3)_2$), −5.08 (1 C, $\mathrm{SiH(}\mathit{C}\mathrm{H}_3)_2$), 44.39 (1 C, C-1), 121.94 (1 C, C-4), 123.39 (1 C, C-7), 124.79 (1 C, C-6), 125.90 (1 C, C-5), 130.19 (1 C, C-3), 135.39 (1 C, C-2), 144.92 (1 C, C-7a), 145.74 (1 C, C-3a).

1-(Trimethylsilyl)indene/1-TMS-Ind (1b)

The synthesis followed that described for **1a**, above, employing chlorotrimethylsilane instead of chlorodimethylsilane. The resulting pale yellow liquid (93%) was used without further purification. ^{1}H NMR (300 MHz, [D$_6$]benzene, 25 °C): δ −0.16 (s, 9 H, TMS), 3.29 (d, ^3J = 1.6 Hz, 1 H, 1-H), 6.46 (dd, ^3J = 1.9 Hz, ^3J = 5.3 Hz, 1 H, 2-H), 6.80 (dd, ^4J = 1.7 Hz, ^3J = 5.3 Hz, 1 H, 3-H), 7.16–7.23 (m, 2 H, 5,6-H), 7.38–7.45 (m, 2 H, 4,7-H). ^{13}C{^{1}H} NMR (75 MHz, [D$_6$]benzene, 25 °C): δ −2.23 (3 C, TMS), 46.95 (1 C, C-2), 121.84 (1 C, C-4), 123.35 (1 C, C-7), 124.49 (1 C, C-6), 125.66 (1 C, C-5), 129.74 (1 C, C-3), 136.05 (1 C, C-2), 144.96 (1 C, C-3a), 146.06 (1 C, C-7a).

1-(Dimethylphenylsilyl)indene/1-DMPS-Ind (1c)

The synthesis followed that described for **1a**, above, employing chlorodimethylphenylsilane instead of chlorodimethylsilane. The resulting pale yellow liquid (96%) was used without further purification. ^{1}H NMR (300 MHz, [D$_6$]benzene, 25 °C): δ −0.12 (s, 3 H, $\mathrm{Si(C}\mathit{H}_3)_2\mathrm{Ph}$), −0.07 (s, 3 H, $\mathrm{Si(C}\mathit{H}_3)_2\mathrm{Ph}$), 3.47 (d, ^3J = 1.8 Hz, 1 H, 1-H), 6.35 (dd, ^3J = 1.9 Hz, ^3J = 5.2 Hz, 1 H, 2-H), 6.71 (dd, ^4J = 1.6 Hz, ^3J = 5.5 Hz, 1 H, 3-H), 6.98 (m, 1 H, 7-H), 7.02–7.12 (m, 5 H, $\mathrm{Si(CH}_3)_2\mathit{Ph}$), 7.24–7.27 (m, 2 H, 5,6-H), 7.29–7.31 (m, 1 H, 4-H). ^{13}C{^{1}H} NMR (75 MHz, [D$_6$]benzene, 25 °C): δ −4.62 (1 C, $\mathrm{Si(}\mathit{C}\mathrm{H}_3)_2\mathrm{Ph}$), −4.03 (1 C, $\mathrm{Si(}\mathit{C}\mathrm{H}_3)_2\mathrm{Ph}$), 46.27 (1 C, C-1), 121.89 (1 C, C-4), 123.71 (1 C, C-7), 124.52 (1 C, C-6), 125.83 (1 C, C-5), 128.49 (2 C, C-2′,6′), 129.99 (1 C, C-3), 130.15 (1 C, C-4′), 134.52 (2 C, C-3′,5′), 135.99 (1 C, C-2), 138.17 (1 C, C-1′), 145.18 (1 C, C-7a), 145.65 (1 C, C-3a).

1-(Diphenylsilyl)indene/1-DPS-Ind (1d)

The synthesis followed that described for **1a**, above, employing chlorodiphenylsilane instead of chlorodimethylsilane and toluene instead of pentane. After addition of the chlorodiphenylsilane, the reaction mixture was heated to 80 °C overnight. Quenching with methanol and subsequent acidic work-up yielded 77% of a white solid. ^{1}H NMR (300 MHz, [D$_6$]benzene, 25 °C): δ 3.93 (m, 1 H, 1-H), 4.92 (d, ^3J = 3.0 Hz, 1 H, $\mathrm{Si}\mathit{H}\mathrm{Ph}_2$), 6.61 (dd, ^3J = 1.8 Hz, ^3J = 5.3 Hz, 1 H, 2-H), 6.79 (ddd, ^5J = 0.7 Hz, ^4J = 1.8 Hz, ^3J = 5.3 Hz, 1 H, 3-H), 7.02–7.11 (m, 4 H, 2′,3′,2″,3″-H), 7.12–7.18 (m, 4 H, 5′,6′,5″,6″-H), 7.28 (m, 1 H, 4′-H), 7.35 (m, 1 H, 4″-H), 7.37–7.41 (m, 4 H, 4,5,6,7-H). ^{13}C{^{1}H} NMR (75 MHz, [D$_6$]benzene, 25 °C): δ 43.13 (1 C, C-1), 122.09 (1 C, C-4), 124.17 (1 C, C-7), 124.75 (1 C, C-6), 126.20 (1 C, C-5), 128.49 (2 C, C-3′,5′), 128.60 (2 C, C-3″,5″), 130.43 (1 C, C-4′), 130.59 (1 C, C-4″), 131.05 (1 C, C-3), 133.26 (1 C, C-1′), 133.33 (1 C, C-1″), 135.13 (1 C, C-2), 135.87 (2 C, C-2′,6′), 136.09 (2 C, C-2″,6″), 144.97 (1 C, C-7a), 145.33 (1C, C-3a).

3-(*tert*-Butyldimethylsilyl)indene/3-TBDMS-Ind (1e)

