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1,2-Bis(dimethylsilyl)phenylidene bridged zirconocene and hafnocene dichloride complexes as precatalysts for ethylene polymerization

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- Catalytic ethylene polymerization

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Abstract

The synthesis and characterization of a new class of ansa bis(indenyl) complexes of zirconium and hafnium is described. Two indenyl moieties are linked at the 1-,1'- positions via a 1,2-bis(dimethylsilyl)benzene unit. The ligand precursor was prepared via three reaction steps including Grignard coupling of chlorodimethylsilane and 1,2-dibromobenzene, $PdCl_2$ -catalyzed chlorination, and the reaction with indenyllithium. The zirconium and hafnium complexes were obtained by deprotonation of the corresponding bis-(indenyl) compound with n-BuLi followed by metalation reactions of MCl_4 (M = Zr, Hf) in tetrahydrofuran. The solid state molecular structures of both complexes were established by single crystal X-ray diffraction analyses. In ethylene polymerization reactions, both complexes exhibited high activities. The zirconocene catalyst **4** showed a higher activity (7610 kg PE/mol cat. h) compared to the hafnium catalyst **5** (3590 kg PE/mol cat. h).

1. Introduction

A wide range of bridged bis(indenyl) metallocene complexes has been synthesized and tested as catalyst precursors for olefin polymerization [1-7]. These complexes include different bridging-type moieties. However, the most commonly used bridges are the dimethylsilylene, ethylidene, isopropylidene, and methylene units [8, 9, 10-14]. The structure of the bridging unit in ansa metallocene complexes has a strong influence on the catalyst activity and the molecular weight of the generated polymers [15]. The activity can be improved by enlarging the reaction space around the metal center, mainly by increasing the metal-centroid distance and the dihedral angle between the two indenyl based π -ligands. In contrast to silylene and alkylidene bridged metallocene complexes, few examples of ansa-metallocene complexes are known containing bulky aromatic groups as bridges. For instance, *o*-xylidene- and naphthylidene-bridged catalysts have recently been synthesized and evaluated as catalysts for ethylene and propylene polymerization after activation with MAO [16, 17]. In this context ansa

bis(indenyl) complexes of Ti, Zr and Hf with dimethylsilylene bridges and sterically demanding 4-aryl substituents proved as highly isoselective catalyst precursors for the polymerization of propylene [18-20]. Herein, a synthesis of new ansa-complexes of zirconium and hafnium is described, with two indenyl ligands linked through a 1,2-bis(dimethylsilyl)phenylidene bridge. The catalytic behavior for ethylene polymerization after activation with methylaluminoxane (MAO) in homogeneous solution is described.



Scheme 1: General structural formula of the prepared metallocene complexes.

2. Results and discussion

2.1. Synthesis of the ligand precursor

1,2-Bis(inden-1-yldimethylsilyl)benzene **3** was prepared via a three step reaction that comprises Grignard coupling of 1,2-dibromobenzene with chlorodimethylsilane to give 1,2-bis(dimethylsilyl)benzene (**1**), followed by chlorination with carbon tetrachloride in the presence of a catalytic amount of palladium dichloride to obtain 1,2-bis(chlorodimethylsilyl)benzene (**2**) [21]. The desired compound was readily prepared by the reaction of compound **2** with two equivalents of indenyllithium (prepared separately via reaction of indene and n-butyllithium in ether) (Scheme 2). This reaction was necessarily conducted in ether at room temperature. If another solvent such as tetrahydrofurane (THF) is used, the undesired monoindenyl spiro compound is formed as a side product. This proceeds by deprotonation at the C1-position in the already silyl bonded indene followed by an intramolecular reaction with the chlorine atom of the same molecule leading to the formation of the cyclic mono substituted indenyl derivative with a sp³- hybridized carbon atom. Compound **3** was initially obtained with trace

amounts of the monoindenyl substituted derivative as side product. Thus, the purity was improved via prolonged evacuation at elevated temperatures.





2.2. Characterization of compound 3

Compound **3** was characterized by ¹H NMR, ¹³C NMR and GC/MS (Experimental, Table 4). The ¹H NMR spectrum of compound **3** (Scheme 3) shows multiplet signals at δ = 7.76-7.73 (m, 2H), 7.50-7.46 (m, 2H), 7.29-7.26 (m, 4H) and 7.14-7.09 ppm (m, 4H) for the aromatic protons of both the bridge and the indenyl moiety (H10, H11, H4, H5, H6 and H7). The two signals appearing at δ = 6.96 (d, ³J(H,H) = 5.2 Hz, 2H) and 6.57 ppm (dd, 2H) can be assigned to the protons at the 3- and 2-positions of the indenyl moiety (H3 and H2). The protons at the 1-positions of the indenyl moieties (H1) produce the signal at δ = 4.00 ppm (s, 2H) while the silyl protons H8 and H9 appear as singlets at δ = 0.19 (s, 6H) and 0.21 ppm (s, 6H) indicating slightly different magnetic environment.



