Chiral Indenes and Group-4 Metallocene Dichlorides Containing α- and β-Pinenyl-Derived Ligand Substituents: Synthesis and Catalytic Applications in Polymerization and Carboalumination Reactions

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The synthesis and characterization of chiral bis(indenyl)zirconium dichlorides containing β-pinenyl-derived ligand substituents is reported. Unbridged metallocene complexes having the {[(1*S*,2*S*,5*S*)-6,6-dimethylbicyclo[3.1.1]hept-2-yl]methyl}dimethylsilyl substituent in both 1- and 2-positions of the indenyl moiety were prepared and isolated in moderate to low yields by reaction of the corresponding indenyllithium salts with $ZrCl_4$ followed by work-up and crystallization procedures. The corresponding tetrahydroindenyl complexes were obtained in excellent yields by catalytic hydrogenation of the indenyl six-membered rings. In a complementary approach, a synthetic route to α-pinenyl-substituted indenyl ligand analogues was briefly evaluated, which however, suffered from low yields. Selected β-pinenyl-substituted indenyl complexes were scanned as catalysts for the dehydropolymerization of phenylsilane upon activation with *n*BuLi, for polymerization of ethylene and propylene upon activation with methylaluminoxane (MAO) as well as for enantioselective carboalumination of 1-octene with triethyl- and trimethylaluminum. The bis(indenyl) complexes catalyzed the carboalumination reaction, albeit only low yields (8–16 %) and low enantioselectivities (*ee* = 0.5–10 %) were obtained. The 2-substituted bis(indenyl)zirconocene/MAO catalyst system produced atactic low-molecular weight polypropylene with low polymerization activity whereas both 1- and 2-substituted complexes showed high activities in ethylene polymerization producing polyethylenes with high molecular weights ($M_w > 440000$).
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Introduction

Chiral group-4 metallocenes are widely used catalysts or catalyst precursors for the stereoselective polymerization of α-olefins,[1–3] and enantioselective cyclopolymerization of nonconjugated dienes,[4,5] and are employed in various enantioselective organic transformations[6,7] including carbon–carbon,[8–13] carbon–hydrogen[14–18] and carbon–oxygen[19,20] bond formation. Commonly employed chiral precatalysts are the conformationally constrained racemic *ansa*-metallocenes and their resolved single enantiomers,[21] but also unbridged bis(indenyl)metallocenes containing chiral substituents[22–27] have been utilized previously in a number of applications in stereo- and/or enantioselective synthesis.

In a recent communication, we presented a simple route to new chirally substituted indenes by reaction of indenyllithium or 2-indenylmagnesium bromide with a β-pinenyl-derived chlorosilane.[28] As a continuation of the previous work, we report here a detailed study on the utilization of these new chiral ligand precursors for the preparation of new chiral group-4 metallocene complexes as well as a brief evaluation of the chiral metallocenes formed for catalytic applications in olefin polymerization, dehydropolymerization of phenylsilane and enantioselective carboalumination reactions. As a complementary approach, the low-yield synthesis of some α-pinenyl-substituted ligand analogues is briefly described.

Results and Discussion

Ligand Precursor and Metallocene Synthesis

The chiral zirconocene dichloride **2** was prepared by deprotonation of the previously described chiral indene **1**[28] with *n*BuLi followed by reaction with 0.5 equiv. $ZrCl_4$ in toluene (Scheme 1). Subsequent work-up and crystallization from pentane at –20 °C provided pure **2** in 37% isolated yield. Due to the position of the chiral substituent, the π-faces of the indenyl ligand are equivalent (i.e., homotopic) and only one product can be formed upon metallation. Complex **2** was further hydrogenated at 50 bar H_2 in dichloromethane in the presence of PtO_2 catalyst to provide the corresponding chiral tetrahydroindenyl complex **3** in 86% isolated yield. The parent compound **2** is obtained as

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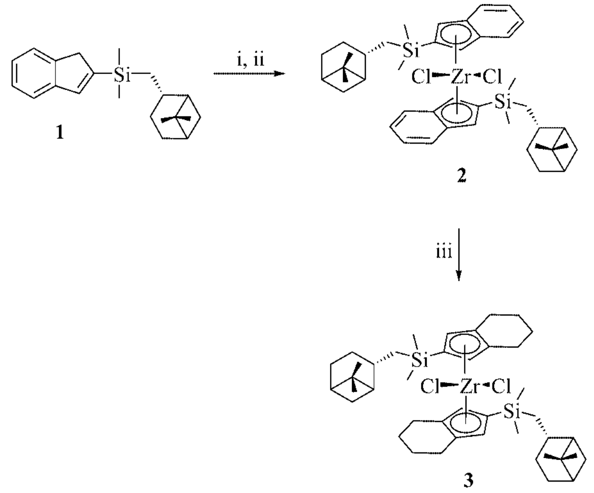
a yellow powder, whereas the hydrogenated congener **3** is a noncrystalline, pale green oil. Apparently, because of the large aliphatic pinenyl substituent, both complexes are remarkably soluble in all common organic solvents including pentane and hexane. Consequently, all our attempts to grow single crystals suitable for X-ray structure determination from either one of the complexes **2** or **3** failed.



Scheme 1. Synthesis of the chiral metallocenes **2** and **3**. (i) *n*BuLi, Et_2O, 0 °C. (ii) $ZrCl_4$, toluene, 50 °C, 37%. (iii) H_2/50 bar/PtO_2, CH_2Cl_2, 86%.

The change in the position of the chiral substituent from 2- to 1- or 3-indenyl renders the π-faces of the ligand precursor inequivalent [planar chirality: (*pR*) vs. (*pS*)] thus potentially resulting in the formation of three isomeric metallocene complexes [combinations of (*pR*)/(*pR*), (*pS*)/(*pS*) and (*pR*)/(*pS*)] upon metallation with group-4 metal tetrahalides (Figure 1).

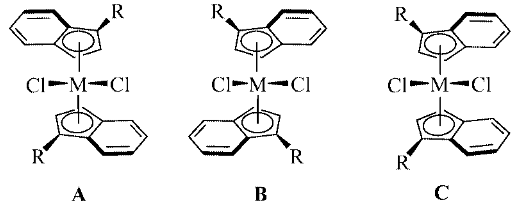
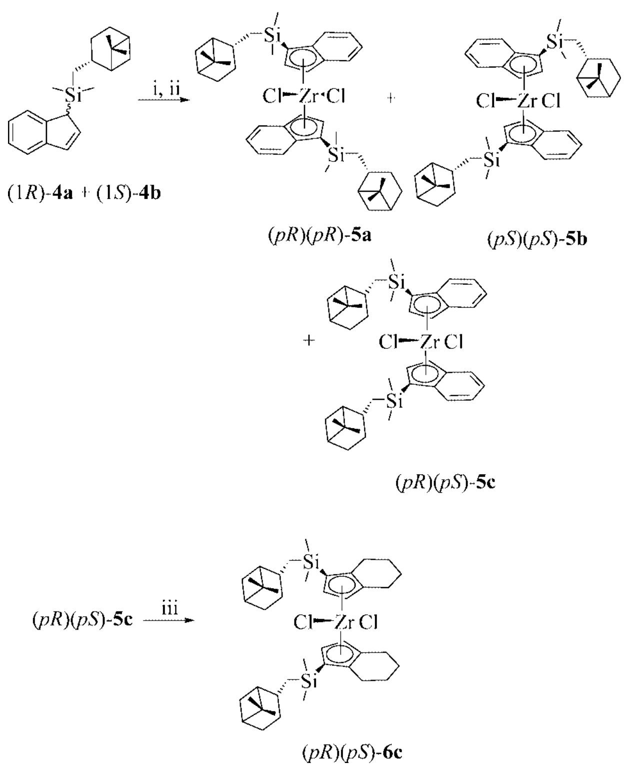


Figure 1. Metallocene diastereomers obtained upon metallation of indenyl ligands with enantiotopic or diastereotopic ligand π-faces [combinations of (*pR*)/(*pR*), (*pS*)/(*pS*) (**A** and **B**) and (*pR*)/(*pS*) (**C**).

If the 1- or 3-indenyl substituent is achiral (*enantiotopic* ligand π-faces), a C_2 symmetric racemic pair of two equienergetic enantiomers (**A** and **B** in Figure 1) is obtained together with a C_s symmetric *meso* form (**C**). A statistical 1:1:2 ratio of the three isomers is observed in most cases. When, as in the present case, the 1- or 3-indenyl substituent is chiral (*diastereotopic* ligand π-faces), a mixture of three diastereomers, two C_2 symmetric “pseudo-racemic” or “racemic-like” complexes (**A** and **B**) and one C_1 symmetric “*meso*-like” diastereomer (**C**), is formed in a ratio depending on the relative energies of the π-face metallation (*pR*) vs. (*pS*) and the mono(indenyl)metallocene trichlorides initially formed.

Thus, when the previously described 1:1 diastereomeric mixture of the chiral 1-substituted indenes (1*R*)-**4a** and (1*S*)-**4b**[28] was deprotonated with *n*BuLi and the resulting chiral indenyl anion lithium salt metallated with 0.5 equiv. of $ZrCl_4$ (Scheme 2), a mixture of the metallocene complexes **5a-c** was obtained in variable ratios depending on the solvent employed in the metallation step, as shown by ^{1}H NMR analyses of the metallocene crude products (Table 1, Figure 2). In all solvents investigated (toluene, Et_2O, THF), the molar ratio between the C_2-symmetric diastereomers (*pR*)(*pR*)-**5a** and (*pS*)(*pS*)-**5b** remained equimolar, consistent with their “pseudo-racemic” character. Formation of the *meso*-like C_1-symmetric diastereomer (*pR*)(*pS*)-**5c** was more favored in the coordinating solvents Et_2O and THF. As observed for the 2-substituted analogue **2**, also complexes **5a–c** displayed unusually high solubilities in all common organic solvents rendering their isolation and purification very difficult. The pure, least soluble C_1-symmetric diastereomer (*pR*)(*pS*)-**5c** was, however, obtained in 11% isolated yield as a bright yellow powder from the reaction carried out in Et_2O after subsequent work-up and crystallization from dichloromethane at –20 °C. The *meso*-like diastereomer (*pR*)(*pS*)-**5c** is easily distinguished from the C_2-symmetric diastereomers (*pR*)(*pR*)-**5a** and (*pS*)(*pS*)-**5b** by its ^{1}H and ^{13}C NMR spectra where, unlike in the cases of **5a** and **5b**, separate signal sets are observed for each of the (*pR*)- and (*pS*)-indenyl ligands coordinated to the central metal atom. The corresponding tetrahydroinde-



Scheme 2. Synthesis of the chiral metallocenes **5a–c** and **6c**. (i) *n*BuLi, Et_2O, 0 °C. (ii) 0.5 $ZrCl_4$, toluene, 50 °C; or 0.5 $ZrCl_4$, Et_2O, room temp.; or 0.5 $ZrCl_4$·2THF, –80 °C. (iii) H_2/50 bar/PtO_2, CH_2Cl_2, 82%.

nyl analogue (*pR*)(*pS*)-**6c** was then obtained in 82% yield after hydrogenation at 50 bar over PtO_2 catalyst in dichloromethane. Again, despite several attempts, crystals suitable for X-ray structure determination could not be grown from either one of the highly soluble complexes **5c** and **6c**.

Table 1. Relative ratios of the metallocene diastereomers **5a**–**c** formed in different solvents.

Solvent	*rac*-like **5a**	*rac*-like **5b**	*meso*-like **5c**
Toluene	42.4%	42.4%	15.2%
THF	22.6%	22.6%	54.8%
Et_2O	28.4%	28.4%	43.2%

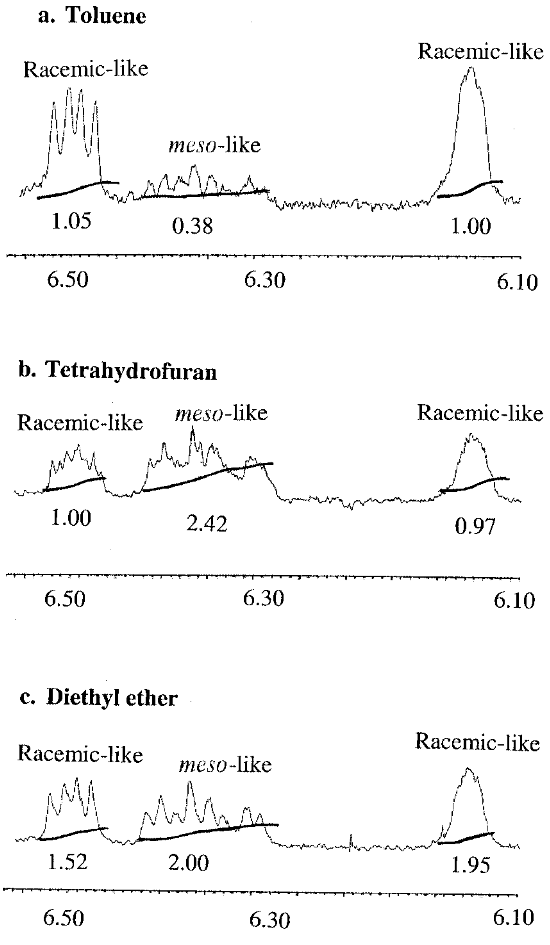
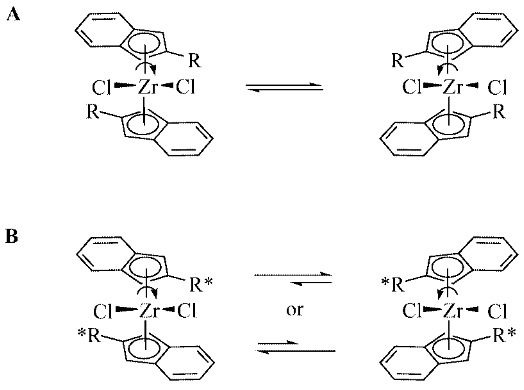


Figure 2. Expansions of the crude product indenyl CH regions of the ^1H NMR spectra of complexes **5a**–**c.**

Unbridged bis(indenyl)zirconocenes with bulky equatorial or σ-ligand substituents may exhibit dynamic behavior in their NMR spectra at subambient temperatures resulting from partially hindered rotation around the Zr–Cp(centroid) axis (Scheme 3).[29] For complexes with achiral ligand substituents the observed interconversion is likely to take place between two C_2 symmetric enantiomeric conformations becoming frozen on the NMR time scale to form a racemic mixture of the interconverting conformational isomers.[30–32] If, however, the ligand substituent is chiral, the interconverting conformational isomers become diastereomeric, one of which could be favored by proper choice of the ligand substitution pattern. Such complexes in turn could prove promising candidates for applications in enantioselective catalysis. In a previous work, Halterman and coworkers demonstrated that for the chiral bis(2-menthyl-4,7-dimethylindenyl)zirconium dichloride one diastereomeric conformation is slightly favored at 223 K (60:40) with a rotational activation barrier of 12.5 ± 0.5 kcal/mol.[25]

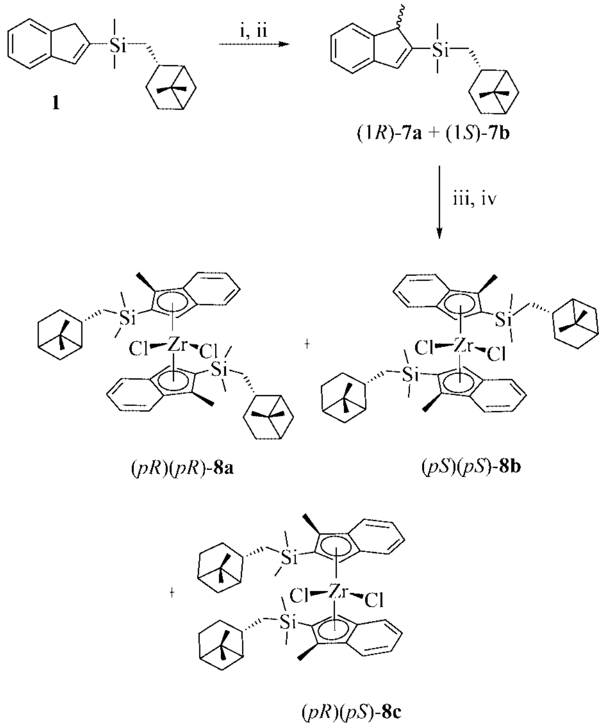


Scheme 3. Conformational equilibration of unbridged bis(indenyl) zirconocenes with (**A**) achiral substituents (enantiomeric conformations), and (**B**) chiral substituents (diastereomeric conformations).

