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Synthesis and olefin polymerization performance of new *ansa*-zirconocene with OSiO-bridged bis(2-indenyl) ligand

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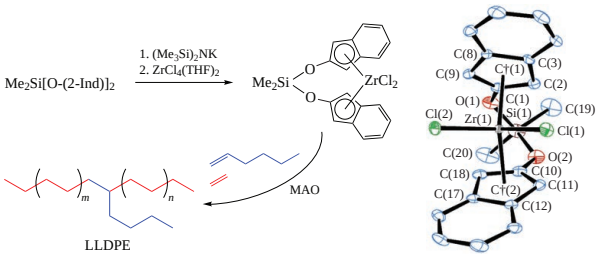
New *ansa*-zirconocene with bis(inden-2-yloxy)dimethylsilane ligand was synthesized and characterized by NMR spectroscopy and X-ray crystallography. The zirconocene was found to be highly active catalyst of ethylene polymerization and ethylene/hex-1-ene copolymerization upon methylaluminoxane activation.



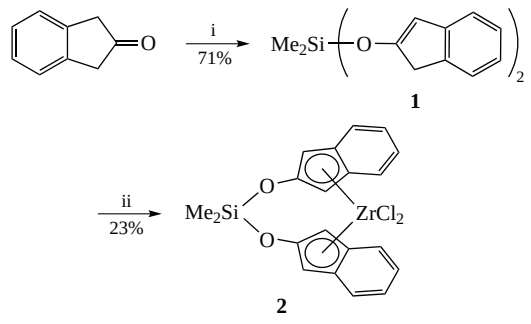
Keywords: *ansa*-metallocenes, LLDPE, olefin polymerization, single-site catalysts, X-ray crystallography.

Group 4 metallocenes have been studied as olefin polymerization catalysts since discovery of methylaluminoxane [$(MeAlO)_n$, MAO] being a powerful alkylating and cationizing agent, which initially was used with unbridged bis(cyclopentadienyl) complexes.[1] Soon after that, bridged metallocenes (or *ansa*-metallocenes) became the mainstream topic in studies of well-defined molecular (so-called single-site) olefin polymerization catalysts for the next decades.[2,3] Introduction of a bridging group in bis(cyclopentadienyl) systems is associated with two effects: (1) a possibility to synthesize catalysts with rigid geometry allowing for stereoselective homopolymerization of prochiral α-olefins such as propylene, and (2) a more open metal center which exhibits a higher comonomer affinity in ethylene/α-olefin copolymerization compared to unbridged systems. The contribution of the latter effect depends on the length, rigidity and geometry of a bridging group, in other words, on its influence on the mutual position of the cyclopentadienyl moieties (bite angle). The vast majority of *ansa*-metallocenes described so far contain silicon-based bridging groups, predominantly one atom R_2Si bridges linking two cyclopentadienyl moieties.[3] *ansa*-Metallocenes with longer silicon-containing bridging groups are less explored, though syntheses of complexes containing $(SiMe_2)_2$,[4–9] $(SiMe_2)_3$,[10–12] R_2CSiR_2,[5,13–15] $SiMe_2OSiMe_2$,[16–21] $SiMe_2NRSiMe_2$,[22] and $SiMe_2(1,2\text{-}C_6H_4)SiMe_2$[23] bridges have been documented. However, their polymerization behavior has been studied just in a few papers.[5–9,14,15,20,23] Besides that, there is still a considerable interest in longer-bridged metallocene catalysts in scientific[23,24] and patent[25–31] literature with applications mostly related to ethylene/α-olefin copolymerization. To date, we are unaware of examples of $OSiR_2O$ bridged metallocene olefin polymerization catalysts, though such ligands seem to be attractive due to the presence of a donor group in the cyclopentadienyl (indenyl) moiety, which has been associated with increased activity and/or molecular weight capability,[32,33] and commercial availability of the ligand precursors, namely, cyclopentenones or indanones, and dichlorodialkylsilanes.

Herein, we report on synthesis of $OSiR_2O$ bridged bis(2-indenyl) zirconocene, its crystal structure and performance in ethylene homopolymerization and ethylene/hex-1-ene copolymerization in the presence of MAO as the cocatalyst. The only two known examples of $OSiR_2O$ bridged metallocenes are ferrocene derivatives, one of which was synthesized by silylation of 1,1′-dihydroxyferrocene,[34] and the other by metathesis reaction of the lithiated ligand with ferrous chloride.[35] Evidently, only the second method could be used for preparation of group 4 metallocenedichlorides.