The ¹³C NMR spectrum of compound **3** (Scheme 4) shows three resonance signals at $\overline{\delta}$ = 145.0, 144.4 and 144.0 ppm attributed to the quaternary carbon atoms C8, C9, and C12. The two signals at $\overline{\delta}$ =136.2 and 135.7 ppm correspond to C2 and C3 of the indene five membered ring, while the CH–type carbon atoms in the indenyl moiety (C4, C5, C6 and C7) give signals at $\overline{\delta}$ =129.7, 125, 123.6, and 123.0 ppm. The two signals at $\overline{\delta}$ =128.3 and 121.0 ppm can be assigned to the carbon atoms of the phenyl ring (C13 and C14). The carbon atom at the 1-position of the indenyl ligand (C1) shows a signal at $\overline{\delta}$ = 45.8 ppm while the silyl methyl groups (C10 and C11) show signals at $\overline{\delta}$ = -1.3 and - 1.9 ppm indicating slightly different magnetic environment.



Scheme 4: ¹³C NMR spectrum of 3 in C₆D₆

The mass spectrum of **3** (Scheme 5) shows the molecular ion peak at m/z = 422 with 88% intensity. The ion formed by the loss of one indenyl unit [M⁺-indenyl] generates the peak at m/z = 306 (intensity 45%) while the loss of two indenyl units from the molecule gives rise to the base peak at m/z = 191.



Scheme 5: Mass spectrum of compound 3.

2.5. Synthesis of 1,2-phenylene-bis(inden-1-yldimethylsilyl) complexes of zirconium (4) and hafnium (5)

The 1,2-phenylidenedisilyl bridged bis(indenyl) complexes of zirconium and hafnium were synthesized by a method that comprises the deprotonation of the bridged bis(indenyl) compound **3** with two equivalents of n-butyllithium (n-BuLi) in ether at -78°C. A subsequent reaction of the resulting dilithium salt with one equivalent of zirconium (IV) chloride or hafnium (IV) chloride in THF at -78°C afforded the mononuclear zirconocene dichloride complex **4** and the hafnocene dichloride complex **5**. The general synthetic method is illustrated in Scheme 6. Reactions of ZrCl₄ and HfCl₄ with the ligand precursor **3** proceeded successfully to afford the corresponding ansa metallocene complexes. However, the reaction of TiCl₄ with compound **3** under various reaction conditions was not successful.



1) 2 n-BuLi / THF, -78°C 2) MCl₄ / THF, 60°C, 72 h -2Bu-H -2LiCl



Scheme 6: Synthesis of complexes 4 and 5.

2.6. Characterization of the complexes 4 and 5

The synthesized metallocene dichloride complexes were characterized by ¹H NMR, ¹³C NMR, mass spectroscopy (Experimental, Table 5), and elemental analysis. The molecular structures of both complexes were determined with single crystal X-ray diffraction (Schemes 10 and 11).

The ¹H and ¹³C NMR spectra of complex **4** are discussed as examples. The ¹H NMR spectrum of complex **4** (Scheme 7) shows a multiplet at $\delta = 7.99-7.97$ ppm (2H) which is assigned to the aromatic protons H13. The overlapping signal appearing at $\delta = 7.59-7.53$ ppm (m, 6H) can be assigned to the protons H14, H4 and H7 while the multiplet signal appearing at $\delta = 7.23-7.20$ ppm (m, 4H) is attributed to the protons H5 and H6 at the six-membered ring of the indenyl ligands. The protons at the 3- and 2-positions of the indenyl moieties (H3 and H2) are characterized by the signals at $\delta = 6.56$ ppm (br, 2H) and $\delta = 5.72$ ppm (br, 2H) The methyl groups (H10 and H11) produce two singlets at $\delta = 0.70$ (6H) and $\delta = 0.61$ ppm (6H) indicating different magnetic environments.



Scheme 7: ¹H NMR spectrum of the complex 4 in CDCl₃

The ¹³C NMR spectrum for complex **4** (Scheme 8) shows a signal at δ = 143.5 ppm corresponding to the quaternary carbon atom C12. The aromatic carbon atoms C13 and C14 give the two signals at δ =136.7 and 129.4 ppm. The two signals appearing at δ =132.4 and 131.9 ppm are generated by the quaternary carbon atoms of the indenyl moiety (C8 and C9). The signal at δ =131.7 ppm is assigned to C3 while the four resonances at 127.1, 126.9, 125.8 and 125.7 ppm are attributed to the CH-type carbon atoms of indene C7, C4, C5, and C6. The signal which appears at δ =110.8 ppm is assigned to C2 while the signal at δ = 107.0 ppm is characteristic for the quaternary carbon atom C1 at the 1-position of the indenyl moiety. The two signals appearing at δ = 3.4 and 1.2 ppm are attributed to the silyl methyl groups C10 and C11 indicating a slightly distorted molecule.