2.78 g (2.4 mL, 10.5 mmol) *tert*-Butyldimethylsilyl triflate was added to 50 mL dry toluene in a 100 mL Schlenk flask and cooled to 0 °C. After 1.17 g (9.6 mmol) indenyl lithium was added as a solid, a condenser was mounted on the Schlenk flask. After heating to 110 °C for 16 h and subsequent quenching with 20 mL 0.1 M hydrochloric acid and phase separation, the organic layer was extracted twice with 25 mL deionised water and dried over magnesium sulfate. Removal of the volatiles afforded 2.16 g (9.3 mmol, 95%) of a colourless liquid. It was identified to be the desired product at 98.4% purity. The major impurity was indene from unreacted, hydrolysed indenyl lithium. ^{1}H NMR (300 MHz, [D$_6$]benzene, 25 °C): δ −0.34 (s, 3 H, $\mathrm{Si(C}\mathit{H}_3)_2(\mathrm{C}_4\mathrm{H}_9)$), 0.07 (s, 3 H, $\mathrm{Si(C}\mathit{H}_3)_2(\mathrm{C}_4\mathrm{H}_9)$), 0.16 (s, 9 H, $\mathrm{Si(CH}_3)_2(\mathrm{C}_4\mathit{H}_9)$), 3.16 (s, 2 H, 1-H), 7.02 (s, 1 H, 2-H), 7.16 (dd, ^3J = 8 Hz, ^3J = 8 Hz, 1 H, 5-H), 7.25 (dd, ^3J = 8 Hz, ^3J = 8 Hz, 1 H, 6-H), 7.36 (d, ^3J = 8 Hz, 2 H, 4,7-H). ^{13}C{^{1}H} NMR (75 MHz, [D$_6$]benzene, 25 °C): δ −7.09 (1 C, $\mathrm{Si(}\mathit{C}\mathrm{H}_3)_2(\mathrm{C(CH}_3)_3)$), −4.36 (1 C, $\mathrm{Si(}\mathit{C}\mathrm{H}_3)_2(\mathrm{C(CH}_3)_3)$), 18.58 (1 C, $\mathrm{Si(CH}_3)_2(\mathit{C}\mathrm{(CH}_3)_3)$), 27.71 (3 C, $\mathrm{Si(CH}_3)_2(\mathrm{C(}\mathit{C}\mathrm{H}_3)_3)$), 45.26 (1 C, C-1), 121.86 (1 C, C-4), 124.03 (1 C, C-7), 124.25 (1 C, C-6), 125.69 (1 C, C-5), 129.35 (1 C, C-3), 136.80 (1 C, C-2), 145.27 (1 C, C-7a), 146.38 (1 C, C-3a). GC/MS (70 eV): *m*/*z* (%): 230 (21) [M$^+$], 173 (28) [M$^+$− C$_4$H$_9$], 145 (21) [$\mathrm{C_9H_7SiH_2}^+$], 115 (24) [$\mathrm{C_9H_7}^+$], 73 (100) [$\mathrm{C_3H_9Si}^+$].

1-(Diphenylmethylsilyl)indene/1-DPMS-Ind (1g)

The synthesis followed that described for **1a**, above, employing chlorodiphenylmethylsilane instead of chlorodimethylsilane. The desired product was obtained from a diethyl ether extraction of the reaction residue and subsequent cooling of the pale yellow solution to −40 °C. Repeated crystallizations gave several crops of a white solid in an 82% overall yield. ^{1}H NMR (300 MHz, [D$_6$]benzene, 25 °C): δ 0.08 (s, 3 H, $\mathrm{Si(C}\mathit{H}_3)\mathrm{Ph}_2$), 3.95 (s, 1 H, 1-H), 6.52 (dd, ^3J = 5.4 Hz, J = 1.8 Hz, 1 H, 2-H), 6.77 (dd, ^3J = 5.1 Hz, J = 2.4 Hz, 1 H, 3-H), 6.94 (ddd, ^3J = 7.2 Hz, ^3J = 7.2 Hz, ^4J = 2.1 Hz, 1 H, 4-H), 7.02–7.18 (m, 7 H, benzo-H, Ph-H), 7.33–7.43 (m, 6 H, benzo-H, Ph-H). ^{13}C{^{1}H} NMR (75 MHz, [D$_6$]benzene, 25 °C): δ −7.09 (1 C, $\mathrm{Si(}\mathit{C}\mathrm{H}_3)\mathrm{Ph}_2$), 44.59 (1 C, C-1), 121.89 (1 C, C-4), 124.14 (1 C, C-7), 124.56 (1 C, C-6), 125.99 (1 C, C-5), 128.51 (2 C, C-3′,5′), 128.55 (2 C, C-3″,5″), 130.07 (1 C, C-4′), 130.22 (1 C, C-4″), 130.67 (1 C, C-3), 135.20 (2 C, C-2′,6′), 135.54 (2 C, C-2″,6″), 135.87 (1 C, C-1′), 135.91 (1 C, C-2), 136.97 (1 C, C-1″), 145.28 (1 C, C-7a), 145.49 (1 C, C-3a).

2-(Dimethylsilyl)indene/2-DMS-Ind (2a)

The synthesis was based on a literature procedure,[20] with some modification. Magnesium turnings (0.99 g, 40.7 mmol) were placed in a 250 mL flask equipped with an addition funnel and Teflon-coated stir bar and cooled with a water bath. Dry THF (30 mL) was added. In a separate flask, 2-bromoindene (5.54 g, 28.4 mmol) was dissolved in 20 mL THF, and the resulting solution was transferred to the addition funnel. 2 mL of the 2-bromoindene solution was added to the magnesium suspension, and then a small amount of iodine was added to initiate the reaction. Within 15 min, the reaction had lost the iodine-derived colour and become cloudy. At this point the remaining 2-bromoindene solution was added dropwise over 30–45 min. The resulting Grignard solution was usually violet–red, but could be as light as orange without apparent change in reactivity. After stirring for an additional 4 h, the unreacted magnesium was filtered off and the Grignard solution was transferred to a second 250 mL flask equipped with an addition funnel and Teflon-coated stir bar and cooled with a water-bath. Chlorodimethylsilane (3.25 mL, 29.3 mmol) and THF (10 mL) were then placed in the addition funnel, and this solution was added dropwise over about 30 minutes. The light-red reaction solution was then stirred overnight at room temperature. Degassed water (25 mL) was added, followed by THF (10 mL) and diethyl ether (20 mL), and then the organic layer was removed and dried over magnesium sulfate. Filtration and removal of the volatiles followed by distillation under vacuum (1 Torr) gave first a colourless fraction boiling at 26 °C. A second fraction boiling at 44–45 °C provided 3.0 g (17.2 mmol, 61%) of 2-(dimethylsilyl)indene. ^{1}H NMR (300 MHz, [D$_6$]benzene, 25 °C): δ 0.07 (d, ^3J = 3.6 Hz, 6 H, $\mathrm{SiH(C}H_3)_2$), 3.04 (d, ^4J = 1.6 Hz, 2 H, 1-H), 4.41 (sept, ^3J = 3.6 Hz, 1 H, $\mathrm{Si}H(\mathrm{CH_3})_2$), 6.93 (t, ^4J = 1.9 Hz, 1 H, 3-H), 7.03 (dd, ^3J = 7.3 Hz, ^4J = 1.2 Hz, 1 H, 5-H), 7.13–7.07 (m, 1 H, 7-H), 7.19–7.21 (m, 2 H, 5,6-H). ^{13}C{^{1}H} NMR (75 MHz, [D$_6$]benzene, 25 °C): δ −3.49 (2 C, $\mathrm{Si(C}H_3)_2$), 43.16 (1 C, C-1), 121.67 (1 C, C-4), 124.30 (1 C, C-7), 125.67 (1 C, C-6), 126.97 (1 C, C-5), 143.09 (1 C, C-3), 145.77 (1 C, C-2), 146.22 (1 C, C-7a), 147.57 (1 C, C-3a). GC/MS (70 eV): *m*/*z* (%): 174 (59) [M$^+$], 159 (100) [M$^+$ − CH$_3$], 143 (21) [M$^+$ − C$_2$H$_7$], 131 (23) [M$^+$ − SiHCH$_3$], 115 (23) [C$_9$H$_7$$^+$], 59 (53) [SiH(CH$_3$)$_2$$^+$].

