Heteroatom-Substituted Group 4 Bis(indenyl)metallocenes

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The synthesis, characterization and applications of heteroatom-substituted group 4 bis(indenyl)metallocene complexes is reviewed. In recent years, an increasing number of group 4 metallocenes with electronically modified cyclopentadienyl ligands have been reported with, in some cases, considerably altered catalytic properties. This microreview focuses on bis(indenyl) complexes of titanium, zirconium and hafnium that contain nitrogen, oxygen and sulfur atoms directly bonded to the five- or six-membered rings of the indenyl ligand framework. The catalytic performance is briefly reviewed, with emphasis on catalytic olefin polymerization.

Introduction

The past decades have witnessed an impressive growth in the application of group 4 metallocene complexes in homogeneous catalysis. Of particular significance is the ability of appropriately substituted bridged and unbridged bis(indenyl)-ligated complexes to stereoselectively control the microstructure of poly-α-olefins produced when activated with methylaluminoxane (MAO) or other cocatalysts.[1−6] In enantioselective synthesis, chiral group 4 bis(indenyl)metallocenes are being employed as reagents or catalysts for various applications ranging from enantioselective cyclopolymerization[7] to carbon−carbon, carbon−hydrogen, and carbon−oxygen bond formation in small molecule syntheses.[8,9] Prototypical chiral bis(indenyl) complexes are the now classic ethylene-bridged *ansa*-metallocenes **1−3** and their hydrogenated tetrahydroindenyl congeners **4−6** (Figure 1) originally described by Brintzinger and co-

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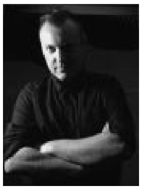

Reko Leino was born in Turku, Finland in 1969. He received his PhD (Doctor of Science in Technology) at Åbo Akademi University in 1998 with Professor Jan H. Näsman, in the field of organometallic synthesis and catalytic olefin polymerization. After a post-doctoral year at Stanford University with Professor Robert M. Waymouth in 1998-1999 working on stereocontrol in syndiospecific propylene polymerization, he briefly returned to the Laboratory of Polymer Technology, Åbo Akademi University to work on polymer-supported chiral catalysts, then for 18 months during 2001-2002 joined the Biopharmaceutical company Carbion Ltd. (later merged with Biotie Therapies Corp.) focusing on the development of carbohydrate-based pharmaceuticals. Since January 2003 he is Professor of Organic Chemistry at Åbo Akademi University with research interests ranging from synthetic organic and organometallic chemistry to polymer synthesis with current focus on stereoselective catalysis, bioorganometallic and carbohydrate chemistry.

Petri Lehmus was born in Helsinki, Finland in 1970. His interest in the polymerization behavior of single-site catalysts was inspired by his studies at Helsinki University of Technology, where he graduated as Doctor of Science in Technology from the research group of Professor Jukka V. Seppälä. Parts of his Ph.D. work were conducted in the group of Professor Bernhard Rieger at the University of Ulm, Germany. In 2000 he joined Borealis Polymers where he currently acts as research manager for Single Site Technology.

Ari Lehtonen was born in 1966. He obtained his MSc in Chemistry in 1990 from the University of Turku and his Doctorate in 1995, also at the University of Turku. During 1999 he worked as a post-doctoral fellow with Prof. Bohumil Štíbr at the Institute of Inorganic Chemistry, Academy of Sciences of the Czech Republic. Presently, he is a lecturer at the University of Turku. His current research interests include coordination chemistry of catalytically interesting high-valent metal compounds, especially molybdenum and tungsten phenoxides.

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workers 20 years ago.[10−13] In the synthesis, the ethylene-bridged C_2-symmetric complexes, together with an unwanted *meso* diastereomer, are formed as racemates, which in an optimal case may be resolved through diastereomeric derivatives to afford the individual (*R*,*R*) and (*S*,*S*) enantiomers.[10,12,14−16] Since the initial reports, a huge number of substituted chiral and achiral group 4 bis(indenyl) complexes have been prepared and studied, and the structure-property relationships, especially in catalytic olefin polymerization, are now relatively well understood.[3,17−20] An excellent review is available covering the synthesis of chiral titanocene and zirconocene dichlorides and their ligand precursors,[21] including those of the bis(indenyl) type, although, with the exclusion of heteroatom-substituted ligands and complexes. An obvious attractive feature of these catalysts is the relative ease with which variations in the ligand-substitution pattern can be carried out using standard synthetic methodology, although the catalytic performance is very often a complicated and, in many cases, inseparable combination of steric as well as electronic effects.

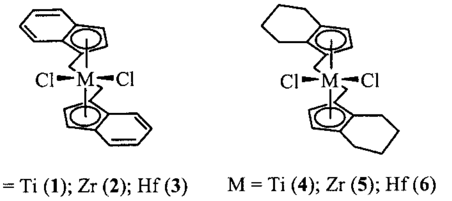

Figure 1. Racemic ethylene-bridged bis(indenyl) and bis(tetrahydroindenyl) group 4 *ansa*-metallocenes **1−6**; only one enantiomer of the racemic pair is shown

Despite the imminent possibilities, the influence of electronic modification of these systems by direct heteroatom ligand substitution has, until recently, remained less explored. This reluctance may, in part, be due to the anticipated problems associated with the combination of highly electrophilic early transition metals with heteroatom-containing substituents. In recent years, however, a large number of group 4 bis(indenyl) complexes containing oxygen, sulfur as well as nitrogen donor atoms directly bonded to the five- or six-membered rings of the indenyl ligand framework have been reported in the literature; in some cases, the catalytic properties are significantly altered. The purpose of this microreview is to cover the recent synthetic efforts towards these complexes, as well as some of their catalytic applications, with the main focus on olefin polymerization. The emphasis lies on bis(indenyl) and bis(tetrahydroindenyl) complexes of the group 4 metals (Ti, Zr, Hf) that contain N, O and S atoms directly linked to the indenyl ligand. Excluded thus from detailed discussion are complexes containing substituted or unsubstituted cyclopentadienyl, fluorenyl and related ligands, complexes with pendant heteroatom substitution where the functional group is separated from the ligand by an inert linker,[22−25] as well as complexes with directly bonded phosphorus,[26] boron,[27−29] and other heteroatom substituents. The so-called constrained-geometry linked amido-cyclopentadienyl and amido-indenyl complexes,[30,31] as well as cyclopentadienyl complexes containing fused heterocyclic ring systems[32−36] that mimic those of indenyl compounds, are excluded as well. The references have been, with a few exceptions, drawn from the authors' own work in the area and the open scientific literature.

Complex Synthesis and Characterization

Amino-Substituted Group 4 Bis(indenyl)metallocenes

An early example of an amino-substituted group 4 metallocene is the 1,1′-bis(dimethylamino)titanocene dichloride **7** reported by Boche and co-workers in 1984 (Figure 2).[37] Since the first reports by Brintzinger,[38] Näsman,[39] and Plenio groups[40] in 1996, a number of 2-amino-substituted bis(indenyl) complexes of titanium and zirconium have been described and characterized (complexes **8−16**).[41−45] Selected compounds have been collected in Figure 3. The numbering system of indene is displayed in Figure 4. Related recently reported complexes include the mixed-ligand titanocene dichloride **17** that incorporates one 2-(dimethylamino)indenyl ligand as described by Bochmann and co-workers,[46] as well as the (aminofluorenyl)zirconium complexes of Miller and Bercaw.[47] Aminocyclopentadienyl compounds have also been incorporated into the donor/acceptor group 4 metallocenes of Ostoja Starzewski, catalyst technology designed for production of thermoplastic elastomers.[48] In addition, a number of mono- and bis(2-aminoindenyl) complexes of manganese, cobalt and iron,[49−52] lithium,[53] and ruthenium[54] have been reported in recent years. Heteroatom-substituted, constrained-geometry titanium complexes including those derived from 2- and 3-aminoindenes have also been described.[55] De Rosa, Resconi and co-workers have recently reported the preparation of a series of silyl-bridged constrained-geometry *tert*-butylamido-indenyl complexes of titanium in which the indenyl ligand has a nitrogen- or sulfur-containing heterocycle condensed onto the five-membered indenyl ring.[56,57]

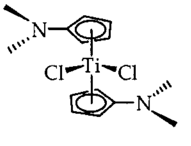

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Figure 2. 1,1′-Bis(dimethylamino)titanocene dichloride (**7**)

Syntheses of the 2-amino-substituted indenes generally follow the original procedures of Edlund,[58−61] which involve the enamine reaction of 2-indanone with a secondary amine in methanol or toluene to produce the corresponding 2-aminoindenes, typically in excellent yields (Scheme 1).[38−40,42−45,49−53] The reaction is applicable to substituted cyclopentenones and also provides access to a

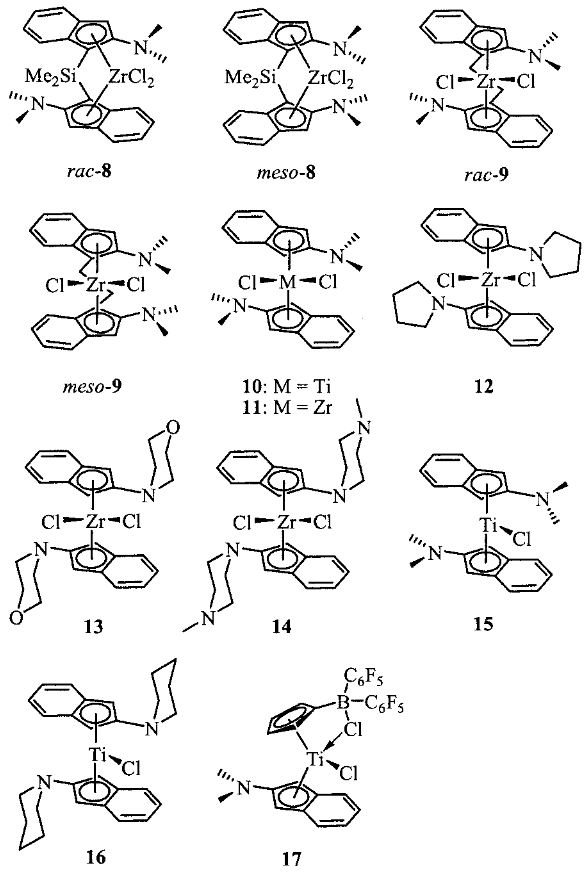


Figure 3. 2-Amino-substituted indenyl complexes of titanium and zirconium described in the literature; for racemic complexes, only one enantiomer of the racemic pair is shown

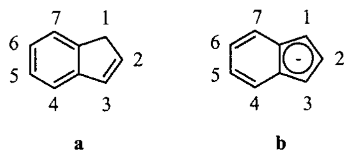
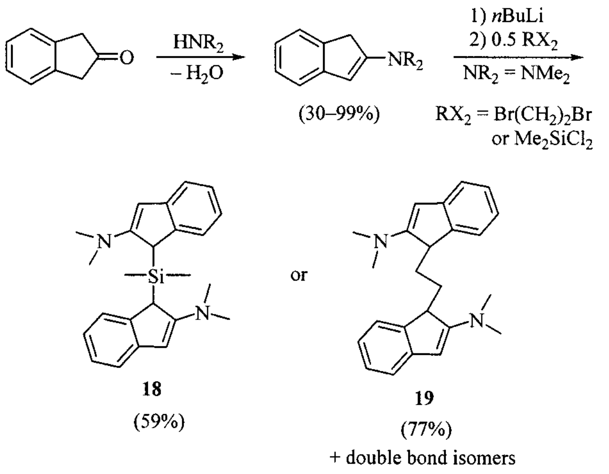


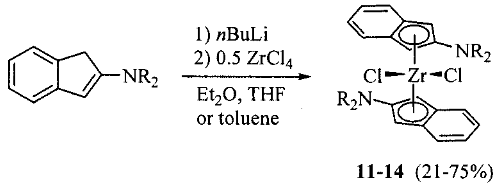
Figure 4. Numbering system for indene (**a**) and the corresponding indenyl anion (**b**)



Scheme 1. Synthesis of 2-aminoindenes and the corresponding bridged bis(indenes)

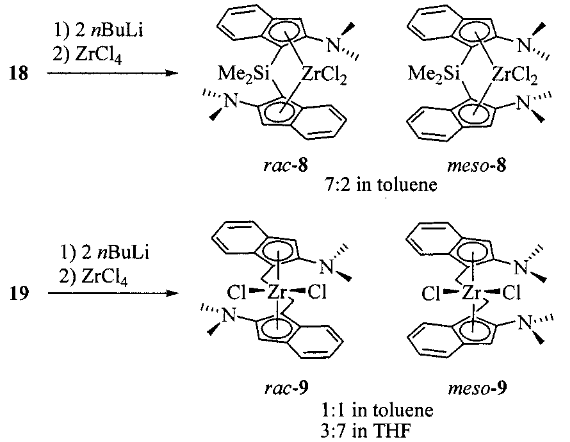
series of amino-substituted cyclopentadienes.[40,44,49,52] For 2-(dimethylamino)indene, the synthesis of both dimethylsilylene-[38] and ethylene-bridged[39] bis(indenyl) analogues **18** and **19** in good yields (59 and 77%, respectively) has been described that employs standard deprotonation/alkylation and deprotonation/silylation procedures in THF or diethyl ether solution (Scheme 1). The synthesis of 3-aminoindenes by enamine reaction of 1-indanone with secondary amines has also been reported.[55,62,63]

The syntheses of the unbridged bis(2-aminoindenyl)zirconocene dichlorides **11–14** proceed in 21–75% yields by reaction of the corresponding 2-aminoindenyllithium salts with $ZrCl_4$ in Et_2O, THF or toluene (Scheme 2) followed by standard workup and crystallization procedures.[38–40,44,45] In terms of metallation yield, toluene appears to be the preferred solvent. The bis(2-dimethylaminoindenyl)titanocene dichloride analogue **10** was obtained in a nearly quantitative yield by oxidation of the corresponding titanium(III) monochloride **15**, which in turn was prepared in over 90% yield by reaction of the 2-(dimethylamino)indenyllithium salt with $TiCl_3 \cdot 3THF$.[43] The piperidinoindenyl analogue **16** was obtained in 70% yield according to a similar procedure.[64] All zirconium complexes **11–14** have been characterized crystallographically (vide infra). The titanium(III) chlorides **15** and **16** reported by Stryker and co-workers have been further converted into a series of (η^3-allyl)titanium and titanacyclobutane complexes, several of which were characterized crystallographically[42,43] and applied in the synthesis of cyclobutanones[64] and substituted cyclobutanimines.[65]



Scheme 2. Synthesis of the unbridged bis(2-aminoindenyl)zirconium dichlorides **11–14**

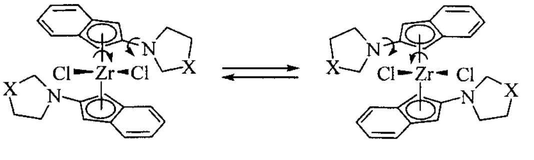
The dimethylsilylene- and ethylene-bridged bis(indenes) **18** and **19** yield, after deprotonation with *n*BuLi and subsequent reactions of the dilithium salts with $ZrCl_4$ in toluene or THF, the corresponding *ansa*-metallocene complexes **8** and **9** (see Figure 3) as mixtures of the racemic and *meso* diastereomers (Scheme 3). In the case of the dimethylsilylene-bridged complex **8**, the reaction in toluene gives a 7:2 *rac*/*meso* mixture in an overall yield of 57%, from which the pure racemic diastereomer *rac*-**8** was obtained in 30% yield by recrystallization, and was characterized crystallographically.[38] The ethylene-bridged analogue **9** in turn shows an unusual case of solvent-dependent *meso* diastereoselectivity in the metallation step, to yield a 1:1 *rac*/*meso* ratio in toluene, from which *rac*-**9** was isolated after fractional crystallization in 33% yield.[39] However, when the metallation was carried out in THF, a 3:7 *rac*/*meso* ratio was obtained from which the pure *meso* diastereomer was isolated in 38% yield.[41] Both diastereomers of **9** have been characterized crystallographically.



