Ligand exchange in zirconocene dichloride–diethylzinc bimetallic systems

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Abstract:

The reaction between zirconocene dichloride and excess diethylzinc in d-6-benzene solution was studied. It was found that the exchange reaction between Cp_2ZrCl_2 and Et_2Zn is accompanied by the formation of such complexes as bis-(cyclopentadienyl)ethylzirconium chloride ($EtZrCp_2Cl$) and bis-(cyclopentadienyl)diethylzirconium (Et_2ZrCp_2). An assessment of the thermodynamic stability of the obtained products is given based on the results of DFT analysis. The description of the NMR spectral data of the obtained organozirconium complexes is carried out.

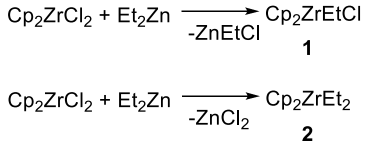
Keywords: Zirconocene dichloride, diethylzinc, bis-(cyclopentadienyl)ethyl zirconium chloride, ligand exchange

Introduction

Chain transfer reactions between compounds of transition metals and alkyls, haloalkanes of Group II – III metals play an important role in the catalysis of homogeneous polymerization of olefins [1, 2]. A special place among chain transfer reactions is occupied by the exchange reactions of zirconocene complexes and organoaluminum compounds of various structures. Despite the low activity of these systems in polymerization reactions, they are important for organic and organometallic chemistry. σ-Ligand exchange between metallocene dichloride- and organoaluminum compounds - based systems underlies the generation of hydride and alkyl organometallic complexes initiating the reactions of hydro-, carbo- and cyclometalation of alkynes and alkenes. Functionally substituted products of hydrometalation and carbometalation obtained *in situ* are important synthons for the organometallic synthesis of various classes of organic molecules [3]. The nature of the interaction of metallocene complexes of zirconium and organoaluminum compounds has been studied in detail and continues to be studied by L.V. Parfenova with co-workers [4,5]. However, there are no literature data on the study of the exchange reactions of zirconocene complexes with organocin reagents. Currently known examples of Cp_2ZrCl_2-catalyzed 2-zincoethylzincation of 5-decyne [6] and substituted 2-alkynylamines [7], as well as ethylzincation of terminal olefins [8] serve as a reliable prerequisite for the alkylation of metallocene dichlorides using diethylzinc. The results of study of the alkylation of such organozirconium complexes as bis(cyclopentadienyl)hafnium dimethyl (Cp2HfMe2, 1Me2) and [N-(2,6-diisopropylphenyl)-α-(2-isopropylphenyl)-6-(1-naphthalenyl)-2-pyridinemethanaminato]hafnium dimethyl ($2Me_2$) with Et_2Zn are preseted in for the first time in [9]. Studying the alkyl transfer processes in the Cp_2ZrCl_2-Et_2Zn system is an important task, since they are central to coordinative chain transfer olefin polymerization catalysis. This work presents the first results of studying the exchange reaction between zirconocene dichloride (Cp_2ZrCl_2) and Et_2Zn.

Results and discussion

We found that the reaction of Cp_2ZrCl_2 with 4 equiv. Et_2Zn in d-6-benzene solution at room temperature is accompanied by the alkylation of zirconocene dichloride and the formation after 5 min bis-(cyclopentadienyl)ethylzirconium chloride ($EtZrCp_2Cl$) **1** (Scheme 1).

