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Synthetic approach to 6-*tert*-butyl-5-methoxy-2-methylindenyl zirconium *ansa*-complexes, bridged in 4-position of indenyl fragment

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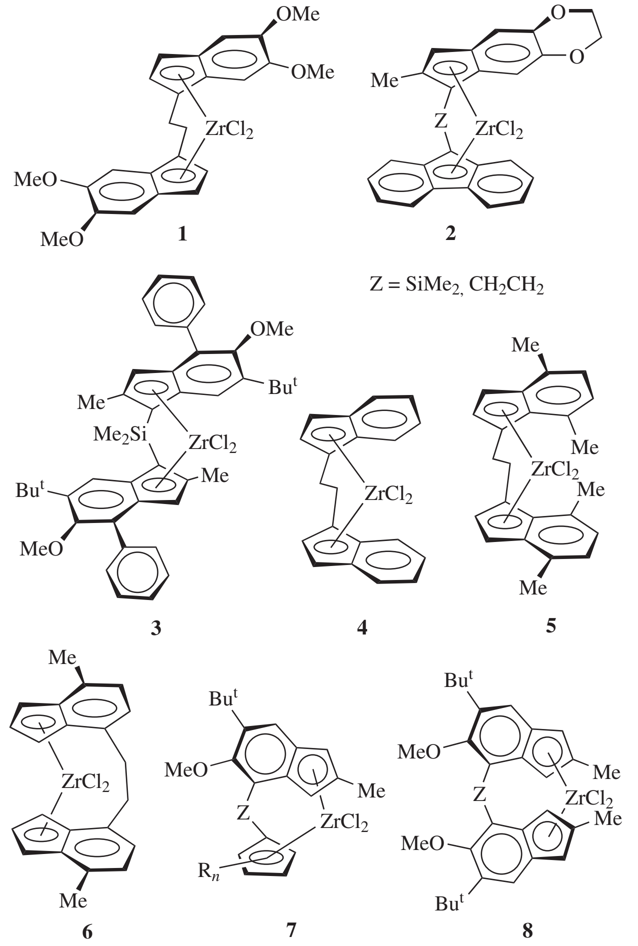
Two novel *ansa*-zirconocenes containing $SiMe_2$ bridge in non-conventional 4-position of 5-methoxy-6-*tert*-butylindenyl fragment have been synthesized, using TMS-protected substituted bromoindanol as a key starting compound. The structure of *rac*-dichlorozirconium μ-4,4′-dimethylsilylene-bis(η^5-6-*tert*-butyl-5-methoxy-2-methylinden-1-ide) was established by X-ray diffraction.

Bis-indenyl *ansa*-zirconocenes are traditionally considered as promising catalysts for homo- and copolymerization of alkenes. Apart from the structural factors, the complex activity and polymer characteristics are also affected by electronic properties of the η^5-coordinated ligands. Some publications considered the influence of electron-donating η^5-coordinated ligands on the stability of catalytically active species[1,2] and discussed the relationship between the presence of electron-donating substituents and the ease of polymer chain transfer processes.[2] A number of publications confirm the expediency of introducing electron-donating fragments for the design of effective polymerization catalysts.[3,4]

A certain progress was achieved by using alkyl,[5,6] trialkylsilyl,[7] and trialkylsiloxy groups.[8–10] The alkoxy group also received its share of researchers' attention; however, back in 1992,[2] Collins demonstrated that the presence of methoxy groups in molecule **1** (Scheme 1) results in complete loss of catalytic activity in the presence of MAO. Later,[11] it was reported that complexes **2** (Scheme 1) exhibit a moderate activity. Previously,[12] we assumed and proved the fact that the alkoxy group still can be used as a structural fragment of an efficient zirconocene polymerization catalyst: for this purpose, it is merely required that the access of the co-catalyst to this group be hampered by neighboring bulky groups (complex **3**, Scheme 1).