At ambient temperature, the ^1H NMR spectra of complexes **2** and **5c** are consistent with unhindered ligand rotation. Upon lowering the monitoring temperature to 213–163 K, complex **2** displays dynamic behavior as indicated by the broadening of the aromatic CH resonances at δ = 5.92 and 5.96 ppm in the five-membered indenyl ring. At the estimated coalescence temperature of 163 K, the signals start to split to the individual resonances resulting from the equilibration of the two C_2 symmetric diastereomeric conformers. However, due to the operational limits of the NMR instrument at such low temperatures, neither the exact point of coalescence nor the associated rotational energy barrier and the eventual predominance of either one of the conformers could be reliably determined.

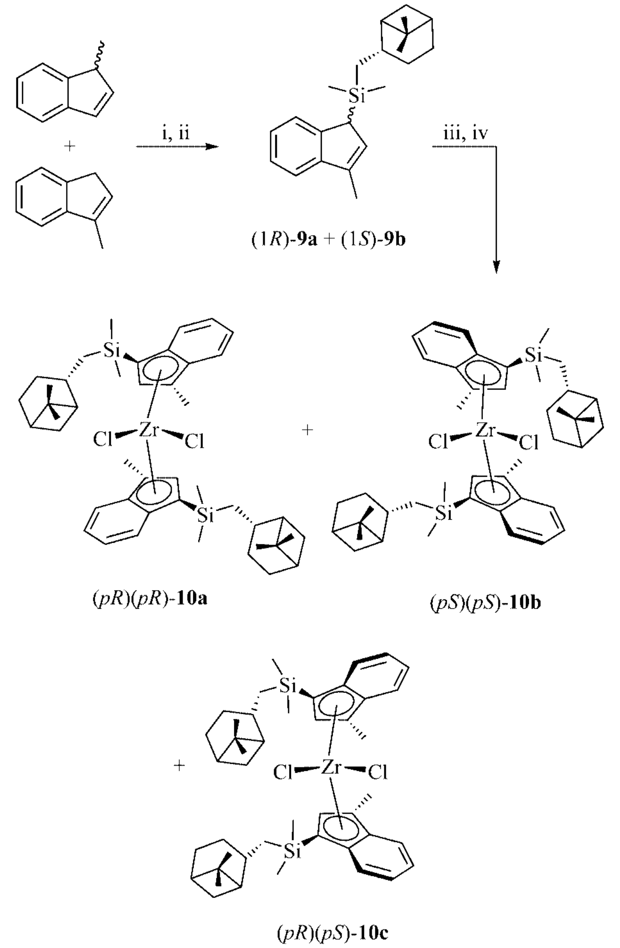
Next, as an attempt to modify the steric properties of the complex family and as a further extension of the use of the pinenyl group as a chiral indenyl ligand substituent, we prepared the monomethylated analogues of compounds **1** and **4a/b**. Thus, deprotonation of **1** with *n*BuLi and the subsequent reaction of the lithium salt formed with excess methyl iodide provided a diastereomeric mixture of the chiral indenes (1*R*)-**7a** and (1*S*)-**7b** in 74% isolated yield after purification by flash chromatography. Deprotonation of **7a/7b** with *n*BuLi and the subsequent reaction with 0.5 equiv. $ZrCl_4$ formed the expected mixture of the diastereomeric metallocene complexes (*pR*)(*pR*)-**8a**, (*pS*)(*pS*)-**8b** and (*pR*)(*pS*)-**8c** in good yield, as evidenced by ^1H NMR analysis of the crude product. All attempts to purify/isolate any of the complexes **8a**–**c** by fractional crystallization techniques failed due to their extremely high solubilities in all common organic solvents. When, however, the crude product was subjected to flash column chromatography using silanized silica gel[33] under argon, elution with pentane provided a mixture of the pure metallocenes **8a**–**c** in 53%

yield (all fractions combined) as a yellow oil. Despite their very similar solubility properties, the diastereomers eluted at slightly different retention times yielding fractions consisting of both **8a/8b** and **8a/8b/8c** in variable ratios. Small differences in the elution properties were observed even between the racemic-like diastereomers **8a** and **8b**, however, due to their high solubilities even in pentane, complete separation was impossible to achieve. Combination of all fractions containing only the racemic-like diastereomers gave an isolated yield of 18% for **8a/8b** obtained as a yellow oil. Crystallization of this mixture from cold pentane (–60 °C) gave 54 mg (3%) of yellow crystals enriched in one of the racemic-like diastereomers in a 53:47 ratio (Scheme 4).



Scheme 4. Synthesis of the chiral indenyl ligand precursor **7a/7b** and the chiral metallocenes **8a**–**c**. (i) *n*BuLi, THF, 0 °C. (ii) MeI, 74%. (iii) *n*BuLi, Et_2O, 0 °C. (iv) 0.5 $ZrCl_4$, 53% (isolated mixture **8a**–**c**), 18% (isolated mixture **8a/8b**).

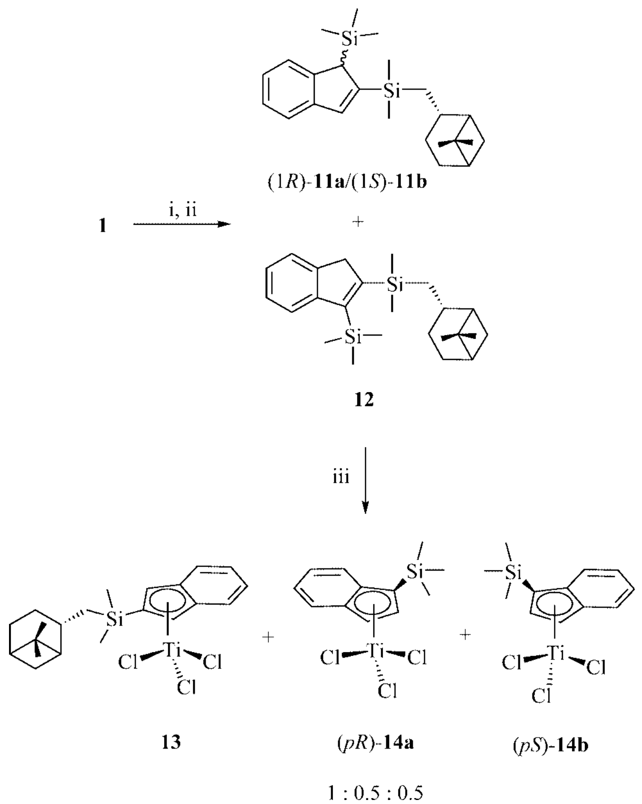
A diastereomeric mixture of the 3-methyl-substituted chiral indenes (1*R*)-**9a** and (1*S*)-**9b** was in turn obtained in 53% isolated yield by deprotonation of a 1-methylindene/3-methylindene mixture with *n*BuLi followed by quenching with excess chloro{[(1*S*,2*S*,5*S*)-6,6-dimethylbicyclo[3.1.1]-hept-2-yl]methyl}dimethylsilane, work-up and purification by flash chromatography. Deprotonation of **9a/9b** with *n*BuLi and the subsequent reaction with 0.5 equiv. $ZrCl_4$ formed the expected mixture of the diastereomeric metallocene complexes (*pR*)(*pR*)-**10a**, (*pS*)(*pS*)-**10b** and (*pR*)(*pS*)-**10c** in good, approximately 70% yield, as evidenced by ^{1}H NMR analysis of the crude product. All attempts to purify/isolate any of the complexes **10a**–**c** by crystallization failed due to their high solubilities in all common organic solvents. In contrast to complexes **8a**–**c**, the 1-silyl-substituted zirconocenes **10a**–**c** were also unstable under the flash column chromatographic conditions (silanized silica gel under argon atmosphere), yielding ligand precursor as the main decomposition product upon elution with pentane (Scheme 5).



Scheme 5. Synthesis of the chiral indenyl ligand precursor **9a/9b** and the chiral metallocenes **10a**–**c**. (i) *n*BuLi, THF, 0 °C. (ii) Chloro{[(1*S*,2*S*,5*S*)-6,6-dimethylbicyclo[3.1.1]hept-2-yl]methyl}dimethylsilane, 53%. (iii) *n*BuLi, Et_2O, 0 °C. (iv) 0.5 $ZrCl_4$, product not isolated.

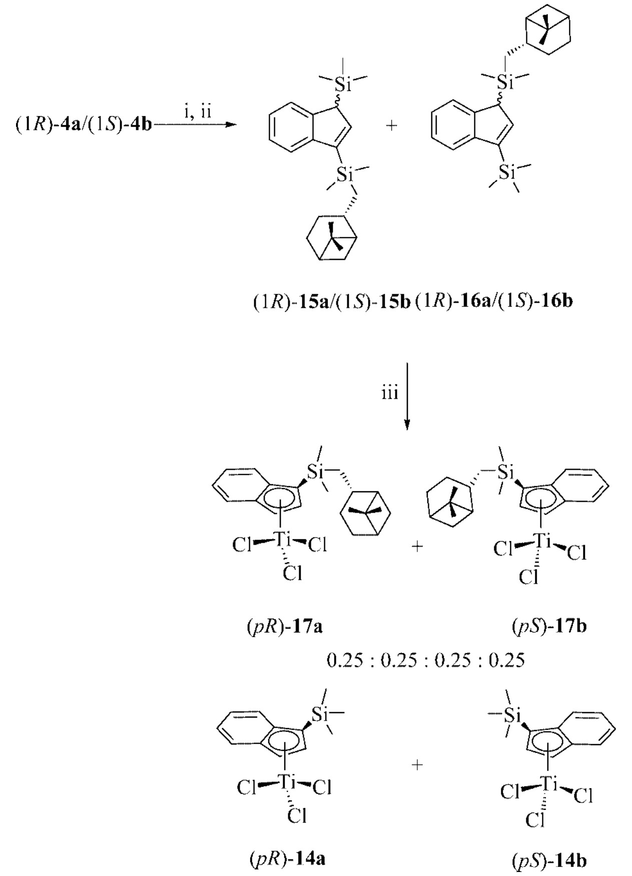
In addition, we briefly evaluated the metalation of the ligand percursors **1** and (1*R*)-**4a**/(1*S*)-**4b** with other group-4 metals. Treatment of the from **1** and (1*R*)-**4a**/(1*S*)-**4b** generated lithium salts with 0.5 equiv. $HfCl_4$ in diethyl ether or toluene yielded the desired metallocene complexes in moderate (approximately 30%) yields as shown by ^{1}H NMR analyses of the corresponding crude products. In contrast to their zirconium analogues, these hafnium complexes proved highly unstable resulting in decomposition upon all purification attempts, even when manipulated under strictly inert atmosphere.

From both compounds **1** and (1*R*)-**4a**/(1*S*)-**4b**, a mixture of the trimethylsilyl-substituted derivatives (1*R*)-**11a**/(1*S*)-**11b** and **12** and mixtures of (1*R*)-**15a**/(1*S*)-**15b**/(1*R*)-**16a**/(1*S*)-**16b** were obtained in high yields by quenching the corresponding lithium salts with chlorotrimethylsilane (Scheme 6 resp. Scheme 7). Treatment of these with one equivalent of $TiCl_4$ in dichloromethane at –78 °C resulted in competing elimination of both the trimethylsilyl- and the pinenyl-substituted silyl groups providing approximately 1:1 mixtures of the mono(indenyl)titanium trichlorides carrying either a trimethysilyl [(*pR*)-**14a**/(*pS*)-**14b**] or {[(1*S*,2*S*,5*S*)-6,6-dimethylbicyclo[3.1.1]hept-2-yl]methyl}-dimethylsilyl substituent [**13** and (*pR*)-**17a**/(*pS*)-**17b**, respectively]. In the case of the mixture of (1*R*)-**11a**/(1*S*)-**11b** and **12**, conversion of the ligand to mono(indenyl)metallocene appears to be nearly quantitative as evidenced by ^1H NMR, whereas in the case of (1*R*)-**15a**/(1*S*)-**15b**/(1*R*)-**16a**/(1*S*)-**16b** the yield of the metallation step is approximately 30%. Due to the similar solubilities of the (trimethylsilylindenyl)-titanium trichloride and the {{[(1*S*,2*S*,5*S*)-6,6-dimethylbicyclo[3.1.1]hept-2-yl]methyl}dimethylsilylindenyl}titanium trichlorides formed, these metallocene mixtures proved inseparable by fractional crystallization techniques.



Scheme 6. Attempted synthesis of 2-chirally substituted mono(indenyl)titanium trichlorides. (i) *n*BuLi, THF, 0 °C. (ii) Chlorodimethylsilane, 71%. (iii) $TiCl_4·CH_2Cl_2$, –78 °C, not purified.

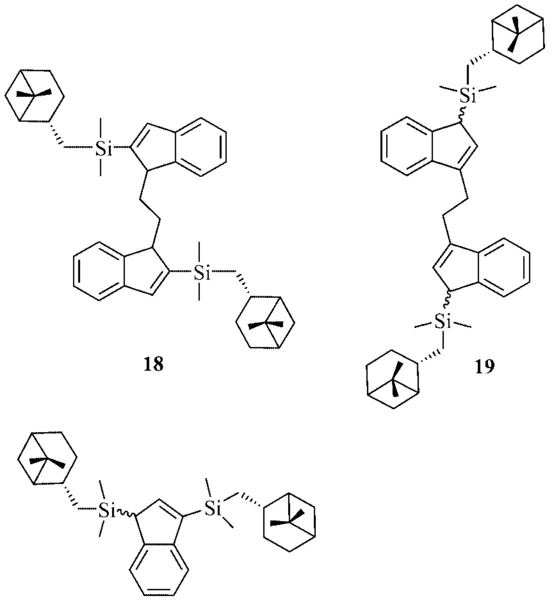
When the lithium salts generated from **1** and (1*R*)-**4a**/(1*S*)-**4b** were treated with 0.5 equiv. $FeCl_2$, the desired ferrocenes were formed in approximately 25% and 40% yields, respectively, as evidenced by ^1H NMR spectroscopy. Also these compounds proved to have extremely high solubilities in all common organic solvents rendering their purification by crystallization impossible. All attempts to purify the oily crude products by silica gel column chromatography likewise failed due to the apparent high sensitivity of these iron complexes.