Synthesis of the target complex is shown in Scheme 1. The pro-ligand, bis(1*H*-inden-2-yloxy)(dimethyl)silane **1** (a silyl enol ether, in our case, the derivative of indan-2-one), was prepared in 71% yield by a procedure previously used for similar transformation of indan-1-one.[36]

Typically, *ansa*-zirconocenes are synthesized in two steps comprising double metalation of a pro-ligand with BuLi followed by metathesis between the intermediate dilithium salt of the ligand with zirconium tetrachloride or its less reactive equivalent

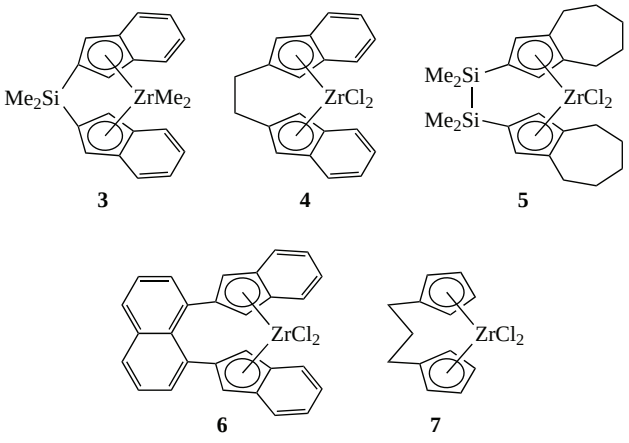


Scheme 1 *Reagents and conditions*: i, Me_2SiCl_2, Et_3N, NaI, MeCN; ii, $(Me_3Si)_2NK$, Et_2O, then $ZrCl_4(THF)_2$.

such as $ZrCl_4(THF)_2$[37] or $Zr(NMe_2)_2Cl_2(THF)_2$.[38] In our case, an attempt to obtain dilithium derivative of **1** by treatment with 2 equiv. of BuLi in ether at ambient temperature caused complete decomposition. The plausible reason is high reactivity of $OSiMe_2O$ moiety towards the organolithium compounds (BuLi, mono- and dilithiated pro-ligand) present in the mixture. A successful application of this method to the synthesis of $OSiR_2O$ bridged ferrocene[35] can be explained by the bulkier *tert*-butyl substituents at the silicon atom, which would hinder side reactions of the $OSiBu^t_2O$ moiety with organolithium compounds. In the described syntheses of 2-R_3SiO-substituted bis-indenyl *ansa*-zirconocenes *via* dilithiation of the proligand with BuLi, the silicon atoms in Bu^tMe_2SiO[39] and Pr^i_3SiO[40] moieties were also sterically hindered. The crucial role of bulky substituents at the silicon atom of R_3SiO moiety for direct lithiation of a pro-ligand was clearly demonstrated[41] on a series of bis(RMe_2SiO) substituted cyclopentadienes (R = Me, Pr^i, Bu^t). In the latter two cases, the cyclopentadienes were successfully metalated with Bu^tLi, but in the case of R = Me decomposition of the pro-ligand was observed.

In this study, the solution was to utilize hindered and weakly nucleophilic base $(Me_3Si)_2NK$ in ether. Deprotonation of ligand **1** with this base proceeded slowly and took about 24 h for completion. Dipotassium salt of the ligand was insoluble in ether, which probably suppressed the side reactions of nucleophilic indenylpotassium species with labile $OSiMe_2O$ moiety. Addition of zirconium tetrachloride to the suspension of dipotassium salt of **1** led to a complex mixture of products. The same result was obtained when $Zr(NMe_2)_2Cl_2(THF)_2$ was used as metal precursor. Subsequent treatment of the crude mixture with Me_3SiCl[42] was also unsuccessful and did not give the desired zirconocene dichloride. Finally, the reaction of $ZrCl_4(THF)_2$ with dipotassium salt of **1** afforded the desired complex **2** along with significant amount of a coordination polymer. It should be noted that a reasonable yield of the target complex was achieved only when the reaction was carried out for 48 h under the conditions used. The novel *ansa*-zirconocene was finally isolated in 23% yield after crystallization of the crude reaction product from toluene solution at –30 °C.

Single crystals suitable for X-ray structure analysis† (Figure 1) were obtained by slow evaporation of toluene solution of compound **2**. Since complex **2** is the first example of OSR_2O-bridged zirconocenes, it was interesting to compare its solid state structure with zirconocenes with similar and shorter bridges so to understand how this bridging group would shape the geometry of the indenyl moieties in the final complex. Table 1 demonstrates some important structural parameters measured for complex **2** in comparison with zirconocenes **3**–**7** with various bridging groups.