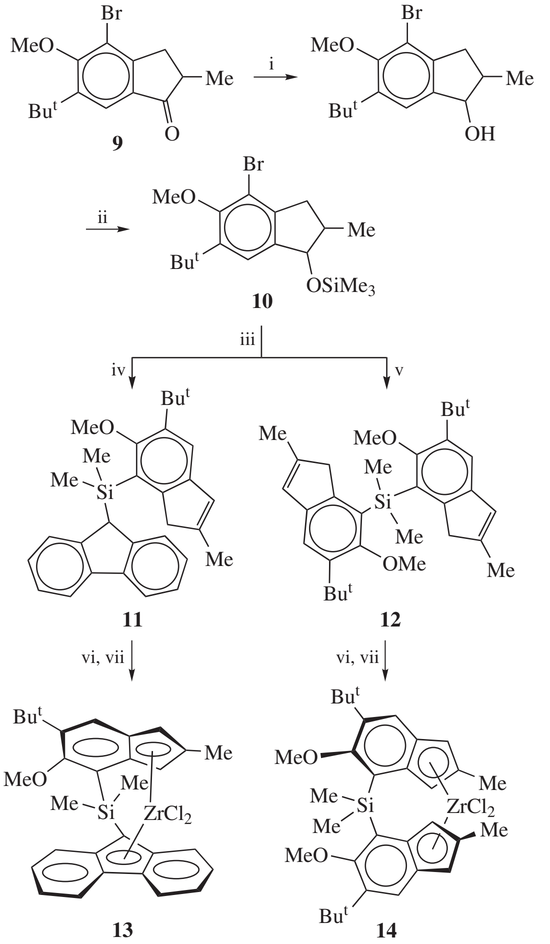
The recent enhancement of the interest in the use of zirconocenes in polymerization of higher α-olefins and copolymerization has extended the range of sources for the design of metallocene systems as it has become possible to 'depart' from the structures optimal for isotactic propylene polymerization. One route to this design is to change crucially the metallocene geometry, in particular, the position of the bridging fragment in the bis-indenyl compound. This type of structural modification (Scheme 1, complex **6** *vs*. 'traditional' **4** and **5**) leads to dramatic enhancement of productivity in copolymerization processes.[13]



Scheme 1

Group 4 metal indenyl complexes, containing methoxy substituents in C_6 rings and bridging fragment in 4(7)-position, look promising in terms of potential catalytic activity. If bridging fragment in the 4-position of indene acts as one of the bulky substituents, methoxy substituent should be in the 5-position, and the rest neighboring position should be occupied by bulky substituent (*tert*-butyl). These considerations lead to general formula **7** and **8** of target zirconocenes (Scheme 1).

Bis-indenes possessing a bridging fragment that links 4-positions of the indenyl fragment can be prepared starting from diarylalkanes (acylation to give bis-indanones followed by reduction and dehydration)[13–15] or from 4-bromoindanones (4-bromoindanols) using acetal (ether) protection, replacement of Br by Li, introduction of the bridging group and subsequent deprotection and reduction/dehydration to give bis-indenyl compound.[15,16] We decided to use the latter approach starting from synthetically accessible[12] substituted bromoindanone **9**. The substrate structure imposes some limitations on the suitable reactions and conditions: the presence of labile methoxy and *tert*-butyl groups is incompatible with acid hydrolysis at elevated temperature, and hence the use of acetal or ether protecting groups is problematic when dealing with compound **9**. As a moderately labile protecting group that first, allows performing the Li/Br exchange reaction and, second, can be removed without noticeable side reactions, we chose the trimethylsilyl (TMS) group and synthesized indanol TMS ether **10** (Scheme 2). As two model ligands for zirconocene of structural types **7** and **8**, we chose unsymmetrical indenyl-fluorenyl (**11**) and bis-indenyl (**12**) compounds. The synthesis was performed in diethyl ether in the presence of catalytic amount of CuCN. The removal of the TMS group by short-term heating of the intermediate silyl ether in benzene in the presence of water and traces of *p*-TSA afforded **11** and **12** (Scheme 2).



Scheme 2 *Reagents and conditions*: i, $NaBH_4$/EtOH, then H_2O; ii, Me_3SiCl/NEt_3, CH_2Cl_2; iii: BuLi/Et_2O; iv, 9-[fluorenyl]$SiMe_2Cl$/CuCN, then TsOH, H_2O, benzene, Δ; v, $SiMe_2Cl_2$/CuCN, then TsOH, H_2O, benzene, Δ; vi, BuLi/Et_2O; vii, $ZrCl_4$/pentane.

Target complexes were synthesized by the reaction of dilithium derivatives of **11** or **12** with $ZrCl_4$ (see Scheme 2).[†] In the case of **13**, this gave only one product having *ansa*-structure, and in the case of **14**, a mixture was produced in which the more stable racemic form predominated.

