

Preliminary communication

Hydride abstraction from (η^2 -acetaldehyde) zirconocene dimer using $B(C_6F_5)_3$

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Abstract

$B(C_6F_5)_3$ reacts with the (η^2 -acetaldehyde)zirconocene dimer (**4**) by hydride transfer from the methyl group of a CH_3CHO ligand to boron. One of the metallaioxirane moieties of the dizirconium complex is then opened to give the salt $\{(\eta^2-CH_3CHO)ZrCp_2 \cdot (H_2C=CHO)ZrCp_2\}^+ [HB(C_6F_5)_3]^-$ (**6**) that was isolated with an 80% yield.

Keywords: Aldehyde; Early transition metals; Group 4; Hydride; Zirconium

Under thermodynamic control (η^2 -formaldehyde)-zirconocene forms a cyclic trimer that contains a central six-membered ring of alternating oxygen and zirconium atoms to three edges of which methylene groups are attached [1]. Under kinetic control the usually applied synthetic entry to the $[(\eta^2-CH_2O)ZrCp_2]_n$ complexes yields a corresponding cyclodimer (**2**) [2]. Here the CH_2 groups are attached to the edges of a central Zr_2O_2 four-membered metaloxide ring. These polymetallacycles have been used as molecular Fischer–Tropsch models. The CH_2 groups of for example **2** can be oligomerized by adding a trialkylborane catalyst [3]. In addition, many insertion reactions into the reactive $Zr-CH_2$ bonds of **2** have been realized [4]. The pronounced metallaioxirane character of the structural subunits of **2** was also utilized in a variety of (η^2 -formaldehyde)-zirconocene transfer reactions leading to novel organometallic substrates [5] (for selected examples see Scheme 1).

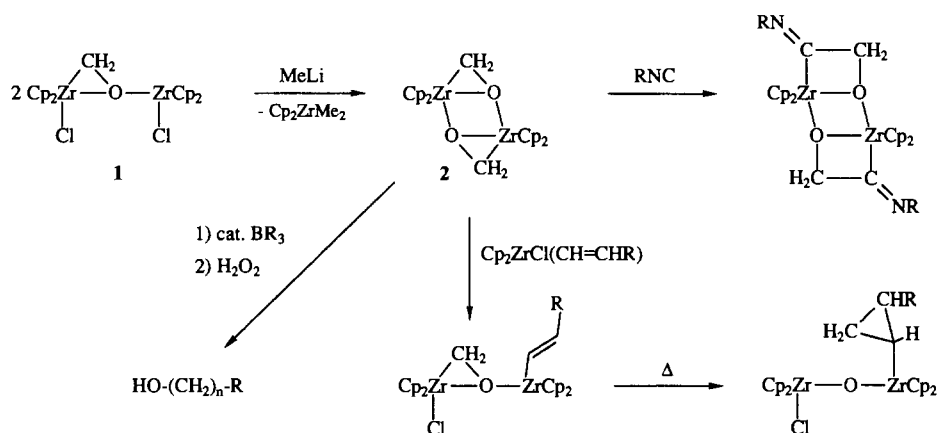
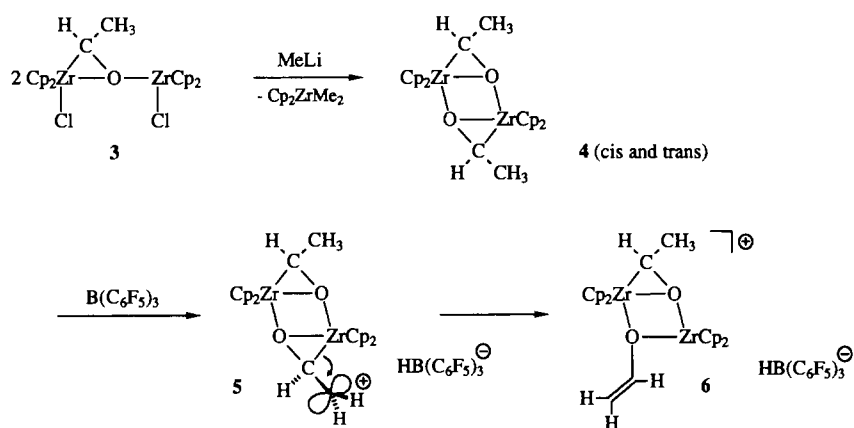
In a similar way we have recently prepared the (η^2 -acetaldehyde)zirconocene dimers (**4**). In this case a mixture of two diastereoisomers is obtained (of C_1 and C_2 -symmetry respectively, in a 1.7:1 ratio under thermodynamic control). The dimetallatricyclic systems of **4** also contain reactive zirconium to carbon σ bonds that undergo the typical insertion chemistry [6]. In addition, the presence of methyl groups at the metal-

laoxirane rings allows for some reactions that have not been observed for the unsubstituted parent system **2**. These seem to make use of some typical “cyclopropane character” of the three-membered metallacyclic ring system in such Group 4 organometallic systems. We here describe a typical example, namely the reaction of the (η^2 -acetaldehyde)zirconocene dimers **4** with the strong Lewis acid $B(C_6F_5)_3$ (Scheme 2).