Scheme 3. Synthesis of the *ansa*-bis[2-(dimethylamino)indenyl]zirconocenes **8** and **9**; only one enantiomer of the racemic pair is shown

The ^{1}H and ^{13}C NMR spectra of all unbridged zirconium complexes **11−14** show time-averaged molecular C_{2v} symmetry at room temperature, consistent with rapid rotation of the aminoindenyl ligands around the Cp(centroid)−Zr axis. The ^{1}H NMR resonances of the 1-H/3-H protons in the five-membered indenyl ring range from δ = 4.42 (complex **12**) to 4.86 ppm (complex **14**); these protons are considerably shielded relative to those of the 2-hydrocarbon-substituted analogues (commonly δ ≈ 6.0−6.5 ppm), indicating increased electron density in the Cp ring induced by the electron-donating amino substituent. For the complexes **12** and **13**, a detailed 600 MHz ^{1}H NMR spectroscopic study in [D$_8$]toluene by Erker and co-workers reveals two different dynamic processes, which freeze on the NMR timescale when the monitoring temperature is lowered (Scheme 4).[44] For complex **12**, a C−N rotational barrier of $\Delta G^{\ddagger}_{(\text{CN-rot})}$ (338 K) = 16.4 ± 0.2 kcal·mol^{-1} and an activation energy for the rotation about the zirconium−Cp(indenyl) vector of $\Delta G^{\ddagger}_{(\text{Ind-rot})}$ (198 K) = 9.1 ± 0.5 kcal·mol^{-1} was determined. For the 2-morpholinoindenyl complex **13**, the corresponding values were measured as $\Delta G^{\ddagger}_{(\text{CN-rot})}$ (268 K) = 12.9 ± 0.2 kcal·mol^{-1} and $\Delta G^{\ddagger}_{(\text{Ind-rot})}$ (178 K) = 7.6 ± 0.5 kcal·mol^{-1}, indicating that, for both of these complexes, a single metallocene rotamer is present in solution at low temperature within the limits of the ^{1}H NMR detection.

In solution, racemic C_2-symmetric ethylene-bridged bis(indenyl)zirconocenes commonly rapidly interconvert between two limiting conformations, indenyl-forward (Π) and indenyl-backward (Y), which arise from the conformational freedom of the five-membered metallacycle formed by the central metal atom, bridgehead carbon atoms, and the carbon atoms of the ethylene bridge (Scheme 5).[66−68] Similarly, for the *meso* diastereomers, two chiral C_1-symmetric, equienergetic, staggered, mirror-image-limiting conformations exist that interconvert in solution through a completely eclipsed conformation (Scheme 6). Bis(indenyl) complexes having one-membered silicon or carbon bridges are considerably more rigid due to the restricted conformational freedom of the four-membered metallacycle formed by the metal atom, bridgehead carbon atoms, and the bridge.

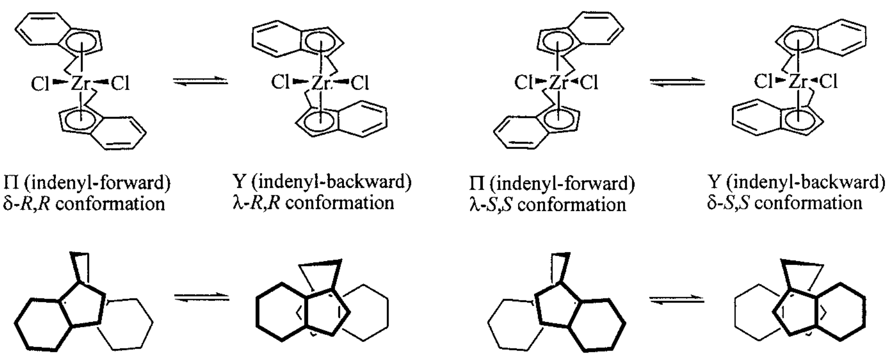


X = -CH$_2$- (**12**); -CH$_2$-O- (**13**)

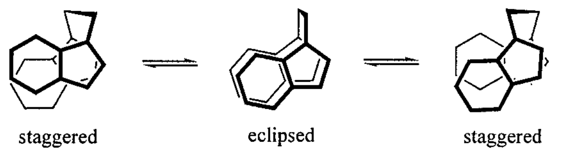
Scheme 4. Dynamic processes in unbridged bis(2-aminoindenyl)zirconium dichlorides

The ^{1}H NMR spectra of both *rac*- and *meso*-ethylene-bridged 2-dimethylamino-substituted bis(indenyl)zirconocenes *rac*-**9** and *meso*-**9** show at room temperature only one set of highly symmetric ligand resonances, which indicate rapid interconversion between the limiting conformations on the NMR time scale.[39,41] For both diastereomers, only one single resonance is observed for the aminomethyl groups indicating rapid rotation around the η^5-C−N bond as well. The β-protons in the five-membered indenyl rings of both *rac*-**9** (δ = 5.99 ppm) and *meso*-**9** (δ = 5.85 ppm) are considerably shielded relative to those of the racemic and *meso* diastereomers of the unsubstituted bis(indenyl) analogue **2** (δ = 6.58 and 6.70 ppm, respectively);[66] this is consistent with donation of electron density from the amino substituent to the Cp ring. Similarly, the β-H of the dimethylsilylene-bridged analogue *rac*-**8** (δ = 6.4 ppm) is strongly shielded relative to that of the unsubstituted racemic parent complex dimethylsilylenebis(indenyl)zirconium dichloride (δ = 6.90 ppm).[69]

Brintzinger and co-workers have reported cyclic voltammograms of the dimethylamino-substituted complexes *rac*-**8** and **11**.[38] In comparison with the unsubstituted analogues *rac*-dimethylsilylenebis(indenyl)zirconium dichloride and bis(indenyl)zirconium dichloride, an additional irreversible oxidation peak was observed at $E_{1/2} \approx 0$ V, indicating instability against oxidation. The Zr$^{\text{IV}}$/Zr$^{\text{III}}$ reduction peaks of these complexes, recorded at $E_{1/2} = -2.48$ V (*rac*-**8**) and −2.42 V (**11**), respectively, are shifted to more negative potentials by 0.28 and 0.43 V relative to the unsubstituted analogues, indicating noticeable increase in the electron density at the Zr centers of the amino-substituted complexes. The electrochemical potentials were measured at a platinum electrode against an Ag/AgNO$_3$ (satd.) reference electrode at 25 °C, with full compensation of the internal resistance (*IR*) of the electrolyte solution, and referenced against the standard potential of the ferrocene/ferrocenium couple ($E_{1/2} = -0.12$ vs. Ag/AgNO$_3$).

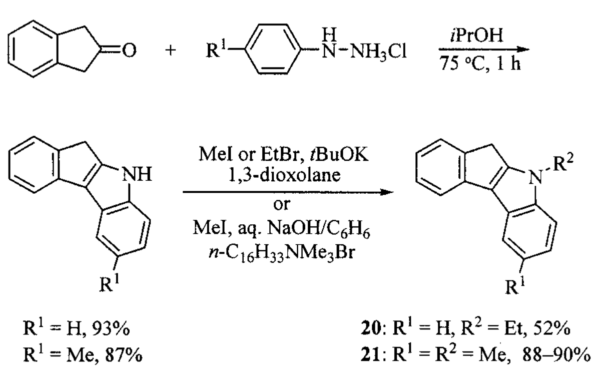


Scheme 5. Schematic presentation of the indenyl-forward/indenyl-backward interconversion for both enantiomers of the racemic ethylene-bis(indenyl)zirconium dichloride **2**



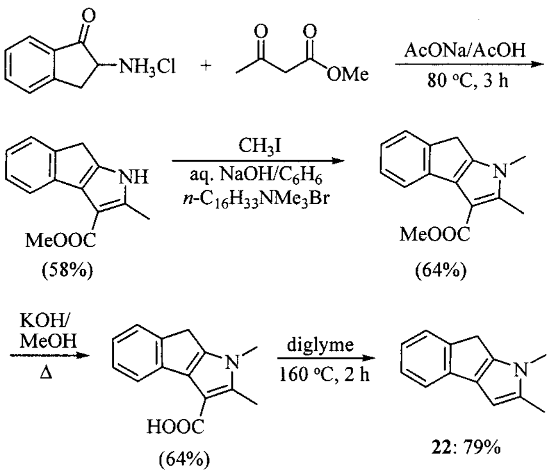
Scheme 6. Conformational freedom in the *meso* diastereomer of ethylene-bridged bis(indenyl)metallocenes

The synthesis of the indenoindole and indenopyrrole ligand precursors **20**−**22** for constrained-geometry type titanium complexes described by Resconi and co-workers are displayed in Schemes 7 and 8, respectively. The indenoindoles **20** and **21** were prepared in high yields by the acid-catalyzed Fischer condensation of 2-indanone with arylhydrazines (Scheme 7). The amines obtained were then alkylated in good yields using methyl iodide or bromoethane.[57]



Scheme 7. Synthesis of the indenoindole ligand precursors **20** and **21**

The *N*,2-dimethyldihydroindeno[2,1-*b*]pyrrole ligand precursor **22** was obtained in 25% overall yield (4 steps) by Knorr condensation between 2-aminoindanone hydrochloride and acetoacetic ester followed by *N*-alkylation, hydrolysis, and decarboxylation of carboxylic acid (Scheme 8).[57]



Scheme 8. Synthesis of the indenopyrrole ligand precursor **22**

Alkoxy-Substituted Group 4 Bis(indenyl)metallocenes

Alkoxy-substituted group 4 indenyl complexes **23**−**32** are collected in Figure 5. Detailed information on bis(indenyl) group 4 metallocenes containing direct alkoxy substitution in the five-membered Cp rings has only appeared in the patent literature. The racemic ethylene-bridged 2- and 3-methoxy-substituted zirconium complexes *rac*-**23** and *rac*-**24**[70] displayed in Figure 5 were obtained by recrystallization of the corresponding 1:1 *rac*/*meso* mixtures from toluene.[71] The 1:1 *rac*/*meso* mixtures had been obtained in 35 and 31% yields, respectively, by treating the lithiated ethylene-bridged ligand precursors with $ZrCl_4$ in THF. The syntheses of 2- and 3-methoxyindenes **33** and **34** are displayed in Scheme 9. Reaction of 1-indanone with trimethyl orthoformate in a mixture of methanol, benzene and a small amount of methanol saturated with dry hydrogen chloride yielded, after workup and distillation, a 59% yield of 3-methoxyindene.[72] A similar reaction of 2-indanone with trimethyl orthoformate in methanolic *p*-toluenesulfonic acid solution reportedly yielded 2-methoxyindene after purification by preparative GLPC, although the yield of the reaction was not described.[73][74] Subsequent deprotonation with *n*BuLi and reaction with 0.5 equiv. of dibromoethane in THF then gave the corresponding bis(methoxyindenyl)ethanes in 45 and 64% yields, respectively.[71] For the 2- and 3-methoxy-substituted zirconocene dichlorides, the five-membered ring β-protons of **23** (*rac*/*meso* mixture: 6.0/6.1 ppm) and the α-protons of **24** (*rac*/*meso* mixture: δ = 5.7/5.9 ppm) are shielded considerably relative to the corresponding β- and α-protons of the unsubstituted ethylene-bridged *rac*/*meso*-**2** (δ = 6.58/6.70 and 6.20/6.55 ppm, respectively);[66] this is consistent with increased electron density in the η^5-Cp rings. In addition to these, dimethylsilylene-bridged constrained-geometry *tert*-butylamidoindenyl complexes of titanium incorporating both 3-methoxy- and 2-ethoxyindenyl ligands have been reported in the open literature.[55] Synthesis of 2-ethoxyindene in 86% yield by reaction of 2-indanone with ethyl orthoformate in a manner similar to those reported for the 2- and 3-methoxyindenes has been described.[75]

