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Preliminary communication

Dynamic NMR spectra and thermolysis of $(RCp)_2Zr(CH_2OCH_3)_2$: Evidence for the insertion of a methylene group from a metallaoxirane into a Zr–C σ-bond

Gerhard Erker *, Rüger Schlund, Markus Albrecht and Christian Sarter
Institut für Organische Chemie der Universität Würzburg, Am Hubland, D-8700 Würzburg (F.R.G.)

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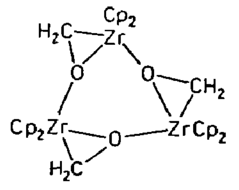
Abstract

The reaction of $(RCp)_2Zr(OCH_3)Cl$ with two molar equivalents of $ClMgCH_2OCH_3$ yields $(RCp)_2Zr(CH_2OCH_3)_2$ (**6**). Thermolysis of **6** at 70 °C gives ethylene and $(RCp)_2Zr(OCH_3)_2$. The low temperature dynamic NMR spectra of **6** indicate the presence of a η^2-CH_2OCH_3 ligand. It is suggested that the thermally-induced insertion of the metallaoxirane methylene unit into the remaining Zr–CH_2OCH_3 σ-bond initiates the reaction sequence leading to $CH_2{=}CH_2$ and dimethoxyzirconocene.

Carbon–carbon coupling and chain growth in the reductive coupling of carbon monoxide on heterogeneous Fischer–Tropsch catalysts is thought to involve reaction of surface-bound CH_2 groups. Methylene groups can thus undergo two main types of reaction at the catalyst surface, namely (a) coupling to give ethylene and (b) hydride insertion to give surface-bound CH_3 groups. The latter may then undergo insertion of additional CH_2, giving rise to chain growth at the catalyst [1]. Steps (a) and (b) have been successfully modelled by systems involving molecular metallaoxirane-type complexes in solution [2].

Such complexes derived from the Group 4 transition metal zirconium have been obtained by two different routes. Carbonylation of the zirconocene hydrides $(Cp_2ZrH_2)_x$ or $(Cp_2ZrHCl)_x$ led to metallaoxiranes **1** or **2**, respectively [3]. Alternatively, stoichiometric reaction of Cp_2ZrCl_2 with α-metallated ethers $LiCPh_2OCH_3$ or $ClMgCH_2OCH_3$ (**3**) gave the zirconocenyl ethers **4** and **5**, respectively, both containing $\overline{ZrOC}$ ring systems [4].

Complexes **2**, **4**, and **5** cleanly undergo alkylidene transfer with metal hydrides. For example, $Cp_2\overline{Zr(Cl)CH_2O}CH_3$ reacts with $(Cp_2Zr(H)Cl)_x$ at 40 °C to give a 1/1 mixture of the methylene insertion product $Cp_2Zr(CH_3)Cl$ and the remaining "template" species $Cp_2Zr(OCH_3)Cl$ [4b]. Further insertion of methylene from the



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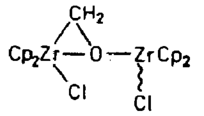

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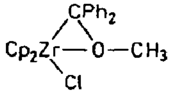

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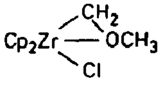

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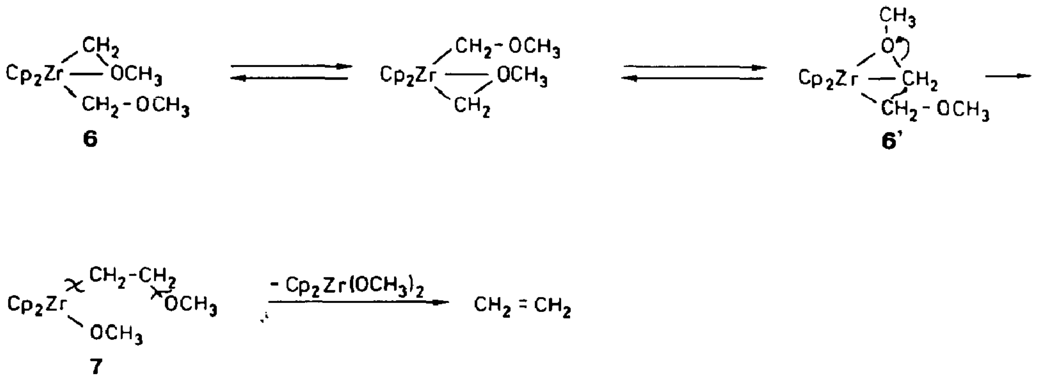
metallaoxirane moiety into the resulting methyl-zirconium unit or into analogous M–C σ-bonds seems to be much less favoured. We have now obtained evidence that such a process does take place in a related system at elevated temperature.