2-(Trimethylsilyl)indene/2-TMS-Ind (2b)

The synthesis was also based on a literature procedure,[19] with modifications. Magnesium turnings (1.5 g, 62.5 mmol) and a grain of iodide were placed in a flask equipped with an addition funnel and stirred in THF (30 mL) for 10 min. The addition funnel was charged with a solution of 2-bromoindene (8.0 g, 41.0 mmol) in THF (40 mL). Upon addition of 1 mL of the 2-bromoindene solution to the magnesium, immediate formation of the Grignard reagent occurred, as the suspension turned pale and cloudy. The remaining 2-bromoindene solution was added dropwise to the gently boiling suspension, and the reaction was stirred for another 30 min, yielding a violet–red suspension. In a second flask also equipped with an addition funnel, chlorotrimethylsilane (5.7 g, 53.1 mmol) was diluted with THF (40 mL). The Grignard suspension was filtered into the second addition funnel and added dropwise over 4 h and under vigorous stirring. The resulting pale red solution was stirred overnight to yield a pink suspension. The reaction was quenched by addition of 20 mL diethyl ether and 20 mL 0.1 mol L^{-1} hydrochloric acid. After evaporation of the organic solvent and subsequent addition of 40 mL diethyl ether, the organic and aqueous phases were separated and the organic phase was washed two times with equal amounts of distilled water. Drying over magnesium sulfate and removal of excess solvent *in vacuo* provided 6.2 g of crude product. High vacuum distillation (0.05 Torr) yielded 4.9 g (26.0 mmol, 64%) of the desired product, boiling at 36–40 °C$_{0.05\ \mathrm{Torr}}$. ^{1}H NMR (300 MHz, [D$_6$]benzene, 25 °C): δ 0.16 (s, 9 H, TMS), 3.04 (d, ^4J = 1.9 Hz, 2 H, 1-H), 6.90 (dt, ^5J = 0.8 Hz, ^4J = 1.9 Hz, 1 H, 3-H), 7.04 (dt, ^5J = 1.1 Hz, ^3J = 7.3 Hz, 1 H, 4-H), 7.10 (m, 1 H, 7-H), 7.23 (m, 2 H, 5,6-H). ^{13}C{^{1}H} NMR (75 MHz, [D$_6$]benzene, 25 °C): δ −0.67 (3 C, TMS), 42.77 (1 C, C-1), 121.21 (1 C, C-4), 124.13 (1 C, C-7), 125.18 (1 C, C-6), 126.75 (1 C, C-5), 140.86 (1C, C-3), 146.30 (1 C, C-2), 147.47 (1 C, C-7a), 150.19 (1 C, C-3a). GC/MS (70 eV): *m*/*z* (%): 188 (37) [M$^+$], 173 (22) [M$^+$ − CH$_3$], 145 (38) [M$^+$ − C$_3$H$_7$], 115 (12) [M$^+$ − TMS], 73 (100) [TMS$^+$].

2-(Dimethylphenylsilyl)indene/2-DMPS-Ind (2c)

The synthesis proceeded in a fashion similar to **2b**. The Grignard solution derived from 2-bromindene (3.14 g, 16.1 mmol) and magnesium turnings (2.0 g, 83 mmol) was added to a solution of chlorodimethylphenylsilane (2.7 mL, 16.2 mmol) in 10 mL THF and stirred overnight at room temperature. Removal of solvent, extraction with toluene and purification by column chromatography with heptane and heptane–toluene (1 : 1) on silica gel (195 g) yielded a white solid (2.94 g, 11.8 mmol, 73%). ^{1}H NMR (300 MHz, [D$_6$]benzene, 25 °C): δ 0.40 (s, 6 H, $\mathrm{Si(C}H_3)_2\mathrm{Ph}$), 3.18 (d, ^4J = 1.9 Hz, 2 H, 1-H), 6.90 (dt, ^4J = 1.9 Hz, ^5J = 0.8 Hz, 1 H, 3-H), 7.04 (ddd, ^3J = 7.3 Hz, ^3J = 7.3 Hz, ^4J = 1.1 Hz, 1 H, 5-H), 7.10–7.16 (m, 1 H, 6-H), 7.22–7.25 (m, 2 H, 4,7-H). ^{13}C{^{1}H} NMR (75 MHz, [D$_6$]benzene, 25 °C): δ −2.00 (2 C, $\mathrm{Si(}C\mathrm{H_3)_2Ph}$), 43.13 (1 C, C-1), 121.72 (1 C, C-4), 124.36 (1 C, C-7), 125.66 (1 C, C-6), 126.99 (1 C, C-5), 128.56 (2 C, C-3′,5′), 129.73 (2 C, C-2′,6′), 134.62 (1 C, C-4′), 138.94 (1 C, C-1′), 143.34 (1 C, C-3), 146.29 (1 C, C-2), 147.15 (1 C, C-7a), 147.75 (1 C, C-3a). GC/MS (70 eV): *m*/*z* (%): 250 (7) [M$^+$], 235 (6) [M$^+$ − CH$_3$], 207 (6), 135 (100) [Si(CH$_3$)$_2$Ph$^+$], 115 (5) [C$_9$H$_7$$^+$], 105 (7) [SiC$_6H_5$].

2-(Diphenylsilyl)indene/2-DPS-Ind (2d)

The synthesis was similar to that described for **2b**, and employed magnesium turnings (0.6 g, 25 mmol), 2-bromoindene (2.0 g, 10.3 mmol), and chlorodiphenylsilane (2.46 g, 11.3 mmol). After the combined Grignard and chlorodiphenylsilane solutions were stirred overnight, the reaction was refluxed for another 24 h. The reaction was quenched with methanol (20 mL). The volatiles was removed under reduced pressure and the resulting solid was extracted with 40 mL of 1 : 1 mixture of toluene and methylene chloride. Filtration and removal of solvent yielded 2.8 g (9.3 mmol, 90% yield) of the product as a white solid. ^{1}H NMR (300 MHz, [D$_6$]benzene, 25 °C): δ 3.33 (d, ^4J = 2.1 Hz, 2 H, 1-H), 5.61 (s, 1 H, $\mathrm{Si}H\mathrm{Ph_2}$), 7.08–7.22 (m, 6 H, 3-H, benzo-H, Ph-H), 7.22–7.28 (ddm, ^3J = 6.6 Hz, ^3J = 6.6 Hz, 3 H, Ph-H), 7.57–7.65 (m, 5 H, benzo-H, Ph-H). ^{13}C{^{1}H} NMR (75 MHz, [D$_6$]benzene, 25 °C): δ 43.88 (1 C, C-1), 122.04 (1 C, C-4), 124.41 (1 C, C-7), 126.09 (1 C, C-6), 127.06 (1 C, C-5), 128.83 (2 C, C-3′,5′), 130.42 (1 C, C-3), 134.31 (1 C, C-4′), 135.11 (1 C, C-2), 136.32 (2 C, C-2′,6′), 141.95 (1 C, C-1′), 146.97 (1 C, C-7a), 148.04 (1 C, C-3a). GC/MS (70 eV): *m*/*z* (%): 298 (12) [M$^+$], 219 (6) [M$^+$ − C$_6$H$_7$], 184 (100) [Ph$_2$SiH$^+$], 115 (7) [C$_9$H$_7$$^+$], 105 (14) [C$_8H_9$$^+$], 78 (3) [C$_6H_6$$^+$].