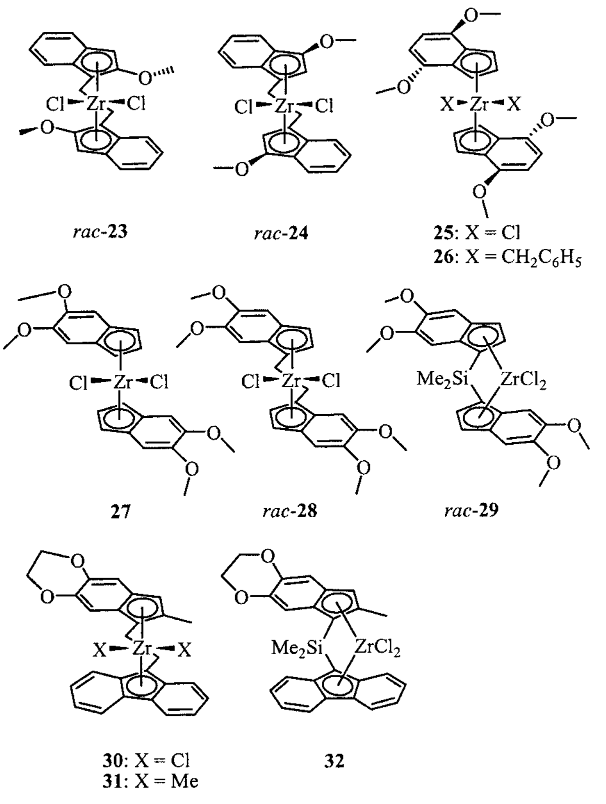
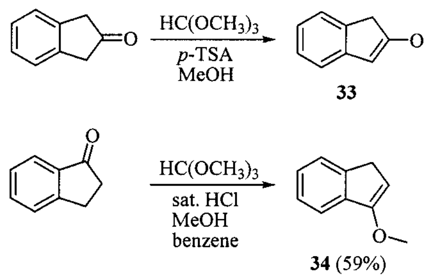
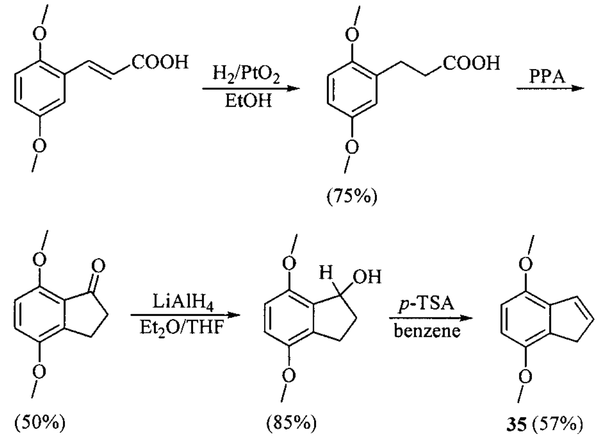


Figure 5. Alkoxy-substituted indenyl complexes of zirconium described in the literature; for racemic complexes only one enantiomer of the racemic pair is shown



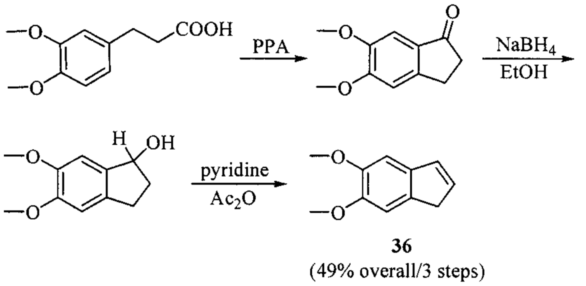
Scheme 9. Synthesis of 2- and 3-methoxyindenes (**33** and **34**)

Bis(indenyl)zirconium complexes containing alkoxy substitution in the six-membered rings of the indenyl ligand system have been reported in both the open and patent literature (complexes **25**−**29** in Figure 5).[71,76,77] Consiglio and co-workers have described the synthesis of 4,7-dimethoxyindene (**35**) in four steps and in 18% overall yield from *trans*-3-(2,5-dimethoxyphenyl)propanoic acid (Scheme 10),[76] according to a modified literature procedure.[78,79] Deprotonation of **35** with *n*BuLi and subsequent reaction with $ZrCl_4$ in THF then gave, after workup and crystallization from toluene/hexane, a 40% yield of the 4,7-dimethoxy-substituted unbridged bis(indenyl)zirconium dichloride **25**.[76] The benzyl analogue **26** was prepared in 68% yield by reaction of **25** with benzylmagnesium chloride in Et_2O followed by crystallization from toluene/hexane.



Scheme 10. Synthesis of 4,7-dimethoxyindene (**35**)

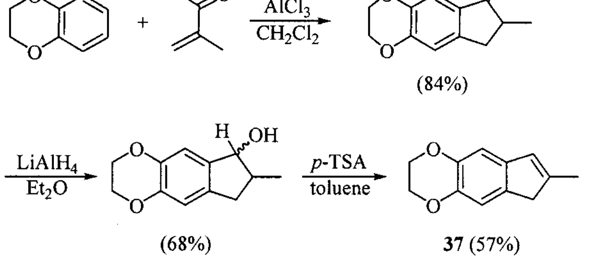
Collins and co-workers have reported the synthesis of the unbridged bis(5,6-dimethoxyindenyl)zirconium dichloride (**27**) in 35% yield by deprotonation of 5,6-dimethoxyindene (**36**) with *n*BuLi in THF followed by reaction with $ZrCl_4$ and subsequent workup and crystallization from toluene.[77] The synthesis of **36** is analogous to that of the 4,7-dimethoxy derivative **35**, which involves cyclization of 3-(3,4-dimethoxyphenyl)propanoic acid with polyphosphoric acid to the corresponding 1-indanone followed by reduction and dehydration steps to yield **36** in 49% overall yield (Scheme 11).[80] The ethylene-bridged ligand derivative was then prepared in 56% yield by reaction of the lithium derivative of **36** with dibromoethane in THF/HMPA solution.[77] Subsequent deprotonation with *n*BuLi and reaction with $ZrCl_4$ in THF gave, after workup and washing with toluene, the racemic ethylenebis(5,6-dimethoxyindenyl)zirconium dichloride (*rac*-**28**) in 24% yield.



Scheme 11. Synthesis of 5,6-dimethoxyindene (**36**)

The dimethylsilylene-bridged analogue *rac*-**29** has been reported in the patent literature only. It was obtained by deprotonation of the dimethylsilylene-bridged ligand precursor with *n*BuLi and subsequent reaction of the isolated dilithium salt with $ZrCl_4$ in CH_2Cl_2 to give, after workup and crystallization from the same solvent, a 3:1 *rac*/*meso* mixture in 35% yield.[71] The pure racemate was then obtained by recrystallization. The dimethylsilylene-bridged ligand was prepared in 55% yield according to standard procedures by lithiation of **36** with *n*BuLi followed by reaction with dichlorodimethylsilane in THF.

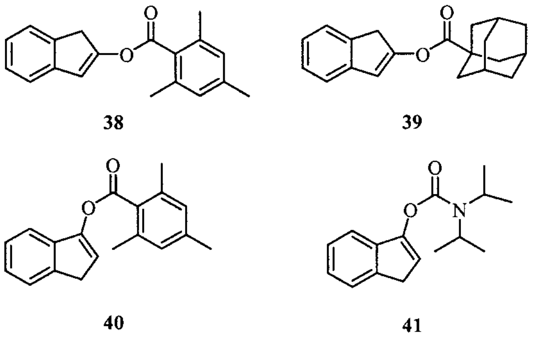
In a recent study, Rieger and co-workers have described a series of C_1-symmetric mixed-ligand *ansa*-zirconium complexes **30**−**32**, which incorporate one 2-methylindenyl ligand with a fused 5,6-ethylenedioxy substituent.[81] The 5,6-(ethylenedioxy)-2-methylindene (**37**) employed was prepared in three steps and 32% overall yield by reaction of 1,2-(ethylenedioxy)benzene with methacryloyl chloride and $AlCl_3$ followed by subsequent reduction and dehydration steps (Scheme 12). The mixed ligand complexes form, upon activation with suitable cocatalysts, active catalyst systems for production of medium-tacticity polypropylenes. A detailed discussion is outside the scope of this review.



Scheme 12. Synthesis of 5,6-(ethylenedioxy)-2-methylindene (**37**)

All unbridged methoxy-substituted zirconium complexes **25**−**27** give, at room temperature, ^{1}H NMR spectra consistent with time-averaged molecular C_{2v} symmetry and unhindered ligand rotation around the Cp(centroid)−Zr axis. The η^5-Cp ring protons of the dichloride complexes **25** (1-H/3-H: δ = 6.11 ppm; 2-H: δ = 6.30 ppm) and **24** (1-H/3-H: δ = 5.91 ppm; 2-H: δ = 6.15 ppm) are considerably less shielded relative to unsubstituted bis(indenyl)zirconium dichloride (1-H/3-H: δ = 6.20 ppm; 2-H: δ = 6.45 ppm)[76,82] than those of the unbridged 2-amino-substituted complexes **11**−**14** (vide supra). Likewise, the racemic ethylene- and dimethylsilylene-bridged complexes **28** and **29** containing methoxy substituents in the six-membered indenyl rings give resonances in their ^{1}H NMR spectra that indicate that the α-H (δ = 5.98 and 5.82 ppm, respectively) and β-H (δ = 6.45 and 6.75 ppm, respectively) atoms are less shielded than the corresponding H atoms in the 2-aminoindenyl analogues, relative to those of the unsubstituted analogues *rac*-ethylenebis(indenyl)zirconium dichloride (**2**)[66] and *rac*-dimethylsilylenebis(indenyl)zirconium dichloride[69] (α-H: δ = 6.20 and 6.08 ppm; β-H: δ = 6.58 and 6.90 ppm, respectively). In the five-membered ring, however, the electron-releasing effect of the methoxy substituent is similar to that of the amino group, as can be seen by the η^5-Cp ring proton resonances of *rac*/*meso*-**23** (β-H: δ = 6.0/6.1 ppm) and *rac*/*meso*-**24** (α-H: δ = 5.7/5.9 ppm).

In addition to alkoxy groups, sterically hindered ester groups have been incorporated at both the 2- and 3-positions of indene by some of us and others (Figure 6).[83,84] All compounds **38**−**41** can be deprotonated with *n*BuLi to generate the corresponding indenyl anions. In all cases the anions were successfully trapped by addition of chlorotrimethylsilane or iodomethane. Complexation of the ester-functionalized ligands with transition metals has, however, not been described.



38
39
40
41

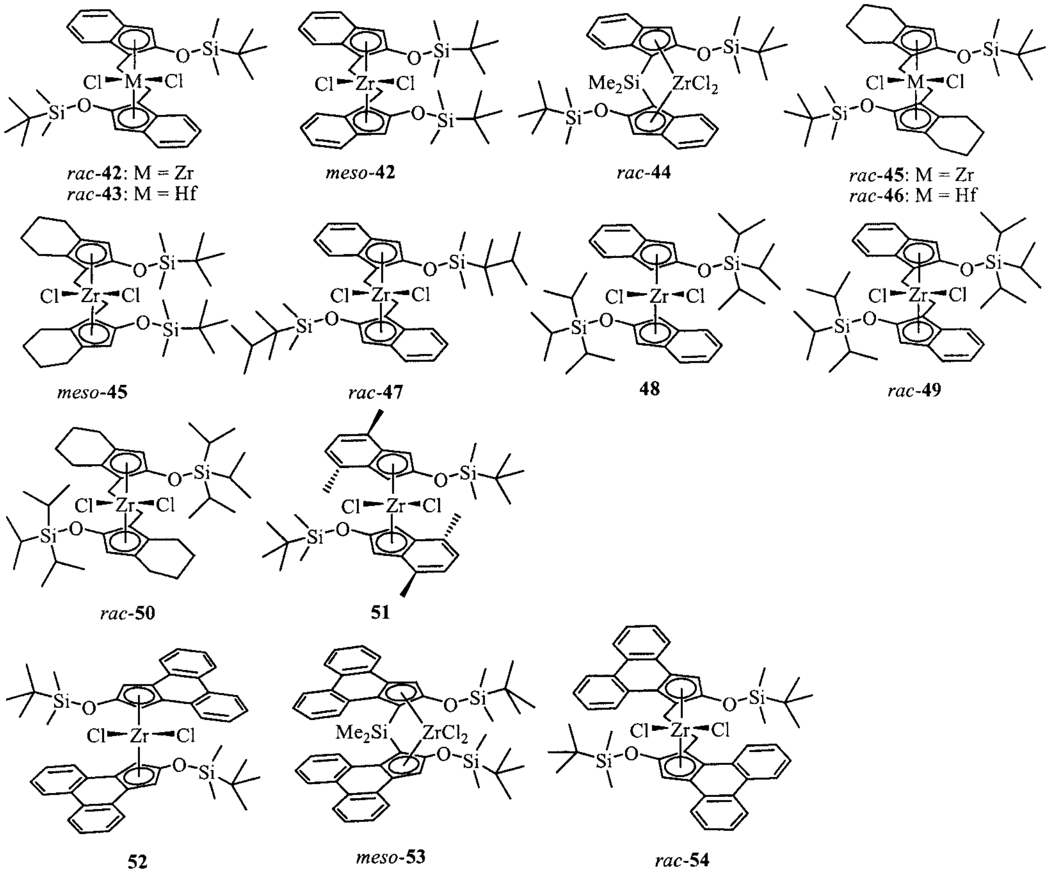
Figure 6. Ester-substituted indenes that can be deprotonated with butyllithium