Scheme 8: ¹³C NMR spectrum of complex 4 in CDCl₃

The mass spectrum of the zirconium complex **4** (Scheme 9) shows the molecular ion peak at m/z = 582 with 62% intensity. Due to the presence of isotopes (Zr, Cl), a characteristic distribution of M⁻⁺ peaks are observed. The ion formed by the loss of one chloro ligand or one HCl molecule produces the peaks around m/z = 544 with 58% intensity. The ionized ligand molecule gives a 10% intensity peak at m/z = 422, while the loss of one indenyl unit from the ligand [ligand-Ind] produces the peak at m/z = 306 with 45% intensity. The base peak at m/z = 172 results from a fragment containing an indenyldimethylsilyl unit.



Scheme 9: Mass spectrum of complex 4

2.7. Crystal structures of complexes 4 and 5

Single crystals suitable for the X-ray diffraction analyses of complexes **4** and **5** were obtained by slow solvent evaporation from concentrated solutions of pentane/toluene mixtures in an approximately 9:1 ratio. The molecular structures of the complexes have been established by single crystal X-ray diffraction analyses. The ORTEP diagrams of **4** and **5** are displayed in Schemes 10 and 11 Selected bond lengths and angles for complexes **4** and **5** are presented in Tables 1 and 2, crystal data and structural refinements in Tables 6 and 7 (Experimental).



Scheme 10: ORTEP diagram of complex **4**, ellipsoids are drawn in 30% probability level. Hydrogen atoms have been omitted for clarity.



Scheme 11: ORTEP diagram of complex **5**, along with atom numbering scheme, ellipsoids are drawn in 30% probability level. Hydrogen atoms are drawn as spheres with fixed small radius. Hydrogen atom names are omitted for clarity.

Table 1: Selected Bond lengths and angles of	4
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Selected bond lengths [Å]		Si(1)-C(1)	1.867(4)
Zr-Cl(1)	2.4230(14)	Si(2)-C(20)	1.872(4)
Zr-Cl(2)	2.4398(11)	Cen1-Zr	2.2513
Zr-C(1)	2.499(3)	Cen2-Zr	2.2114
Zr-C(2)	2.634(3)	Cen1-Cen2	4.0520
Zr-C(7)	2.654(3	Selected bonds a	ngles[°]
Zr-C(8)	2.506(4)	Cl(1)-Zr-Cl(2)	96.81(5)

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Zr-C(9)	2.490(3)	C(1)-Si(1)-C(12)	111.68(18)
Zr-C(20)	2.491(3)	C(20)-Si(2)-C(17)	114.49(16)
Zr-C(21)	2.465(3)	C(2)-C(1)-Si(1)	126.2(3)
Zr-C(22)	2.479(3)	C(28)-C(20)-Si(2)	129.1(3)
Zr-C(23)	2.565(4)	Dihedral angle	51.36(8)
Zr-C(28)	2.617(4)	Cen1-Zr-Cen2	130.453

Table 2: Selected Bond lengths and angles of 5

Selected bond le	ngths [Å]	Si(1)-C(1)	1.868(4)
Hf-Cl(1)	2.4095(14)	Si(2)-C(10)	1.855(4)
Hf-Cl(2)	2.3921(14)	Cen1-Hf	2.194(4)
Hf-C(1)	2.469(4)	Cen2-Hf	2.231(5)
Hf-C(2)	2.449(4)	Cen1-Cen2	4.024(8)
Hf-C(3)	2.464(4)	Selected bonds a	ngles[°]
Hf-C(4)	2.549(4)	CI(1)-Hf-CI(2)	95.91(4)
Hf-C(9)	2.596(4)	C(1)-Si(1)-C(23)	113.77(15)
Hf-C(10)	2.473(4)	C(10)-Si(2)-C(24)	111.32(19)
Hf-C(11)	2.452(4)	C(9)-C(1)-Si(1)	129.7(3)
Hf-C(12)	2.485(4)	C(18)-C(10)-Si(2)	125.8(3)
Hf-C(13)	2.644(4)	Dihedral angle	51.478(150)
Hf-C(18)	2.625(4)	Cen1-Hf-Cen2	130.813(10)