3 **4** **5**

6 **7**

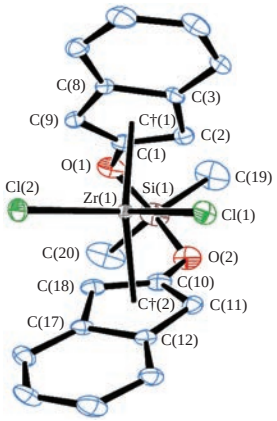


Figure 1 ORTEP diagram of **2**. Thermal ellipsoids are given for 50% probability. Hydrogen atoms are omitted of clarity. Selected bond lengths, Å: Zr(1)–C(1) 2.571(2), Zr(1)–C(2) 2.489(2), Zr(1)–C(3) 2.569(2), Zr(1)–C(8) 2.556(3), Zr(1)–C(9) 2.513(2), Zr(1)–C(10) 2.565(2), Zr(1)–C(11) 2.503(2), Zr(1)–C(12) 2.560(3), Zr(1)–C(17) 2.576(3), Zr(1)–C(18) 2.480(2), Zr(1)–Cl(1) 2.4241(5), Zr(1)–Cl(2) 2.4233(5), Si(1)–O 1.6617(18), Si(1)–O 1.6669(18), O–C(1) 1.357(3), O–C(10) 1.362(2). Selected angles, deg: Ct(1)–Zr(1)–Ct(2) 124.5, O(1)–Si–O(2) 103.32(7), C(1)–O(1)–Si 126.07(15), C(10)–O(2)–Si 124.37(15), Cl(1)–Zr(1)–Cl(2) 97.24(2).

The zirconium atom in **2** is in pseudotetrahedral coordination environment formed by two η^5-coordinated indenyl ligands and two chlorine atoms. The Cp_{cent}–Zr–Cp_{cent} angle (124.5°) is common for zirconocene dichlorides[3] and slightly smaller than those for zirconocenes **4**–**7** (from 125.5° in **4** to 131.7° in **5**). The same is true for the Cl–Zr–Cl angle (97.2°) which is close to the range of values found for zirconocenes **4**–**7** (from 98.4° in **5** to 100.3° in **6**). The C_{Cp}–Si–O angles (124.4, 126.1°) are close to those in unconstrained non-cyclic $Fc_2O_2SiMe_2$ (126.0–131.0° in two crystallographically independent molecules),[34] and ferrocenophane (ferrocene-1,1′-diyl)O_2SiMe_2 (123.9°, mean value),[34] whereas O–Si–O angle (103.3°) is smaller than that in the two ferrocenes (109.4 and 108.5°, respectively[34]), indicating the presence of some strain. The strain is also evidenced by deviation of the oxygen atoms of the bridging unit from the mean planes of cyclopentadienyl moieties by an average value of ~0.20 Å, which is not unusual for bridged metallocenes.[46]

The values of bite angle (angle between the mean planes of cyclopentadienyl moieties) in the series decrease predictably along with elongation of the bridge being largest for zirconocene **3** with short $SiMe_2$ bridge and smallest for zirconocene **7** with three-atom $(CH_2)_3$ bridge. Bite angle in zirconocene **2** (57.1°) is somewhat between the values found for complexes **6** (naphthalene-1,8-diyl bridge) and **5** ($SiMe_2SiMe_2$ bridge).

Zirconocene **3** with the shortest $SiMe_2$ bridge in the series adopts C_{2v} symmetry in the crystal state, which means that the Cp rings are situated exactly one above the other, the bridging

† *Crystal data for* **2**. The crystal of $C_{20}H_{18}Cl_2O_2SiZr$ is monoclinic, space group C_2, a = 17.0381(8), b = 10.2952(5) and c = 13.9766(10) Å, β = 125.6830(10)°, V = 1991.4(2) Å^3, Z = 4. Reflections collected 16357, of which 5841 unique reflections (R_{int} = 0.0186) were used in all calculations. The final parameters are R_1 = 0.0210, wR_2 = 0.0489 [$I > 2\sigma(I)$] and R_1 = 0.0212, wR_2 = 0.0491 (all data). GOOF = 1.152. Completeness 99.7%. Data were collected on a Bruker Apex II CCD diffractometer with MoKα radiation (λ = 0.71073 Å) using the φ- and ω-scan techniques. The structures were solved and refined by direct methods using SHELX. Data were corrected for absorption effects using the multi-scan method (SADABS). All non-hydrogen atoms were refined anisotropically using SHELX. The coordinates of the hydrogen atoms were calculated from geometrical positions.

CCDC 1980388 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

Table 1 Comparison of structural parameters of selected zirconocenes.

Zirconocene	Bridge	n^a	Symmetry[b]	Bite angle[c]	Tilt angle[c]	Reference
2	$OSiMe_2O$	3	C_2	57.1	39.4	this work
3	$SiMe_2$	1	C_{2v}	63.9	0.0	CCDC 1413171
4	CH_2CH_2	2	C_2	61.0	8.7	43
5	$SiMe_2SiMe_2$	2	C_s	54.1	0.0	44
6	naphthalene-1,8-diyl	3	C_2[d]	58.1/58.6[e]	37.0/33.2[e]	45
7	$CH_2CH_2CH_2$	3	C_s	50.2	1.5	46

[a] Number of atoms in the bridge; [b] of the ligand framework in the solid state; [c] in degrees; [d] distorted from ideal symmetry; [e] values for each of the two crystallographically independent molecules in the unit cell.