Siloxy-Substituted Group 4 Bis(indenyl)metallocenes

A series of 1-(3-) and 2-trialkylsiloxy-substituted bis(indenyl) and bis(tetrahydroindenyl) complexes of zirconium and hafnium were reported by Leino, Luttikhedde, Näsman and co-workers between 1996 and 2000, with focus on the electronic effects in catalytic olefin polymerization (Figures 7 and 8).[85−97] Parts of this work have been briefly reviewed previously.[98] Prior to our work, both 2- and 3-trimethylsilylindenes had been reported in the literature;[73,99−103] however, the complexation of silyl ether substituted indenyl ligands with transition metals was undisclosed. Instead of the acid-labile and sterically less shielded trimethylsiloxy group, our initial attempts were focused on the use of the more stable *tert*-butyldimethylsilyl ether and its analogues as electron-donating indenyl ligand substituents.[104][105] The synthesis of 2-trialkyl/arylsiloxy-substituted indenes utilizing the keto-enol tautomerism of 2-indanone[73] is shown in Scheme 13. Thus, reaction of 2-indanone with *tert*-butylchlorodimethylsilane,[85] chlorodimethyl(thexyl)silane,[93] chlorotriisopropylsilane,[90] chloro(cyclohexyl)dimethylsilane,[106] and *tert*-butylchlorodiphenylsilane using the base/solvent combinations of DMF/imidazole or DBU/benzene gave the corresponding 2-siloxyindenes **64**−**68** as distillable oils in 69−90% yields. The six-membered ring substituted ligand analogues 2-(*tert*-butyldimethylsiloxy)-4,7-dimethylindene (**69**)[91] (distillable oil) and 2-(*tert*-butyldimethylsiloxy)cyclopenta[*l*]phenanthrene (**70**)[89] (powderous solid) were prepared in 85 and 72% yields, respectively, by reaction of 4,7-dimethyl-2-indanone[91] and 1,3-dihydro-2-oxocyclopenta[*l*]phenanthrene[107,108] (Scheme 14) with *tert*-butylchlorodimethylsilane/DBU in benzene. Analogously, the reaction of 1-indanone with *tert*-butylchlorodimethylsilane[92] and chlorotriisopropylsilane[90] using DBU/dichloromethane gave the corresponding 3-siloxyindenes **72** and **73** in 92 and 70% yields, respectively (Scheme 15). The 2-methyl-substituted analogue 3-(*tert*-butyldimethylsiloxy)-2-methylindene (**73**)[105] was prepared from 2-methyl-1-indanone[109] in 81% yield according to a similar procedure.[110]

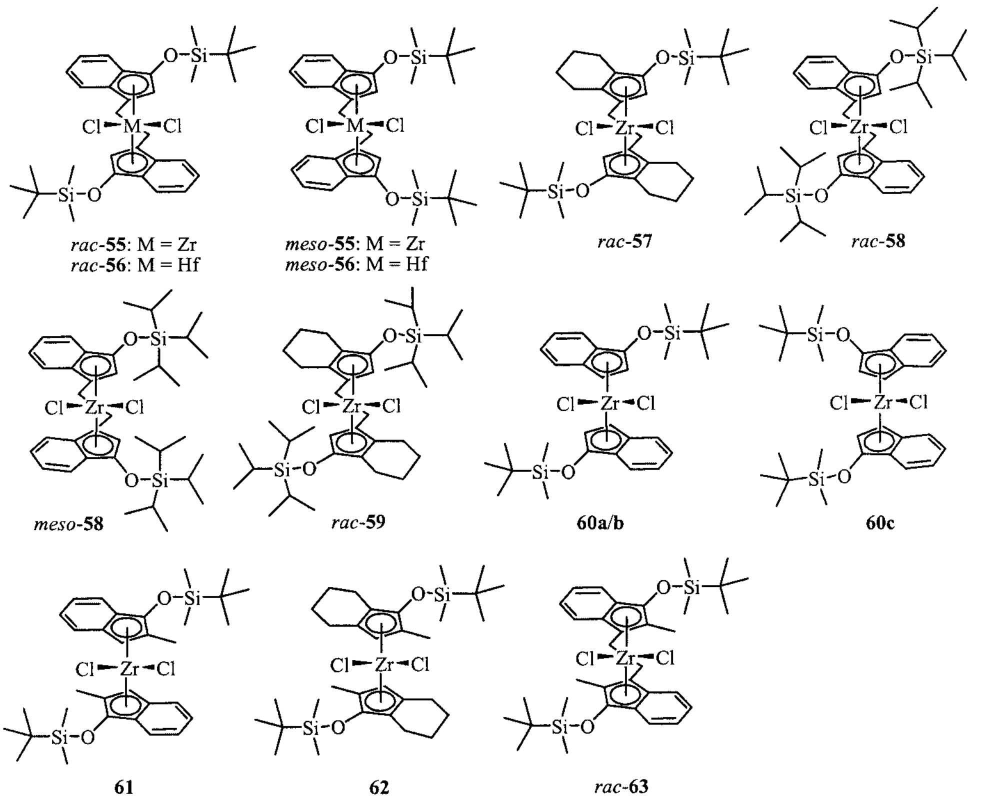
The synthesis of the unbridged 2-siloxy-substituted bis(indenyl)zirconium dichlorides **48**,[90] **51**[91] and **52**[89] was carried out using standard procedures involving deprotonation of the indenyl ligand precursor with *n*BuLi in Et_2O or THF followed by metallation with $ZrCl_4$ in the same solvent or toluene (Scheme 16). The unbridged metallocenes were isolated after workup and crystallization in 32−42% yields. Of these, complex **51** was characterized crystallographically (vide infra). Attempts to prepare the analogous unbridged zirconium complexes from 2-(*tert*-butyldimethylsiloxy)indene (**64**) and 2-[dimethyl(thexyl)-siloxy]indene (**65**) likewise resulted in the formation of the desired metallocenes, as evidenced by EIMS, and ^1H and ^{13}C NMR analyses. Due to their extremely high solubilities in all common organic solvents, these complexes were, however, always obtained as inseparable powderous 5:3−5:2 mixtures containing also the unchanged indenyl ligand precursor as the minor component.[110] Obviously, a bulkier substitution pattern, as in complexes **48**, **51** and **52**, is required for obtaining unbridged 2-siloxy-substituted complexes in pure crystalline form.

The unbridged 2-siloxy-substituted zirconocene dichlorides **48**, **51** and **52** show at room temperature highly symmetric ^1H and ^{13}C NMR spectra consistent with time-averaged molecular C_{2v} symmetry and rapid rotation of the siloxyindenyl ligands around the Cp(centroid)−Zr axis. For example, in the ^1H NMR spectrum of complex **51** at ambient temperature five singlets are observed at $\delta = 6.84$, 5.83, 2.32, 1.08 and 0.34 ppm in a 2:2:6:9:6 ratio assigned to the



rac-**42**: M = Zr
rac-**43**: M = Hf
meso-**42**
rac-**44**
rac-**45**: M = Zr
rac-**46**: M = Hf
meso-**45**
rac-**47**
48
rac-**49**
rac-**50**
51
52
meso-**53**
rac-**54**

Figure 7. 2-Trialkylsiloxy-substituted bis(indenyl) and bis(tetrahydroindenyl) group 4 metallocenes; for racemic complexes, only one enantiomer of the racemic pair is shown



rac-**55**: M = Zr
rac-**56**: M = Hf

meso-**55**: M = Zr
meso-**56**: M = Hf

rac-**57**

rac-**58**

meso-**58**

rac-**59**

60a/b

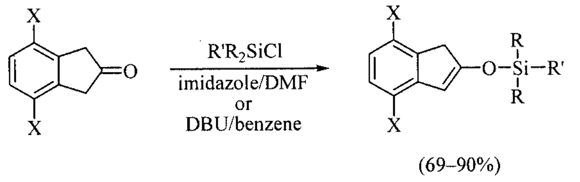
60c

61

62

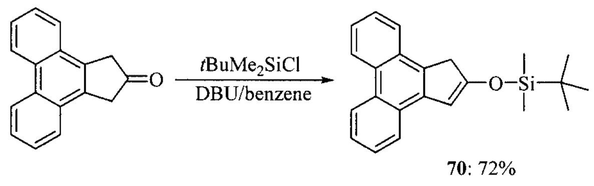
rac-**63**

Figure 8. 1-Trialkylsiloxy-substituted bis(indenyl) and bis(tetrahydroindenyl) group 4 metallocenes; for racemic complexes, only one enantiomer of the racemic pair is shown



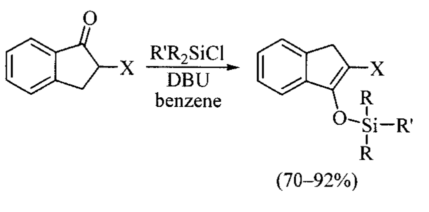
	64	65	66	67	68	69
X	H	H	H	H	H	Me
R'	*t*Bu	thex	*i*Pr	cyhex	*t*Bu	*t*Bu
R	Me	Me	*i*Pr	Me	Ph	Me

Scheme 13. Synthesis of 2-siloxyindenes **64**–**69**



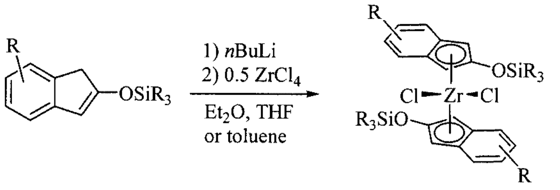
70: 72%

Scheme 14. Synthesis of 2-(*tert*-butyldimethylsiloxy)cyclopenta[*l*]-phenanthrene (**70**)



	71	72	73
X	H	H	Me
R'	*t*Bu	*i*Pr	*t*Bu
R	Me	*i*Pr	Me

Scheme 15. Synthesis of 3-siloxyindenes **71**–**73**

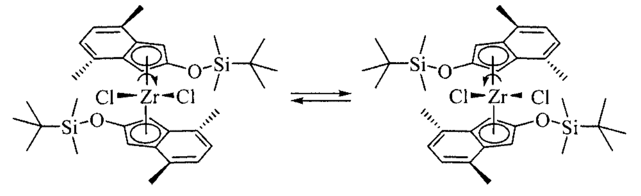


48, **51**, **52** (32-42%)

Scheme 16. Synthesis of the unbridged bis(2-siloxyindenyl)zirconium dichlorides

aromatic methine CH, five ring CH, the methyl groups of the aromatic ring, silicon-bound *tert*-butyl and methyl groups, respectively. The 1-H/3-H protons in the five-membered indenyl rings of complexes **48** (δ = 5.51 ppm)[90] and **51** (δ = 5.83 ppm)[91] are considerably more shielded than those observed for the 2-hydrocarbon-substituted analogues (commonly δ ≈ 6.0−6.5 ppm), indicating increased electron density in the Cp ring induced by the electron-donating siloxy substituent. In complex **52**, the observed deshielding of this proton resonance (δ = 6.24 ppm)[89] is apparently caused by the increased π-electron delocalization induced by the fused benzo substituents.

Variable-temperature NMR spectroscopic measurements were carried out on both complexes **51**[91] and **52**, and indicate dynamic behavior upon lowering the monitoring temperature. For **51**, the ^{1}H NMR resonance of the methyl signal at δ = 2.32 ppm becomes appreciably broadened at 218−198 K, and below coalescence (T_c = 193−190 K) two resonances of equal intensities are observed. In a similar fashion, the methyl signal at δ = 0.34 ppm and the methine signals at δ = 6.84 and 5.83 ppm show considerable broadening at 218−188 K, and split into two resonances below 178 K. Finally, at 173 K a 6.3 Hz ^3J coupling was observed for the methine protons of the six-membered ring. Similar splitting was observed for most of the ^{13}C NMR signals of **51** recorded at 173 K. Analogous to the amino-substituted zirconocenes **12** and **13** described by Erker and co-workers, and discussed earlier in this microreview (vide supra),[44] the signal splitting indicates a single C_2-symmetric bent-metallocene conformation that is detected when the equilibration of **51** with its nonsuperimposable mirror image becomes frozen on the NMR time scale (Scheme 17).[111] The calculated activation barrier for **51**, $\Delta G^{\ddagger}_{(\mathrm{Ind\text{-}rot})}$ (190−193 K) = 9.1−9.3 kcal·mol^{-1}, is of similar magnitude to those observed by Erker and co-workers for the amino-substituted complexes,[44] and by Waymouth et al. for dibenzylbis(2-phenylindenyl)zirconium for which $\Delta G^{\ddagger}_{(\mathrm{Ind\text{-}rot})}$ (203 K) = 10.7 kcal·mol^{-1} has been reported.[112] For complex **52**, a coalescence temperature of T_c = 173−174 K was estimated from the extensive broadening of the ^{1}H NMR signals at 173 K.[113] An activation barrier $\Delta G^{\ddagger}_{(\mathrm{Ind\text{-}rot})}$ (173 K) = 8.91 kcal·mol^{-1} was calculated using the splitting of the ^{13}C NMR Si−CH$_3$ resonance at this temperature.



Scheme 17. Dynamic behavior in bis[2-(*tert*-butyldimethylsiloxy)-4,7-dimethylindenyl]zirconium dichloride (**51**)

The 3-(*tert*-butyldimethylsiloxy)indenes **71** and **73** were likewise converted into the corresponding bis(indenyl)zirconium dichlorides **60** and **61** by deprotonation with *n*BuLi in Et$_2$O followed by reaction of the isolated lithium salts with 0.5 equiv. of ZrCl$_4$ in toluene (Scheme 18). In contrast to 2-substituted indenyl complexes, the presence of a 3-(or 1-)indenyl substituent renders the ligand system prochiral. The attachment of the metal atom can occur from either enantiotopic face of the five-membered ring system, thus resulting in diastereomeric metallocene complexes consisting of a pair of racemic-like enantiomers **A** and **B**, and their *meso*-like diastereomer **C** (Figure 9).[114−116] In the case of complex **60**, workup and crystallization from Et$_2$O provided a first crop of a diastereomerically pure bright yellow powder in 15% yield, possibly corresponding to the enantiomeric **60a/b** mixture. Further concentration and cooling of the mother liquor then provided the other diastereomer (tentatively **60c**) in 12% yield, contaminated with traces of the other diastereomer.[117] As both diastereomers give highly symmetrical NMR spectra and similar EIMS fragmentation patterns, assignment of the diastereomers is not possible based on the spectroscopic data of the dichlorides only. Similar types of complexes have previously been assigned by Erker and co-workers based on conversion of the dichloride complexes to dimethylzirconium compounds where the *rac*-type isomer exhibits only one ^{1}H NMR resonance, whereas two resonances in a 1:1 ratio are observed for the *meso*-like diastereomer.[116] In the case of the sterically more hindered ligand precursor **73** that contains an additional 2-methyl substituent in the indenyl fragment, the ^{1}H NMR spectrum of the crude product indicates an approximately 1:1 mixture of two metallocene diastereomers. From a crude yield of 40%, diastereomerically pure complex **61** (tentatively the racemic-like isomer) was isolated in 13% yield after recrystallization from toluene. Complex **61** was further hydrogenated to yield the corresponding tetrahydroindenyl complex **62** in 65% isolated yield.[110] Despite several attempts, crystals suitable for X-ray structure determination were not obtained from any of the complexes **60**−**62**.