The solid state crystal structure analysis shows that the metallocene dichloride complexes 4 and 5 are isostructural and adopt a pseudotetrahedral coordination geometry around the metal atom formed by two chlorine atoms and two η^5 -coordinated indenyl ligands. As both complexes have closely equivalent bond lengths and angles, the following description of complex 4 is also valid for 5. One of the important features is that the indenyl ligand planes in the molecule are twisted from being perfectly C₂symmetric thus leading to a distorted rac orientation. In 4, the angle Cl(1)-Zr-Cl(2) is 96.81° which is comparable to that of the unbridged zirconocene complex Ind₂ZrCl₂ (94.71°) [22] and the Me₂Si bridged metallocene complex Me₂Si(Ind)₂ZrCl₂ (98.76°) [23]. The angle that comprises the zirconium atom and the two five membered ring planes, Cen-Zr-Cen, is 130.45° which is larger than that of Ind₂ZrCl₂ (128.3°) and the bridged Me₂Si(Ind)₂ZrCl₂ (127.8°). The Zr-C bond distances are different; the quaternary carbon atoms between the five- and six-membered rings, C(2), C(7), C(23), and C(28), are apparently further away from the zirconium atom compared to the three remaining carbon atoms. These two common carbon atoms are covalently bonded to three other carbon atoms, which reduces their bonding ability to zirconium [24]. The value of the dihedral angle between the two planes of the five ring centroids is 51.37° which is smaller than that of Me₂Si(Ind)₂ZrCl₂ with a difference of Δ = 10.57°. For metallocene complexes prepared for catalytic functions, the greater dihedral angle allows better access of the monomer molecules to the cationic metal center. Therefore, catalysts with wider dihedral angles should show comparatively higher activities. The distance between the zirconium and the Cen1 plane is 2.2513 Å being slightly longer than the Zr-Cen2 distance (2.2114 Å), the distance between the two centroids is 4.05 Å and the zirconium atom is located 0.935 Å out of this Cen1-Cen2 vector.

2.9. Ethylene polymerization experiments with complexes 4 and 5

Complexes **4** and **5** are ansa bis(1-indenyl) metallocene dichloride complexes, the two indenyl ligands are tethered via a 1,2-bis(dimethylsilyl) phenylene bridge.



The catalytic activities of complexes **4** and **5** in the homogeneous polymerization of ethylene along with the results of the polymer analyses are summarized in Table 3. Methylaluminoxane (MAO) was used as a cocatalyst (M:AI = 1:2000), the experiments were conducted at a polymerization temperature of 60° C, 10 bar ethylene pressure, and in 250 ml of pentane for one hour. The produced polyethylene samples were analyzed by GPC, DSC and viscosimetry.

Table 3: Ethylene polymerization activities and analyses of the polymers produced with complexes **4/**MAO and **5/**MAO.

Complex				DSC		M _n [g/mol]
No.	IVI	Activity	∆H _m [J/g]	Т _т [°С]	[α]	
4	Zr	7610	124.5	135.5	0.43	366000
5	Hf	3590	124.6	135.5	0.43	375000

^a (kg PE/mol cat. h)

Both MAO-activated zirconium and hafnium catalysts were active in ethylene polymerization. The zirconium catalyst **4**/MAO gave a higher activity compared to the hafnium complex derived from the same ligand while the hafnium catalyst **5**/MAO produced polyethylene with apparently higher molecular weight. This result is consistent with the experience that zirconocene catalysts provide higher activities while the

hafnocene analogues produce polyolefins with greater molecular weights [25]. The difference in the polymerization behavior between Zr- and Hf-based catalysts could be attributed to thermodynamically stronger σ -bonds between hafnium and the polymer chain (Hf-C), slowing down not only the chain propagation but also the release of the chain, giving rise to less activities and higher molecular weight polyethylenes [26]. In line with this assumption, a recent study of hafnocene catalysts demonstrated that the activation energies for chain propagation and termination are significantly higher compared with zirconium catalysts [27]. The catalytic activity of 4/MAO in homogeneous polymerization of ethylene is, as expected, lower, than the activities observed for the unbridged bis-indenyl metallocene complex [28] and that of the single atom bridged metallocene complexes such as -CH2- [29,30], -Me2C- [31,32], and -Me₂Si-[33,34] bridged species. Similar results are observed when comparing the activity of 4/MAO with the widely known ethylidene bridged catalyst precursor, [35,36] rac-[Et(Ind)₂)]ZrCl₂ ("Brintzinger catalyst"). However, in terms of molecular weight, catalyst 4/MAO produces a polyethylene with the highest molecular weight compared with the above mentioned catalysts (except the Me₂Si-bridged one). The comparatively lower activity of 4/MAO can be rationalized by the existence of the 4 atoms-bridge, 1,2bis(dimethylsilyl)phenylene, incorporating 2 C and 2 Si atoms. This rigid and long bridge resulted in a smaller dihedral angle and thus the zirconium center becomes more shielded. From the crystal structure data of complex 4 (Table 1), the value of the dihedral angle was determined to 51.4° , whereas the dihedral angles reported for CH₂-, Me₂C-, Me₂Si-, and C₂H₄-bridged metallocene complexes are 72.4°, 70.9°, 61.6° and 62.1°. A greater value of the dihedral angle between the ligand planes enhances the activity in olefin polymerization by increasing the reaction space of the metal center [34]. Catalyst 4 exhibited a far better catalytic performance in terms of both activity and molecular weight compared with the known metallocene catalysts comprising 4-atombridges such as o-xylidene-bridge [24] and (-Me₂Si-CH₂-CH₂-Me₂Si-)-bridged [37] catalysts. This distinction could be explained by the favourable replacement of the two methylene groups with two dimethylsilyl groups in 4. In this context it also must be considered that the silicon atoms in the bridge can behave as Lewis acids and interact with the Lewis basic oxygen atoms of the MAO counter anion of the activated catalyst in an advantageous manner. Changing the metal centre in this catalyst system seems to have no influence on the melting points and crystallinity values of the polyethylenes.