2-(*tert*-Butyldimethylsilyl)indene/2-TBDMS-Ind (2e)

The synthesis was based on a literature procedure,[23] with modifications. 2-(Dimethylsilyl)indene (2.0 g, 11.5 mmol) was placed in a Schlenk flask with 50 mL diethyl ether and cooled to −90 °C. After addition of *tert*-butyllithium (13.5 mL, 22.9 mmol) *via* syringe, the reaction was allowed to warm to room temperature and afforded a yellow suspension. Removal of solvent and washing with pentane (30 mL, 3 × 20 mL) provided 1.80 g (7.6 mmol, 66%) of a white powder. For spectroscopic characterisation, 57 mg (241 µmol) of the lithium salt were quenched with diluted hydrochloric acid, extracted with water and dried over magnesium sulfate to yield 30 mg (130 µmol) of the desired product. ^{1}H NMR (300 MHz, [D$_6$]benzene, 25 °C): δ 0.14 (s, 6 H, $\mathrm{Si(C}H_3)_2\mathrm{(C_4H_9)}$), 0.91 (s, 9 H, $\mathrm{Si(CH_3)_2(C_4}H_9)$), 3.26 (s, 2 H, 1-H), 7.08 (m, 1 H, 3-H), 7.13–7.20 (m, 1 H, 5-H), 7.20–7.28 (dd, ^3J = 7.8 Hz, ^3J = 7.8 Hz, 1 H, 6-H), 7.37 (d, ^3J = 8.1 Hz, 2 H, 4,7-H). ^{13}C{^{1}H} NMR (75 MHz, [D$_6$]benzene, 25 °C): δ −5.14 (2 C, $\mathrm{Si(}C\mathrm{H_3)_2(C_4H_9)}$), 17.40 (1 C, $\mathrm{Si(CH_3)_2(}C\mathrm{(CH_3)_3)}$), 27.19 (3 C, $\mathrm{Si(CH_3)_2(C(}C\mathrm{H_3)_3)}$), 44.40 (1 C, C-1), 121.57 (1 C, C-4), 124.21 (1 C, C-7), 125.51 (1 C, C-6), 126.97 (1 C, C-5), 143.23 (1 C, C-3), 146.33 (1 C, C-7a), 146.76 (1 C, C-3a), 147.56 (1 C, C-2). GC/MS (70 eV): *m*/*z* (%): 230 (9) [M$^+$], 173 (100) [M$^+$ − C$_4$H$_9$], 145 (40) [C$_9$H$_9$Si$^+$], 115 (7) [C$_9$H$_7$$^+$], 73 (6) [SiC$_3H_9$$^+$]. Characterisation of the lithium salt: ^{1}H NMR (300 MHz, [D$_8$]THF, 25 °C): δ 0.38 (s, 6 H, $\mathrm{Si(C}H_3)_2\mathrm{(C_4H_9)}$), 1.07 (s, 9 H, $\mathrm{Si(CH_3)_2(C_4}H_9)$), 6.30 (s, 2 H, 1,3-H), 6.57 (m, 2 H, 5,6-H), 7.46 (m, 2 H, 4,7-H). ^{13}C{^{1}H} NMR (75 MHz, [D$_8$]THF, 25 °C): δ −3.88 (2 C, $\mathrm{Si(}C\mathrm{H_3)_2(C(CH_3)_3)}$), 18.14 (1 C, $\mathrm{Si(CH_3)_2(}C\mathrm{(CH_3)_3)}$), 26.66 (3 C, $\mathrm{Si(CH_3)_2(C(}C\mathrm{H_3)_3)}$), 101.29 (2 C, C-1,3), 114.63 (2 C, C-5,6), 120.04 (2 C, C-4,7), 120.55 (1 C, C-2), 130.27 (2 C, C-3a,7a).

2-(Phenylsilyl)indene/2-PS-Ind (2f)

The synthesis of 2-indenidemagnesium bromide was conducted in a fashion similar to **2b**, employing 0.80 g (33.3 mmol) magnesium turnings and 2.47 g (12.7 mmol) 2-bromoindene in

20 mL THF. The Grignard reagent was added to 32 g (151 mmol) phenyltrichlorosilane in 30 mL THF at −40 °C in a second flask. The solution was allowed to stir overnight and warm to room temperature. Prior to volume reduction by 50%, the yellow orange solution was briefly heated until boiling. The solution was filtrated *via* a canula into the addition funnel of a third flask charged with 4 g (105 mmol) lithium aluminium hydride in 60 mL of diethyl ether. Dropwise addition of the chlorosilane solution and stirring for 48 h at room temperature yielded a colourless suspension. Insolubles were removed by filtration through a D4-frit. Volatiles were removed under reduced pressure (0.05 Torr) and 1.16 g (5.2 mmol) of a yellowish residue was obtained and identified to be the desired product in 41% yield. ^{1}H NMR (300 MHz, [D$_6$]benzene, 25 °C): δ 3.20 (d, J = 3.0 Hz, 2 H, 1-H), 4.98 (s, 2 H, SiH_2Ph), 5.29 (s, 1 H, 3-H), 7.06–7.30 (m, 5 H, benzo-H, Ph-H), 7.47–7.56 (m, 4 H, benzo-H, Ph-H). ^{13}C{^{1}H} NMR (75 MHz, [D$_6$]benzene, 25 °C): δ 43.84 (1 C, C-1), 121.95 (1 C, C-4), 124.33 (1 C, C-7), 126.11 (1 C, C-6), 127.04 (1 C, C-5), 128.84 (2 C, C-3′,5′), 130.45 (1 C, C-3), 132.18 (1 C, C-4′), 136.19 (2 C, C-2′,6′), 139.42 (1 C, C-2), 145.84 (1 C, C-1′), 146.86 (1 C, C-7a), 147.95 (1 C, C-3a). GC/MS (70 eV): *m*/*z* (%): 222 (40) [M$^+$], 207 (25) [M$^+$ − CH$_3$], 143 (45) [$C_9H_7Si^+$], 115 (74) [$C_9H_7^+$], 107 (100) [$PhSiH_2^+$].

1- or 2-(Trisubstituted silyl)indenyl lithium

A published procedure[36] was followed similarly for all silylindenyl lithium salts. The salts were not characterised except for their successful use in the following reactions or where necessary. The yields of the isolated salts were as follows: 1-(dimethylsilyl)indenyl lithium, 97%; 1-(trimethylsilyl)indenyl lithium, 93%; 1-(dimethylphenylsilyl)indenyl lithium, 94%; 1-(diphenylsilyl)indenyl lithium, 82%; 1-(*tert*-butyldimethylsilyl)indenyl lithium, 67%; 1-(diphenylmethylsilyl)indenyl lithium, 92%; 2-(dimethylsilyl)indenyl lithium, 93%; 2-(trimethylsilyl)indenyl lithium, 98%; 2-(dimethylphenylsilyl)indenyl lithium, 82%. The low yield in the deprotonation of 3-(*tert*-butyldimethylsilyl)indene is due to a deficiency in solvent leading to a gelatinous mass. Addition of 2 mL diethyl ether provided a fine precipitate at the expense of some salt being dissolved.