Scheme 7. Attempted synthesis of 1-chirally substituted mono(indenyl)titanium trichlorides. (i) *n*BuLi, THF, 0 °C. (ii) Chlorodimethylsilane, 76%. (iii) $TiCl_4·CH_2Cl_2$, –78 °C, not purified/isolated.

In our previous communication,[28] we also described the preparation of the ethylene-bridged bis(indenyl) ligand analogues of **1** and **4a**/**4b** (compounds **18** and **19**), as well as the 1,3-chirally disubstituted indene analogue **20** (Figure 3). When the dilithium salt of **18** was reacted with $ZrCl_4$ in Et_2O, no metallocene could be detected by ^1H NMR or EIMS analysis of the crude product. Reaction of the dilithium salt of **19** with $ZrCl_4$ in THF showed no formation of the desired bis(indenyl)metallocenes. By carrying out the metallation in toluene only traces of zirconium complex diastereomers could be detected together with large amounts of impurities. In Et_2O, however, metallation of **19**-Li_2 with $ZrCl_4$ consumed all of the ligand precursor and formation of zirconocene diastereomers could be proven by both ^1H NMR and EIMS analyses, the latter of which gave the observed isotope peak distibutions for [M^+] in matching ratios with the theoretically calculated values. Unfortunately, again apparently due to the very high solubilities of the metallocene complexes formed, all attempts to isolate pure compounds by crystallization from Et_2O, *i*Pr_2O, hexane, THF, toluene and dichloromethane failed.

All our attempts to metallate either the lithium or potassium salt of the 1,3-disubstituted indene **20** with $ZrCl_4$ in Et_2O, toluene and dichloromethane under various reaction conditions failed. In none of the attempts could we observe



18 **19** **20**

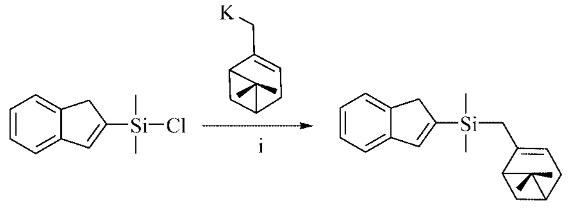
Figure 3. Ethylene-bridged and 1,3-chirally disubstituted ligand precursors **18**–**20**.

any formation of the desired bis(indenyl)metallocene complex. Considering that the analogous 1,3-bis(trimethylsilyl)indenyl and other 1,3-bis(trialkyl/arylsilyl)indenyl-derived anions were recently successfully complexed with zirconium and iron in moderately high yields by Chirik and coworkers,[34,35] the observation here is quite surprising and hardly explained by steric factors only. Other examples of both 1,2- and 1,3-trimethylsilyl-substituted bis(indenyl)iron(II) complexes have also been reported recently.[36]

Finally, in a complementary approach, we investigated the possibility of using α-pinene as the chiral indenyl substituent. By deprotonation of α-pinene with *n*BuLi/*t*BuOK at 50 °C using excess α-pinene[37] and the subsequent reaction of the obtained α-pinenyl potassium salt with 2-(chlorodimethylsilyl)indene[38] **21** or 1-(chlorodimethylsilyl)indene[39] (1*R*)-**23a**/(1*S*)-**23b**, the corresponding 1- and 2-chirally substituted indenes **22** and (1*R*)-**24a**/(1*S*)-**24b**/**25** were obtained in low (3% and 21%, respectively) yields (Scheme 8 and Scheme 9). The amount of the 3-silyl isomer **25** in the **24a**/**24b**/**25** mixture was estimated to 15% by ^{1}H NMR spectroscopy. All attempts to react α-pinenyl potassium with either 2-indanone or 2-bromoindene failed. Due to the low isolated yields and preparations in small scale, further attempts to utilize the compounds **22** and (1*R*)-**24a**/(1*S*)-**24b**/**25** as ligand precursors for transition metal complexes were not pursued.

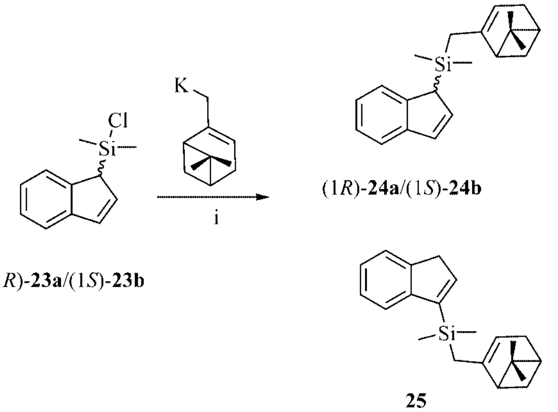
Dehydropolymerization of Phenylsilane

Dehydropolymerization of phenylsilane to poly(phenylsilane) with *n*BuLi activated transition-metal catalysts is a well-known reaction.[40,41] Harrod and co-workers reported in 1985 the first effective transition-metal catalyst for silane



21 **22**

Scheme 8. Synthesis of the 2-chirally substituted indenyl ligand precursor **22**. (i) THF, –72 °C, 3%.

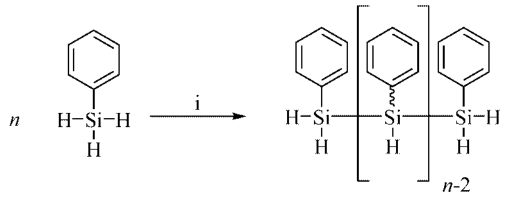


Scheme 9. Synthesis of the 1-chirally substituted indenyl ligand precursors (1*R*)-**24a**/(1*S*)-**24b**/**25**. (i) THF, –72 °C, 21%.

dehydrocoupling[42] and during the past 20 years a number of metallocene-based catalyst systems have been reported to polymerize phenylsilane.[43–50] Several shortcomings are, however, still to be overcome. Firstly, catalysts producing polyphenylsilanes with narrower polydispersities and with higher molecular weights than the presently existing systems, which seldom yield polymers with M_w's exceeding 5×10^3, would be desirable. Secondly, cleaner reaction mixtures not containing intractable oligo-/polysilane mixtures are required. Finally, the issue of stereocontrol in phenylsilane polymerization remains largely unsolved and only essentially atactic polymers are obtained regardless of chirality/achirality of the initiating catalyst system.

During the course of the present investigation, the chiral metallocenes **2**, **3**, (*pR*)(*pS*)-**5c** and (*pR*)(*pS*)-**6c** were briefly evaluated as catalysts for the dehydropolymerization of phenylsilane using zirconocene dichloride ([Cp_2ZrCl_2]) as reference catalyst (Scheme 10). The polymerization reactions were carried out in neat phenylsilane under argon by activation of 1 mol-% of the metallocene dichloride with 2 mol-% of *n*BuLi. The results are summarized in Table 2.

With the exception of the 1-substituted *meso*-like chiral complex (*pR*)(*pS*)-**5c**, the silane polymerization activities of the pinenyl-substituted systems were significantly lower than obtained with the zirconocene dichloride reference. The 2-substituted bis(indenyl) complex **2** gave polysilane with similar molecular weight to the reference catalyst whereas both 1-substituted complexes **5c** and **6c** and the 2-substituted tetrahydroindenyl analogue **3** produced lower molecular weight polymers. All catalysts investigated pro-



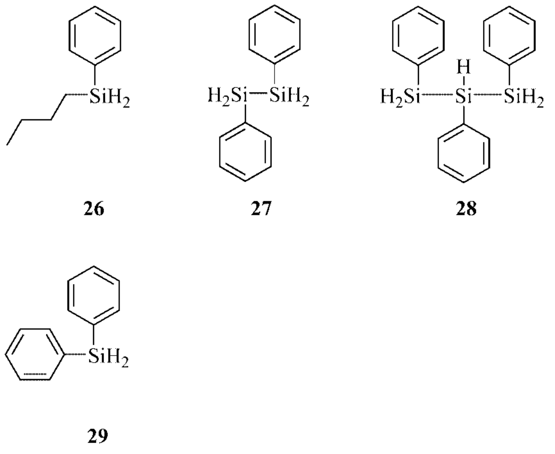
Scheme 10. Zirconocene-catalyzed dehydropolymerization of phenylsilane. (i) 1 mol-% **2**, **3**, (*pR*)(*pS*)-**5c** or (*pR*)(*pS*)-**6c**, 2 mol-% *n*BuLi.

Table 2. Dehydropolymerization of phenylsilane over chiral metallocenes **2**, **3**, (*pR*)(*pS*)-**5c** and (*pR*)(*pS*)-**6c** and the reference catalyst [Cp_2ZrCl_2].

Catalyst[a]	Conv.[b]	A[c]	M_w[d]	M_n[d]	MP[d][e]	PDI[d][f]
Cp_2ZrCl_2	98	116.3	715	680	707	1.05
2	97	36.2	705	646	691	1.09
3	46	27.3	n.d.[g]	n.d.[g]	n.d.[g]	n.d.[g]
(*pR*)(*pS*)-**5c**	90	124.9	366[h]	336[h]	274	1.09
(*pR*)(*pS*)-**6c**	25	73.1	n.d.[g]	n.d.[g]	n.d.[g]	n.d.[g]

[a] 1 mol-% of metallocene activated with 2 mol-% *n*BuLi in neat phenylsilane. [b] Conversion in % = (g of polymer)·(g of monomer)$^{-1}$. [c] Activity = (kg of polymer)·(mol of cat.)$^{-1}$·(mol of monomer)$^{-1}$·h^{-1}. [d] Determined by GPC. [e] The place (g/mol) of the top of the molecular mass peak. [f] PDI = M_w/M_n. [g] Not determined. [h] The values reported are indicative only, due to the detection limit (500 g/mol) of the column employed.

duced atactic polysilanes as confirmed by $^{29}Si\{^1H\}$ NMR analysis. As the sole significant difference between zirconocene dichloride and the investigated pinenyl-substituted complexes, it could be shown by ^1H NMR analysis of the polysilanes produced that catalysts **2**, **3**, **5c** and **6c** produced only linear polysilanes whereas mixtures of cyclic and linear poly-/oligomers were obtained with the Cp_2ZrCl_2/*n*BuLi catalyst system. The formation of oligomers and other coupling products was further investigated with GC-MS with compounds detected shown in Figure 4. All by-products **26**–**29** were detected in polymerizations catalyzed by complexes **2** and (*pR*)(*pS*)-**5c**, whereas complex **3** only yielded compounds **26** and **27** and complex **6c** yielded compound **26**. In the reaction catalyzed by the reference catalyst only compounds **26** and **29** were formed.


26 **27** **28**

29

Figure 4. Oligomers/by-products formed in the dehydropolymerization of phenylsilane catalyzed by [Cp_2ZrCl_2], **2**, **3**, **5c** and **6c**/*n*BuLi

Olefin Polymerization

Complexes **2** and (*pR*)(*pS*)-**5c** were activated with methylaluminoxane (MAO) for polymerization of propylene in toluene (T = 50 °C, P = 5.34 bar, [Al]:[Zr] = 2000:1). The results are summarized in Table 3. Under the conditions investigated, the 2-pinenyl-substituted **2**/MAO catalyst system produced only low molecular weight atactic polypropylene (*a*PP) (colorless oil) with low activity, whereas the 1-substituted **5c**/MAO was totally inactive toward propylene intake, most likely due to its greater steric hindrance toward monomer coordination in the vicinity of the metal site induced by placement of the bulky substituents. The experimental pentad distribution for the *a*-PP obtained with **2**/MAO as determined by quantitative ^{13}C NMR with inverse gated ^1H-decoupling is as follows: [*mmmm*] = 5.5%, [*mmmr*] = 8.8%, [*rmmr*] = 5.5%, [*mmrm*] + [*rmrr*] = 25.3%, [*mrmr*] = 16.5%, [*rrrr*] = 8.8%, [*rrrm*] = 11.0% and [*mrrm*] = 7.7%. End group analysis by ^{13}C NMR indicated the presence of *n*-propyl, vinylidene, isobutenyl, *cis*-2-butenyl and *trans*-2-butenyl chain ends (Figure 5).

Table 3. Polymerization of propylene over **2**/MAO and (*pR*)(*pS*)-**5c**/MAO.

Catalyst[a]	A[b]	M_w[c]	M_n[c]	M_v[c]	PDI[d]
2/MAO	125	3670	1900	3110	1.93
5c/MAO	–	–	–	–	–

[a] 20 µmol of **2** or (*pR*)(*pS*)-**5c** activated with 40 mmol of MAO (30 vol-% in toluene) in 200 mL dry toluene at T = 50 °C, P = 5.34 bar, [Al]:[Zr] = 2000:1, t = 2 h. [b] Polymerization activity in (kg of PP)·(mol of cat.)$^{-1}$·h^{-1}. [c] By GPC. [d] PDI = M_w/M_n.

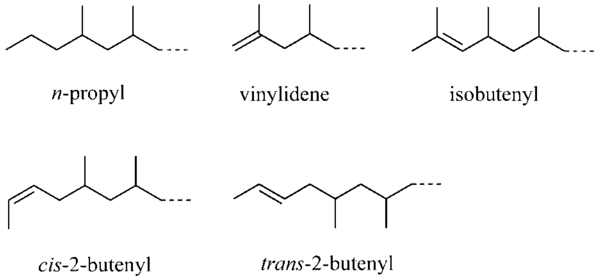


Figure 5. End groups present in the atactic polypropylene produced with **2**/MAO

The MAO-activated bis(indenyl) complexes **2** and (*pR*)(*pS*)-**5c** were further tested in the polymerization of ethylene in toluene (T = 50 °C, P = 3.95 bar, [Al]:[Zr] = 2000:1). In contrast to the propylene polymerization experiments, both catalysts **2**/MAO and **5c**/MAO polymerized ethylene with fairly high activities (2300–2550 kg PE/mol Zr/h) to high molecular weight polyethylene (M_w > 440000), the latter being slightly more active of the two. The polymerization results and characterization data are collected in Table 4 with results of IR-analyses of the polymer end group composition in Table 5. Both catalysts produced polyethylenes with vinylidene, terminal vinyl and *trans*-vinylene end groups (Figure 6) in slightly different ratios. The fact that the **5c**/MAO catalyst polymerizes ethylene with comparable activity to that of **2**/MAO further suggests that its inactivity toward propylene is most likely of steric origin and a consequence of the orientation of the 1-indenyl substituents over the metal center.