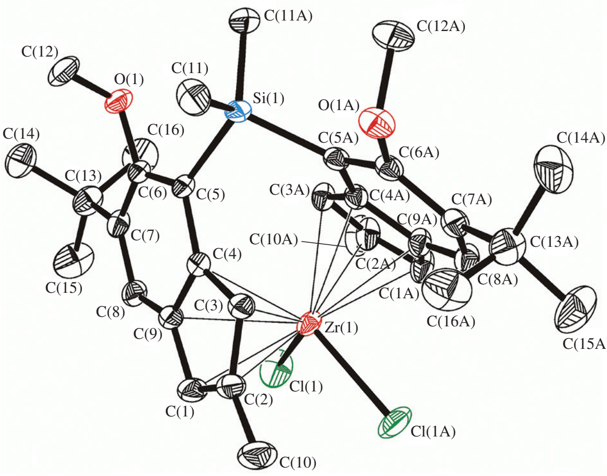


Figure 1 Molecular structure of **14**. Displacement ellipsoids are shown at 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Zr(1)–Cl(1) 2.4292(6), Zr(1)–C(3) 2.4707(19), Zr(1)–C(1) 2.519(2), Zr(1)–C(4) 2.5379(17), Zr(1)–C(9) 2.5486(18), Zr(1)–C(2) 2.563(2), Zr(1)–$Cp_{centroid}$ 2.221(1), Si(1)–C(11) 1.867(2), Si(1)–C(5) 1.8925(18). Selected bond angles (°): Cl(1)–Zr(1)–Cl(1A) 97.39(3), $Cp_{centroid}$–Zr(1)–$Cp(A)_{centroid}$ 127.9, C(11)–Si(1)–C(11A) 112.62(15), C(11)–Si(1)–C(5) 108.84(8), C(11)–Si(1)–C(5A) 113.29(9), C(5)–Si(1)–C(5A) 99.31(10) [symmetry transformation: (A) $-x+1, y, -z+3/2$].

The molecule of racemic complex **14** (Figure 1)[‡] lies on 2-fold rotation axis passing through Zr(1) and Si(1) atoms. The coordination environment of Zr atom may be regarded as a distorted tetrahedron (assuming that η^5-C_5 rings occupy one coordination site). The Zr–C distances vary in wide range 2.471(2)–2.563(2) Å. The latter is typical of indenyl zirconium complexes[17,18] and reflects the tendency of Zr atoms to form η^3, η^2 linkage with indenyl ligands. Both indenyl ligands are planar within 0.090(1) Å and form dihedral angle 49.28(4)°. The main geometric parameters for molecule **14** are very close to the respective average values for closely related bis(indenyl)-zirconocene dichlorides retrieved from CSD.[19]

In conclusion, two novel *ansa*-zirconocenes containing $SiMe_2$ bridge in non-conventional 4-position of 5-methoxy-6-*tert*-butyl-indenyl fragment have been synthesized and characterized. Trimethylsiloxy protection has been shown to be effective for methoxyindanol metallation, the key stage in the ligand preparation.

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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.2015.11.012.

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[†] For synthetic procedures and characteristics of compounds **9**–**14**, see Online Supplementary Materials.

[‡] *Crystallographic data for* **14**: $C_{32}H_{42}Cl_2O_2SiZr$, $M = 648.87$, monoclinic, space group *C*2/*c*, $a = 21.882(5)$, $b = 10.523(2)$ and $c = 14.853(3)$ Å, $\beta = 113.402(3)°$, $V = 3138.6(11)$ Å^3, $Z = 4$, $d_{calc} = 1.373$ g cm^{-3}, $F(000) = 1352$, μ(MoKα) = 0.586 mm^{-1}, $T = 173(2)$ K, $\theta_{min} = 2.03°$, $\theta_{max} = 27.00°$, 14726 reflections measured, 3436 independent reflections ($R_{int} = 0.0330$), 179 parameters, $R_{1\,obs} = 0.0299$ [2970 reflections with $I > 2\sigma(I)$], $wR_{2\,obs} = 0.0765$, $R_{1\,all} = 0.0370$, $wR_{2\,all} = 0.0796$, GOF = 1.052, $\Delta\rho_{max} = 0.377$ e Å^{-3}, $\Delta\rho_{min} = -0.397$ e Å^{-3}.

CCDC 774771 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.

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