Reaction of 1-(diphenylsilyl)indene (2d) with potassium hydride

Potassium hydride (275 mg, 6.7 mmol) was placed in a 50 mL Schlenk flask equipped with a rubber septum. Addition of 20 mL THF provides a homogeneous, though slightly cloudy solution, which was cooled to −90 °C. The 2-(diphenylsilyl)indene (620 mg, 2.1 mmol) was added as a solid and the solution was allowed to warm to room temperature overnight, yielding a green suspension. Removal of the volatiles, subsequent washing of the green residue with equal aliquots of pentane (3 × 10 mL) and drying under high vacuum provided 445 mg (1.3 mmol, 63%) of a dark green powder. ^{1}H NMR (300 MHz, [D$_6$]benzene, 25 °C): δ 5.78 (s, 1 H, SiHPh$_2$), 6.02 (s, 2 H, 1,3-H), 6.90 (m, 2 H, benzo-H), 7.31 (m, 6 H, Ph-H), 7.41 (m, 2 H, benzo-H), 7.69 (m, 4 H, Ph-H).

meso-Bis[1-(dimethylsilyl)indenyl]zirconium dichloride (3a)

Zirconium tetrachloride (1.11 g, 4.76 mmol) and 1-(dimethylsilyl)indenyl lithium (1.79 g, 9.93 mmol) were placed in a 100 mL flask and cooled to 0 °C. Diethyl ether (30 mL) was added in 10 mL aliquots to give an orange–yellow suspension. The reaction was allowed to warm to room temperature while stirring overnight. After 16 h, the volatiles were removed from the orange–yellow reaction mixture, and the resulting residue was washed twice with 20 mL portions of pentane. After removing any residual pentane, the yellow pentane insolubles were extracted with two 40 mL aliquots of toluene. Concentration and cooling gave first 0.60 g of a yellow, microcrystalline powder, followed by 0.28 g of a second crop of a pale orange microcrystalline powder, in total 0.88 g (1.73 mmol, 36%). ^{1}H NMR analyses showed the presence of two isomers, with the *meso* isomer constituting *ca.* 85% of the first crop and 25% of the second crop. A portion of the initially isolated powder (0.25 g) was extracted with diethyl ether (50 mL). The insoluble fraction was isolated and dissolved in toluene (30 mL). Cooling of this yellow solution to −40 °C gave pure *meso* isomer as fine yellow needles. The relatively similar solubility of both isomers in diethyl ether precluded isolation of pure *rac*-isomer. An analytically pure sample could only be obtained by high-vacuum sublimation. Found: C 51.82, H 5.21. $C_{22}H_{26}Cl_2Si_2Zr$ requires C 51.94, H 5.15%. *meso*-isomer: ^{1}H NMR (300 MHz, [D$_6$]benzene, 25 °C): δ 0.32 (d, ^3J = 3.9 Hz, 6 H, SiH(CH_3)$_2$), 0.42 (d, ^3J = 3.9 Hz, 6 H, SiH(CH_3)$_2$), 4.95 (dq, ^3J = 3.9 Hz, ^3J = 3.9 Hz, 2 H, SiH(CH$_3$)$_2$), 5.84 (dd, ^5J = 0.8 Hz, ^3J = 3.3 Hz, 2 H, 3-H), 6.38 (d, ^3J = 3.0 Hz, 2 H, 2-H), 6.98 (m, 4 H, 5,6-H), 7.35 (m, 2 H, 4-H), 7.74 (m, 2 H, 7-H). ^{13}C{^{1}H} NMR (75 MHz, [D$_6$]benzene, 25 °C): δ −2.84 (2 C, SiH(CH$_3$)$_2$), −2.19 (2 C, SiH(CH$_3$)$_2$), 106.74 (2 C, C-2), 113.10 (2 C, C-1), 125.92 (2 C, C-5), 126.63 (2 C, C-6), 126.93 (2 C, C-4), 127.51 (2 C, C-7), 129.54 (2 C, C-3a), 129.69 (2 C, C-3), 132.96 (2 C, C-7a). *rac*-isomer: ^{1}H NMR (300 MHz, [D$_6$]benzene, 25 °C): δ 0.33 (d, ^3J = 3.9 Hz, 6 H, SiH(CH_3)$_2$), 0.39 (d, J = 3.9 Hz, 6 H, SiH(CH_3)$_2$), 4.94 (dq, ^3J = 3.9 Hz, 2 H, SiH(CH$_3$)$_2$), 5.98 (d, ^3J = 3.4 Hz, 2 H, 3-H), 6.28 (d, ^3J = 3.4 Hz, 2 H, 2-H), 6.98 (m, 4 H, 5,6-H), 7.28 (m, 2 H, 4-H), 7.74 (m, 2 H, 7-H).

meso-Bis[1-(trimethylsilyl)indenyl]zirconium dichloride (3b)

The reaction was conducted analogous to that for **3a**, employing zirconium tetrachloride (0.80 g, 3.4 mmol) and 1-(trimethylsilyl)indenyl lithium (1.34 g, 6.9 mmol) in 50 mL diethyl ether. Work-up was conducted similarly. Concentration and cooling of the toluene extracts gave two crops of a yellow crystalline solid totalling 0.42 g (0.78 mmol, 23% yield). Each crop of crystals was washed after isolation with 5 mL pentane to remove any residual **1b**. ^{1}H NMR (300 MHz, [D$_6$]benzene, 25 °C): δ 0.42 (s, 18 H, TMS), 5.95 (dd, ^3J = 3.3 Hz, ^4J = 0.9 Hz, 2 H, 3-H), 6.44 (d, ^3J = 3.3 Hz, 2 H, 2-H), 6.95 (dd, ^3J = 8.4 Hz, ^3J = 6.6 Hz, ^4J = 1.2 Hz, 2 H, 5-H), 7.00 (dd, ^3J = 8.4 Hz, ^4J = 6.9 Hz, ^4J = 1.5 Hz, 2 H, 6-H), 7.26 (dd, ^3J = 7.8 Hz, ^4J = 1.2 Hz, 2 H, 4-H), 7.27 (dd, ^3J = 8.4 Hz, ^4J = 1.2 Hz, 2 H, 7-H). ^{13}C{^{1}H} NMR (75 MHz, [D$_6$]benzene, 25 °C): δ 0.99 (6 C, TMS), 106.24 (2 C, C-2), 125.86 (2 C, C-5), 126.32 (2 C, C-6), 126.62 (2 C, C-4), 127.35 (2 C, C-7), 127.82 (2 C, C-1), 128.23 (2 C, C-3), 130.01 (2 C, C-3a), 134.64 (2 C, C-7a).