Table 4. Polymerization of ethylene over **2**/MAO and (*pR*)(*pS*)-**5c**/MAO.

Catalyst[a]	A[d]	M_w[e]	M_n[e]	M_v[e]	PDI[f]	T_m[g]
2/MAO[b]	2300	489000	169000	428000	2.9	122–128
5c/MAO[c]	2550	449000	178000	395000	2.5	124–134

[a] 2 µmol of **2** or (*pR*)(*pS*)-**5c** activated with 4 mmol of MAO (30 vol-% in toluene) in 200 mL dry toluene at T = 50 °C, P = 3.95 bar, [Al]:[Zr] = 2000:1. [b] Polymerization time = 0.58 h. [c] Polymerization time = 0.75 h. [d] Polymerization activity in (kg of PE)-(mol of cat.)$^{-1}$ h^{-1}. [e] By GPC. [f] PDI = M_w/M_n. [g] Melting interval in °C by DSC.

Table 5. End group distribution [C=C/1000] in polyethylenes produced by **2**/MAO and (*pR*)(*pS*)-**5c**/MAO.

Catalyst[a]	Vinylidene	Terminal vinyl	*trans*-Vinylene
2/MAO	0.69	1.54	1.11
5c/MAO	0.52	3.85	0.35

[a] By IR.

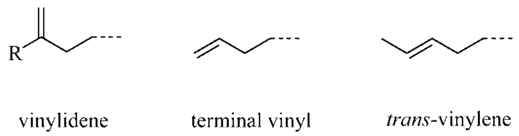
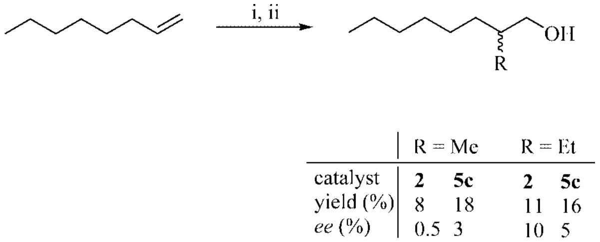


Figure 6. End groups present in polyethylenes produced with **2**/MAO and **5c**/MAO

Carboalumination Reactions

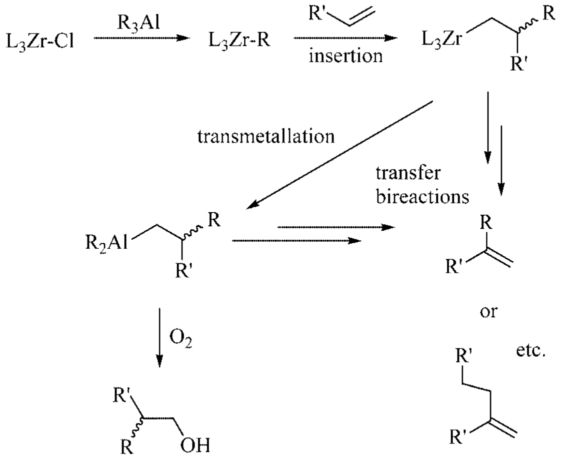
Catalytic asymmetric carboalumination of unactivated terminal alkenes using chiral zirconocene catalysts has considerable synthetic potential as oxidation of the organoaluminum products with molecular oxygen potentially provides access to the corresponding chiral alcohols.[9–13] Recently, this reaction, initially developed by Negishi and coworkers, has been applied successfully e.g., in natural product synthesis via the obtained chiral polypropionate building blocks.[51–53] Of several zirconocene catalysts evaluated previously, high yields and moderate enantioselectivities are almost exclusively obtained by use of the chiral unbridged bis(1-neomenthylindenyl)zirconium dichloride [(NMI)$_2$-ZrCl$_2$], initially developed by Erker and co-workers.[22] Accordingly, we felt motivated to briefly investigate the applicability of the easily prepared chiral zirconocenes **2**, **3**, (*pR*)(*pS*)-**5c** and (*pR*)(*pS*)-**6c** as catalysts for carboalumination reactions. Thus, by reaction of 1-octene with triethylaluminum or trimethylaluminum in the presence of catalytic amounts of the chiral zirconocene complexes **2** and (*pR*)(*pS*)-**5c**, 2-ethyl-1-octanol and 2-methyl-1-octanol were indeed obtained after oxidation with O_2, albeit in disappointingly low yields ranging from 8 to 18% (Scheme 11). Also enantiomeric excesses were low ranging from marginal to 10% as determined by ^{1}H and ^{19}F NMR analysis of the corresponding Mosher esters.[54] By measuring the optical rotations of the enantiomeric product mixtures it could be deduced that the 2-substituted complex **2** produced, in both cases, a slight excess of the (+)-enantiomer of 2-alkyl-1-octanols whereas a slight excess of the (–)-enantiomers was obtained with (*pR*)(*pS*)-**5c**. The hydrogenated congeners **3** and (*pR*)(*pS*)-**6c** proved totally inactive as carboalumination catalysts.



	R = Me		R = Et	
catalyst	**2**	**5c**	**2**	**5c**
yield (%)	8	18	11	16
ee (%)	0.5	3	10	5

Scheme 11. Carboalumination of 1-octene with chiral zirconocene catalysts. (i) Et_3Al or Me_3Al, **2** or (*pR*)(*pS*)-**5c**, dichloromethane. (ii) O_2.

A simplified mechanistic scheme of the carboalumination reaction is displayed in Scheme 12. Based on the previous work by Negishi, Waymouth and others, the NMI_2ZrCl_2 catalyst appears to have an optimal disposal of the chiral ligands coupled with conformational flexibility driving the reaction towards the carboalumination product which in turn can be oxidized to the chiral alcohol. With other catalysts investigated previously, larger amounts of alkene products resulting from hydrometalation/carbometalation and/or hydrogen transfer sequences are often produced. The ligands in **2** and (*pR*)(*pS*)-**5c** are apparently not bulky enough for efficient blocking of the side reactions resulting in low carboalumination yields and selectivities.



Scheme 12. Simplified mechanism for zirconocene catalyzed carboalumination.

Nevertheless, some enantiocontrol was obtained with the simple ligand design presented in this work and the results obtained could be considered promising. Unfortunately our attempts to modify the steric properties of these precatalysts by additional methyl substituents were hampered by the difficult (or impossible) isolation and purification of complexes **8a**–**c** and **10a**–**c**. Furher variations in ligand structure are currently in progress.

Summary and Conclusions

In this paper we have reported the synthesis of some new indenes containing a β-pinenyl-derived, chiral substituent and investigated the metallation of these ligand precursors, as well as some previously described ligand analogues,[28] with group-4 metals. Due to the simple accessibility of the ligand precursors and the successful metallations in some of the cases, the route appears attractive for the preparation of new chiral transition metal complexes. The main drawback of the complexes described are the high solubilities of both the ligand precursors and the corresponding metallocenes in nearly all common organic solvents which render their isolation and purification unusually difficult in many cases. The high solubilities in turn are likely a consequence of the high rotational and conformational freedom of the pinenyl part in these molecules.

In addition, we have investigated the catalytic activity of selected metal complexes in polymerization and carboalumination reactions. Metal complexes **2** and (*pR*)(*pS*)-**5c** polymerized ethylene with high activity and polyethylene with high molecular weight was obtained whereas only complex **2** was active in propylene polymerization producing atactic polypropylene with low molecular weight. All of the catalysts investigated produced atactic poly(phenylsilane) with low molecular weight. In catalytic carboalumination reactions, complexes **2** and (*pR*)(*pS*)-**5c** showed to induce some (0.5–10% *ee*) enantioselectivity in the carboalumination of 1-octene with triethyl- and trimethylaluminum whereas their tetrahydroindenyl analogues **3** and (*pR*)(*pS*)-**6c** were not active at all. Nevertheless, we believe that the simple chiral catalyst structures described herein, may prove valuable starting points for further developoment by structural modifications.

Experimental Section

General Comments: All air and moisture sensitive reactions were conducted under argon using standard techniques. Commercially available reagents were used without further purification. Methylindene,[55] α-pinenylpotassium,[37] 2-(chlorodimethylsilyl)indene[38] and 1-(chlorodimethylsilyl)indene[39] were synthesized essentially according to literature procedures. Chloro{[(1*S*,2*S*,5*S*)-6,6-dimethylbicyclo[3.1.1]hept-2-yl]methyl}dimethylsilane was prepared by hydrosilylation of β-pinene with chlorodimethylsilane in the presence of Karstedt's catalyst.[56,57] Diethyl ether and tetrahydrofuran were distilled from sodium/benzophenone ketyl prior to use. Dichloromethane was distilled from calcium hydride and toluene was purified by passage through a series of activated 3-Å molecular sieves and copper catalyst columns. Flash chromatography was performed on silica gel 60 (40–63 μm). Silanized silica gel was prepared according to a literature procedure.[33] NMR spectra were recorded at 298 K with a Bruker Avance 600 (^{1}H NMR 600 MHz, ^{13}C NMR 150.9 MHz), Jeol JNM-A500 (^{1}H NMR 500 MHz, ^{13}C 125.8 MHz), Jeol L-400 (^{1}H NMR 400 MHz, ^{13}C 100.6 MHz, ^{29}Si 79.5 MHz) or Bruker 250 MHz (1H NMR 250 MHz) NMR spectrometer. ^{1}H NMR were referenced against residual ^{1}H-impurities in the solvent and ^{13}C NMR to the solvent signals. In the ^{29}Si NMR experiments TMS was used as external reference. The NMR spectra were recorded in δ values with $CDCl_3$ or CD_2Cl_2 as the solvent. Mass spectra were recorded with a high-resolution mass spectrometer (Fison's ZapSpec). A Hewlett–Packard Series II 5890/Hewlett Packard 5971A Mass selective detector was used in GC-MS analysis. Molecular weights and molecular weight distributions of polysilanes were measured at 30 °C in THF by size exclusion chromatography (GPC) relative to polystyrene standards using a Waters 515 high-pressure liquid chromatography pump, GPC fitted with Styragel columns HR 2, HR 4, and HR 6, a UV detector Waters 2487 and a refractive-index detector Waters 2410. Melting intervals were measured with Perkin–Elmer DSC 7. Polyethylene end group analyses were carried out with a Perkin–Elmer FT-IR spectrometer Spectrum 1000. The optical rotation measurements were made using Perkin–Elmer Polarimeter 241. The molecular weights of the polyethylene and polypropylene samples were determined using a Waters Alliance 2000 GPC equipped with a refractometer, viscometer, and three Waters Styragel HMW columns covering the molecular weight range from 10^2 to 10^8 g/mol. 1,2,4-Trichlorobenzene was used as solvent and the chromatograms were collected at 140 °C. The molecular weights were calculated with the universal calibration based on 11 narrow polystyrene standards.

Bis{2-[(7,7-dimethylnorpinanylmethyl)dimethylsilyl]indenyl}-zirconium Dichloride (2): To 2-[(7,7-dimethylnorpinanylmethyl)dimethylsilyl]indene (**1**) (2.4076 g, 7.8 mmol) in diethyl ether (35 mL) at 0 °C was added *n*BuLi (2.5 M in *n*-hexane, 3.2 mL, 7.8 mmol). The yellow solution was stirred at room temperature for 4 h. The solvent was removed under vacuum leaving a pale yellow foam. Next, $ZrCl_4$ (0.9634 g, 4.1 mmol) was added and the solids were mixed a few minutes before 50 mL of toluene was added. After stirring at 50 °C for 18 h, the suspension was filtered and the filtrate was concentrated under vacuum. The product was crystallized from *n*-pentane at –20 °C yielding 1.1157 g (37%) of pure **2** as a yellow powder. ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): δ = 7.81 (m, 4 H, arom. CH in six-membered ring), 7.30 (m, 4 H, arom. CH in six-membered ring), 5.97 (dd, J = 0.92 Hz, 2.14 Hz, 2 H, arom. CH in five-membered ring), 5.94 (dd, J = 0.76 Hz, 2.14 Hz, 2 H, arom. CH in five-membered ring), 1.92 (m, 2 H, aliph. CH in pinenyl ring), 1.87 (m, 2 H, aliph. CH in pinenyl ring), 1.77 (m, 2 H, aliph. CH in pinenyl ring), 1.65 (m, 4 H, aliph. CH_2 in pinenyl ring), 1.55 (m, 2 H, aliph. CH in pinenyl ring), 1.35 (dt, J = 1.32 Hz, 5.57 Hz, 2 H, aliph. CH in pinenyl ring), 1.28 (d, J = 9.92 Hz, 2 H, aliph. CH in pinenyl ring), 1.11 (m, 2 H, aliph. CH in pinenyl ring), 1.06 (s, 6 H, CH_3 in pinenyl ring), 0.69 (s, 6 H, CH_3 in pinenyl ring), 0.53 (dd, J = 7.55 Hz, 14.50 Hz, 2 H, aliph. CH between Si and pinenyl ring), 0.45 (dd, J = 6.56 Hz, 14.50 Hz, 2 H, aliph. CH between Si and pinenyl ring), 0.11 (s, 6 H, CH_3 attached to Si), 0.10 (s, 6 H, CH_3 attached to Si) ppm. ^{13}C NMR (100.6 MHz, CD_2Cl_2, 25 °C): δ = 141.83 (2 C_q), 130.02 (4 C_q), 126.32 (4 arom. CH in six-membered ring), 126.06 (4 arom. CH in six-membered ring), 112.47 (2 arom. CH in five-membered ring), 112.30 (2 arom. CH in five-membered ring), 49.44 (2 aliph. CH in pinenyl ring), 41.30 (2 aliph. CH in pinenyl ring), 39.93 (2 C_q in pinenyl ring), 31.46 (2 aliph. CH in pinenyl ring), 27.15 (2 CH_3 in pinenyl ring), 26.23 (4 aliph. CH in pinenyl ring), 25.31 (4 aliph. CH in pinenyl ring), 25.10 (2 aliph. CH_2 between Si and pinenyl ring), 23.32 (4 aliph. CH in pinenyl ring), 20.18 (2 CH_3 in pinenyl ring), –1.16 (2 CH_3 attached to Si), –1.47 (2 CH_3 attached to Si) ppm. ^{29}Si NMR (79.5 MHz, CD_2Cl_2, 25 °C): δ = –4.45 (2 Si) ppm. In the EIMS mass spectrum parent ions of composition $C_{42}H_{58}Cl_2Si_2Zr^+$ were observed in the appropriate ratios at *m*/*z* = 778–786. $C_{42}H_{58}Cl_2Si_2Zr$ (781.18): calcd. C 64.57, H 7.48; found C 64.58, H 7.59.