Reaction of $Cp_2Zr(OCH_3)Cl$, obtained from the oligomeric $(Cp_2ZrHCl)_x$ and CH_3OH at −75 °C, with two molar equivalents of the reagent $ClMgCH_2OCH_3$ [5] led cleanly to $Cp_2Zr(CH_2OCH_3)_2$ (**6a**). Complex **6a** was isolated in 87% yield. It is characterized by very simple ^1H and ^{13}NMR spectra at ambient temperature, each comprising three separate signals for Cp (δ(H) 5.57; δ(C) 106.8), CH_2 (δ(H) 2.92; δ(C) 76.7), and CH_3 (δ(H) 3.30; δ(C) 65.2) groups. When a toluene solution of complex **6a** is heated at 70 °C, there is a rapid controlled decomposition, which gives $Cp_2Zr(OCH_3)_2$ and $CH_2{=}CH_2$ as the main products (> 80%).

The recent development of routes to $[(MeCp)_2Zr(H)Cl]_x$ (either from $[(MeCp)_2ZrH_2)]_x$ and $(MeCp)_2ZrCl_2$ or involving treatment of $(MeCp)_2ZrCl_2$ with lithium aluminum hydride in tetrahydrofuran) [6,7] provided us with the Cp-substituted starting material $(MeCp)_2Zr(OCH_3)Cl$ via methanol addition at −75 °C. Subsequent treatment with 2 equivalents of **3** produced $(MeCp)_2Zr(CH_2OCH_3)_2$ (**6b**) NMR (CS_2/C_6D_6, (10/1), ambient temperature: δ(H) 5.44 (m, 4 H), 5.55 (m, 4 H), 1.88 (s, 6 H, η-$C_5H_4CH_3$); 2.92 (s, 4 H), 3.34 (s, 6 H, CH_2OCH_3); δ(C) 14.5, 104.4, 109.7, 118. 1 (MeCp), 64.6 (OCH_3), 77.4 (CH_2).

As the temperature is lowered all the NMR resonances of **6b** broaden except for the ^1H and ^{13}C Cp-methyl singlets. In 10/1 CS_2/C_6D_6 at 4.7 Tesla splitting of the methylene ^1H NMR singlet into two separate signals ($\Delta\delta$ 170 Hz) was observed at 163 K ($T_{coal.} \approx 173$ K). In the ^{13}C NMR spectrum at the lowest temperature possible with the 10/1 CS_2/C_6D_6 solvent mixture (163 K), there was separation into four Me–Cp methine (δ 101.5, 103.5, 108.7, 111.1) and two $\mathit{C}H_2OCH_3$ resonances ($\Delta\delta$ 1080 Hz). Under these conditions, the σ-ligand ^{13}C methyl signal was still very broad.

The dynamic NMR spectra of **6b** provide clear evidence for the presence of two chemically different methoxymethyl ligands in the $(RCp)_2Zr(CH_2OCH_3)_2$ complexes. In view of the preferred metallaoxirane type structure of **5** (shown by X-ray diffraction) and the similar NMR chemical shifts of one of the methoxymethyl ligands in **6b** and **5** [4b], it appears that complexes **6** are metallaoxirane type compounds containing both a η^1- and a η^2-CH_2OCH_3 ligand. Their rapid interconversion ($\Delta G^\ddagger$ (173K) $\approx 7.8 \pm 0.4$ kcal/mol estimated from the ^1H NMR $C\mathit{H}_2OCH_3$ coalescence) should provide a kinetically feasible pathway for the mutual rearrangement of the respective η^2-O-inside and η^2-O-outside isomers, the former probably representing the overall minimum for complex type **6**, in keeping with the known preferred structure of **5** [8]. The η^2-O-outside isomer **6′** would allow for CH_2-inser-



tion into the Zr–CH_2OCH_3 σ-bond to give **7**. Subsequent rapid β-OCH_3 elimination makes this a very attractive mechanism for the observed formation of ethylene and dimethoxyzirconocene.

The observed methylene insertion from the three membered $\overline{\text{ZrCH}_2\text{O}}\text{R}$ ring system of **6** into the adjacent metal–carbon σ-bond provides further confirmation of the validity of using metallaoxiranes as molecular models for Fischer–Tropsch type chemistry [9].

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