The polyethylene produced with the zirconium catalyst **4**/MAO was analyzed by high temperature gel permeable chromatography, GPC. The values of polymer molecular weights and PD are as follows; $M_n = 90116$, $M_w = 265361$ (g/mole); PD = 2.94

The molecular weight distribution of the polymer sample produced with **4**/MAO is shown in Scheme 12



Scheme 12: Molecular weight distribution curve of the polyethylene produced with 4/MAO

3. Experimental

3.1 General

All reactions were carried out under an inert gas atmosphere of pure oxygen-free argon using standard Schlenk techniques. n-Pentane, n-hexane, diethyl ether, toluene, and tetrahydrofuran were purified by distillation over Na/K alloy. Diethyl ether was additionally distilled over lithium aluminum hydride. Toluene was additionally distilled over phosphorus pentoxide. Methylene chloride and carbon tetrachloride were dried over phosphorus pentoxide. Deuterated organic solvents (CDCl₃, CD₂Cl₂, and C₆D₆) for NMR spectroscopy were purchased from Euriso-Top and stored over molecular sieves (3 Å). Argon (5.0) and ethylene (3.5) were purchased from Rießner Company. Methylaluminoxane (10% in toluene) was purchased from Chemtura Europe Limited (Bergkamen). All other starting materials were commercially available and used without further purification.

3.2 NMR spectroscopy

NMR spectra were recorded with Bruker ARX (250 MHz), Varian Inova (300 MHz) or Varian Inova (400 MHz) spectrometers. All spectra were recorded at 298 K. In the ¹H-NMR spectra, the chemical shift of the residual proton signal of the solvent was used as a reference ($\delta = 7.24$ ppm for chloroform, $\delta = 5.32$ ppm for methylene chloride, $\delta = 7.16$ ppm for benzene). In the ¹³C-NMR spectra, the chemical shift of the solvent was used as a reference ($\delta = 77.0$ ppm for chloroform-d₁, $\delta = 54.0$ ppm for methylene chloride-d₂, $\delta = 128.0$ ppm for benzene-d₆).

3.3 GC/MS

GC/MS spectra were recorded with a Thermo FOCUS gas chromatograph combined with a DSQ mass detector. A 30 m HP-5 fused silica column (internal diameter 0.32 mm, film 0.25 µm and flow 1 ml/min) was used and helium (4.6) was applied as carrier gas. The measurements were recorded using the following temperature program: Starting temperature: 50 °C, duration: 2 minutes; Heating rate: 20 °K/minute, duration: 12 minutes; Final temperature: 290 °C, duration: 27 minutes.

3.4 Mass spectrometry

Mass spectra were recorded with a VARIAN MAT CH-7 instrument (direct inlet, EI, E = 70 EV) and a VARIAN MAT 8500 spectrometer at the Zentrale Analytik of the University of Bayreuth.

3.5 Elemental analysis

Elemental analyses were performed with a Vario EL III CHN instrument. Therefore, 4-6 mg of the complex were weighed into a standard tin pan. The tin pan was carefully

closed and introduced into the auto sampler of the instrument. The values of C, H and N were calibrated using acetamide as a standard.

3.6 High temperature gel permeable chromatography GPC

The molecular weights (Mw/Mn) of the ethylene polymers were determined by gel permeation chromatography, HT-GPC PL-220 chromatograph at 150°C using 1,2,4-trichlorobenzene as the mobile phase. The sample was prepared by dissolving the polymer (0.2 mg/l) in the mobile phase solvent in an external oven and was run without filtration. The molecular weight was referenced to polystyrene (Mw = 510 - 3100000 g/mol) standards. The reported values are the average of at least two independent determinations.