Bis{2-[(7,7-dimethylnorpinanylmethyl)dimethylsilyl]4,5,6,7-tetrahydro-1-indenyl}zirconium Dichloride (3): A suspension of **2** (0.1124 g, 0.1 mmol) and PtO_2 (a catalytic amount) in dichloromethane (50 mL) was hydrogenated in a steel autoclave under 50 bar H_2 for 20 h at room temperature. The catalyst was filtered off and the filtrate was evaporated yielding 0.095 g (86%) of the pure title compound as a pale green oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 6.22 (m, 4 H, arom. CH in five-membered ring), 2.78 (m, 4 H, aliph. CH in six-membered ring), 2.59 (m, 4 H, aliph. CH in six-membered ring), 1.86 (m, 10 H, aliph. CH in six-membered ring and in pinenyl ring), 1.62 (m, 10 H, aliph. CH in six-membered ring and in pinenyl ring), 1.45 (m, 2 H, aliph. CH in pinenyl ring), 1.29 (d, *J* = 9.92 Hz, 2 H, aliph. CH in pinenyl ring), 1.14 (m, 2 H, aliph. CH in pinenyl), 1.12 (s, 6 H, CH_3 in pinenyl ring), 0.73 (s, 6 H, CH_3 in pinenyl ring), 0.58 (m, 4 H, CH_2 between Si and pinenyl ring), 0.28 (s, 6 H, CH_3 attached to Si), 0.27 (s, 6 H, CH_3 attached to Si) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 135.15 (2 C_q), 135.02 (2 C_q), 122.26 (2 C_q), 121.09 (2 arom. CH in five-membered ring), 120.81 (2 arom. CH in five-membered ring), 48.85 (2 C, aliph. C in six-membered ring or in pinenyl ring), 40.54 (2 C, aliph. C in six-membered ring or in pinenyl ring), 39.44 (2 C_q in pinenyl ring), 30.97 (2 C, aliph. C in six-membered ring or in pinenyl ring), 26.91 (2 C, aliph. C in six-membered ring or in pinenyl ring), 26.01 (2 C, aliph. C in six-membered ring or in pinenyl ring), 25.59 (2 C, aliph. C in six-membered ring or in pinenyl ring), 25.40 (2 C, aliph. C in six-membered ring or in pinenyl ring), 25.12 (2 C, aliph. C in six-membered ring or in pinenyl ring), 24.71 (2 C, aliph. C in six-membered ring or in pinenyl ring), 22.90 (2 C, aliph. C in six-membered ring or in pinenyl ring), 22.26 (6 C, aliph. C in six-membered ring or in pinenyl ring), 19.94 (2 C, aliph. C in six-membered ring or in pinenyl ring), –0.45 (2 CH_3–Si), –0.88 (2 CH_3–Si) ppm. ^{29}Si NMR (79.5 MHz, $CDCl_3$, 25 °C): δ = –4.71 (2 Si) ppm. In the EIMS mass spectrum parent ions of composition $C_{42}H_{66}Cl_2Si_2Zr^+$ were observed in the appropriate ratios at *m*/*z* = 786–794.

(*pR*)(*pS*)-Bis{1-[(7,7-dimethylnorpinanylmethyl)dimethylsilyl]-indenyl}zirconium Dichlorides (5c): To a diastereomeric mixture of 1-[(7,7-dimethylnorpinanylmethyl)dimethylsilyl]indene (**4a/4b**) (5.5281 g, 17.8 mmol) in diethyl ether (100 mL) at 0 °C was added *n*BuLi (2.5 M in *n*-hexane, 7.2 mL, 18.0 mmol). The yellow solution was stirred at room temperature for 4.5 h. The reaction mixture was cooled to 0 °C and $ZrCl_4$ (2.0870 g, 9.0 mmol) was added. After stirring the suspension at room temperature for 19 h, the solvents were removed under vacuum. The residue was dissolved in dichloromethane, filtered and the filtrate was concentrated. Crystallization from dichloromethane at –20 °C provided 0.7782 g (11%) of the pure (*pR*)(*pS*)-**5c** diastereomer as a yellow powder. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 7.67 (m, 4 H, arom. CH in six-membered ring), 7.25 (m, 4 H, arom. CH in six-membered ring), 6.41 (m, 2 H, arom. CH in five-membered ring), 6.34 (m, 2 H, arom. CH in five-membered ring), 1.94 (m, 4 H, aliph. CH in pinenyl ring), 1.78 (m, 2 H, aliph. CH in pinenyl ring), 1.59 (m, 6 H, aliph. CH in pinenyl ring), 1.44 (m, 2 H, aliph. CH in pinenyl ring), 1.27 (m, 2 H, aliph. CH in pinenyl ring), 1.15 (m, 2 H, aliph. CH in pinenyl ring), 1.07 (s, 6 H, CH_3 in pinenyl ring), 0.76 (m, 4 H, aliph. CH_2 between Si and pinenyl ring), 0.67 (s, 3 H, CH_3 in pinenyl ring), 0.64 (s, 3 H, CH_3 in pinenyl ring), 0.44 (s, 3 H, CH_3 attached to Si), 0.42 (s, 3 H, CH_3 attached to Si), 0.37 (s, 3 H, CH_3 attached to Si), 0.35 (s, 3 H, CH_3 attached to Si) ppm. ^{13}C NMR (150.9 MHz, $CDCl_3$, 25 °C): δ = 145.59 (C_q), 144.37 (C_q), 136.05 (2 C_q), 134.73 (C_q), 134.41 (C_q), 127.35 (2 arom. CH in six-membered ring), 127.31 (2 arom. CH in five-membered ring), 126.42 (arom. CH in six-membered ring), 126.39 (arom. CH in six-membered ring), 126.01 (arom. CH in six-membered ring), 125.96 (arom. CH in six-membered ring), 125.24 (2 arom. CH in six-membered ring), 104.89 (arom. CH in five-membered ring), 104.86 (arom. CH in five-membered ring), 49.16 (aliph. C in pinenyl ring), 49.13 (aliph. C in pinenyl ring), 40.71 (2 aliph. C in pinenyl ring), 39.60 (C_q in pinenyl ring), 39.58 (C_q in pinenyl ring), 31.23 (2 aliph. C in pinenyl ring), 26.98 (CH_3 in pinenyl ring), 26.95 (CH_3 in pinenyl ring), 25.73 (aliph. C in pinenyl ring), 25.68 (aliph. C in pinenyl ring), 25.15 (CH_2 between Si and pinenyl ring), 25.12 (CH_2 between Si and pinenyl ring), 24.88 (2 aliph. C in pinenyl ring), 23.06 (aliph. C in pinenyl ring), 23.05 (aliph. C in pinenyl ring), 20.04 (CH_3 in pinenyl ring), 20.00 (CH_3 in pinenyl ring), 0.06 (CH_3–Si), –0.48 (CH_3–Si), –0.57 (CH_3–Si), –0.81 (CH_3–Si) ppm. ^{29}Si NMR (79.5 MHz, $CDCl_3$, 25 °C): δ = –4.82 (2 Si) ppm. In the EIMS mass spectrum parent ions of composition $C_{42}H_{58}Cl_2Si_2Zr^+$ were observed in the appropriate ratios at *m*/*z* = 778–786. ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C) analysis of the filtrate containing a mixture of diastereomers (*pR*)(*pS*)-bis{1-[dimethyl(7,7-dimethylnorpinanylmethyl)silyl]indenyl}zirconium dichlorides (**5a** and **5b**): δ = 7.73 (m, 4 H, arom. CH in six-membered ring in **5a** and/or **5b**), 7.54 (m, 4 H, arom. CH in six-membered ring in **5a** and/or **5b**), 7.28 (m, 8 H, arom. CH in six-membered ring in **5a** and/or **5b**), 6.49 (m, 4 H, arom. CH in five-membered ring in **5a** and/or **5b**), 6.15 (m, 4 H, arom. CH in five-membered ring in **5a** and/or **5b**), 1.07 (s, 12 H, CH_3 in pinenyl ring in **5a** and/or **5b**), 0.67 (s, 6 H, CH_3 in pinenyl ring in **5a** and/or **5b**), 0.63 (s, 6 H, CH_3 in pinenyl ring in **5a** and/or **5b**), 0.47 (m, 12 H, CH_3 attached to Si in **5a** and/or **5b**), 0.40 (m, 12 H, CH_3 attached to Si in **5a** and/or **5b**), 2.23–0.75 (m, 44 H, aliph. CH in pinenyl substituent in **5a** and **5b**) ppm, signals from the aliph. protons in pinenyl ring in **5a** and **5b** are overlapping with each other and other signals in the region 2.23–0.75 ppm.

{*pR*)(*pS*)-Bis{1-[(7,7-dimethylnorpinanylmethyl)dimethylsilyl]-4,5,6,7-tetrahydro-1-indenyl}zirconium Dichloride (6c): A suspension of **5c** (0.1190 g, 0.2 mmol) and PtO_2 (a catalytic amount) dichloromethane (50 mL) was hydrogenated in a steel autoclave under 50 bar H_2 for 20 h at room temperature. The catalyst was filtered off and the filtrate was evaporated yielding 0.096 g (82%) of pure **6c** as a pale green powder. Recrystallization from dichloromethane at –20 °C yielded 0.037 g (31%) of a pale green solid. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 6.51 (m, 2 H, arom. CH in five-membered ring), 5.58 (m, 2 H, arom. CH in five-membered ring), 3.00 (m, 4 H, aliph. CH in six-membered ring), 2.50 (m, 4 H, aliph. CH in six-membered ring), 1.96 (m, 4 H, aliph. CH in six-membered ring and in pinenyl ring), 1.80 (m, 6 H, aliph. CH in six-membered ring and in pinenyl ring), 1.62 (m, 12 H, aliph. CH in six-membered ring and in pinenyl ring), 1.31 (d, *J* = 10.15 Hz, 1 H, aliph. CH in pinenyl ring), 1.30 (d, *J* = 10.15 Hz, aliph. CH in pinenyl ring), 1.20 (m, 2 H, aliph. CH in pinenyl ring), 1.14 (s, 3 H, CH_3 in pinenyl ring), 1.01 (s, 3 H, CH_3 in pinenyl ring), 0.75 (s, 3 H, CH_3 in pinenyl ring), 0.73 (s, 3 H, CH_3 in pinenyl ring), 0.67 (m, 4 H, CH_2 between Si and pinenyl ring), 0.26 (s, 3 H, CH_3 attached to Si), 0.25 (s, 3 H, CH_3 attached to Si), 0.17 (s, 6 H, CH_3

attached to Si) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 140.48 (C_q), 140.42 (C_q), 136.24 (C_q), 136.18 (C_q), 118.86 (C_q), 118.68 (C_q), 116.42 (arom. CH), 116.38 (arom. CH), 111.96 (arom. CH), 111.85 (arom. CH), 49.02 (aliph. C in six-membered ring or in pinenyl ring), 48.82 (aliph. C in six-membered ring or in pinenyl ring), 40.60 (aliph. C in six-membered ring or in pinenyl ring), 40.59 (aliph. C in six-membered ring or in pinenyl ring), 39.53 (C_q in pinenyl ring), 39.44 (C_q in pinenyl ring), 31.11 (aliph. C in six-membered ring or in pinenyl ring), 31.01 (aliph. C in six-membered ring or in pinenyl ring), 26.91 (aliph. C in six-membered ring or in pinenyl ring), 26.86 (aliph. C in six-membered ring or in pinenyl ring), 26.10 (aliph. C in six-membered ring or in pinenyl ring), 26.06 (aliph. C in six-membered ring or in pinenyl ring), 25.68 (aliph. C in six-membered ring or in pinenyl ring), 25.61 (aliph. C in six-membered ring or in pinenyl ring), 25.18 (aliph. C in six-membered ring or in pinenyl ring), 25.16 (aliph. C in six-membered ring or in pinenyl ring), 24.76 (aliph. C in six-membered ring or in pinenyl ring), 24.73 (aliph. C in six-membered ring or in pinenyl ring), 24.56 (aliph. C in six-membered ring or in pinenyl ring), 24.54 (aliph. C in six-membered ring or in pinenyl ring), 22.93 (aliph. C in six-membered ring or in pinenyl ring), 22.91 (aliph. C in six-membered ring or in pinenyl ring), 22.64 (2 aliph. C in six-membered ring or in pinenyl ring), 22.26 (aliph. C in six-membered ring or in pinenyl ring), 22.24 (aliph. C in six-membered ring or in pinenyl ring), 19.97 (2 aliph. C in six-membered ring or in pinenyl ring), –0.52 (CH_3–Si), –0.74 (CH_3–Si), –0.99 (CH_3–Si), –1.34 (CH_3–Si) ppm. ^{29}Si NMR (79.5 MHz, $CDCl_3$, 25 °C): δ = –6.37, –6.47 ppm. In the EIMS mass spectrum parent ions of composition $C_{42}H_{66}Cl_2Si_2Zr^+$ were observed in the appropriate ratios at *m*/*z* = 786–794.

A Diastereomeric Mixture of (6,6-dimethylbicyclo[3.1.1]hept-2-ylmethyl)dimethyl(1-methyl-1*H*-inden-2-yl)silanes (7a/7b): To **1**[28] (3.4065 g, 11.0 mmol) in tetrahydrofuran (50 mL) at 0 °C was added *n*BuLi (2.5 M in *n*-hexane, 4.5 mL, 11.1 mmol). The orange solution was stirred at room temperature for 3.5 h and to this solution was added dropwise methyl iodide (1.4 mL, 21.9 mmol) at 0 °C. The resulting red reaction mixture was stirred at room temperature for 1.5 h before saturated aqueous NH_4Cl solution (50 mL) was added. The layers formed were separated and the aqueous layer was further extracted with diethyl ether (30 mL). The combined organic layers were dried with Na_2SO_4, filtered and the solvents evaporated to dryness. The crude product was purified with silica gel column chromatography using hexane as eluent providing 2.6259 g (74%) of **7a**/**7b** (a mixture of two diastereomers) as a colorless oil. ^1H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 7.45 (m, 1+1 H, arom. CH), 7.39 (m, 1+1 H, arom. CH), 7.28 (m, 1+1 H, arom. CH), 7.22 (m, 1+1 H, arom. CH), 7.06 (m, 1+1 H, olefinic CH in five-membered ring), 3.59 (m, 1+1 H, aliph. CH in five-membered ring), 2.21 (m, 1+1 H, CH in pinenyl ring), 2.05 (m, 1+1 H, CH in pinenyl ring), 1.88 (m, 1+1 H, CH in pinenyl ring), 1.74 (m, 3+3 H, CH in pinenyl ring), 1.68 (m, 1+1 H, CH in pinenyl ring), 1.42 (m, 1+1 H, CH in pinenyl ring), 1.39 (m, 3+3 H, CH_3 attached to five-membered ring), 1.30 (m, 1+1 H, CH in pinenyl ring), 1.21 (s, 3 H, CH_3 in pinenyl ring), 1.20 (s, 3 H, CH_3 in pinenyl ring), 0.85 (m, 1+1 H, bridging CH between Si and pinenyl ring), 0.84 (s, 3 H, CH_3 in pinenyl ring), 0.83 (s, 3 H, CH_3 in pinenyl ring), 0.75 (m, 1+1 H, bridging CH between Si and pinenyl ring), 0.28 (m, 6+6 H, CH_3 attached to Si) ppm. ^{13}C NMR (150.9 MHz, $CDCl_3$, 25 °C): δ = 155.20 (C_q), 155.14 (C_q), 152.51 (C_q), 152.48 (C_q), 144.36 (2 C_q), 140.01 (olefinic CH in five-membered ring), 140.00 (olefinic CH in five-membered ring), 126.48 (2 arom. CH), 124.98 (2 arom. CH), 122.58 (2 arom. CH), 120.84 (2 arom. CH), 49.51 (CH in pinenyl ring), 49.37 (CH in pinenyl ring), 49.33 (aliph. CH in five-membered ring), 49.32 (aliph. CH in five-membered ring), 40.79 (CH in pinenyl ring), 40.77 (CH in pinenyl ring), 39.69 (2 C_q in pinenyl ring), 31.39 (CH in pinenyl ring), 31.38 (CH in pinenyl ring), 27.07 (2 CH_3 in pinenyl ring), 25.81 (CH_2 in pinenyl ring), 25.69 (CH_2 in pinenyl ring), 24.92 (2 CH_2 in pinenyl ring), 24.35 (bridging CH_2 between Si and pinenyl ring), 24.22 (bridging CH_2 between Si and pinenyl ring), 23.13 (2 CH_2 in pinenyl ring), 20.18 (2 CH_3 in pinenyl ring), 17.24 (CH_3 attached to five-membered ring), 17.20 (CH_3 attached to five-membered ring), –0.78 (CH_3 attached to Si), –1.02 (CH_3 attached to Si), –1.17 (CH_3 attached to Si), –1.38 (CH_3 attached to Si) ppm. ^{29}Si NMR (119.3 MHz, $CDCl_3$, 25 °C): δ = –8.30, –8.43 ppm. EIMS (70 eV) calcd. for $C_{22}H_{32}Si$ 324.2273, found 324.2273.