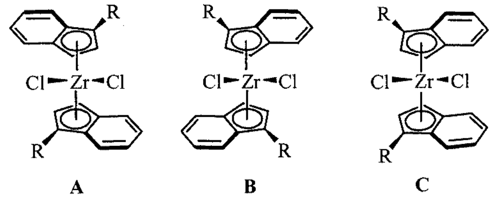
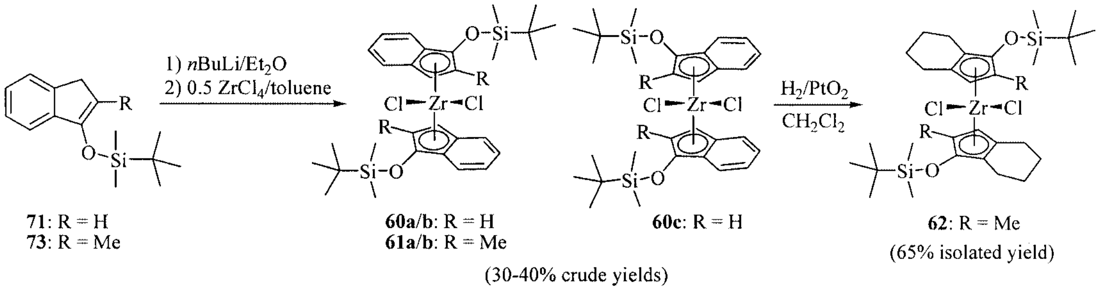


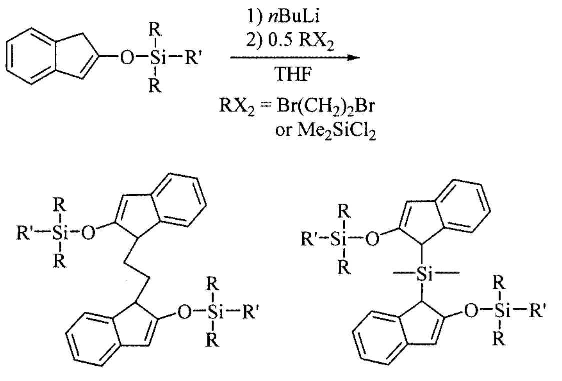
Figure 9. Diastereomers of 3-(1-)substituted bis(indenyl)metallocenes: racemic-like (**A**/**B**) and *meso*-like (**C**)



Scheme 18. Synthesis of unbridged 1-siloxy-substituted bis(indenyl) and bis(tetrahydroindenyl)zirconium dichlorides **60**−**62**; for racemic complexes only one enantiomer of the racemic pair is shown

The synthesis of bridged 2,2′- and 3,3′-siloxy-substituted bis(indenyl) ligands was carried out according to standard procedures. Thus, all 2-siloxy-substituted indenes **64–68** were successfully converted into the corresponding ethylene-bridged bis(indenyl) derivatives **74–78** in 28–58% yields (crystalline solids) by lithiation with *n*BuLi followed by reaction with 0.5 equiv. of dibromoethane in THF, subsequent workup and purification by crystallization (Scheme 19). In contrast to bis(indenyl)ethane for which the 3,3′-indenyl-bridged isomer predominates,[10,66,118] all siloxy-substituted indenes yield exclusively the 1,1′-bridged product.[85,90,93,106] Only in the case of the six-membered ring substituted 2-siloxyindenes **69**[91] and **70**[106] were the yields for the ethylene-bridged bis(indenyl) ligands **79** and **80** (Figure 10) low (4.8 and 3.9%, respectively), which resulted from the nearly exclusive predomination of the spirocyclopropane adducts formed by intramolecular bis(alkylation) reactions of the substituted indene.[8,67,77,119] Both 2-(*tert*-butyldimethylsiloxy)indene (**64**) and 2-[dimethyl(thexyl)siloxy]indene (**65**) were further converted into the dimethylsilylene-bridged bis(indenyl) ligand analogues **81** and **82** in high yields by deprotonation with *n*BuLi followed by reaction with 0.5 equiv. of dichlorodimethylsilane.[106] The racemic diastereomers of the dimethylsilylene-bridged ligands were obtained as crystalline solids in 42 and 30% yields, respectively, and the *meso* diastereomers were isolated as oils in similar yields after exhaustive washing of the mother liquor with cold pentane. The benzo-fused dimethylsilylene-bridged bis[2-(*tert*-butyldimethylsiloxy)cyclopenta[*l*]phenanthryl] ligand (**83**, Figure 10) was prepared from **70** according to a similar procedure and isolated as a high-melting solid (m.p. 273–274 °C) in 25% yield.[89]

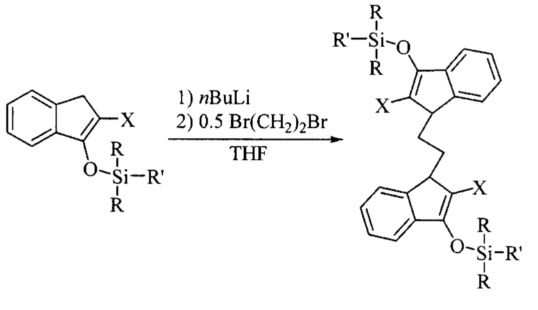
All 3-siloxy-substituted indenes **71–73** were converted into the corresponding ethylene-bridged bis(indenyl) analogues **84**,[92] **85**[90] and **86**[110] in variable yields ranging from 14% (compound **86**) to nearly quantitative (compound **85**) by deprotonation with *n*BuLi followed by reaction with dibromoethane in THF (Scheme 20).



	74	**75**	**76**	**77**	**78**
R'	*t*Bu	thex	*i*Pr	cyhex	*t*Bu
R	Me	Me	*i*Pr	Me	Ph
yield (%)	58	52	43	28	41

	81	**82**
R'	*t*Bu	thex
R	Me	Me
yield (%)	~80	~60

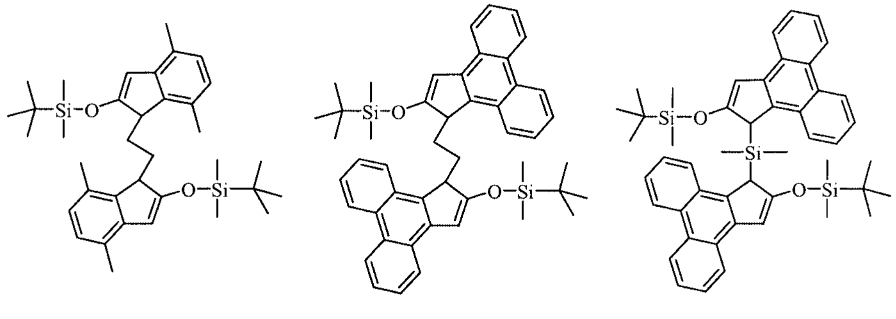
Scheme 19. Synthesis of the bis(2-siloxyindenyl)ethanes **74–78** and the dimethylbis(2-siloxyindenyl)silanes **81** and **82**



	84	**85**	**86**
X	H	H	Me
R'	*t*Bu	*i*Pr	*t*Bu
R	Me	*i*Pr	Me
yield (%)	63	99	14

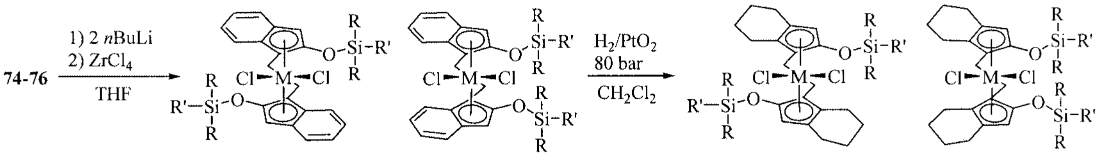
Scheme 20. Synthesis of the bis(3-siloxyindenyl)ethanes **84–86**

The ethylene-bridged bis(2-siloxyindenes) **74–76** yield, after deprotonation with *n*BuLi and subsequent reactions of the dilithium salts with $ZrCl_4$ in THF, the corresponding *ansa*-zirconocene complexes **42**, **47** and **49** (Scheme 21).[85,90,93,97] The bulkiness of the siloxy group in the α-position to the ethylene bridge influences the *rac*/*meso* ratio of the metallocenes formed. In the case of the 2-*tert*-butyldimethylsiloxy-substituted complex **42**, metallation with $ZrCl_4$ in THF initially produces a *rac*/*meso* ratio of 14:1 as determined by ^1H NMR spectroscopic analysis of the crude product, whereas an entirely *rac*-selective metall-



79 (5%) **80** (4%) **83** (25%)

Figure 10. Ethylene- and dimethylsilylene-bridged bis[2-(*tert*-butyldimethylsiloxy)indenes] **79**, **80** and **83**, having substituents in the six-membered rings



	rac-**42**	*meso*-**42**	*rac*-**43**	*rac*-**47**	*rac*-**49**
R'	*t*Bu	*t*Bu	*t*Bu	thex	*i*Pr
R	Me	Me	Me	Me	*i*Pr
M	Zr	Zr	Hf	Zr	Zr
yield (%)	21-26	-	13	22	28

	rac-**45**	*meso*-**45**	*rac*-**46**	*rac*-**49**
R'	*t*Bu	*t*Bu	*t*Bu	*i*Pr
R	Me	Me	Me	*i*Pr
M	Zr	Zr	Hf	Zr
yield (%)	80	-	75	67

Scheme 21. Synthesis of the ethylene-bridged 2-siloxy-substituted bis(indenyl)- and bis(tetrahydroindenyl)metallocene complexes **42**, **43**, **45**−**47**, **49** and **50**; for racemic complexes only one enantiomer of the racemic pair is shown

ation was observed for the 2-triisopropylsiloxy-substituted analogue **49**. Pure *rac*-**42** was obtained in 21−26% yield after crystallization/recrystallization from dichloromethane,[85,97] and pure *meso*-**42** after repeated recrystallization from a large-scale synthesis of **42**.[97] The analogous hafnium complex *rac*-**43** was isolated in 13% yield according to a similar procedure.[86] The racemic 2-[dimethyl(thexyl)-siloxy]-[93] and 2-triisopropylsiloxy-substituted[90] zirconium complexes *rac*-**47** and *rac*-**49** were isolated in 22 and 28% yields, respectively, after crystallization from dichloromethane or toluene. All attempts to metallate the dilithium salts of the ligand precursors **77**−**79** failed. The ethylene-bridged benzo-fused ligand precursor **80** was, however, successfully deprotonated with *n*BuLi, and treated with $ZrCl_4$ in THF. Workup and washing of the residue with toluene and hexane provided in total 22 mg of the corresponding metallocene *rac*-**54** (Figure 7) in 7% yield, tentatively assigned as the racemic diastereomer based on the highly isotactic polypropylene obtained upon activation of this complex with MAO and subsequent exposure to gaseous propylene.[113]

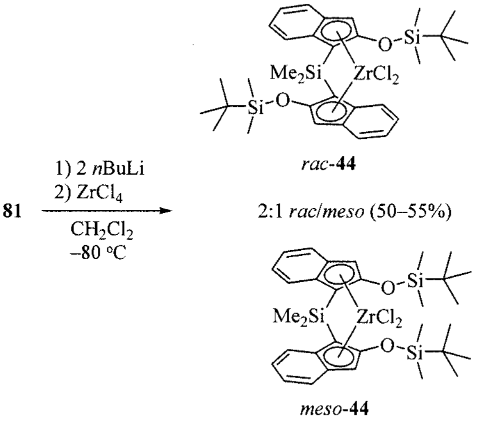
The racemic zirconium complexes *rac*-**42** and *rac*-**49** were further hydrogenated to yield the corresponding tetrahydroindenyl analogues *rac*-**45** and *rac*-**50**, isolated in 80% and 67% yields, respectively.[86][90] A small amount of pure *meso*-**45** was isolated after repeated recrystallization of the product obtained from hydrogenation of a *rac*/*meso*-**42** mixture.[120] Hydrogenation of the hafnium complex *rac*-**43** provided the corresponding tetrahydroindenyl complex *rac*-**46** in 75% isolated yield.[121] All of the ethylene-bridged 2-siloxy-substituted bis(indenyl)- and bis(tetrahydroindenyl)-metallocene complexes, with the exception of the bis(indenyl)hafnocene *rac*-**43**, are remarkably stable in air and towards moisture. The 2-siloxy-substituted bis(indenyl) complexes are generally soluble in cyclohexane, diethyl ether, toluene and dichloromethane. The hydrogenated congeners also dissolve readily in aliphatic solvents such as pentane and hexane. The increased stability in polar solvents is exemplified by complex *rac*-**42**, which is readily recrystallized from acetone.

The X-ray crystal structures of complexes *rac*-**42**,[85] *rac*-**45**,[87] *rac*-**46**,[121] *rac*-**47**,[93] *rac*-**49**,[90] *rac*-**50**[90] and *meso*-**45**[120] were determined and are discussed separately (vide infra).

