Synthesis and molecular structures of the racemate and the *meso*-form of 2,2′-propylidene-bis(η^5-indenyl)zirconium dichloride

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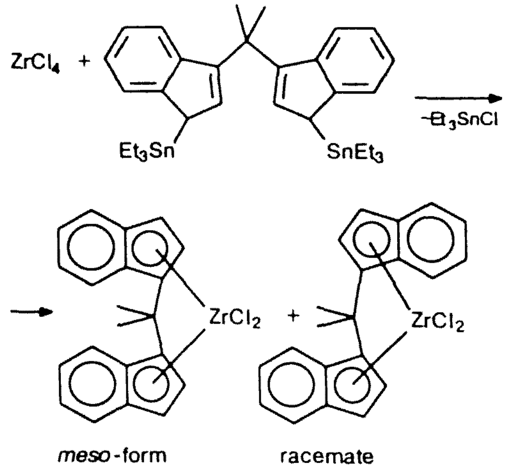
A mixture of *rac*- and *meso*-2,2′-propylidene-bis(η^5-indenyl)zirconium dichlorides was obtained in 95 % yield. The compounds were separated, and their structures were established by X-ray structural analysis.

Key words: *ansa*-zirconocene dichlorides, synthesis, molecular structure.

Recently, *ansa*-zirconocenes have attracted much interest both of leading chemical companies and chemists involved in fundamental research. This is, primarily, caused by the ability of the racemic form of these compounds to catalyze stereoselective polymerization and copolymerization of olefins.[1–5] Synthesis of promising *ansa*-zirconocenes, separation of their mixtures into the individual racemate and the *meso* form, as well as structural study of the complexes are laborious problems. This is because the products are obtained in low yields, sometimes they are poorly soluble, it is difficult to separate the mixtures and, as such, it is hard to grow single crystals suitable for X-ray structural study.

Previously,[6] the racemate of 2,2′-propylidene-bis(η^5-indenyl)zirconium dichloride was synthesized in low yield by the reaction of the dilithium salt of 2,2′-bis(indenyl)propane and $ZnCl_4$ taken in stoichiometric amounts. In Ref. 6, the formation of the corresponding isomeric *meso*-zirconocene dichloride was not mentioned. Apparently, the low yield of the racemate is due to the use of the very active organolithium reagent, which nonselectively forms oligomeric and polymeric zirconocene dichlorides containing bridging indenyl ligands.

In this work, an alternative method of the synthesis of the racemate of 2,2′-propylidene-bis(η^5-indenyl)zirconium dichloride and its *meso*-form by the reaction of $ZrCl_4$ and 2,2-bis[3-(triethyltin)indenyl]propane in toluene (reaction (1)) is considered. This reaction affords a stoichiometric mixture of the racemate and *meso*-2,2′-propylidene-bis(η^5-indenyl)zirconium dichloride in a yield of up to 95 %. Individual compounds (racemate and *meso*-form) were isolated in an analytically pure form in a yield of approximately 45 % each after fractional crystallization from CH_2Cl_2.



(1)

The obtained compounds have been studied by X-ray structural analysis. There are two independent molecules of the *meso*-form per asymmetric unit. The Zr—C bond lengths are in the range 2.438(3)—2.618(3) Å and 2.431(5)—2.629(6) Å for the racemate and the *meso*-form. The Zr—Cl bond lengths are 2.417(1) Å and 2.402(2)—2.441(2) Å for the racemate and the *meso*-form, respectively. The values of the angles formed by the bonds between the carbon atoms of the indenyl rings and the quaternary carbon atom of the propylidene bridge (111.2, 99.6°, and 100.4°, for the racemate and the *meso*-form, respectively) are indicative of the greater

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steric hindrance of the *meso* form. In the future, we plan to study the reactivities of the compounds obtained in detail, the possibility of their synthesis, and the reactivities of the analogous *ansa*-metallocenes.