3.7 DSC analysis

Differential scanning calorimetry experiments were conducted at a heating rate of 10°C/min under N₂ atmosphere with a Mettler Toledo DSC/SDTA 821e instrument. Melting enthalpies and melting points were taken from the second heating phase. The values were calibrated using indium as a standard (m.p. 429.78 K, H_m = 28.45 J/g).

3.8 Viscosimetry analysis

Viscosimetry analyses for the determination of the viscosity average molecular weights $[M_{\eta}]$ of the polyethylene samples were performed on an Ubbelohde precision capillary viscometer in cis/trans-decalin at 135 ± 0.1 °C. For the preparation of the sample solutions, an amount of 50 mg of the polymer was dissolved in decalin (45 ml) by heating for 3 hours at 135 °C. M_{η} values were determined by comparing the obtained values with calibration curves available for different polymer concentrations.

3.9 Single crystal X-rays diffraction

The crystal structure analysis of complex **4** was performed with a STOE-IPDS II diffractometer equipped with an Oxford Cryostream low-temperature unit. The crystal structure analysis of complex **5** was performed with a MarIP MAR345DTB devise (Mo-K α radiation, $\lambda = 0.71073$ Å).

Crystal data:

Complex **4**: Yellow cubic crystals, crystal system is triclinic; space group is P-1; a = 9.1925 (18) Å, b = 10.110(2) Å, c = 15.726(3) Å; α = 91.36(3)°, β = 100.26(3)°, γ = 111.24(3)°; volume is 1333.6(5) Å³; d _(calc) = 1.451 g/cm³; wavelength = 0.71073 Å; absorption coefficient = 0.718 mm⁻¹; F(000) = 596; reflections collected 6271; independent reflections 4372 [R(int) = 0.0396]; Goodness-of-fit = 0.938; R indices (R1 = 0.0547, wR2 = 0.1022).

Complex **5**: Yellow cubic crystals, crystal system is triclinic; space group is P-1;, a = 9.1624 (16) Å, b = 10.0503(18) Å, c = 15.643(3) Å; α = 91.567(19)°, β =100.285(18)°, γ = 111.167(8)°; volume is 1315.0(4) Å³; d = 1.6918 g/cm³; wavelength = 0.71069 Å; absorption coefficient = 4.276 mm⁻¹; F(000) = 660; no. of all reflections 11018; no. of observed reflections 8001 [R(int) = 0.056]; GOF (obs/all) = 1.01/-0.87; R(F) = 0.0422 (wR(F) = 0.0395).

Crystallographic data on (4) and (5) have been deposited at the Cambridge Crystallographic Data Centre. The data can be retrieved free of charge under numbers CCDC 1557277 for (4) and CCDC 1557278 for (5).

3.10 Polymerization of ethylene

Few milligrams of the complexes were dissolved or suspended in toluene (5-10 ml) and mixed with the appropriate amount of methylaluminoxane (MAO). The activated complexes were suspended in pentane (250 ml) in a 1I Schlenk flask and then transferred under argon to a 1I Büchi autoclave. The temperature of the thermostat was adjusted to the desired value and an ethylene pressure of 10 bar was applied for one hour. After releasing the pressure, the obtained polymer was filtered over a frit, washed with dilute hydrochloric acid, water, and finally with acetone and dried under vacuum.

3.11. Synthesis procedures

3.11.1 Preparation of 1,2-bis(chlorodimethylsilyl)benzene (2)

A solution of 1,2-dibromobenzene (16.5 g, 70 mmol) in 70 ml of THF was added slowly to a stirred mixture of magnesium powder (3.7 g, 147 mmol) and chlorodimethylsilane (14.0 g, 147 mmol) in 15 ml of THF. The mixture was refluxed for 3 hours. After cooling, the solution was decanted from solid magnesium salts and the solvent was removed under vacuum. The residual oil was extracted and washed with a large amount of n-hexane. After removal of the solvent, the residue was purified by distillation under reduced pressure to afford 1,2-bis(dimethylsilyl)benzene (1) in 60% yield. Compound 1 (20 mmol) was mixed with 40 ml of dry carbon tetrachloride and 0.2 g of palladium dichloride in a 100 ml two necked flask equipped with a reflux condenser. The mixture was refluxed for 3 hours and excess carbon tetrachloride and chloroform were removed by evacuation. The residual oil was distilled at 85 °C (1 mbar) to obtain compound **2** in 90% yield.

3.11.2. General synthesis of the ligand precursor 3

An amount of 16 mmol of indene was dissolved in 70 ml of diethyl ether and cooled to -5 °C. Subsequently, n-butyllithium (16 mmol) was added dropwise over 30 minutes followed by stirring at room temperature for 2 hours. To this mixture, another solution of 1,2-bis(chlorodimethylsilyl)benzene (8 mmol) in 50 ml of diethyl ether was added dropwise from a dropping funnel equipped with a pressure equalizer. After the addition was completed, the solution was stirred for one hour and filtered from the solid lithium chloride. The solution was evaporated and methylene chloride (200ml) was added. After filtration, the solvent was removed under high vacuum. Compounds **3** was obtained as heavy brownish waxy material in 80-90% yields.