The ^1H NMR spectra of all ethylene-bridged racemic and *meso*-2-siloxy-substituted bis(indenyl)- and bis(tetrahydroindenyl)metallocene dichlorides show, at ambient temperature, one set of highly symmetrical ligand resonances indicating rapid interconversion between the limiting ligand conformers on the NMR time scale. The interconversion is analogous to that discussed earlier in this microreview for the 2-dimethylamino-substituted complexes *rac*/*meso*-**9** (Schemes 5 and 6), and by Resconi and co-workers for *rac*/*meso*-ethylenebis(indenyl)zirconium dichloride **2** and its 4,7-dimethyl-substituted analogue.[66,67] Likewise, analogous to the 2-amino-substituted complexes *rac*- and *meso*-**9**, the β-protons in the five-membered rings of all ethylene-bridged *rac*- and *meso*-2-siloxy-substituted bis(indenyl) complexes **42**, **43**, **47** and **49** are shielded and the signals shifted by 0.6−0.7 ppm to a higher field relative to the corresponding resonances of the 2-alkyl or unsubstituted analogues. Similar effects are observed in the ^{13}C NMR spectra for the chemical shifts of the β-carbon atoms of the five-membered rings. The only exception in this series is the benzo-fused complex *rac*-**54**, for which a ^1H NMR β-H resonance of $\delta = 6.51$ ppm, similar to that observed for the unsubstituted parent complex *rac*-ethylenebis(indenyl)zirconium dichloride *rac*-**2** ($\delta = 6.58$ ppm),[66][118] was detected.[113] The observed shielding effects are consistent with increased electron densities in the five-membered rings induced by the electron-donating siloxy substituents. For the benzo-fused complex *rac*-**54** the observed deshielding is apparently a consequence of the increased π-electron delocalization, as observed also for its unbridged congener **52** (vide supra). In the ^{29}Si NMR spectrum of the 2-*tert*-butyldimethylsiloxy-substituted ethylene-bridged ligand precursor **74**, the Me_2Si resonance is observed at $\delta = 22.45$ ppm; however, in the corresponding racemic bis(indenyl)- and bis(tetrahydroindenyl)zirconium complexes *rac*-**42** and *rac*-**45**, lower field ^{29}Si NMR resonances of $\delta = 26.64$ and 25.21 ppm, respectively, are observed, which are possibly influenced by electron donation to the aromatic five-membered rings and the Lewis-acidic zirconium atoms.[98] The subsequent decrease in the local electron densities of the oxygen atoms of the metallocene complexes then result in inductive electron withdrawal from the silicon to the oxygen atom, thus contributing to the lower field ^{29}Si NMR resonances.

The dimethysilylene-bridged ligand precursor **81** gave, upon deprotonation and reaction of the dilithium salt with $ZrCl_4$ in CH_2Cl_2 and subsequent workup and crystallization from the same solvent, a 2:1 mixture of fairly pure *rac*-

and *meso*-dimethylsilylenebis[2-(*tert*-butyldimethylsiloxy)indenyl]zirconium dichlorides (**44**) in approximately 50−55% yield (Scheme 22).[98,106] Surprisingly, in contrast to the ethylene-bridged complexes, the silylene-bridged analogue is highly sensitive towards air and moisture, and only a small sample of fairly pure racemic diastereomer *rac*-**44** was obtained after tedious recrystallization from Et_2O. Likewise, the diastereocontrol in favor of the racemic isomer in the metallation step is inferior to that observed for the ethylene-bridged analogues. The ^1H NMR chemical shift of β-H in *rac*-**44** ($\delta = 6.22$ ppm) is of the same magnitude as that observed for the 2-dimethylamino-substituted analogue *rac*-**8** ($\delta = 6.4$ ppm)[38] (vide supra) and strongly shielded relative to that observed for the parent *rac*-dimethylsilylenebis(-indenyl)zirconium dichloride ($\delta = 6.90$ ppm).[69] The benzo-fused dimethylsilylene-bridged ligand **83** gave after deprotonation with *n*BuLi and subsequent reaction with $ZrCl_4$ in toluene a 1:9 *rac*/*meso* mixture of the corresponding zirconium complex **53**, as indicated by ^1H NMR spectroscopic analysis of the crude product.[89] Both diastereomers of **53** decompose rapidly in common organic solvents; the racemic isomer is the more unstable one. After rapid workup and crystallization from dichloromethane, pure *meso*-**53** was, however, obtained in 40% isolated yield.



Scheme 22. Synthesis of the dimethylsilylene-bridged 2-*tert*-butyldimethylsiloxy-substituted bis(indenyl) complex **44**; only one enantiomer of the racemic pair is shown

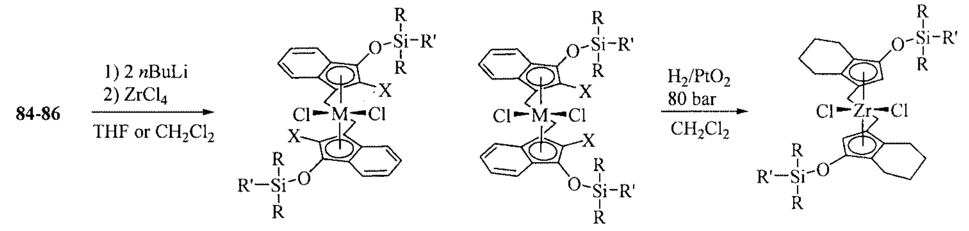
The ethylene-bridged 3-siloxy-substituted ligand precursors **84**−**86** were likewise deprotonated with *n*BuLi in Et_2O or THF, and the obtained dilithium salts reacted with $ZrCl_4$ (ligands **84**−**86**)[90][92][110] and $HfCl_4$ (ligand **84**) in THF or dichloromethane to yield the corresponding 1-(3-)siloxy-substituted *ansa*-metallocene complexes **55**, **56**, **58** and **63** as mixtures of the *rac* and *meso* diastereomers (Scheme 23). In the case of the 1-*tert*-butyldimethylsiloxy-substituted zirconium and hafnium complexes **55** and **56**, metallation of the dilithiated ligand precursor with MCl_4 (M = Zr, Hf) initially produces a 5:1 mixture of the corresponding *rac* and *meso* diastereomers, isolated after workup and crystallization from Et_2O in 20 and 15% yields, respectively. A small amount of analytically pure racemic zirconium complex *rac*-**55** was obtained after tedious recrystallization from toluene.[92] Recrystallization of the *rac*/*meso*-hafnocene mixture from Et_2O finally provided a 28:1 mixture of *rac*-**56**/*meso*-**56** used for characterization of the racemic hafnium complex.[110] Pure *meso* diastereomers *meso*-**55** and *meso*-**56** were obtained in 4 and 8% isolated yields, respectively, after tedious recrystallization from dichloromethane or toluene. Crystals suitable for X-ray structure determination were obtained from the *meso*-zirconocene **55**.[92] Separation of the diastereomers of the *tert*-butyldimethylsiloxy-substituted complexes **55** and **56** is hampered by the *slightly lower solubilities* of the minor *meso* diastereomers in common crystallization solvents such as Et_2O and toluene. An inverse order for the solubilities was observed for the 1-(3-)-triisopropylsiloxy-substituted congeners *rac*- and *meso*-**58**, of which the fairly pure racemic diastereomer was obtained in 44% yield by simply washing the crude product with Et_2O.[90] Analytically pure *rac*-**58** was then obtained by recrystallization from toluene. Recrystallization of the Et_2O extracts from hexane provided pure *meso*-**58** in 6% isolated yield. The more highly substituted 1-*tert*-butyldimethylsiloxy-2-methyl-substituted zirconium complex **63** was obtained, after workup and crystallization from hexane, as an inseparable 18:1 mixture of the *rac* and *meso* diastereomers in 7% yield.[110] A 9:1 *rac*/*meso*-**55** mixture and the pure racemic diastereomer of **58** were further hydrogenated to yield the corresponding tetrahydroindenyl complexes **57** and *rac*-**59** in 84 and 67% isolated yields, respectively. The *tert*-butyldimethylsiloxy-substituted tetrahydroindenyl complex was obtained, after crystallization from hexane, as the initial 9:1 *rac*/*meso* mixture. Samples of pure *rac*-**57** were then obtained after careful recrystallization from the same solvent and characterized crystallographically.[92]

The ^1H NMR chemical shifts of the α-protons in the five-membered rings of the racemic 1-siloxy-substituted bis(indenyl)zirconium complexes *rac*-**55** ($\delta = 5.60$ ppm)[92] and *rac*-**58** ($\delta = 5.63$ ppm)[90] are shielded in comparison with those observed for *rac*-ethylenebis(indenyl)zirconium dichloride (**2**) ($\delta = 6.20$ ppm)[66] and *rac*-ethylenebis(1-trimethylsilylindenyl)zirconium dichloride ($\delta = 6.10$ ppm),[70] consistent with electron donation from the siloxy substituent to the aromatic five-membered ring. Similarly, for the tetrahydroindenyl complexes *rac*-**57** ($\delta = 4.96$ ppm)[92] and *rac*-**59** ($\delta = 5.01$ ppm),[90] the α-Hs are shielded relative to that of *rac*-**5** ($\delta = 5.61$ ppm).[118]

In addition to the siloxy-substituted group 4 bis(indenyl) complexes reported by us, a series of siloxy-substituted mono- and bis(cyclopentadienyl) complexes of iron, manganese, tungsten, titanium and zirconium have been described by Plenio and co-workers.[122−125]

Thio-Substituted Group 4 Bis(indenyl)metallocenes

To the best of our knowledge, the only examples of thio-substituted group 4 bis(indenyl)metallocene complexes are those claimed in the patent literature (Figure 11).[126] Explicit yields for the metallation step were not given, characterization data for the ligands and metallocenes were also not given. Complexes **87**−**90** were claimed to be catalysts



	55	**56**	*rac*-**58**	*meso*-**58**	**63**
X	H	H	H	H	Me
R'	*t*Bu	*t*Bu	*i*Pr	*i*Pr	*t*Bu
R	Me	Me	*i*Pr	*i*Pr	Me
M	Zr	Hf	Zr	Zr	Zr
rac/*meso*	5:1	5:1			18:1
yield (%)	20	15	44	6	7

	rac-**57**	*rac*-**59**
R'	*t*Bu	*i*Pr
R	Me	*i*Pr
rac/*meso*	9:1	
yield (%)	84	67

Scheme 23. Synthesis of the ethylene-bridged 1-siloxy-substituted bis(indenyl)- and bis(tetrahydroindenyl)metallocene complexes **55**−**59** and **63**; for racemic complexes only one enantiomer of the racemic pair is shown

both in solution homopolymerization of ethylene, as well as copolymerization of ethylene and propylene, with few details of polymer characterization given in the patent application.

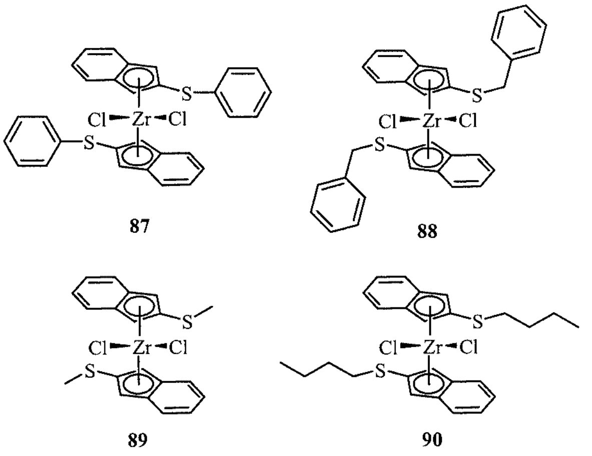
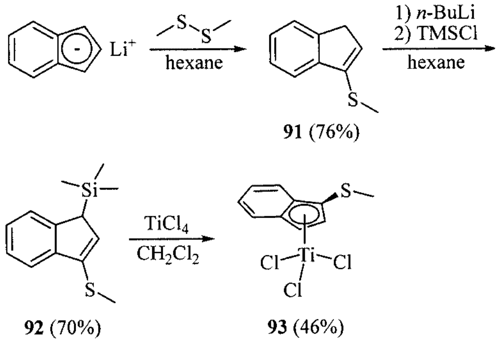


Figure 11. Thio-substituted bis(indenyl)zirconium complexes **87**−**90** reported in the patent literature

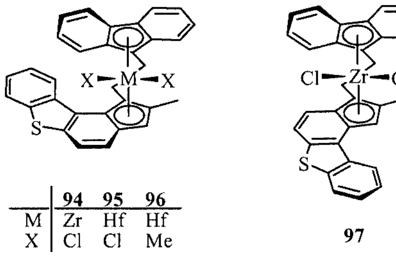
Related to these, Rausch and co-workers have reported the synthesis of the monoindenylmetallocene trichloro[1-(thiomethyl)indenyl]titanium (**93**) and its application in the syndiospecific polymerization of styrene (Scheme 24).[127] The 3-(methylthio)indene (**91**) employed as ligand precursor was prepared from indenyllithium and dimethyl disulfide in 76% yield according to the procedure of Hartke.[128] Subsequent deprotonation with *n*BuLi and reaction with chlorotrimethylsilane gave the TMS adduct **92** in 70% yield, which upon reaction with $TiCl_4$ in dichloromethane eliminates TMSCl to form the half-sandwich titanocene **93** in 46% yield after crystallization from toluene. Introduction of the methylthio group appears to have a detrimental effect on the styrene polymerization activity, presumably due to interaction of the sulfur lone pairs with the MAO cocatalyst.