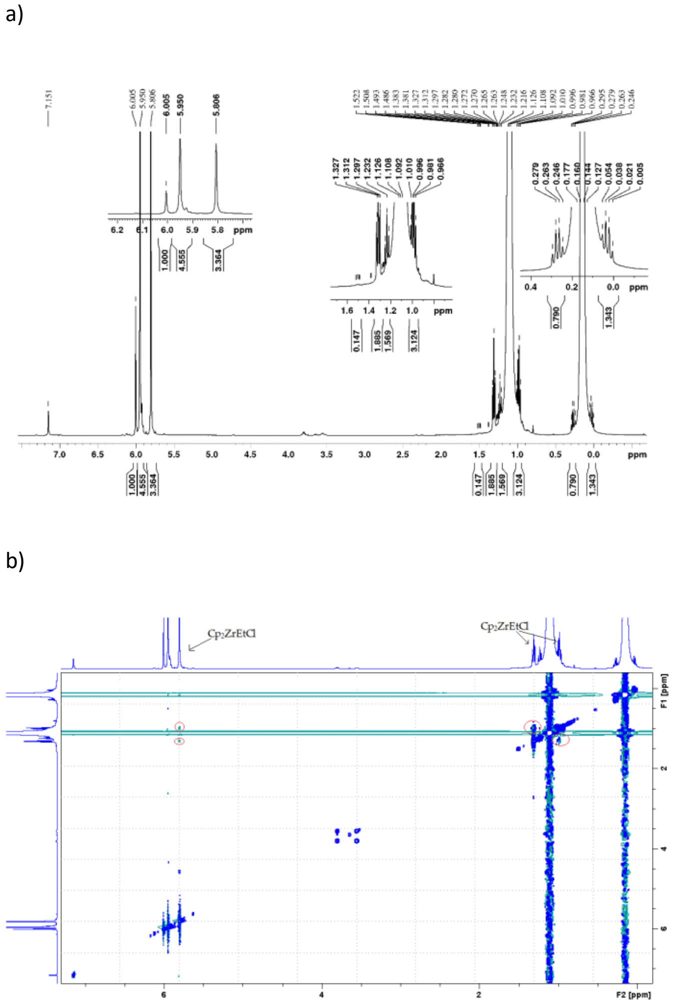


$$Cp_2ZrCl_2 + Et_2Zn \xrightarrow[-ZnEtCl]{} Cp_2ZrEtCl \quad \mathbf{1}$$

$$Cp_2ZrCl_2 + Et_2Zn \xrightarrow[-ZnCl_2]{} Cp_2ZrEt_2 \quad \mathbf{2}$$

Scheme 1 Ligand exchange in zirconocene dichloride–diethylzinc bimetallic systems.

The structural identification of the obtained compounds was carried out by 1D and 2D methods of NMR spectroscopy under standard conditions. The ratio of intensities of three singlet signals of protons of cyclopentadiene rings (δ = 5.81, 5.95, and 6.01 ppm) is equal to 1: 4: 3, that confirms the presence of a residue of unreacted zirconocene dichloride (δ = 6.01 ppm) and, respectively, the formation of three products as a result of the reaction ligand exchange. The presence of compound **1** in the resulting reaction mixture is indicated by the nuclear Overhauser effect, that was observed in the NOESY spectrum between the protons of the ethyl group (δ = 0.96 - 1.01 ppm and δ = 1.29 - 1.33 ppm, ^1H NMR) and protons of cyclopentadiene rings (δ = 5.81 ppm) (Scheme 2, Figures a) and b)). Analysis of the ^1H NMR spectral data shows that the signal with a chemical shift δ = 5.95 ppm refers to two products with different concentrations. Signals of the protons of the methylene groups in the range δ = 0.24 - 0.29 ppm, as well as of the methyl group in the range of δ = 1.22 - 1.25 ppm. at the ^1H NMR spectrum, according to the conclusions of [10], may indicate the formation of the second component of the reaction mixture. Determination of the nature of the second component of the reaction mixture requires additional experiments, which is the subject of our further studies. At this stage of the study of the detected transformation, we believe that the formation of the product is result of the reaction of Cp_2ZrCl_2 with an excess of Et_2Zn via bimetallic β-C-H activation. The experimentally observed intense gas evolution after addition of Et_2Zn to a solution of Cp_2ZrCl_2 and benzene serves as additional evidence of the formation of the complex under consideration. Spectral data for compound with a similar structure, formed as a result of the reaction of Cp_2ZrCl_2 with Et_3Al, are presented in the work of Negishi [10]. The authors of [11], when they examined the interaction of Cp_2ZrCl_2 with $AlMe_3$, note a low rate of formation of the corresponding zirconium-aluminum organic complex relative to the target product Cp_2ZrMe. The ratio of signal intensities at the ^1H NMR spectrum may also indicate for the formation of bimetallic complex in minor amounts. The structure of the product of complete ethylation of zirconocene dichloride **2** is identified in the ^1H NMR spectrum by signals of ethyl groups (δ = 0.005 - 0.05 ppm, δ = 0.24 - 0.29 ppm, and δ = 1.22 - 1.25), as well as a singlet signal of protons of cyclopentadiene rings (δ = 5.95 ppm), which is equivalent to the signal of the cyclic part of the the second component of the reaction mixture.