Bis[1-(dimethylphenylsilyl)indenyl]zirconium dichloride (3c)

A Schlenk flask was charged with zirconium tetrachloride (0.50 g, 2.15 mmol) and 1-(dimethylsilyl)indenyl lithium (1.14 g, 4.43 mmol). Diethyl ether (30 mL) was added, and the resulting yellow–orange heterogeneous reaction was stirred overnight. The volatiles were removed from the now yellow heterogeneous reaction. The remaining orange–yellow residue was first washed with pentane (2 × 30 mL), and then extracted with toluene (3 × 50 mL). The volatiles were removed from the combined toluene extracts to give an orange–yellow solid (0.62 g, 44% crude yield). ^{1}H NMR spectroscopic analysis of the solid showed a mixture of *meso* and *rac* isomers in an approximate 7 : 3 ratio. Extraction of the isolated solid with 25 mL toluene provided a crude separation of isomers: The light orange toluene solution was enriched to >90% *meso*-isomer, while the insoluble fraction contained *ca.* 85% of the *rac*-isomer. Pure *meso*-isomer was obtained by dissolution of the enriched *meso* fraction in 3 mL toluene, removal of the insolubles by filtration, cooling of the yellow solution to −40 °C, and isolation of the resulting yellow solid by filtration (0.14 g). Addition of warm toluene (50 mL) to the enriched *rac*-isomer, followed by cooling to −40 °C and isolation of the fluffy yellow precipitate gave pure *rac*-isomer

(0.09 g). Despite repeatedly washing each isolated isomer with pentane, small (<2%) amounts of free **1c** can be detected by ^{1}H NMR spectroscopy. An analytically pure sample could only be obtained by high-vacuum sublimation. Found: C 61.84, H 5.19. $C_{34}H_{34}Cl_2Si_2Zr$ requires C 61.79, H 5.19%. *meso*-Isomer: ^{1}H NMR (300 MHz, [D$_6$]benzene, 25 °C): δ 0.72 (s, 6 H, Si(CH_3)$_2$Ph), 0.78 (s, 6 H, Si(CH_3)$_2$Ph), 5.64 (dd, ^{3}J = 3.3 Hz, ^{5}J = 0.8 Hz, 2 H, 3-H), 6.45 (d, ^{3}J = 3.3 Hz, 2 H, 2-H), 6.90 (m, 4 H, 5,6-H), 7.15 (m, 8 H, 2′,3′,5′,6′-H), 7.48 (m, 4 H, 4,4′-H), 7.70 (m, 2 H, 7-H). ^{13}C{^{1}H} NMR (75 MHz, [D$_6$]benzene, 25 °C): δ −0.48 (2 C, Si(CH$_3$)$_2$Ph), −0.03 (2 C, Si(CH$_3$)$_2$Ph), 106.51 (2 C, C-2), 114.33 (2 C, C-1), 125.86 (2 C, C-5), 126.36 (2 C, C-6), 126.71 (2 C, C-4), 127.91 (2 C, C-7), 128.34 (2 C, C-4′), 128.59 (4 C, C-3′,5′), 129.94 (2 C, C-3), 130.43 (2 C, C-3a), 134.69 (2 C, C-7a), 134.91 (4 C, C-2′,6′), 139.12 (2 C, C-1′). *rac*-Isomer: ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C): δ 0.64 (s, 6 H, Si(CH_3)$_2$Ph), 0.67 (s, 6 H, Si(CH_3)$_2$Ph), 6.05 (dd, ^{5}J = 0.9 Hz, ^{3}J = 3.2 Hz, 2 H, 3-H), 6.40 (d, ^{3}J = 3.2 Hz, 2 H, 2-H), 7.17 (ddd, ^{3}J = 8.4 Hz, ^{3}J = 8.4 Hz, ^{4}J = 1.2 Hz, 2 H, 5-H), 7.23 (ddd, ^{3}J = 8.4 Hz, ^{3}J = 8.4 Hz, ^{4}J = 1.2 Hz, 2 H, 6-H), 7.32–7.37 (m, 6 H, Ph-H), 7.44–7.49 (m, 4 H, Ph-H), 7.57 (tm, ^{3}J = 8.9 Hz, 4 H, 4,7-H). ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$, 25 °C): δ −1.53 (2 C, Si(CH$_3$)$_2$Ph), −0.86 (2 C, Si(CH$_3$)$_2$Ph), 105.11 (2 C, C-2), 113.38 (2 C, C-1), 125.29 (2 C, C-5), 125.95 (2 C, C-6), 126.26 (2 C, C-4), 126.83 (2 C, C-7), 126.93 (2 C, C-4′), 127.78 (4 C, C-3′,5′), 129.16 (2 C, C-3), 129.57 (2 C, C-3a), 133.94 (4 C, C-2′,6′), 134.25 (2 C, C-7a), 138.14 (2 C, C-1′).

Bis[1-(diphenylsilyl)indenyl]zirconium dichloride (3d)

Zirconium tetrachloride (0.45 g, 1.93 mmol) and 1-(diphenylsilyl)indenyl lithium (1.18 g, 3.88 mmol) were combined in a 100 mL flask and cooled to 0 °C. Diethyl ether (30 mL) was added, and the resulting orange–yellow mixture was gradually warmed to room temperature with stirring for 18 h. The volatiles from the now yellow heterogeneous reaction mixture were removed, and the remaining yellow residue was washed with pentane (2 × 30 mL). The reaction residue was extracted two times with 30 mL diethyl ether, and the volatiles from combined yellow diethyl ether extracts were removed *in vacuo* to give 0.46 g of a bright yellow powder, which was analyzed by ^{1}H NMR as impure *rac*-isomer. The remaining reaction residue was extracted two times with 60 mL toluene. Removal of the volatiles from the combined yellow solutions gave 0.39 g of a yellow powder, which was identified as impure *meso*-isomer. The combined yield is 0.85 g (1.12 mmol, 58% crude yield). The *rac*-isomer enriched crop was extracted with 5 mL diethyl ether and solidified by solvent removal. Washing with 4 mL of pentane yielded 175 mg (232 µmol, 12%) of the pure *rac*-isomer. The purification of the *meso*-isomer was achieved by washing the crude product with two aliquots of 10 mL diethyl ether and drying the remaining solid *in vacuo* overnight, which yielded 240 mg (317 µmol, 16%). An analytically pure sample could only be obtained by high-vacuum sublimation. Found: C 66.58, H 4.53. $C_{42}H_{34}Cl_2Si_2Zr$ requires C 66.64, H 4.53%. *meso*-isomer: ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C): δ 5.26 (d, ^{3}J = 3.3 Hz, 2 H, 3-H), 5.66 (s, 2 H, SiHPh$_2$), 6.40 (d, ^{3}J = 3.1 Hz, 2 H, 2-H), 7.02 (dd, ^{3}J = 6.5 Hz, ^{4}J = 1.4 Hz, 2 H, benzo-H), 7.10–7.27 (m, 12 H, Ph-H), 7.45 (dd, ^{3}J = 5.2 Hz, ^{4}J = 1.8 Hz, 6 H, Ph-H), 7.48 (d, ^{3}J = 8.4 Hz, 2 H, benzo-H), 7.64–7.67 (m, 4 H, Ph-H, benzo-H), 7.68 (d, ^{3}J = 2.1 Hz, 2 H, benzo-H). ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$, 25 °C): 105.42 (2 C, C-2), 106.56 (2 C, C-1), 124.44 (2 C, C-5), 125.65 (2 C, C-6), 126.28 (2 C, C-4′), 126.43 (2 C, C-4″), 127.24 (2 C, C-4), 127.90 (4 C, C-3′,5′), 128.30 (4 C, C-3″,5″), 129.76 (2 C, C-7), 130.39 (2 C, C-3), 132.54 (2 C, C-3a), 132.68 (2 C, C-7a), 133.41 (2 C, C-1′), 133.47 (2 C, C-1″), 135.07 (4 C, C-2′,6′), 136.18 (4 C, C-2″,6″). *rac*-isomer: ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C): δ 5.42 (dd, ^{3}J = 3.3 Hz, ^{4}J = 0.6 Hz, 2 H, 3-H), 5.79 (s, 2 H, SiHPh$_2$), 6.34 (d, ^{3}J = 3.3 Hz, 2 H, 2-H), 7.07–7.29 (m, 14 H, benzo-H, Ph-H), 7.31–7.52 (m, 10 H, Ph-H), 7.66 (dd, ^{3}J = 7.8 Hz, ^{4}J = 1.8 Hz, 4 H, benzo-H). ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$, 25 °C): δ 106.99 (2 C, C-2), 108.36 (2 C, C-1), 125.12 (2 C, C-5), 125.81 (2 C, C-6), 126.73 (2 C, C-4′), 126.95 (2 C, C-4″), 127.70 (2 C, C-4), 127.90 (4 C, C-3′,5′), 127.98 (4 C, C-3″,5″), 129.74 (2 C, C-7), 130.03 (2 C, C-3), 130.56 (2 C, C-3a), 132.00 (2 C, C-7a), 132.67 (2 C, C-1′), 133.36 (2 C, C-1″), 135.43 (4 C, C-2′,6′), 136.11 (4 C, C-2″,6″).