Table 2 Ethylene homopolymerization and ethylene/hex-1-ene copolymerization data for zirconocenes **2**, **3**, and **6**.[a]

Zirconocene	H (%)[b]	Activity[c]	M_n[d]	M_w[d]	PDI[e]	H_{cop} (%)[f]
2	–	1207	148	380	2.6	–
2	10.0	126	62	145	2.3	0.5
2	40.0	92	45	94	2.1	2.0
3	–	671	3	6	2.0	–
3	10.0	704	3	6	2.0	1.5
3	40.0	150	3	6	2.0	5.8
6	–	493	46	108	2.3	–
6	10.0	904	44	92	2.1	0.5
6	40.0	605	35	71	2.0	1.9

[a] Polymerization conditions: P_{total} = 65 psi, T = 80 °C, t = 30 min, [Al] = 2.0 mM; [b] vol% of hexene in the feed; [c] in kg mmol^{-1} $[C_2H_4]^{-1}$ h^{-1}; [d] in kDa; [e] M_w/M_n; [f] mol% of the incorporated hexene units.

silicon atom is located on the Cp_{cent}–Zr–Cp_{cent} plane and connects atoms in the Cp-rings which are proximal to each other. The slightly elongated CH_2CH_2 bridge in **4** crosses the Cp_{cent}–Zr–Cp_{cent} plane and forces the Cp-rings to tilt relative to each other by an angle of 6.2° [torsion angle C(1)–Cp_{cent}–Cp'_{cent}–C(1′), where C(1) and C(1′) are atoms in the Cp moieties bonded with the bridging group], the symmetry is thus lowered to C_2. Further elongation of the bridge in **6** results in a higher value of the tilt angle (35.2°) while the symmetry still remains C_2. Longer bridges are unable to connect the proximal two carbon atoms in the Cp-rings and thus can only be located at one side of the Cp_{cent}–Zr–Cp_{cent} plane; the symmetry in such metallocenes in the crystal state is C_s. This is the case of complexes **5** and **7**. Although one may expect that the novel zirconocene **2** with a three-atom flexible $OSiMe_2O$ bridge would adopt the C_s-symmetric geometry, in fact, it is of C_2-symmetry with the tilt angle of 39.4°, which makes it also similar to metallocene **6** (37.0/33.2°). One may assume zirconocene **7** with flexible three-atom $(CH_2)_3$ bridge to be a closest structural analogue of **2** due to the same number of atoms in the bridge and nearly same sums of bond lengths (~6.05 Å in **2** and ~6.02 Å in **7**) in the bridges. However, it appeared that **2** is quite different in geometry to **7**. In contrast, having compared the data for the bridged zirconocenes (see Table 1), we can make a counterintuitive conclusion that **2** is a very close structural analogue of complex **6** with a rigid aromatic naphthalene-1,8-diyl bridge notwithstanding the significant differences in composition and flexibility of the bridging groups.

Although the geometry of the catalytically active cationic species, formed from a zirconocene precatalyst after reaction with a perfluoroarylborate or MAO activator, is obviously not exactly the same as the crystal structure in the solid state, we considered it interesting to check whether the structural similarity of zirconocenes **2** and **6** translates into the similarity of polymerization performance (Table 2). Ethylene homopolymerization and ethylene/hex-1-ene copolymerization experiments at two levels of hex-1-ene feed were performed using a setup of high-throughput reactors previously described,[47,48] and used extensively in various polymerization studies.[49–53] Complex **3** with a $SiMe_2$ bridge, a zirconium dimethyl version of a known zirconocene dichloride,[54] was used for comparison (its synthesis is described in Online Supplementary Materials). The new zirconocene **2** modified with MAO appeared to be more active in ethylene homopolymerization compared to the rest two complexes, however, it was less active in ethylene/hex-1-ene copolymerization. To our excitement, the catalytic behavior of structurally similar complexes **2** and **6** in polymerization appeared to be very close in terms of molecular weight capabilty and comonomer response (degree of hex-1-ene incorporation), but with notable exception of the activity values. Expectedly, a significantly more open metallocene **3** displayed higher comonomer incorporation, but only formed oligomers.

In conclusion, we have synthesized a novel bis(2-indenyl) zirconocene dichloride **2** with a fairly chemically unstable $OSiMe_2O$ bridge and studied its structure by X-ray crystallography. In the crystal state, molecule **2** adopts C_2-symmetry and has a surprisingly similar geometry to naphthalene-1,8-diyl bridged zirconocene **6**, which can be a reason for the observed significant similarity of behavior of these zirconocenes in ethylene/hex-1-ene copolymerization.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2020.07.014.

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