Scheme 2 (a) ^1H NMR spectra of a 1/1 mixture of Cp_2ZrCl_2 and $ZnEt_2$ in d-6-benzene. (b) ^1H – ^1H NOESY spectrum recorded at 298 K.

The optimization of the geometric parameters of the compounds under study and the solution of the vibrational problem were carried out in the GAUSSIAN 09 program [12] within the framework of the density functional theory (DFT) using the B3LYP functional and the LANL2DZ basis set. The absence of imaginary frequencies of normal vibrations in each case indicates the thermodynamic stability of molecules **1**, and **2**. The values of the Gibbs free energy presented in Table 1 cause the shift of thermodynamic equilibrium in the reaction system towards the reaction products.

Table 1. Thermodynamic parameters of the compounds under study,T = 298 K

№	(-G) ккал/моль	(-H) ккал/моль	S,кал/(моль*К)
Cp_2ZrCl_2	291539,4792	291575,8516	121,9940
1	331809,4014	331770,2793	131,2180
2	372038,2060	371996,4848	139,9330

Conclusions

Thus, as a result of our study, we have discovered for the first time ligand exchange between zirconocene dichloride and diethylzinc. It was found that the interaction of Cp_2ZrCl_2 with an excess of Et_2Zn in a d-6-benzene solution leads to the formation of organometallic complexes such as bis-(cyclopentadienyl)ethylzirconium chloride ($EtZrCp_2Cl$) and bis-(cyclopentadienyl)diethylzirconpium (Et_2ZrCp_2). For all the compounds received, the thermodynamic stability was assessed based on the analysis of the results of the DFT study.

Experimental section

General information

All experiments were carried out under argon using Schlenk techniques. Commercially available Et_2Zn, ≥52 wt. % Zn basis (Aldrich); bis(cyclopentadienyl)zirconium(IV) dichloride (Aldrich) and benzene-d_6, anhydrous, ≥99.6 atom % D, (Aldrich) were involved in the reactions. **CAUTION**: *Pyrophoric nature of diethylzinc compounds requires special safety precautions in their handling*. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AVANCE-500 spectrometer (400.13 MHz (^{1}H), 100.62 MHz (13C)). As the solvents and the internal standard, benzene-d6 were employed. 1D and 2D NMR spectra (COSY, HSQC, HMBC, NOESY) were recorded using standard Bruker pulse sequences.

NMR Examination of the Reaction of Cp_2ZrCl_2 with 4 Equiv of Et_2Zn.

An argon-filled dry round-bottomed flask was charged with Cp_2ZrCl_2 (0.5 mmol, 0,146 g), benzene-d6 (0.7 ml), and $ZnEt_2$ (2 mmol, 0.2 ml). The mixture was stirred at room temperature for 5 min and transfer via cannula to NMR tube. NMR spectra were recorded at 298 K. NMR examination of the reaction mixture indicated that $Cp_2ZrEtCl$ **1** was formed in 83% yield: ^{1}H NMR (benzene-d6): 0.96 – 1.01 (q, *J* = 7 Hz, *J* = 14 Hz, 2H, CH_2), 1.29 – 1.33 (t, J = 14 Hz, *J* = 7 Hz, 3H, CH_3), 5.81 (s, 10H, 2Cp). ^{13}C NMR (benzene-d6): 18.10 (CH_3), 48.03 (CH_2), 112.32 (2Cp). NMR examination of the reaction mixture indicated that **2** was formed. ^{1}H NMR (benzene-d6): 0.005 – 0.05 (q, J = 16 Hz, J = 8Hz, 2H, $2CH_3$), 0.24 – 0.29 (q, *J* = 16 Hz, *J* = 8 Hz, 2H, CH_2), 1.22 – 1.25 (t, *J* = 8 Hz, 3H, CH_3), 5.95 (s, 10H, 2Cp).

Conflicts of interest

The authors declare no competing financial interest.

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