The (η^2 -acetaldehyde)zirconocene dimer (**4**) (kinetic 1:1.5 mixture of the *trans* and *cis* diastereoisomers) was dissolved in toluene and then treated with approximately twofold molar excess of tris(pentafluorophenyl)borane at room temperature. The product precipitated from the solution and was isolated as an orange–yellow solid (**6**), yield about 500 mg (80%); melting point (differential scanning calorimetry), 47°C (decomposition). Anal. Found: C, 47.69, H, 2.90. $C_{42}H_{28}BF_{15}O_2Zr_2$ calc.: (1042.9) C 48.37, H 2.71%. The ^{11}B NMR spectrum (d, $^1J_{BH} = 90$ Hz at -25.5 ppm in CD_2Cl_2 solution at 64.2 MHz, 300 K) and the IR spectrum ($\nu_{(B-H)} = 2377$ cm^{-1}) revealed the presence of the hydrido-tris(pentafluorophenyl)borate anion [7,8]. The IR spectrum exhibits additional strong features at $\tilde{\nu} = 3121, 2970, 2914, 2875, 1641, 1616, 1510, 1461, 1371, 1272, 1158, 1150, 1103, 1080, 1019, 976$ and 813 cm^{-1} .

The newly formed compound **6** still contains one intact (η^2 -acetaldehyde)zirconocene moiety inside the framework of the cationic dizirconocene complex. This is evident from the 1H and ^{13}C NMR features of the CH_3CHO group. 1H NMR: δ 1.88 (d, $^3J = 6.2$ Hz, 3H,

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Scheme 1. Synthesis and selected reactions of the (η^2 -formaldehyde)zirconocene dimer.

Scheme 2.

CH₃), 4.48 (q, $^3J = 6.2$ Hz, 1H, CH) ppm. ^{13}C NMR: δ 24.8 ($^1J_{\text{CH}} = 126$ Hz, CH₃), 93.4 ($^1J_{\text{CH}} = 155$ Hz, CHO) ppm. The methine coupling constant of $^1J_{\text{CH}} = 155$ Hz is very typical of the metallaioxirane moiety [2–6]. The (η^2 -CH₃CHO)Zr subunit contains a center of chirality. Therefore the cyclopentadienyl ligands at each bent metallocene group of the dinuclear complex **6** are diastereotopic. Accordingly, four ^1H and ^{13}C NMR Cp resonances are found. ^1H NMR (CD₂Cl₂, 300 K) δ 6.53, 6.48, 6.06, 6.04 ppm. ^{13}C NMR: δ 116.6, 116.4, 110.3, 110.1 ppm. The remaining signals of the ^1H NMR spectrum of **6** exhibit a three proton AMX pattern ($\delta = 6.62, 4.50, 4.10$ ppm with coupling constants $^3J = 13.7$ and 6.0 Hz, $^2J = 2.8$ Hz). We think that this vinyl group is connected to oxygen, which is in accord with the observed ^{13}C NMR chemical shifts $\delta = 155.1$ ($^1J_{\text{CH}} = 183$ Hz, $-\text{CH}=\text{CH}_2$), 97.3 ($^1J_{\text{CH}} = 154$ and 165 Hz, $-\text{CH}=\text{CH}_2$) ppm.

The formation of **6** can readily be explained if some metallaioxirane character of the (η^2 -acetaldehyde)zirconocene moiety is assumed. Hydride transfer from the methyl group to B(C₆F₅)₃ creates a heteroanalogous cyclopropylcarbinyl cation system **5** that might find

some electronic stabilization in the bisected conformation [9] as depicted in Scheme 2. Subsequent cleavage of the adjacent endocyclic zirconium to carbon σ bond seems to represent the most favorable pathway of stabilization of the intermediate **5**, that directly leads to the formation of the organometallic onium complex **6**. We conclude that this typical reaction of **4** with the hydride abstractor B(C₆F₅)₃ provides additional evidence of the pronounced metallaioxirane character of the (η^2 -aldehyde)zirconocene species.

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