Bis{2-[(7,7-dimethylnorpinanylmethyl)dimethylsilyl](1-methyl)-indenyl}zirconium Dichlorides [(*pR*)(*pR*)-8a, (*pS*)(*pS*)-8b, (*pR*)(*pS*)-8c]: To a mixture of **7a**/**7b** (1.2887 g, 4.0 mmol) in diethyl ether (30 mL) at 0 °C was added *n*BuLi (2.5 M in *n*-hexane, 1.6 mL, 4.0 mmol). The yellow solution was stirred at room temperature for 4 h. The reaction mixture was cooled to 0 °C and $ZrCl_4$ (0.4626 g, 2.0 mmol) was added. After stirring the suspension at room temperature for 18 h, the solvents were removed under vacuum. The residue was dissolved in dichloromethane, filtered and the filtrate was concentrated. The crude product was purified with silanized silica gel column chromatography under argon using pentane as eluent providing 0.8499 g (53%) of a mixture of **8a**–**c** as a yellow oil. Combination of fractions containing only the racemic-like diastereomers (*pR*)(*pR*)-**8a** and (*pS*)(*pS*)-**8b** yielded 0.2938 g (18%) of a such mixture. When to this mixture was added cold pentane at –60 °C a small sample (0.054 g, 3%) of **8a**/**8b** was obtained as yellow crystals enriched in one of the racemic-like diastereomers in a 57:43 ratio. ^1H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 7.97 (m, 4 H, arom. CH in **8a** and **8b**), 7.59 (m, 4 H, arom. CH in **8a** and **8b**), 7.33 (m, 4 H, arom. CH in **8a** and **8b**), 7.20 (m, 4 H, arom. CH in **8a** and **8b**), 5.14 (m, 2 H, olefinic CH in five-membered ring in **8a** and **8b**), 5.13 (m, 2 H, olefinic CH in five-membered ring in **8a** and **8b**), 2.46 (s, 6 H, CH_3 attached to five-membered ring in **8a** and **8b**), 2.45 (s, 6 H, CH_3 attached to five-membered ring in **8a** and **8b**), 1.87 (m, 4 H, CH in pinenyl ring in **8a** and **8b**), 1.77 (m, 8 H, CH in pinenyl ring in **8a** and **8b**), 1.60 (m, 8 H, CH in pinenyl ring in **8a** and **8b**), 1.49 (m, 4 H, CH in pinenyl ring in **8a** and **8b**), 1.23 (m, 8 H, CH in pinenyl ring in **8a** and **8b**), 1.06 (m, 4 H, CH in pinenyl ring in **8a** and **8b**), 1.01 (s, 6 H, CH_3 attached to pinenyl ring in **8a** or **8b**), 0.99 (s, 6 H, CH_3 attached to pinenyl ring in **8a** or **8b**), 0.64 (s, 6 H, CH_3 attached to pinenyl ring in **8a** or **8b**), 0.63 (s, 6 H, CH_3 attached to pinenyl ring in **8a** or **8b**), 0.43 (m, 4 H, bridging CH_2 between pinenyl ring and Si in **8a** or **8b**), 0.35 (m, 4 H, bridging CH_2 between pinenyl ring and Si in **8a** or **8b**), 0.19 (s, 12 H, CH_3 attached to Si in **8a** or **8b**), –0.08 (s, 6 H, CH_3 attached to Si in **8a** or **8b**), –0.10 (s, 6 H, CH_3 attached to Si in **8a** or **8b**) ppm. ^{13}C NMR (150.9 MHz, $CDCl_3$, 25 °C): δ = 139.13 (2 C_q), 139.08 (2 C_q), 131.65 (2 C_q), 131.64 (2 C_q), 126.15 (4 arom. CH in **8a** and **8b**), 125.74 (2 C_q), 125.72 (2 C_q), 125.04 (4 arom. CH in **8a** and **8b**), 124.79 (4 arom. CH in **8a** and **8b**), 124.52 (4 C_q), 123.96 (2 arom. CH in **8a** and **8b**), 123.93 (2 arom. CH in **8a** and **8b**), 106.70 (4 olefinic CH in five-membered ring in **8a** and **8b**), 48.82 (2 CH in pinenyl ring in **8a** and **8b**), 48.79 (2 CH in pinenyl ring in **8a** and **8b**), 40.71 (2 CH in pinenyl ring in **8a** and **8b**), 40.67 (2 CH in pinenyl ring in **8a** and **8b**), 39.45 (4 C_q in pinenyl ring in **8a** and **8b**), 30.96 (2 CH in pinenyl ring in **8a** and **8b**), 30.87 (2 CH in pinenyl ring in **8a** and **8b**), 26.89 (2 CH_3 attached to pinenyl ring in **8a** or **8b**), 26.83 (2 CH_3 attached to pinenyl ring in **8a** or **8b**), 25.86 (2 CH in pinenyl ring in **8a** and **8b**), 25.80 (2 CH in pinenyl ring in **8a** and **8b**), 25.05 (2 bridging CH_2 between pinenyl ring and

Si in **8a** or **8b**), 24.96 (2 bridging CH_2 between pinenyl ring and Si in **8a** or **8b**), 24.86 (4 CH in pinenyl ring in **8a** and **8b**), 22.95 (2 CH in pinenyl ring in **8a** and **8b**), 22.92 (2 CH in pinenyl ring in **8a** and **8b**), 20.00 (2 CH_3 attached to pinenyl ring in **8a** or **8b**), 19.95 (2 CH_3 attached to pinenyl ring in **8a** or **8b**), 13.83 (2 CH_3 attached to five-membered ring in **8a** or **8b**), 13.80 (2 CH_3 attached to five-membered ring in **8a** or **8b**), –0.52 (2 CH_3 attached to Si in **8a** or **8b**), –0.86 (2 CH_3 attached to Si in **8a** or **8b**), –1.03 (2 CH_3 attached to Si in **8a** or **8b**), –1.45 (2 CH_3 attached to Si in **8a** or **8b**) ppm. ^{29}Si NMR (119.3 MHz, $CDCl_3$, 25 °C): δ = –4.29 (2 Si in **8a** or **8b**), –4.31 (2 Si in **8a** or **8b**) ppm. In the EIMS mass spectrum parent ions of composition $C_{44}H_{62}Cl_2Si_2Zr^+$ were observed in the appropriate ratios at *m*/*z* = 806–814.

A Diastereomeric Mixture of (6,6-Dimethylbicyclo[3.1.1]hept-2-ylmethyl)dimethyl(3-methyl-1*H*-inden-1-yl)silanes (9a/9b): To methylindene[55] (2.1064 g, 16.2 mmol) in tetrahydrofuran (20 mL) at 0 °C was added *n*BuLi (2.5 M in *n*-hexane, 6.6 mL, 16.3 mmol). The brownish green solution was stirred at room temperature for 4 h. The lithium salt was the added dropwise at 0 °C to a solution of the chiral chlorosilane (3.9218 g, 17.0 mmol) in tetrahydrofuran (10 mL). The resulting orange reaction mixture was stirred at room temperature for 2 h before saturated aqueous NH_4Cl solution (50 mL) was added. The layers formed were separated and the aqueous layer was further extracted with diethyl ether (30 mL). The combined organic layers were dried with Na_2SO_4, filtered and the solvents evaporated. The crude product was purified with silica gel column chromatography using hexane as eluent providing 2.7974 g (53%) of **9a/9b** (a mixture of two diastereomers) as a pale yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 7.43 (m, 1+1 H, arom. CH), 7.40 (m, 1+1 H, arom. CH), 7.28 (m, 1+1 H, arom. CH), 7.19 (m, 1+1 H, arom. CH), 6.30 (m, 1+1 H, olefinic CH in five-membered ring), 3.38 (m, 1+1 H, aliph. CH in five-membered ring), 2.23 (s, 3+3 H, CH_3 attached to five-membered ring), 2.01 (m, 2+2 H, 2 CH in pinenyl ring), 1.01 (m, 1+1 H, CH in pinenyl ring), 1.73 (m, 2+2 H, 2 CH in pinenyl ring), 1.67 (m, 1+1 H, CH in pinenyl ring), 1.55 (m, 1+1 H, CH in pinenyl ring), 1.32 (m, 2+2 H, 2 CH in pinenyl ring), 1.22 (m, 1+1 H, CH in pinenyl ring), 1.18 (s, 3 H, CH_3 in pinenyl ring), 1.17 (s, 3 H, CH_3 in pinenyl ring), 0.79 (s, 3 H, CH_3 in pinenyl ring), 0.78 (s, 3 H, CH_3 in pinenyl ring), 0.53 (m, 1+1 H, bridging CH between Si and pinenyl ring), 0.45 (m, 1+1 H, bridging CH between Si and pinenyl ring), –0.00 (s, 3 H, CH_3 attached to Si), –0.04 (s, 3 H, CH_3 attached to Si), –0.07 (s, 3 H, CH_3 attached to Si), –0.11 (s, 3 H, CH_3 attached to Si) ppm. ^{13}C NMR (150.9 MHz, $CDCl_3$, 25 °C): δ = 146.23 (2 C_q), 145.38 (2 C_q), 137.03 (2 C_q), 130.97 (2 olefinic CH in five-membered ring), 124.75 (2 arom. CH), 123.66 (2 arom. CH), 122.91 (2 arom. CH), 118.98 (2 arom. CH), 49.45 (CH in pinenyl ring), 49.33 (CH in pinenyl ring), 44.38 (aliph. CH in five-membered ring), 44.36 (aliph. CH in five-membered ring), 40.74 (2 CH in pinenyl ring), 39.66 (2 C_q in pinenyl ring), 31.76 (CH in pinenyl ring), 31.16 (CH in pinenyl ring), 27.06 (2 CH_3 in pinenyl ring), 25.74 (CH_2 in pinenyl ring), 25.62 (CH_2 in pinenyl ring), 24.90 (CH_2 in pinenyl ring), 24.88 (CH_2 in pinenyl ring), 23.08 (2 CH_2 in pinenyl ring), 22.77 (bridging CH_2 between Si and pinenyl ring), 22.70 (bridging CH_2 between Si and pinenyl ring), 20.16 (2 CH_3 in pinenyl ring), 13.09 (2 CH_3 attached to five-membered ring), –2.54 (CH_3 attached to Si), –2.74 (CH_3 attached to Si), –2.80 (CH_3 attached to Si), –3.03 (CH_3 attached to Si) ppm. ^{29}Si NMR (119.3 MHz, $CDCl_3$, 25 °C): δ = –4.13 (2 Si) ppm. EIMS (70 eV) calcd. for $C_{22}H_{32}Si$ 324.2273, found 324.2275.

Bis{3-[(7,7-Dimethylnorpinanylmethyl)dimethylsilyl]-1-methylindenyl}zirconium Dichlorides [(*pR*)(*pR*)-10a, (*pS*)(*pS*)-10b, (*pR*)(*pS*)-10c]: To a mixture of **9a/9b** (0.5294 g, 1.6 mmol) in diethyl ether (10 mL) at 0 °C was added *n*BuLi (2.5 M in *n*-hexane, 660 µL, 1.7 mmol). The pale orange solution was stirred at room temperature for 4 h. The reaction mixture was cooled to 0 °C and $ZrCl_4$ (0.2011 g, 0.9 mmol) was added. After stirring the suspension at room temperature for 20 h, the solvent was removed under vacuum. The residue was dissolved in dichloromethane, filtered and the filtrate was evaporated. The residue was dried in vacuo and the crude product was analyzed with 600 MHz ^{1}H NMR spectroscopy. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 7.71 (m, 4 H, arom. CH in **10a** and/or **10b** and/or **10c**), 7.54 (m, 4 H, arom. CH in **10a** and/or **10b** and/or **10c**), 7.47 (m, 4 H, arom. CH in **10a** and/or **10b** and/or **10c**), 7.38 (m, 2 H, arom. CH in **10a** and/or **10b** and/or **10c**), 7.29 (m, 2 H, arom. CH in **10a** and/or **10b** and/or **10c**), 7.22 (m, 8 H, arom. CH in **10a** and/or **10b** and/or **10c**), 6.41 (m, 2 H, olefinic CH in five-membered ring in **10a** and/or **10b** and/or **10c**), 5.92 (m, 4 H, olefinic CH in five-membered ring in **10a** and/or **10b** and/or **10c**), 2.51 (m, 6 H, CH_3 attached to five-membered ring in **10a** and/or **10b** and/or **10c**), 2.31 (m, 12 H, CH_3 attached to five-membered ring in **10a** and/or **10b** and/or **10c**), 1.10 (m, 18 H, CH_3 in pinenyl ring in **10a** and/or **10b** and/or **10c**), 0.72 (m, 12 H, bridging CH between Si and pinenyl ring in **10a** and/or **10b** and/or **10c**), 0.64 (m, 18 H, CH_3 in pinenyl ring in **10a** and/or **10b** and/or **10c**), 0.38 (m, 36 H, CH_3 attached to Si in **10a** and/or **10b** and/or **10c**), 1.95–1.12 (m, 54 H, aliph. CH in pinenyl ring in **10a** and/or **10b** and/or **10c**), signals from the aliph. protons in pinenyl ring in **10a**, **10b** and **10c** are overlapping with each other and other signals in the region 1.95–1.12 ppm. From the Cp-H (5.92, 6.28 and 6.41 ppm) and Cp-CH_3 signals (2.21, 2.31 and 2.51 ppm) it could be calculated that the amount of the mixture of formed metallocenes was approximately 70%.