rac-Bis[1-(*tert*-butyldimethylsilyl)indenyl]zirconium dichloride (3e)

The reaction was conducted in a manner similar to **3a**, employing 0.70 g (3.0 mmol) 1-(*tert*-butyldimethylsilyl)indenyl lithium and 343 mg (1.5 mmol) zirconium tetrachloride. The reaction mixture was filtered through a D4-frit charged with a 1 cm thick layer of magnesium sulfate. The filter residue was washed two times with 10 mL diethyl ether. The filtrate volume was reduced to 10 mL and refrigerated to −40 °C to yield a yellow precipitate. ^{1}H NMR analysis showed a *rac*/*meso* mixture of 9 : 1 for the precipitate and a 1 : 1 mixture for solid residue obtained from the mother liquor. The former precipitate was dissolved in 17 mL diethyl ether and refrigerated to yield 220 mg (355 µmol, 24%) of light yellow needles. Found: C 57.92, H 6.85. $C_{30}H_{42}Cl_2Si_2Zr$ requires C 58.03, H 6.82%. ^{1}H NMR (300 MHz, [D$_6$]benzene, 25 °C): δ 0.43 (s, 6 H, Si(CH_3)$_2$(C(CH$_3$)$_3$)), 0.68 (s, 18 H, Si(CH$_3$)$_2$(C(CH_3)$_3$)), 0.79 (s, 6 H, Si(CH_3)$_2$(C(CH$_3$)$_3$)), 5.79 (d, ^{3}J = 3 Hz, 2 H, 2-H), 6.24 (d, ^{3}J = 3 Hz, 2 H, 3-H), 6.98 (ddd, ^{3}J = 6.3 Hz, ^{3}J = 6.6 Hz, ^{4}J = 1.4 Hz, 2 H, 5-H), 7.03 (ddd, ^{3}J = 5.8 Hz, ^{3}J = 6.9 Hz, ^{4}J = 1.7 Hz, 2 H, 6-H), 7.36 (dd, ^{3}J = 6.6 Hz, ^{4}J = 1.6 Hz, 2 H, 4-H), 7.89 (dd, ^{3}J = 7.8 Hz, ^{4}J = 1.8 Hz, 2 H, 7-H). ^{13}C{^{1}H} NMR (75 MHz, [D$_6$]benzene, 25 °C): δ −4.67 (2 C, Si(CH$_3$)$_2$(C(CH$_3$)$_3$)), −4.27 (2 C, Si(CH$_3$)$_2$(C(CH$_3$)$_3$)), 19.14 (2 C, Si(CH$_3$)$_2$(C(CH$_3$)$_3$)), 27.14 (6 C, Si(CH$_3$)$_2$(C(CH$_3$)$_3$)), 104.43 (2 C, C-2), 116.69 (2 C, C-1), 125.92 (2 C, C-5), 126.92 (2 C, C-6), 127.00 (2 C, C-4), 127.71 (2 C, C-7), 129.79 (2 C, C-3a), 130.59 (2 C, C-3) 133.41 (2 C, C-7a).

Bis[2-(dimethylsilyl)indenyl]zirconium dichloride (4a)

Zirconium tetrachloride (0.65 g, 2.79 mmol) and 2-(dimethylsilyl)indenyl lithium (1.00 g, 5.55 mmol) were placed in a 100 mL flask. Ether (30 mL) was added at 0 °C, and the resulting yellow slurry was stirred at room temperature for 17 h. The volatiles were removed *in vacuo*, and the residue extracted with toluene (30 mL). The insolubles were filtered off and washed with toluene (20 mL). The filtrate and wash were combined, giving a murky, yellow solution, and were cooled to −40 °C. Successive crystallisations from toluene provided three crops of orange crystals totalling 1.02 g (2.00 mmol, 72%). X-Ray quality crystals were obtained *via* recrystallisation from diethyl ether at −40 °C. An analytically pure sample could only be obtained by high-vacuum sublimation. Found: C 51.96, H 5.10. $C_{22}H_{26}Cl_2Si_2Zr$ requires C 51.94, H 5.15%. ^{1}H NMR (300 MHz, [D$_6$]benzene, 25 °C): δ 0.36 (d, ^{3}J = 3.7 Hz, 12 H, SiH(CH_3)$_2$), 4.70 (sept, ^{3}J = 3.7 Hz, 2 H, SiH(CH$_3$)$_2$), 6.22 (s, 4 H, 1,3-H), 7.03 (m$_{AA'XX'}$, 4 H, 5,6-H), 7.48 (m$_{AA'XX'}$, 4 H, 4,7-H). ^{13}C{^{1}H} NMR (75 MHz, [D$_6$]benzene, 25 °C): δ −2.81 (4 C, SiH(CH$_3$)$_2$), 113.49 (4 C, C-1,3), 125.81 (4 C, C-5,6), 126.34 (4 C, C-4,7), 130.44 (4 C, C-3a,7a), 132.96 (2 C, C-2).

Bis[2-(trimethylsilyl)indenyl]zirconium dichloride (4b)

The synthesis was performed analogously to that for **4a** and provided three crops of fine yellow needles totalling 1.02 g (1.90 mmol, 75%). **4b** can also be crystallised from diethyl ether. Crystals for single-crystal XRD analysis were grown from a solution of 86.0 mg (160 µmol) in 6.0 mL diethyl ether at −40 °C. The crystals were dried *in vacuo* after removal of excess solvent. ^{1}H NMR (300 MHz, [D$_6$]benzene, 25 °C): δ 0.16 (s, 18 H, TMS), 5.88 (s, 4 H, 1,3-H), 6.94 ($m_{AA'XX'}$, ^3J = 6.8 Hz, ^3J = 5.0 Hz, ^4J = 4.6 Hz, ^5J = 0.8 Hz, 4 H, 5,6-H), 7.53 ($m_{AA'XX'}$, ^3J = 6.8 Hz, ^3J = 5.0 Hz, ^4J = 4.6 Hz, ^5J = 0.9 Hz, 4 H, 4,7-H). ^{13}C{^{1}H} NMR (75 MHz, [D$_6$]benzene, 25 °C): δ 0.11 (6 C, TMS), 112.11 (4 C, C-1,3), 125.68 (4 C, C-5,6), 126.46 (4 C, C-4,7), 130.00 (4 C, C-3a,7a), 141.46 (2 C, C-2).