3.11.3. General synthesis of the transition metal complexes 4 and 5

A quantity of 2 mmol of 1,2-bis(1-indenyldimethylsilyl)benzene (**3**) was dissolved in 50 ml of THF and cooled to -78 °C. To this solution, n-butyllithium (4 mmol, 1.6 M in hexanes) was slowly syringed. This solution was allowed to warm to room temperature and stirred for further 3 hours till no more gas evolution was observed. The resulting solution was transferred via cannula to a solution of zirconium tetrachloride (2 mmol) or hafnium tetrachloride (2 mmol) in 20 ml of THF at -78 °C. After warming to room temperature, the mixture was subsequently stirred for 48 hours at 60-65 °C. The solvent was removed in vacuo and toluene (100) ml was added. The toluene suspension was filtered, the clear solution was concentrated to approximately 5 ml and the complexes were precipitated by the addition of n-pentane. After filtration, the precipitate was washed several times with n-pentane and dried in vacuo to obtain the desired complexes as yellow powders in 70-75% yields. Both complexes were crystallized from concentrated pentane/toluene mixtures to obtain yellow cubic crystals suitable for X-ray crystallography analysis. Elemental analysis:

No.	C _{exp} %	C _{theor} %	H _{exp} %	H _{theor} %
4	57.65	57.70	4.79	4.84
5	49.75	50.19	4.25	4.21

Table 4: ¹ H,	¹³ C NMR	and GC/MS	data for com	pounds 1-3
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No.	¹ H NMR	¹³ C NMR	MS [m/z] (%)
1 ^a	7.64-7.60 m (2H) 7.44-7.38 m (2H) 4.78-4.72 m (2H) 0.43 s (6H, Si-CH ₃) 0.41 s (6H, Si-CH ₃)	144.3 (C _q) 134.3, 128.4 (CH) -2.6 (Si(CH ₃) ₂)	194 [M⁺] (10) 179 M⁺-Me (46) 134 (100)
2 ^a	7.90-7.88 m (2H) 7.47-7.45 m (2H) 0.80 s (12H, Si(CH ₃) ₂)	141.7 (C _q) 135.5, 129.3 (CH) 5.2 (Si(CH ₃) ₂)	247.0 M⁺-Me (100) 211 M⁺-HCI (38) 119 (23)

3 ^b	7.76-7.73 m (2H) 7.50-7.46 m (4H) 7.29-7.26 m (2H) 7.14-7.09 m (4H) 6.96 d (3 J =5.2 Hz, 2H, C ₃ -Ind) 6.57 dd (2H, C ₂ -Ind) 4.00 s (2H, C ₁ -Ind) 0.22 s (6H, Si-CH ₃) 0.20 s (6H, Si-CH ₃)	145.0, 144.4, 144.0 (C_q) 136.2 (CH, C ₂ -Ind) 135.7 (CH, C ₃ -Ind) 129.7, 128.3, 125.0, 123.6 123.0, 121.0 (CH) 45.8 (CH, C ₁ -Ind) -1.3, -1.9 (Si(CH ₃) ₂)	422 M ⁺ (88) 306 M ⁺ -Ind (45) 135 (85) 191 M ⁺ -2Ind (100)
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^a δ (ppm) rel. CDCl₃ (7.24 ppm, ¹H NMR and 77.0 ppm, ¹³C NMR) at 298 K.

^b δ (ppm) rel. C₆D₆ (7.16 ppm, ¹H NMR and 128.0 ppm, ¹³C NMR) at 298 K.

Table 5: ¹H, ¹³C NMR and MS data for complexes 4 and 5.