Experimental

X-ray diffraction study was performed on a CAD-4 diffractometer (Mo K_α radiation, graphite monochromator, $\theta \le 27°$). The structures were solved by the heavy-atom method using the SHELX program based on 1885 (racemate) or 5022 (*meso*-form) reflections with $F > 4\sigma(F)$. Correction for absorption was applied using three azimuthal scan curves. The structures were refined anisotropically by the least-squares method with fixed positions of hydrogen atoms.

All synthesis procedures were carried out under a purified argon atmosphere *in vacuo* in Schlenk flasks. Solvents were purified by the standard procedures. $ZrCl_4$ (Reakhim) and 2,2′-bis[3-(triethyltin)indenyl]propane (GNIIKhTEOS) were used without additional purification.

The racemate and the *meso*-form of 2,2′-propylidene-bis(η^5-indenyl)zirconium dichloride. A mixture of $ZrCl_4$ (4.60 g, 41.2 mmol) and 2,2-bis[3-(triethyltin)indenyl]propane (28.11 g, 41.2 mmol) in toluene (150 mL) was stirred at 80 °C for 3 h. Then the solvent was evaporated, and the residue was washed with hexane (2×50 mL) and dried. As a result, the equimolar mixture of the racemate and the *meso*-form of 2,2′-propylidene-bis(η^5-indenyl)zirconium dichloride (according to the results of NMR) was obtained. The mixture was separated by fractional crystallization from CH_2Cl_2. Bright-orange crystals of the racemate (7.98 g, 45 %) and the *meso*-form (8.09 g, 45 %) of 2,2′-propylidene-bis(η^5-indenyl)zirconium dichloride were obtained.

The racemate of 2,2′-propylidene-bis(η^5-indenyl)zirconium dichloride forms monoclinic crystals (a = 15.903(9), b = 11.105(7), c = 11.520(9) Å, β = 121.61(4)°, Z = 4, space group $C2/c$, R = 0.0297, R_w = 0.0297); the corresponding *meso*-form gives triclinic crystals (a = 9.739(2), b = 12.798(4), c = 15.322(4) Å, α = 101.18(2), β = 121.61(4), g = 90.54(6)°, Z = 4, space group $P\bar{1}$, R = 0.0391, R_w = 0.0391).

The racemate of 2,2′-propylidene-bis(η^5-indenyl)zirconium dichloride. Found (%): C, 58.27; H, 4.06. $C_{21}H_{18}Cl_2Zr$. Calculated (%): C, 58.32; H, 4.19. ^{1}H NMR (360 MHz; $CDCl_3$; δ): 2.34 (s, 6 H, $C(CH_3)_2$), 6.18 (d, 2 H, H(2) of the indenyl ligand), 6.65 (d, 2 H, H(3) of the indenyl ligand), 6.96—7.76 (m, 8 H, H(5,6,7,8) of the indenyl ligand).

The *meso* form of 2,2′-propylidene-bis(η^5-indenyl)zirconium dichloride. Found (%): C, 58.47; H, 4.23. $C_{21}H_{18}Cl_2Zr$. Calculated (%): C, 58.32; H, 4.19. ^{1}H NMR (360 MHz; $CDCl_3$; δ): 2.18 (s, 3 H, CH_3), 2.65 (s, 3 H, CH_3) 6.09 (d, 2 H, H(2) of the indenyl ligand), 6.67 (d, 2 H, H(3) of the indenyl ligand), 6.84—7.83 (m, 8 H, H(5,6,7,8) of the indenyl ligand).

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Preparation of *N*-nitrohydroxylamines by the substituting nitration method

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N-Nitro-*N*-methyl-*O*-substituted hydroxylamines were synthesized in high yields by nitration of appropriate *N*-acetylhydroxylamines with nitrogen pentoxide.

Key words: *N*-acetylhydroxylamines, nitration, *N*-nitrohydroxylamines, nitrogen pentoxide.

In the previous report,[1] for a number of examples we have shown that *N,O*-disubstituted *N*-nitrohydroxylamines (NHA) can be obtained by the sustituting nitration method from the corresponding *N*-acetylhydroxylamines (HA) by the action of nitronium salts and/or N_2O_5. In the present work, new possibilities and limita-

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