Scheme 24. Synthesis of 3-(methylthio)indene (**91**) and the corresponding half-sandwich titanium dichloride complex **93**

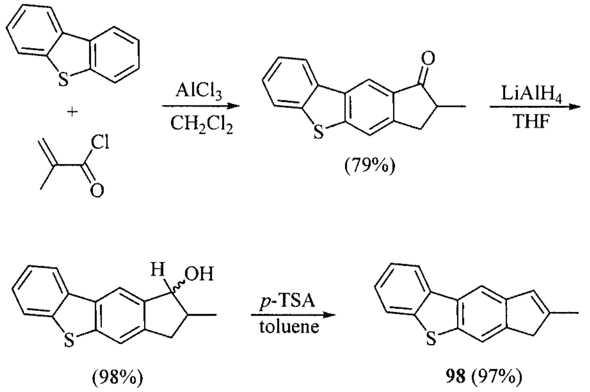
Preparation of C_1-symmetric, mixed-ligand ethylene-bridged group 4 *ansa*-metallocenes (Zr, Hf) **94**−**97** containing one benzothiophene-fused indenyl ligand and one fluorenyl ligand was recently described by Rieger (Figure 12).[129] The 2-methyl-1-*H*-benzo[*b*]indeno[4,5-*d*]thiophene (**98**) precursor was prepared in good yield by Friedel−Crafts acylation of dibenzothiophene with methacrylic chloride in a manner similar to that described for the 5,6-ethylenedioxy-fused ligand (Scheme 10), followed by subsequent Nazarov cyclization, ketone reduction and water elimination (Scheme 25). The mixed-ligand complexes, upon activation with MAO, form high-performance catalysts for production of controlled tacticity polypropylenes. A detailed discussion is outside the scope of this review.

The related indenyl ligand precursor 2-methyl-8*H*-indeno[2,1-*b*]thiophene (**99**), having a sulfur-containing heterocycle condensed to the indenyl *five-membered ring* and reported by Resconi and co-workers for use in constrained-geometry titanium complexes, was prepared from 4-bromo-2-methylthiophene in 30% overall yield (three steps), as displayed in Scheme 26.[57] The 2-methyl-4-phenylthiophene was obtained in 70% yield after reaction of the bromo compound with phenylmagnesium bromide. Sub-



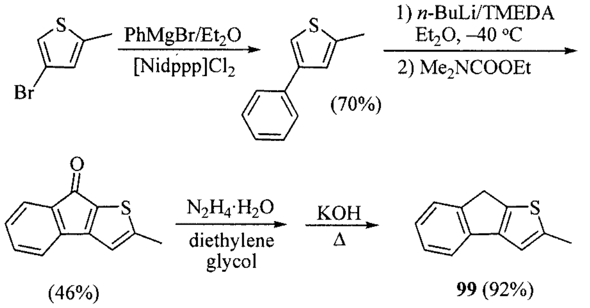
	94	95	96
M	Zr	Hf	Hf
X	Cl	Cl	Me

Figure 12. Benzothiophene-fused mixed-ligand *ansa*-(fluorenyl)(indenyl)metallocenes **94−97**



Scheme 25. Synthesis of 2-methyl-1*H*-benzo[*b*]indeno[4,5-*d*]thiophene (**98**)

sequent dimetallation with *n*BuLi was followed by reaction with ethyl *N*,*N*-dimethylcarbamate and Wolff−Kishner reduction of the obtained ketone to furnish **99**.



Scheme 26. Synthesis of 2-methyl-8*H*-indeno[2,1-*b*]thiophene (**99**)

Additionally, a few examples of bis(cyclopentadienyl) group 4 metallocenes containing phenylthio-[130] and propylthio-substituted[131,132] Cp ligands have been reported in the literature.

Theoretical Studies

Pakkanen and co-workers have studied the geometry prediction of a large set of bridged zirconocene dichloride complexes by ab initio Hartree−Fock, MP2, BLYP and B3LYP methods; with basis sets range from 3-21G* to 6-311G**.[133] Selected calculated geometrical parameters of close to 60 zirconocene dichloride complexes, including several amino- and siloxy-substituted bis(indenyl) and bis(tetrahydroindenyl)zirconocenes, were compared with the experimentally determined crystal structures. The least expensive HF/3-21G* method was verified to be notably accurate for such predictions by a comprehensive data set of 62 bridged zirconocene dichlorides. In a separate study by the same authors,[134] factors controlling the accessibility of cationic metal sites in zirconocene polymerization catalysts was investigated by the ab initio Hartree−Fock method at the 3-21G* level. Special emphasis was laid on the influence of the electronic effects and the ligand structure on the accessibility, stabilization and destabilization of the active center. Several heteroatom-substituted indenyl complexes, including both amino and siloxy substitution, were modeled successfully. A detailed description is outside the scope of this microreview.

In yet another study by Pakkanen et al., conformational preferences of racemic ethylene-bridged bis(indenyl)zirconocenes were investigated using the ab initio Hartree−Fock method with emphasis on the influence of the ligand-substitution pattern on the relative stabilities of the limiting indenyl-backward (Y) and indenyl-forward (Π) conformations (Scheme 5) and their interconversion.[135] Conformational interconversion of several ethylene-bridged methyl- and 1- or 2-trialkylsiloxy-substituted bis(indenyl)- and bis(tetrahydroindenyl)zirconium dichlorides was evaluated as part of this investigation.

Solid-State Structures

Table 1 presents selected bonding parameters for several unbridged, ethylene-bridged and silicon-bridged bis(indenyl) group 4 metallocene dichlorides and their hydrogenated congeners.[38−41,44,45,6,85,86,88,90,92,93,120,121,136−139] Each studied molecule represents the closely related overall structure of the metal-centered unit, i.e. bent-sandwich geometry around the pseudotetrahedrally coordinated metal ion.

Of the unbridged zirconium complexes, the parent bis(indenyl)zirconium dichloride (Ind)$_2$ZrCl$_2$ displays a staggered conformation in the solid state,[136] whereas the 2-amino-substituted analogues **11−14** all crystallize in an *anti* conformation having a crystallographically imposed C_2-axial symmetry. Crystallization of the unbridged 2-siloxy-substituted zirconium complex bis[2-(*tert*-butyldimethylsiloxy)-4,7-dimethylindenyl]zirconium dichloride (**51**) arranges two rotamers in the asymmetric unit corresponding to a C_1-symmetric, "central/lateral:*gauche*" conformation and a C_2-symmetric, "bis(central):*syn*" conformation, respectively.[114] In both rotamers the metallocene C_5 rings are nearly eclipsed.

The combination of ethylene bridge with bis(indenyl)-based ancillary ligands results in the potential formation of *meso* and *rac* diastereomers. All of the crystallographically characterized *meso* isomers display a chiral C_1-symmetric conformation due to the staggered placement of the two indenyl ligand moieties (Scheme 6). The racemic ethylene-bridged bis(indenyl) and bis(tetrahydroindenyl)metallocenes show the ordinary C_2-symmetric bent-metallocene structure adopting one of the two limiting conformations,

Table 1. Selected bonding parameters for group 4 bis(indenyl)- and bis(tetrahydroindenyl)metallocene dichlorides

Metallocene	Indenyl conformation	M−Cl [Å]	M−Cn [Å]	Cl−M−Cl [°]	Cn−M−Cn [°]	Cp−Cp [°]	Ref.
$(\mathrm{R}^n\mathrm{Ind})_2\mathrm{ZrCl}_2$:							
[R = H]	[staggered]	2.440	2.223	94.7	129.1	63.5	[136]
R = 2-Me$_2$N (**11**)	anti	2.455	2.228	95.1	133.1	49.8	[38]
R = 2-Me$_2$N (**11**)	anti	2.455	2.229	94.9	132.8	49.1	[39]
R = 2-Pyr (**12**)	anti	2.446	2.233	95.2	133.0	49.6	[40]
R = 2-Morph (**13**)	anti	2.446	2.225	95.8	132.5	50.1	[44]
R = 2-(*N*-Me-Piper) (**14**)	anti	2.440	2.216	94.8	132.4	49.2	[45]
R = 2-TBSO-4,7-Me$_2$ (**51**)	gauche	2.414	2.253	96.9	130.3	51.5	[91]
R = 2-TBSO-4,7-Me$_2$ (**51**)	*syn*	2.426	2.242	97.1	127.3	54.9	[91]
rac-Et$(\mathrm{R}^n\mathrm{Ind})_2\mathrm{ZrCl}_2$:							
R = H (*rac*-**2**)	forward	2.388	2.219	99.1	125.3	63.5	[66]
R = 2-Me$_2$N (*rac*-**9**)	forward	2.427	2.238	94.8	127.2	62.3	[39]
R = 2-TBSO (*rac*-**42**)	backward	2.412	2.254	99.3	125.9	61.0	[85]
R = 2-TDSO (*rac*-**47**)	backward	2.433	2.243	97.9	120.3	58.6	[93]
R = 2-TIPSO (*rac*-**49**)	forward	2.414	2.237	94.3	125.5	57.7	[90]
rac-Et$(\mathrm{R}^n\mathrm{IndH}_4)_2\mathrm{ZrCl}_2$:							
R = H (*rac*-**5**)	forward	2.439	2.214	98.6	125.2		[118]
R = 2-TBSO (*rac*-**45**)	backward	2.439	2.231	98.2	125.2	58.6	[86]
R = 2-TIPSO (*rac*-**50**)	backward	2.431	2.228	94.3	125.1	57.8	[90]
R = 1-TBSO (*rac*-**57**)	forward	2.415	2.238	98.7	126.4	63.6	[92]
rac-Et$(\mathrm{R}^n\mathrm{IndH}_4)_2\mathrm{HfCl}_2$:							
R = 2-TBSO (*rac*-**46**)	backward	2.412	2.210	97.1	126.1	57.6	[121]
meso-Et$(\mathrm{R}^n\mathrm{Ind})_2\mathrm{ZrCl}_2$:							
R = H (*meso*-**2**)	staggered	2.426	2.227	97.6	126.2	62.3	[66]
R = 2-Me$_2$N (*meso*-**9**)	staggered	2.440	2.231	96.9	127.5	58.0	[41]
R = 1-TBSO (*meso*-**55**)	staggered	2.431	2.252	96.2	126.4	64.6	[92]
meso-Et$(\mathrm{R}^n\mathrm{IndH}_4)_2\mathrm{ZrCl}_2$:							
R = H (*meso*-**5**)	staggered	2.439	2.217	98.7	125.2	62.0	[137]
R = 2-TBSO (*meso*-**45**)	staggered	2.439	2.231	98.2	125.2	58.6	[120]
rac-R$_2$Si$(\mathrm{R}'\mathrm{Ind})_2\mathrm{ZrCl}_2$:							
R = Me, R′ = H	−	2.431	2.293	98.8	119.0	62.0	[69]
R^2 = C$_4$H$_8$, R′ = H	−	2.447	2.225	98.2	127.6	64.1	[138]
R = Me, R′ = 2-Me$_2$N (*rac*-**8**)	−	2.424	2.237	94.9	129.1	59.2	[38]
rac-R$_2$Si$(\mathrm{R}'\mathrm{IndH}_4)_2\mathrm{ZrCl}_2$:							
R = Me, R′ = H	−	2.441	2.231	97.3	126.4	62.1	[139]
R^2 = C$_4$H$_8$, R′ = H	−	2.430	2.231	99.4	126.5	57.2	[138]
meso-R$_2$Si$(\mathrm{R}'\mathrm{Ind})_2\mathrm{ZrCl}_2$:							
R^2 = C$_4$H$_8$, R′ = H	−	2.430	2.250	97.3	127.7	63.1	[138]

indenyl-forward (Π) and indenyl-backward (Y), as discussed previously in this microreview (vide supra). Representative examples of ethylene-bridged parent and heteroatom-substituted bis(indenyl) and bis(tetrahydroindenyl) complexes are displayed in Figures 8 and 9, respectively.

In most cases, racemic ethylene-bridged bis(indenyl)-type metallocenes crystallize in the Π conformation. However, nearly all of the racemic 2-siloxy-substituted complexes crystallize in the less common Y conformation, apparently resulting from the diminished repulsion between the bridge and the 2-substituent of the indenyl ring.[135] As an exception, *rac*-ethylenebis(2-triisopropylsiloxyindenyl)zirconium dichloride *rac*-**49** crystallizes in the indenyl-forward conformation; however, its hydrogenated congener *rac*-**50** again adopts the indenyl-backward conformation in the solid state (Figure 15).[90] Complexes with large equatorial substituents favor the Y conformation, albeit the energy differences between the Π and Y conformations appear to be

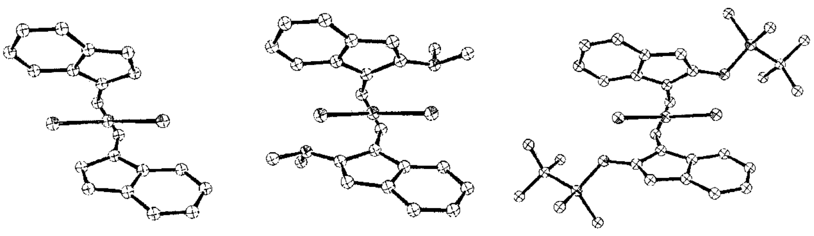


Figure 13. Molecular structures of *rac*-ethylenebis(indenyl)zirconium dichloride (*rac*-**2**) (indenyl-forward conformation),[66] *rac*-ethylenebis(2-dimethylaminoindenyl)zirconium dichloride (*rac*-**9**) (indenyl-forward),[39] and *rac*-ethylenebis(2-*tert*-butyldimethylsiloxyindenyl)zirconium dichloride (*rac*-**42**) (indenyl-backward)[85]

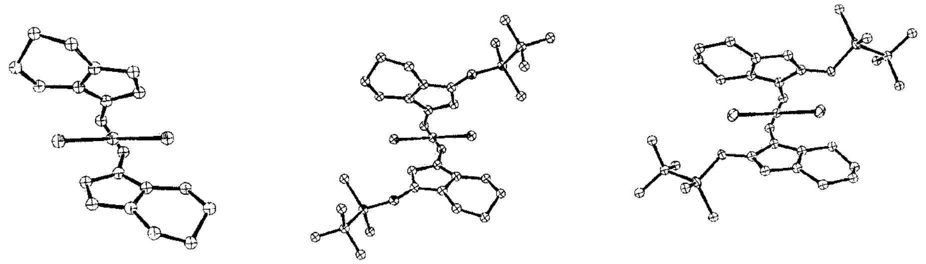


Figure 14. Molecular structures of *rac*-ethylenebis(4,5,6,7-tetrahydroindenyl)zirconium dichloride (*rac*-**5**) (indenyl-forward conformation),[118] *rac*-ethylenebis(1-*tert*-butyldimethylsiloxy-4,5,6,7-tetrahydroindenyl)zirconium dichloride (*rac*-**57**) (indenyl-forward),[92] and *rac*-ethylenebis(2-*tert*-butyldimethylsiloxy-4,5,6,7-tetrahydroindenyl)hafnium dichloride (*rac*-**46**) (indenyl-backward)[121]