Bis[2-(dimethylphenylsilyl)indenyl]zirconium dichloride (4c)

The synthesis was performed analogously to that for **4a**, starting from zirconium tetrachloride (0.331 g, 1.42 mmol) and 2-(dimethylphenylsilyl)indenyl lithium (0.73 g, 2.85 mmol). Three crops of yellow powder totalling 0.63 g (0.95 mmol, 67%) were isolated after extraction of the reaction residue with toluene (50 mL). Each batch of isolated powder was washed with 10 ml pentane to remove any residual **2c**. Found: C 61.76, H 5.23. $C_{34}H_{34}Cl_2Si_2Zr$ requires C 61.79, H 5.19%. ^{1}H NMR (300 MHz, [D$_6$]benzene, 25 °C): δ 0.54 (s, 12 H, Si(CH_3)$_2$Ph), 5.97 (s, 4 H, 1,3-H), 6.86 ($m_{AA'XX'}$, 4 H, 5,6-H), 7.04 (m, 6 H, 2′,4′,6′-H), 7.22 (m, 4 H, 3′,5′-H), 7.44 ($m_{AA'XX'}$, 4 H, 4,7-H). ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$, 25 °C): δ −1.76 (4 C, Si(CH$_3$)$_2$Ph), 112.94 (4 C, C-1,3), 125.87 (4 C, C-5,6), 126.39 (4 C, C-4,7), 128.29 (4 C, C-3′,5′), 129.44 (2 C, C-4′), 129.97 (4 C, C-3a,7a), 134.43 (4 C, C-2′,6′), 138.81 (2 C, C-1′), 139.72 (2 C, C-2).

meso-Bis[1-(trimethylsilyl)indenyl]dimethylzirconium (5a)

In an NMR tube, **3b** (0.014 g, 26.1 µmol) was dissolved in [D$_6$]benzene. Methyllithium (0.05 mL, 55 µmol) was added *via* a syringe. Within minutes, the yellow solution became colourless and a small amount of precipitate formed. After 30 min, quantitative formation of the desired product was observed. ^{1}H NMR (300 MHz, [D$_6$]benzene, 25 °C): δ −1.17 (s, 3 H, Zr(CH_3)$_2$), −0.02 (s, 3 H, Zr(CH_3)$_2$), 0.30 (s, 18 H, TMS), 5.50 (d, ^3J = 3.3 Hz, 2 H, 3-H), 6.08 (d, ^3J = 3.3 Hz, 2 H, 2-H), 6.96 (m, 4 H, 5,6-H), 7.63 (m, 4 H, 4,7-H).

rac-Bis[1-(*tert*-butyldimethylsilyl)indenyl]dimethylzirconium (5e)

The chloride/methyl exchange was carried out in a similar fashion to **5a**. ^{1}H NMR (300 MHz, [D$_6$]benzene, 25 °C): δ −1.01 (s, 6 H, Zr(CH_3)$_2$), 0.21 (s, 6 H, Si(CH_3)$_2$^{t}Bu), 0.60 (s, 6 H, Si(CH$_3$)$_2$^{t}Bu), 0.83 (s, 18 H, Si(CH$_3$)$_2$(C(CH_3)$_3$)), 5.82 (d, ^3J = 3.0 Hz, 2 H, 2-H), 5.91 (dd, ^3J = 3.0 Hz, ^5J = 0.8 Hz, 2 H, 3-H), 6.94 (ddd, ^3J = 8.5 Hz, ^3J = 8.5 Hz, ^4J = 1.1 Hz, 2 H, 5-H), 7.03 (ddd, ^3J = 8.5 Hz, ^3J = 8.5 Hz, ^4J = 1.1 Hz, 2 H, 6-H), 7.23 (ddd, ^3J = 8.3 Hz, ^4J = 1.1 Hz, ^4J = 1.1 Hz, 2 H, 4-H), 7.70 (dd, ^3J = 8.5 Hz, ^4J = 0.8 Hz, 2 H, 7-H).

Crystal structure determination for 4a [37]

A yellow platelet with dimensions 0.85 × 0.33 × 0.10 mm was mounted on a glass fibre. Pertinent data for the crystal and solution are collected in Table 5. Reflections were measured on a Siemens SMART 1000 CCD-diffractometer using Mo-Kα radiation. The data collections with SMART [38a] included three sets of exposures with the detector set at $2\theta = 26$ and crystal-to-detector distance 50 mm. Data integration and cell refinement was carried out by SAINT,[38b] while absorption correction was carried out by SADABS.[38c] SHELXTL [38d] 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.

Crystal structure determination for 4b [37]

The experimental procedure and data evaluation was conducted similarly to **4a** but utilized a Bruker APEX CCD-instrument.

Table 5 Crystallographic data, collection and refinement parameters for **4b** and **4b**

Parameter	**4a**	**4b**
Formula	$C_{22}H_{26}Cl_2Si_2Zr$	$C_{24}H_{30}Cl_2Si_2Zr$
M_r	508.75	536.78
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a/Å	10.6354(1)	9.7631(6)
b/Å	13.4550(2)	34.995(3)
c/Å	16.3064(1)	8.1505(7)
β/°	98.783(1)	112.415(2)
V/Å^3	2306.07(4)	2574.3(3)
Z	4	4
Radiation	Mo-Kα	Mo-Kα
λ/Å	0.71073	0.71073
T/°C	−123	−120
D_c/g cm^3	1.465	1.385
μ/mm^{-1}	0.818	0.737
$R(F_o)$	0.0371 [a]	0.0374 [b]
$R_w(F_o^2)$	0.0917 [c]	0.0959 [d]
GOF	1.023	1.110

[a] Calculated on 12448 reflections with $I > 2\sigma(I)$. [b] Calculated on 8494 reflections with $I > 2\sigma(I)$. [c] Calculated on all 18142 reflections. [d] Calculated on all 9196 reflections.

CCDC reference numbers 226076 and 226077.

See http://www.rsc.org/suppdata/dt/b4/b400505h/ for crystallographic data in CIF or other electronic format.

Computational details

Hybrid DFT calculations were performed with the Gaussian98 package.[39] The B3LYP functional with the 6-31G* basis set was employed for our purposes and proved to be suitable.[40] Results from MP2-level single-point energy calculations with 6-31G* and 6-311G** basis sets did not lead to any different conclusions than those obtained by means of B3LYP/6-31G*. For Zr, a modified version of the LANL2DZ ECP basis was used.[41] 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 two, one and one primitive functions, respectively.

Polymerisation procedure

Polymerisations 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 2 h and flushed three times with argon. At 30 °C, the reactors were charged with 50 mL aliquots of freshly distilled toluene, 50 mg of solid MAO and subsequently pressurised with 1.2 bar of ethene until no further ethene consumption could be registered by the massflow controllers. Polymerisation was initiated by injection of the appropriate volume of a toluenic solution of the catalyst precursor. Typically, the catalyst precursor solutions had concentrations of 1.0×10^{-3} mol L^{-1}. The reaction was stopped by addition of 5 mL methanol. Work-up of the polymers included extraction of the toluenic suspension with methanol–hydrochloric acid (9 : 1) to remove inorganic residues. Products were filtered off, washed with methanol and dried under high vacuum for two days.

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37 Questions and comments regarding the X-ray crystallography of **4a** and **4b** should be directly addressed to C.-H. Görbitz and J. Kopf, respectively.

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