Complex	¹ H-NMR	¹³ C-NMR	MS [m/z] (%)
4 ^a	7.99-7.97 m (2H) 7.59-7.53 m (6H) 7.23-7.20 m (4H) 6.56 br (2H, C ₃ -Ind) 5.72 br (2H, C ₂ -Ind) 0.70 s (6H, Si-CH ₃) 0.61 s (6H, Si-CH ₃)	$\begin{array}{c} 143.5 \ (C_q) \\ 136.7 \ (CH) \\ 132.4, \ 131.9 \ (C_q) \\ 131.7 \ (CH, \ C_3\text{-Ind}) \\ 129.4, \ 127.1, \ 126.9, \\ 125.8, \ 125.7 \ (CH) \\ 110.8 \ (CH, \ C_2\text{-Ind}) \\ 107.0 \ (C_q, \ C_1\text{-Ind}) \\ 3.4, \ 1.2 \ (Si(CH_3)_2) \end{array}$	582 M ⁺ (62) 544 M ⁺ -HCI (58) 422 M ⁺ -ZrCl ₂ (10) 307 (46) 172 (100)
5 ^a	7.98-7.95 q (2H) 7.57-7.48 m (6H) 7.20-7.17 q (4H) 6.54 br (2H, C ₃ -Ind) 5.58 br (2H, C ₂ -Ind) 0.68 s (6H, Si-CH ₃) 0.59 s (6H, Si-CH ₃)	$\begin{array}{c} 143.7 \ (C_q) \\ 136.6 \ (CH) \\ 131.9 \ (C_q) \\ 131.5 \ CH \ (C_3\text{-Ind}) \\ 131.1 \ (C_q) \\ 129.4, \ 127.0, \ 126.9, \\ 125.7, \ 125.5 \ (CH) \\ 108.0 \ (CH, \ C_2\text{-Ind}) \\ 103.8 \ (C_q, \ C_1\text{-Ind}) \\ 3.5, \ 1.0 \ (Si(CH_3)_2) \end{array}$	670 M ⁺ (85) 634 M ⁺ -HCI (10) 421 M ⁺ -HfCI₂-H (30) 172 (100)

 $^{a)}$ δ (ppm) rel. CDCl_3 (7.24 ppm, 1H NMR and 77.0 ppm, ^{13}C NMR) at 298 K.

Table 6: Crystal data and structure refinement for 4.

Chemical formula	$C_{28}H_{28}CI_2Si_2Zr$
M _r	582.80
Temperature (K)	293(2)
Space group, crystal system	P-1, Triclinic
<i>a</i> (Å)	9.1925(18)
b (Å)	10.110(2)
<i>c</i> (Å)	15.726(3)
α (°)	91.63(3)
eta (°)	100.26(3)
γ(°)	111.24(3)
Volume (ų)	1333.6(5)
Z	2
Density (calculated) (g/cm ³)	1.451
Wavelength (Å)	0.71073
Absorption coefficient (mm ⁻¹)	0.718
Crystal size (mm ³)	0.28 x 0.18 x 0.16
$[\sin(\theta)/\lambda]_{max}$ (Å ⁻¹)	0.6170
Absorption correction	None
Unique reflections, all	4372
observed $[I > 2\sigma(I)]$	3350
R _{int}	0.0396
Completeness up to $\theta = 26.01^{\circ}$	83.0 %
GoF (obs/all)	0.938
wR2 (obs/all)	0.0956 / 0.1022
R1 (obs/all)	0.0398 / 0.0547
No. of parameters	298
$\Delta ho_{max} / \Delta ho_{min}$ (eÅ ⁻³)	0.534 / -0.314

Chemical formula	CallaSiaHf
M.	670 10
Temperature (K)	293
Space group, crystal system	<i>P</i> -1. Triclinic
a (Å)	9.1624(16)
b (Å)	10.0503(18)
c (Å)	15.643(3)
α (°)	91.567(19)
β(°)	100.285(18)
γ (°)	111.167(8)
Volume (Å ³)	1315.0(4)
Z	2
Density (g cm ⁻³)	1.692
Wavelength (Å)	0.71069
Absorption coefficient (mm ⁻¹)	4.276
Crystal size (mm ³)	0.3 imes 0.2 imes 0.2
$[\sin(\theta)/\lambda]_{max}$ (Å ⁻¹)	0.8709
Absorption correction	Empirical, multiscan
Unique reflections, all	11018
observed $[I > 3\sigma(I)]$	8001
R _{int}	0.056
Completeness up to $\theta = 38.24^{\circ}$	75.8 %
GoF (obs/all)	1.61/1.79
wR _F (obs/all)	0.0395 / 0.0663
R _F (obs/all)	0.0422 / 0.0446
No. of parameters	299
$\Delta ho_{max} \Delta ho_{min}$ (eÅ ⁻³)	1.01/-0.87

Conclusions

This contribution confirms the statement for ansa metallocene catalysts: the bridge makes the difference. On the first look, this is hard to understand because the bridge of ansa metallocene complexes is far away from the active center. However, the bridge has an influence on the dihedral angle the aromatic ligands are forming and hence on the kinetics of the incoming monomer and the produced polymer chain. In

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addition, the bridge seems to interact with the bulky MAO counteranion that is formed in the activation process of the catalyst precursor. Since the bridge of the catalyst precursors contains the Lewis acidic heteroatom silicon, an advantageous electronic effect of the bridge must also be considered.

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Highlights:

- ansa Bis(indenyl) complexes
- Bis(dimethylsilyl)phenylidene bridge
- Zirconium and hafnium complexes
- X-ray structures
- Catalytic ethylene polymerization