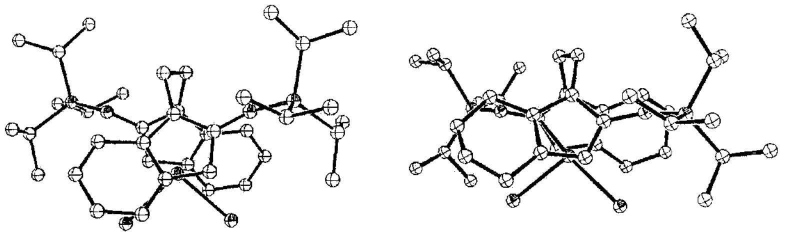


Figure 15. Top views of the molecular structures of *rac*-ethylenebis(2-triisopropylsiloxyindenyl)zirconium dichloride (*rac*-**49**) (indenyl-forward) and of *rac*-ethylenebis(2-triisopropylsiloxy-4,5,6,7-tetrahydroindenyl)zirconium dichloride (*rac*-**50**) (indenyl-backward)[90]

small.[66,67,135] In addition to the siloxy-substituted complexes, the indenyl-backward conformation has also been observed in the solid state by Brintzinger and co-workers for the racemic ethylenebis(4,5,6,7-tetrahydroindenyl)titanium[*O*-acetyl-(*R*)-mandelate],[12,140] by Jordan et al. for the racemic ethylenebis(4,5,6,7-tetrahydroindenyl)zirconium(η^2-CH_2Ph)(CH_3CN)$^+$ cation[141] and racemic ethylenebis(indenyl)hafnium(NMe_2)$_2$,[142] and by Kaminsky and co-workers for racemic ethylenebis(2,4,7-trimethylindenyl)zirconium dichloride.[68]

X-ray crystal structures of the silicon-bridged bis(indenyl)metallocene derivatives display mainly racemic, C_2-symmetric molecules. The coordination sites are surrounded in an equal fashion, in accordance with the conditions for equivalent enantiofacial coordination of prochiral ligands. Structure determinations of the unbridged, amino-substituted complexes reveal that the amino groups are approximately planar.[38−40,44,45] The short C−N bond lengths of about 1.35 Å indicate that the nitrogen lone pair is considerably delocalized into the indenyl five-membered ring. Even so, related planar amino groups and short N−C distances are not found in the silicon- or ethylene-bridged bis(aminoindenyl)zirconium complexes due to the steric interaction of the amino groups with the interannular bridges.[39,41] The nitrogen−chlorine distances are typically slightly shorter than the sum of their van der Waals radii (3.3 Å), and there is no significant bonding. Aforementioned electron donation from the nitrogen atom may result in adequate electron deficiency that allows these short intermolecular distances. For the C_2-symmetric ethylene-bridged 2-siloxy-substituted complexes, the indenyl-backward conformation brings the chlorine and oxygen atoms in closer contact (3.53−3.85 Å) than in the indenyl-forward conformation (4.06 Å).[85,86,90,93,121] In the unbridged 2-siloxy-substituted complex **51**, the Cl−O distance is even shorter (3.141 Å), being shorter than the sum of their relevant van der Waals radii (3.20 Å).[91] Similar short contacts (3.15−3.30 Å) are also found for 1-siloxy-substituted complexes.[92] Then again, the electron donation from the heteroatom to the zirconocene center can result in a sufficient electron shortage that permits the short intramolecular distances.

UV/Vis Spectroscopic Studies

Recently, Mäkelä-Vaarne and co-workers have utilized UV/Vis spectroscopy to study the activation of siloxy-substituted bis(indenyl) complexes with MAO.[143−145] Interestingly, the position of the siloxy substituent was found to have a drastic influence on the activation behavior of the complex. The activation of 2-siloxy-substituted and unsubstituted bis(indenyl) complexes was observed to proceed relatively quickly, contrary to the slow activation of a 1-siloxy-substituted complex, which showed in the UV/Vis spectrum a sequence of three time-consuming reaction steps. With the aid of molecular modeling studies, the reason for the slow activation of the 1-siloxy-substituted complex was interpreted as resulting from an interaction between the oxygen donor atom of the siloxy group and the electron-deficient zirconium atom. According to UV/Vis studies at ambient temperature, to overcome this interaction took several hours, while formation of the final active species occurred for the 2-siloxy-substituted complex in less than a minute.[145]

On increasing the [Al]/[Zr] ratio for the 1-siloxy-substituted bis(indenyl) complex, the UV/Vis spectrum showed an LMCT band shift to higher energies. This shift is indicative of an interaction between the cocatalyst and the siloxy substituent, the net result of which is a decrease in the catalytic activity. At low [Al]/[Zr] ratios this band shift was not observed, which can be correlated with the optimum polymerization performance under such conditions in terms of activity and shortened induction times.[86,95,146]

Polymerization Catalysis

Polymerization catalysis will be discussed here with focus on polymerization activity, molecular weight control and copolymerization ability. Optimally, heteroatom substitution can be utilized to tune the electronic properties of catalyst precursors to stabilize the active cationic species by electron donation, which improves the polymerization activity. Noteworthy, it is to a large extent the interaction of the cocatalyst and the functional groups of the catalyst precursor that determine the net result of the electronic effect on the active cationic center.

Olefin Homopolymerization

To study the electronic effects of ligand substituents, Piccolrovazzi et al.[76] and Collins et al.[77] introduced methoxy groups in the 4,7- and 5,6-positions, respectively, of indenyl ligands. Activation with MAO led to a drastic decrease in the polymerization activity relative to the unsubstituted complexes. This was explained by interaction of MAO with the methoxy groups, which resulted in net electron withdrawal and destabilization of the active center. A similar reasoning can also be used to explain the low activities reported for 2-methoxy-substituted bis(indenyl)zirconocenes.[71] Introduction of 2-amino groups into an indenyl ligand framework was found by Brintzinger et al.[38] and Näsman and co-workers[39] to result in modest activity after an induction period of several hours. The induction time was explained to result from inhibition of the reaction generating the active species, probably again as a consequence of an unfavorable interaction of the donor substituents with the cocatalyst MAO. A similar induction period was reported for a 1-siloxy-substituted bis(indenyl) complex,[95,146] and recently explained to be, in addition to an unfavorable interaction with the cocatalyst, a consequence of an interaction between the donor oxygen atom and the electron-deficient zitconium atom.[145]

Increasing the temperature from 40 to 80 °C or adding triisobutylaluminum to the reaction medium was found to shorten the induction period.[95,146] In contrast to 1-siloxy-substituted bis(indenyl) complexes, 2-siloxy-substituted complexes have been reported not to suffer from such induction periods, which according to molecular modeling studies was explained to result from a weaker O(siloxy)−Zr and a weaker (MAO)Al−O(siloxy) interaction of the latter complexes.[145]

Overall, both 1- and 2-siloxy-substituted bis(indenyl) complexes show a considerable increase in ethylene polymerization activity at low [Al]/[Zr] ratios relative to their unsubstituted analogues. Thus, the polymerization behavior of siloxy-substituted bis(indenyl) systems has been extensively studied.[85−89,91,93−98] It was shown that the optimal catalyst activity for siloxy-substituted bis(indenyl) complexes in homogeneous olefin polymerization is achieved at a remarkably low [Al]/[Zr] ratio of 250. A similar low [Al]/[Zr] ratio for the optimal activity was recently reported by Rieger and co-workers for the heteroatom-substituted C_1-symmetric complexes **30** and **32**.[81] Several reasons for the increased polymerization activity at low [Al]/[Zr] ratios have been suggested.[81,85,86,95] Sufficiently shielded heteroatoms, such as oxygen in trialkylated siloxy substituents or oxygen atoms embedded in a dioxane ring, can be understood to be protected against the attack by the Lewis-acidic aluminum cocatalyst. As a result, the heteroatoms preserve their electron-donating nature in the presence of low amounts of MAO, which facilitates the formation of the active site and stabilizes the cationic metal center. In addition, the weaker bonding of the counterion to the cationic alkylmetallocene might increase the rate of monomer insertion into the metal−alkyl bond and thus the chain propagation rate. One further reason could simply be that the polar oxygen substituents promote the approach of the Lewis-acidic aluminum cocatalyst towards the complex and thus promote the activation reaction in the apolar polymerization medium.

Facilitated activation has also been reported by Kallio and co-workers, who showed that siloxy-substituted bis(indenyl) complexes are more readily activated by higher aluminoxanes, such as hexaisobutylaluminoxane than their unsubstituted analogues.[147]

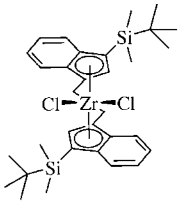
Besides the polymerization activity, the ability to produce sufficiently high-molecular weight polymers is a key factor when evaluating the performance of an olefin polymerization catalyst. Siloxy substitution[85,86,95] and dioxane substitution[81] were found to enhance the probability of chain transfer to aluminum, which was the dominant mechanism for chain termination in propylene polymerization and resulted in rather low polypropylene molecular weights. Chain termination to aluminum has also been reported for 2-amino-substituted complexes in propylene polymeri zation.[38] Rieger et al. reported that borate activation of the dimethylated complex **31** doubled the molecular weight compared with MAO activation of the dichloride.[81] Contrary to propylene polymerization, in ethylene polymerization chain transfer to aluminum has been found to be insignificant for the siloxy-substituted complexes. At 80 °C and with a moderate ethylene concentration of 0.2 mol/dm^3 chain transfer to monomer was found to be the dominant termination mechanism for siloxy-substituted bis(indenyl) complexes, resulting in a number-average molecular weight of 40 kg/mol. For the hydrogenated analogues, chain transfer to monomer was present but less pronounced, and also transfer of β-H to the Zr atom became significant. The number-average molecular weight, 110 kg/mol, was higher than that found for the bis(indenyl) system.[95]

Olefin Copolymerization

Finally, the ability to incorporate comonomers is important when considering the usefulness of a complex to produce linear low-density polyethylene. Table 2 compares the effect of siloxy substituents on the 1-hexene copolymerization ability in ethylene polymerization for bis(indenyl)- and bis(tetrahydroindenyl)zirconium complexes.[95,97] Siloxy substitution in the 1-position of the indenyl ligand was found to markedly improve the α-olefin copolymerization ability, reducing the reactivity ratio of ethylene from 48 to 19 for bis(indenyl) complexes, and from 71 to 30 for the corresponding hydrogenated complexes. The reason for the improved copolymerization ability of 1-siloxy-substituted complexes was explained by their increased coordination gap aperture, which is a parameter generally known to affect comonomer accessibility. Replacing the methyl groups at the silicon atom by isopropyl groups has been reported to further improve the copolymerization ability.[94] In contrast to 1-siloxy substitution, 1-*tert*-butyldimethylsilyl substitution, as reported by Ekholm and co-workers for *rac*-ethylenebis(1-*tert*-butyldimethylsilylindenyl)zirconium dichloride (**100**) (Figure 16), clearly reduced the copolymerization ability and resulted in low molecular weight polymers due to excessive chain transfer after primary comonomer insertion, probably as a consequence of the extensive steric hindrance in the vicinity of the active site.[146] Siloxy substitution in the 2-indenyl position resulted in a slightly reduced copolymerization ability relative to that of the unsubstituted complex.[95]

Table 2. Reactivity ratios r_E for MAO-activated racemic ethylene-bridged C_2-symmetric complexes[95,97,148]

	rac-**2**	*rac*-**55**	*rac*-**42**	*rac*-**5**	*rac*-**57**	*rac*-**100**
1-Hexene:						
T_p = 40 °C	–	15	36	–	14	64
T_p = 80 °C	48	19	55	71	30	100
1-Hexadecene:						
T_p = 80 °C	51	25	63	–	–	–



100

Figure 16. *rac*-Ethylenebis(1-*tert*-butyldimethylsilylindenyl)zirconium dichloride (**100**); only one enantiomer of the racemic pair is shown

Conclusions and Outlook

As shown above, modification of group 4 metallocene complexes with electron-donating heteroatom substituents provides an efficient means for modulating the steric as well as electronic features of this class of organometallic compounds. In most cases, the synthesis of such complexes is straightforward employing conventional organic and organometallic synthesis methods for both ligand and metallocene construction. For example, broad varieties of both 2- and 3-amino-, as well as 2- and 3-siloxyindenes, are obtained in high yields in a single reaction step from 2- and 1-indanones and the corresponding secondary amines or chlorosilanes. Accordingly, a large number of bis(indenyl) group 4 complexes, in particular zirconocenes, containing nitrogen and oxygen atoms directly linked to the indenyl ligand have appeared in the literature in recent years. Most recently, while this microreview was being finalized for publication, Erker and co-workers disclosed the synthesis of 4,7-bis(dimethylamino)indene and zirconocene complexes derived thereof.[149]

In terms of the catalytic applications, remarkable effects have been observed in catalytic olefin polymerization where properly shielded electron-donating substituents on the indenyl ligand can be used to control the electron density of the active metal center and thus its ability to control the formation of the cationic active species, monomer-coordination and chain-termination events in the homo- or copolymerization reaction. For example, the siloxy-substituted bis(indenyl)zirconium complexes reach their maximum activities in the polymerizations of ethylene and propylene at significantly reduced concentrations of the expensive MAO cocatalyst, most likely due to the efficient shielding of the donor atoms from unfavorable coordination of alkylaluminum compounds, allowing them to retain the electron-donating character, which in turn facilitates the formation of the active species. Considering the various promising applications of chiral group 4 metallocenes in stereo- and enantioselective organic synthesis, interesting applications for the electronically modified analogues may be anticipated in these areas as well, while such applications hitherto have remained virtually unexplored.

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