Mixture of a Diastereomeric Mixture of 2-[6,6-(Dimethylbicyclo[3.1.1]hept-2-ylmethyl)dimethylsilyl]-1-trimethylsilyl-1*H*-indenes (11a/11b) and 2-[(6,6-dimethylbicyclo[3.1.1]hept-2-ylmethyl)dimethylsilyl]-3-trimethylsilyl-1*H*-indene (12): To **1** (3.3786 g, 10.9 mmol) in tetrahydrofuran (40 mL) at 0 °C was added *n*BuLi (2.5 M in *n*-hexane, 4.4 mL, 11.0 mmol). The orange solution was stirred at room temperature for 3 h and to this solution was added dropwise chlorodimethylsilane (1.4 mL, 10.9 mmol) in tetrahydrofuran (10 mL) at 0 °C. The resulting brownish-orange reaction mixture was stirred at room temperature for 1.5 h before saturated aqueous NH_4Cl solution (50 mL) was added. The layers formed were separated and the aqueous layer was further extracted with diethyl ether (30 mL). The combined organic layers were dried with Na_2SO_4, filtered and the solvents evaporated to dryness. The crude product was purified with silica gel column chromatography using hexane as eluent providing 2.9362 g (71%) of a mixture of **11a/11b** (a mixture of two diastereomers) and **12** as an orange oil. The chemical shifts are largely overlapping both in the ^{1}H NMR and in the ^{13}C NMR spectrum. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 7.53–6.70 (m, 14 H, arom. CH in six-membered ring and olefinic CH in five-membered ring in **11a**, **11b** and **12**), 3.77–3.49 (m, 4 H, aliph. CH in five-membered ring in **11a**, **11b** and **12**), 2.06–1.30 (m, 27 H, aliph. CH in pinenyl ring in **11a**, **11b** and **12**), 1.20 (m, 9 H, CH_3 in pinenyl ring in **11a**, **11b** and **12**), 0.95–0.77 (m, 15 H, CH_3 in pinenyl ring in **11a**, **11b** and **12** and bridging CH between Si and pinenyl ring in **11a**, **11b** and **12**), 0.32 (m, 18 H, CH_3 attached to Si in **11a**, **11b** and **12**), 0.05 (m, 27 H, CH_3 attached to Si in **11a**, **11b** and **12**) ppm. ^{13}C NMR (150.9 MHz, $CDCl_3$, 25 °C): δ = 151.09, 150.95, 149.14, 148.99, 144.83 (10 overlapping C_q in **11a**, **11b** and **12**), 140.26–140.07 and 124.77–120.78 (12 arom. CH in six-membered ring and 2 olefinic CH in five-membered ring in **11a**, **11b** and **12**), 51.21–48.71 (aliph. CH in pinenyl ring in **11a**, **11b** and **12**), 40.77–40.64 (aliph. CH in pinenyl ring in **11a**, **11b** and

12), 39.68–39.58 (C_q in **11a**, **11b** and **12**), 31.39–30.65 (aliph. CH in pinenyl ring in **11a**, **11b** and **12**), 27.04 (CH_3 in pinenyl ring in **11a**, **11b** and **12**), 24.93–22.79 (aliphtic CH in pinenyl ring in **11a**, **11b** and **12**), 20.17–20.08 (CH_3 in pinenyl ring in **11a**, **11b** and **12**), 0.74 – (–2. 42) (CH_3 attached to Si in **11a**, **11b** and **12**) ppm. EIMS (70 eV) calcd. for $C_{24}H_{38}Si_2$ 382.2512, found 382.2510.

Mixture of [2-({[(1*S*,2*S*5*S*)-6,6-Dimethylbicyclo[3.1.1]hept-2-yl]-methyl}dimethylsilyl)indenyl]titanium Trichloride (13) and [1-(Trimethylsilyl)indenyl]titanium Trichlorides (14a and 14b): To a solution of a mixture of **11a**, **11b** and **12** (0.6153 g, 1.6 mmol) in dichloromethane (4 mL) at –78 °C was added $TiCl_4$·DCM (1.6 mL, 1.6 mmol) in drops. The resulting dark red reaction mixture was gradually warmed to room temperature and after stirring the reaction mixture at room temperature for 19 h the solvent was removed. The reaction product was crystallized from *n*-pentane at –78 °C yielding a 1:1:1 mixture of **13**, **14a** and **14b** as a black solid. ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): δ = 7.79 (m, 6 H, arom. CH in **13** and/or **14a** and/or **14b**), 7.51 (m, 6 H, arom. CH in **13** and/or **14a** and/or **14b**), 7.37 (6 H, olefinic CH in five-membered ring in **13**, **14a** and **14b**), 2.12 (m, 1 H, aliph. CH in pinenyl ring in **13**), 1.99 (m, 1 H, aliph. CH in pinenyl ring in **13**), 1.84 (m, 1 H, aliph. CH in pinenyl ring in **13**), 1.75 (m, 2 H, aliph. CH in pinenyl ring in **13**), 1.87 (m, 3 H, aliph. CH in pinenyl ring in **13**), 1.33 (m, 1 H, aliph. CH in pinenyl ring in **13**), 1.12 (s, 3 H, CH_3 in pinenyl ring in **13**), 0.85 (m, 2 H, bridging CH_2 between Si and pinenyl ring in **13**), 0.76 (s, 3 H, CH_3 in pinenyl ring in **13**), 0.46 (m, 24 H, CH_3 attached to Si in **13**, **14a** and **14b**).

Mixture of Diastereomeric Mixtures of 3-[(6,6-Dimethylbicyclo[3.1.1]hept-2-ylmethyl)dimethylsilyl]-1-trimethylsilyl-1*H*-indenes (15a/15b) and 1-[(6,6-Dimethylbicyclo[3.1.1]hept-2-ylmethyl)dimethylsilyl]-3-trimethylsilyl-1*H*-indenes (16a/16b): To a diastereomeric mixture of 1-[dimethyl(7,7-dimethylnorpinanylmethyl)silyl]indene (**4a**/**4b**) (2.9742 g, 9.6 mmol) in tetrahydrofuran (30 mL) at 0 °C was added *n*BuLi (2.5 M in *n*-hexane, 3.9 mL, 9.7 mmol). The orange solution was stirred at room temperature for 3 h and to this solution was added dropwise chlorodimethylsilane (1.3 mL, 9.6 mmol) in tetrahydrofuran (8 mL) at 0 °C. The resulting yellowish-brown reaction mixture was stirred at room temperature for 1.5 h before saturated aqueous NH_4Cl solution (50 mL) was added. The layers formed were separated and the aqueous layer was further extracted with diethyl ether (30 mL). The combined organic layers were dried with Na_2SO_4, filtered and the solvents evaporated to dryness. The crude product was purified with silica gel column chromatography using hexane as eluent providing 2.3547g (76%) of a mixture of the diastereomeric mixtures **15a**/**15b** and **16a**/**16b** as an orange oil. The chemical shifts are largely overlapping both in the ^{1}H NMR and in the ^{13}C NMR spectrum. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 7.56–7.18 (m, 16 H, arom. CH in **15a**, **15b**, **16a** and **16b**), 6.93–6.67 (m, 4 H, olefinic CH in five-membered ring in **15a**, **15b**, **16a** and **16b**), 3.62–3.43 (m, aliph. CH in five-membered ring in **15a**, **15b**, **16a** and **16b**), 2.23–1.30 (m, 36 H, aliph. CH in pinenyl ring in **15a**, **15b**, **16a** and **16b**), 1.16 (m, 12 H, CH_3 in pinenyl ring in **15a**, **15b**, **16a** and **16b**), 0.83 (m, 8 H, CH_2 bridging between Si and pinenyl ring in **15a**, **15b**, **16a** and **16b**), 0.78 (m, 12 H, CH_3 in pinenyl ring in **15a**, **15b**, **16a** and **16b**), 0.33 (m, 24 H, CH_3 attached to Si in **15a**, **15b**, **16a** and **16b**), –0.04 (m, 36 H, CH_3 attached to Si in **15a**, **15b**, **16a** and **16b**) ppm. ^{13}C NMR (150.9 MHz, $CDCl_3$, 25 °C): δ = 147.65, 146.58, 141.57 (12 overlapping C_q in **15a**, **15b**, **16a** and **16b**), 145.73–145.58 (4 overlapping olefinic CH in five-membered ring in **15a**, **15b**, **16a** and **16b**), 124.88–121.13 (16 overlapping aromatic CH in **15a**, **15b**, **16a** and **16b**), 49.48–46.44, 40.81–40.74, 31.50–31.14 (16 overlapping aliph. CH in five-membered ring and in pinenyl ring in **15a**, **15b**, **16a** and **16b**), 39.69 (4 C_q in pinenyl ring in **15a**, **15b**, **16a** and **16b**), 27.07 (4 CH_3 in pinenyl ring in **15a**, **15b**, **16a** and **16b**), 25.89–22.56 (12 overlapping CH_2 in pinenyl ring in **15a**, **15b**, **16a** and **16b**), 20.18 (4 CH_3 in pinenyl ring in **15a**, **15b**, **16a** and **16b**), –0.66 – (–3.09) (20 overlapping CH_3 attached to Si in **15a**, **15b**, **16a** and **16b**). EIMS (70 eV) calcd. for $C_{24}H_{38}Si_2$ 382.2512, found 382.2518.

Mixture of {1-{{[(1*S*,2*S*5*S*)-6,6-Dimethylbicyclo[3.1.1]hept-2-yl]-methyl}dimethylsilyl}indenyl}titanium Trichloride (17a and 17b) and [1-(Trimethylsilyl)indenyl]titanium Trichlorides (14a and 14b): To a solution of a mixture of **15a**, **15b**, **16a** and **16b** (0.6045 g, 1.6 mmol) in dichloromethane (4 mL) at –78 °C was added $TiCl_4$·DCM (1.6 mL, 1.6 mmol) in drops. The resulting dark red reaction mixture was gradually warmed into room temperature and after stirring the reaction mixture at room temperature for 19 h the solvent was removed. The crude product was analyzed with ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 7.90, 7.82, 7.57, 7.46, 7.38, 7.22 (m, 12 H, overlapping signals from aromatic CH in **17a** and **17b** and olefinic CH in five-membered ring in **17a** and **17b**), 7.82 (m, 4 H, arom. CH in **14a** and **14b**), 7.53 (m, 4 H, arom. CH in **14a** and **14b**), 7.38 (m, 4 H, olefinic CH in five-membered ring in **14a** and **14b**), 2.21–1.24 (m, 18 H, overlapping signals from aliph. CH in pinenyl ring in **17a** and **17b**), 1.18 (s, 3 H, CH_3 in pinenyl ring in **17a** or **17b**), 1.12 (m, 3 H, CH_3 in pinenyl ring in **17a** or **17b**), 0.88 (m, 4 H, bridging CH_2 between Si and pinenyl ring in **17a** or **17b**), 0.82 (s, 3 H, CH_3 in pinenyl ring in **17a** or **17b**), 0.73 (m, 3 H, CH_3 in pinenyl ring in **17a** or **17b**), 0.52 (m, 24 H, CH_3 attached to Si in **17a**, **17b**, **14a** and **14b**), 0.40 (m, 6 H, CH_3 attached to Si in **17a** and **17b**) ppm.

(6,6-Dimethylbicyclo[3.1.1]hept-2-en-2-ylmethyl)-(1*H*-inden-2-yl)dimethylsilane (22): To α-pinene potassium salt (4.4 mmol) in α-pinene (2.1 mL, 13.1 mmol) were added THF (2 mL) and 2-(chlorodimethylsilyl)indene (**21**) (0.9141g, 4.4 mmol) in THF (2 mL) at –72 °C. The resulting brown reaction mixture was taken into room temperature and stirred for 1 h before saturated aqueous NH_4Cl solution (50 mL) was added. The layers formed were separated and the aqueous layer was further extracted with diethyl ether (30 mL). The combined organic layers were dried with Na_2SO_4, filtered and the solvents evaporated. The excess α-pinene was separated from the crude product by distillation under reduced pressure. The residue was further purified with silica gel column chromatography using hexane as eluent providing 0.0378 g (3%) of **22** as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 7.49 (m, 1 H, arom. CH), 7.41 (m, 1 H, arom. CH), 7.28 (m, 1 H, arom. CH), 7.19 (m, 1 H, arom. CH), 7.12 (m, 1 H, olefinic CH in five-membered ring), 5.06 (m, 1 H, olefinic CH in pinenyl ring), 3.46 (m, 2 H, aliph. CH_2 in pinenyl ring), 2.35 (m, 1 H, aliph. CH in pinenyl ring), 2.22 (m, 2 H, 2 aliph. CH in pinenyl ring), 2.06 (m, 1 H, aliph. CH in pinenyl ring), 1.93 (m, 1 H, aliph. CH in pinenyl ring), 1.77 (d, *J* = 14.9 Hz, 1 H, aliph. CH between Si and pinenyl ring), 1.61 (d, *J* = 14.9 Hz, 1 H, aliph. CH between Si and pinenyl ring), 1.25 (s, 3 H, CH_3 in pinenyl ring), 1.18 (d, *J* = 9.1 Hz, 1 H, aliph. CH in pinenyl ring), 0.88 (s, 3 H, CH_3 in pinenyl ring), 0.24 (s, 3 H, CH_3 attached to Si), 0.23 (s, 3 H, CH_3 attached to Si) ppm. ^{13}C NMR (150.9 MHz, $CDCl_3$, 25 °C): δ = 148.60 (C_q), 146.92 (C_q), 145.76 (C_q), 145.22 (C_q), 141.16 (olefinic CH in five-membered ring), 126.37 (arom. CH), 124.83 (arom. CH), 123.77 (arom. CH), 120.95 (arom. CH), 114.69 (olefinic CH in pinenyl ring), 48.27 (aliph. CH in pinenyl ring), 42.67 (aliph. CH_2 in five-membered ring), 40.68 (aliph. CH in pinenyl ring), 38.07 (C_q), 31.96 (aliph. CH_2 in pinenyl ring), 31.52 (aliph. CH_2 in pinenyl ring), 27.33 (aliph. CH_2 between Si and pinenyl ring), 26.63 (CH_3 in pinenyl), 21.42 (CH_3 in pinenyl), –2.06 (CH_3 attached to Si), –2.23 (CH_3 attached to Si) ppm.

^{29}Si NMR (119.3 MHz, $CDCl_3$, 25 °C): δ = –9.39 ppm. EIMS (70 eV) calcd. for $C_{21}H_{28}Si$ 308.1960, found 308.1965.

Mixture of a Diastereomeric Mixture of (6,6-Dimethylbicyclo[3.1.1]hept-2-en-2-ylmethyl)-(1*H*-inden-1-yl)dimethylsilanes (24a/24b) and (6,6-Dimethylbicyclo[3.1.1]hept-2-en-2-ylmethyl)-(3*H*-inden-1-yl)dimethylsilane (25): To α-pinene potassium salt (20.6 mmol) in α-pinene (9.8 mL, 62.0 mmol) were added THF (20 mL) and a diastereomeric mixture of 1-(chlorodimethylsilyl)indenes (**23a/23b**) (0.9141g, 4.4 mmol) in THF (40 mL) at –72 °C. The resulting dark brown reaction mixture was taken into room temperature and stirred there for 2 h before saturated aqueous NH_4Cl solution (70 mL) was added. The layers formed were separated and the aqueous layer was further extracted with diethyl ether (50 mL). The combined organic layers were dried with Na_2SO_4, filtered and the solvents evaporated. The residue was purified with silica gel column chromatography using hexane as eluent. The obtained yellow oil still contained some α-pinene, which was separated by distillation under reduced pressure. The yellow residue provided 1.3523 g (21%) of a mixture of diastereomers **24a/24b** and **25**. The amount of the minor product **25** was 15%. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 7.67 (m, 1 H, arom CH in **25**), 7.62 (m, 5 H, arom. CH in **24a**, **24b** and **25**), 7.43 (m, 1 H, arom. CH in **25**), 7.39 (m, 2 H, arom. CH in **24a** and **24b** or 2 arom. CH in **24a** or **24b**), 7.32 (m, 3 H, arom. CH in **24a** and **24b** or 2 arom. CH in **24a** or **24b** and arom. CH in **25**), 7.07 (m, 2 H, olefinic CH in five-membered ring in **24a** and **24b**), 6.90 (m, 1 H, olefinic CH in five-membered ring in **25**), 6.81 (m, 2 H, olefinic CH in five-membered ring in **24a** and **24b**), 5.22 (m, 3 H, olefinic CH in pinenyl ring in **24a**, **24b** and **25**), 3.71 (m, 2 H, aliph. CH in five-membered ring in **24a** and **24b**), 3.54 (m, 2 H, aliph. CH_2 in five-membered ring in **25**), 2.51 (m, 2 H, aliph. CH in pinenyl in **24a** and **24b**), 2.46 (m, 1 H, aliph. CH in pinenyl in **25**), 2.39 (m, 4 H, aliph. CH_2 in pinenyl in **24a** and **24b**), 2.23 (m, 2 H, aliph. CH in pinenyl in **24a** and **24b**), 2.05 (m, 3 H, aliph. CH in pinenyl in **24a** and **24b** and aliph. CH between Si and pinenyl ring in **25**), 1.86 (m, 1 H, aliph. CH between Si and pinenyl ring in **25**), 1.76 (d, J = 13.5 Hz, 1 H, aliph. CH between Si and pinenyl ring in **24a** or **24b**), 1.71 (d, J = 13.5 Hz, 1 H, aliph. CH between Si and pinenyl ring in **24a** or **24b**), 1.59 (d, J = 13.5 Hz, 1 H, aliph. CH between Si and pinenyl ring in **24a** or **24b**), 1.53 (d, J = 13.5 Hz, 1 H, aliph. CH between Si and pinenyl ring in **24a** or **24b**), 1.42 (s, 9 H, CH_3 in pinenyl ring **24a**, **24b** and **25**), 1.35 (m, 4 H, 2 aliph. CH in pinenyl ring in **24a** and **24b**), 1.06 (s, 9 H, CH_3 in pinenyl ring **24a**, **24b** and **25**), 0.49 (s, 6 H, CH_3 attached to Si in **25**), 0.13 (s, 3 H, CH_3 attached to Si in **24a** or **24b**), 0.10 (s, 3 H, CH_3 attached to Si in **24a** or **24b**), 0.04 (s, 3 H, CH_3 attached to Si in **24a** or **24b**), 0.01 (s, 3 H, CH_3 attached to Si in **24a** or **24b**). Almost all signals from the aliph. protons in pinenyl ring (except signal from one CH) in **25** are overlapping with signals from **24a/24b** and the chemical shifts of these overlapping signals are not listed here ppm. ^{13}C NMR (150.9 MHz, $CDCl_3$, 25 °C): δ = 148.11 (C_q in **25**), 145.34 (C_q in **24a** or **24b**), 145.30 (C_q in **24a** or **24b**), 145.11 (C_q in **25**), 144.73 (C_q in **24a** or **24b**), 144.67 (C_q in **24a** or **24b** and olefinic CH in five-membered ring in **25**), 144.60 (C_q in **25**), 144.53 (C_q in **25**), 144.33 (C_q in **24a** or **24b**), 144.27 (C_q in **24a** or **24b**), 135.60 (olefinic CH in five-membered ring in **24a** and **24b**), 129.12 (olefinic CH in five-membered ring in **24a** or **24b**), 129.09 (olefinic CH in five-membered ring in **24a** or **24b**), 126.16 (arom. CH in **25**), 124.92 (arom. CH in **24a** and **24b**), 124.36 (arom. CH in **25**), 123.83 (arom. CH in **25**), 123.77 (arom. CH in **24a** and **24b**), 122.87 (arom. CH in **24a** and **24b**), 122.16 (arom. CH in **25**), 121.17 (arom. CH in **24a** and **24b**), 115.13 (olefinic CH in pinenyl ring in **24a** and **24b**), 114.72 (olefinic CH in pinenyl ring in **25**), 48.25 (aliph. CH in pinenyl ring in **24a** or **24b**), 48.20 (aliph. CH in pinenyl ring in **24a** or **24b**), 45.73 (aliph. CH in five-membered ring in **24a** or **24b**), 45.72 (aliph. CH in five-membered ring in **24a** or **24b**), 40.86 (aliph. CH_2 in five-membered ring in **25**), 40.65 (aliph. CH in pinenyl ring in **24a** or **24b**), 40.63 (aliph. CH in pinenyl ring in **24a** or **24b**), 38.00 (C_q in **24a** and **24b**), 37.97 (C_q in **25**), 31.97 (aliph. CH_2 in pinenyl ring in **24a** or **24b**), 31.94 (aliph. CH_2 in pinenyl ring in **24a** or **24b**), 31.56 (aliph. CH_2 in pinenyl ring in **24a** and **24b**), 26.85 (aliph. CH_2 between Si and pinenyl ring in **25**), 26.61 (CH_3 in pinenyl ring in **24a**, **24b** and **25**), 25.85 (aliph. CH_2 between Si and pinenyl ring in **24a** or **24b**), 25.79 (aliph. CH_2 between Si and pinenyl ring in **24a** or **24b**), 21.41 (CH_3 in pinenyl ring in **24a**, **24b** and **25**), –2.10 (CH_3 attached to Si in **25**), –2.45 (CH_3 attached to Si in **25**), –3.56 (CH_3 attached to Si in **24a** or **24b**), –3.65 (CH_3 attached to Si in **24a** or **24b**), –3.88 (CH_3 attached to Si in **24a** or **24b**), –3.97 (CH_3 attached to Si in **24a** or **24b**). Almost all signals from the aliph. carbons in pinenyl ring (except signal from quaternary carbon) in **25** are overlapping with signals from **24a/24b** and the chemical shifts of these overlapping signals are not listed here ppm. ^{29}Si NMR (119.3 MHz, $CDCl_3$, 25 °C): δ = 3.13 (Si in **24a** or **24b**), 3.09 (Si in **24a** or **24b**), –10.08 (Si in **25**) ppm. EIMS (70 eV) calcd. for $C_{21}H_{28}Si$ 308.1960, found 308.1965.

Dehydropolymerization of Phenylsilane. General Procedure: A tube was charged with 1 mol-% of the metallocene catalyst, evacuated and backfilled with argon. Phenylsilane was added by syringe and the reaction mixture was degassed three times. The catalyst was activated at room temperature by addition of 2 mol-% of *n*BuLi. The reaction mixture was stirred at room temperature for 24 h. The formed viscous solution was dissolved in tetrahydrofuran and filtered through kiselguhr. The filtrate was concentrated in vacuo to leave the polysilane. The polymer obtained was analyzed by GC-MS, ^{1}H NMR, ^{29}Si{^{1}H} NMR and GPC.

Polymerization of Phenylsilane with [Cp_2ZrCl_2]: By applying the general procedure, [Cp_2ZrCl_2] (0.0111 g, 0.04 mmol), *n*BuLi (31 µL, 0.08 mmol) and phenylsilane (480 µL, 3.86 mmol) gave 0.41 g (98%) of polysilane as a yellow, highly viscous oil.

Polymerization of Phenylsilane with 2: By applying the general procedure, **2** (0.0943 g, 0.12 mmol), *n*BuLi (97 µL, 0.24 mmol) and phenylsilane (1.5 mL, 12.1 mmol) gave 1.26 g (97%) of polysilane as a yellow oil.

Polymerization of Phenylsilane with 3: By applying the general procedure, **3** (0.060 g, 0.08 mmol), *n*BuLi (62 µL; 0,16 mmol) and phenylsilane (950 µL, 7.64 mmol) gave 0.38 g (46%) of polysilane as a pale yellow oil.

Polymerization of Phenylsilane with (*pR*)(*pS*)-5c: By applying the general procedure, (*pR*)(*pS*)-**5c** (0.0261 g, 0.03 mmol), *n*BuLi (27 µL, 0.07 mmol) and phenylsilane (420 µL, 3.34 mmol) gave 0.33 g (90%) of polysilane as a yellow oil.

Polymerization of Phenylsilane with (*pR*)(*pS*)-6c: By applying the general procedure, (*pR*)(*pS*)-**6c** (0.0125 g, 0.02 mmol), *n*BuLi (13 µL, 0.03 mmol) and phenylsilane (198 µL, 1.59 mmol) gave 0.04 g (25%) of polysilane as a yellow oil.

Polymerization of Ethylene and Propylene: The olefin polymerization reactions were performed in a steel reactor rinsed with 200 mL of a 0.3% methylaluminoxane (MAO) solution in toluene prior to use. After evacuation of the steel reactor, 200 mL of dry toluene was cannulated in. MAO was added to the reactor by syringe. The system was saturated with the gas (monomer) and after complete saturation and thermal equilibrium of the system (50 °C) the polymerization was started by adding the prepared catalyst solution (in toluene) to the reactor. Gas (monomer) was continuously added and the pressure was kept constant during the polymerization reaction and the gas consumption was monitored. The polymerization was quenched by adding the reaction mixture to a dilute hydrochloric acid/methanol mixture. The produced polyethylene, which was insoluble in toluene, was washed with a dilute hydrochloric acid/methanol mixture, filtered, washed further with methanol, filtered and dried at 60 °C overnight. The polypropylene produced was mixed with a dilute hydrochloric acid/methanol mixture and the formed layers were separated and the polypropylene was further washed two times with methanol. The oily polypropylene obtained was dried under vacuum.

Methyl- and Ethyl- Carboalumination of 1-Octene. General Procedure: In a glove box, trimethylaluminum or triethylaluminum was placed in a reaction vessel followed by addition of a catalyst solution in dichloromethane (3 mL) under argon atmosphere. To this mixture was then added 1-octene and the reaction mixture was stirred at room temperature for 19 h. After cooling to 0 °C, oxygen was bubbled through the solution until all volatiles were evaporated. The resulting yellow oil was treated with 15% aqueous NaOH solution and extracted with diethyl ether (40 mL). The organic layer was dried with $NaSO_4$, filtered and the solvents evaporated to dryness. The crude product was purified by silica gel column chromatography (eluent: 1:1 diethyl ether/hexane).

Synthesis of 2-Methyl-1-octanol Using 2 or (*pR*)(*pS*)-5c: By applying the general procedure, 1-octene (157 µL, 1 mmol), trimethylaluminum (96 µL, 1 mmol) and **2** (0.0623 g, 0.08 mmol) or (*pR*)(*pS*)-**5c** (0.0623 g, 0.08 mmol) gave after purification by column chromatography 2-methyl-1-octanol as a colorless oil in 8% (11.7 mg) and 18% (26.2 mg) yields, respectively. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 3.49 (m, 1 H, CH next to OH), 3.40 (m, 1 H, CH next to OH), 2.03 (br. s, 1 H, OH), 1.60 (m, 1 H, CH), 1.38 (m, 2 H, 2 CH), 1.25 (m, 7 H, 3 CH_2 and CH), 1.08 (m, 1 H, CH), 0.90 (d, *J* = 6.7 Hz, 3 H, CH_3), 0.86 (t, *J* = 6.9 Hz, 3 H, CH_3) ppm. ^{13}C NMR (150.9 MHz, $CDCl_3$, 25 °C): δ = 68.64 (CH_2–OH), 35.98 (CH), 33.23 (CH_2), 31.96 (CH_2), 29.71 (CH_2), 27.04 (CH_2), 22.88 (CH_2), 16.69 (CH_3), 14.29 (CH_3). EIMS (30eV) calcd. for $C_{19}H_{20}O$ 144.1514, found 144.1499 (reaction using **2**), found 144.1487 (reaction using (*pR*)(*pS*)-**5c**). Enantiomeric excesses were determined from the ^{1}H NMR spectra of the esters formed with (*S*)-(+)-MTPA-Cl using a literature procedure.[54] For the reaction catalyzed by complex **2**: *ee* = 0.5%, $[\alpha]_D^{24}$ = +0.09 (*c* = 0.0117 g/mL $CHCl_3$). For the reaction catalyzed by (*pR*)(*pS*)-**5c**: *ee* = 3%, $[\alpha]_D^{24}$ = –0.6 (*c* = 0.0120 g/mL $CHCl_3$).

Synthesis of 2-Ethyl-1-octanol Using 2 or (*pR*)(*pS*)-5c: By applying the general procedure, 1-octene (157 µL, 1 mmol), triethylaluminum (137 µL, 1 mmol) and **2** (0.0623 g, 0.08 mmol) or (*pR*)(*pS*)-**5c** (0.0623 g, 0.08 mmol) gave after purification by column chromatography 2-ethyl-1-octanol as a colorless oil in 11% (16.8 mg) and 16% (26.0 mg) yields, respectively. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 3.54 (m, 2 H, CH_2 next to OH), 1,37 (m, 3 H, CH and CH_2 in ethyl), 1,27 (m, 11 H, 5 CH_2 and OH), 0,88 (m, 6 H, 2 CH_3) ppm. ^{13}C NMR (150.9 MHz, $CDCl_3$, 25 °C): δ = 65.55 (CH_2–OH), 42.24 (CH), 32.03 (CH_2), 30.62 (CH_2), 29.89 (CH_2), 27.02 (CH_2), 23.48 (CH_2 in ethyl), 22.82(CH_2), 14.30 (CH_3 in ethyl), 11.58 (CH_3). EIMS (30eV) calcd. for $C_{10}H_{22}O$ 158.1671, found 158.1639 (reaction using **2**), found 158.1655 (reaction using (*pR*)(*pS*)-**5c**). Enantiomeric excesses were determined from the ^{1}H NMR spectra of the esters formed with (*S*)-(+)-MTPA–Cl using a literature procedure.[54] For the reaction catalyzed by complex **2**: *ee* = 10%, $[\alpha]_D^{24}$ = +0.48 (*c* = 0.00084 g/mL $CHCl_3$). For the reaction catalyzed by (*pR*)(*pS*)-**5c**: *ee* = 5%, $[\alpha]_D^{24}$ = –0.18 (*c* = 0.0109 g/mL $CHCl_3$).

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