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Synthesis, ethylene polymerization and dynamic features of titanium and zirconium complexes bearing chelating malonate-based enaminoketonato ligands

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Synthesis of new titanium and zirconium dichloro complexes bearing malonate-based enaminoketonato (N,O) ligand is described. NMR studies of the catalyst precursors reveal that synthesized complexes have different configurational isomers in solution state and that they undergo structural change within NMR timescale. After MAO activation complexes exhibited low to moderate activities in ethylene polymerization producing bi- or multimodal polyethylenes.

1. Introduction

Extensive research, both in academia and in industry, has been dedicated for the development of non-metallocene olefin-polymerization catalysts [1–6]. Group IV metal complexes with a wide range of heteroatom-donor ligands have been prepared and used as catalyst precursors in ethylene polymerization [7–19]. Complexes bearing (N,O)-type chelating ligands, like Fujita's FI-catalysts, and enaminoketonato-complexes, have attracted considerable interest [20–24]. These types of complexes have shown both high polymerization activities and interesting possibilities for example in the areas of living polymerization [25,26], co-polymerization [27,28] and polymerization of higher α-olefins [29].

The versatility of these complexes arises from the variation of the ligand structure which leads to significant changes in the catalytic activity and in the properties of the produced polymer products [28]. It has been also shown that in some cases enaminoketonato complexes are more active than the corresponding alkoxy-complexes [23–31]. This led us to develop new enaminoketonato complexes where the ligand-structure is based on malonate-ester backbone which we have previously used as ligand precursor [32]. Reported herein is the synthesis, structure, solution behavior and ethylene polymerization of new malonate based enaminoketonato titanium and zirconium complexes.

2. Results and discussion

2.1. Synthesis and characterization of complexes **1Ti–3Ti** and **1Zr–2Zr**

A general synthetic route for the titanium **1Ti**–**3Ti** and zirconium **1Zr**–**2Zr** complexes is presented in Scheme 1. Ligand precursors **1**–**3** were prepared with chosen anile compounds using ethyl 3-ethoxy-3-imino-propionate hydrochloride as a starting material [33]. Corresponding complexes **1Ti**–**3Ti** and **1Zr**–**2Zr** were synthesized through lithium salts under mild conditions. The desired titanium complexes were obtained from toluene solutions as dark red powders while their zirconium analogues were light yellow. All the complexes were synthesized with reasonable yields (29–36%).

The light yellow crystals of the complex **1Zr** suitable for X-ray structure determination were grown from saturated toluene solution at −60 °C. The solid-state structure of this complex is shown in Fig. 1 and selected bond lengths and angles are given in Table 1. In solid state complex **1Zr** adopts distorted octahedral coordination around the metal center with *trans* oxygen atoms, *cis* nitrogen atoms and *cis* chlorine atoms. The Zr–N and Zr–O bond lengths resemble those of FI-catalysts reported by Fujita and coworkers [34]. This might indicate that in **1Zr** the oxygen is more anionic in nature whereas the bond between nitrogen and zirconium resembles more of coordination type of bonding.

2.2. Solution behavior of complexes **1Ti–3Ti** and **1Zr–2Zr**

It is known that complexes bearing (N,O)-type ligands can adopt different configurational isomers [20,24,35] as displayed in

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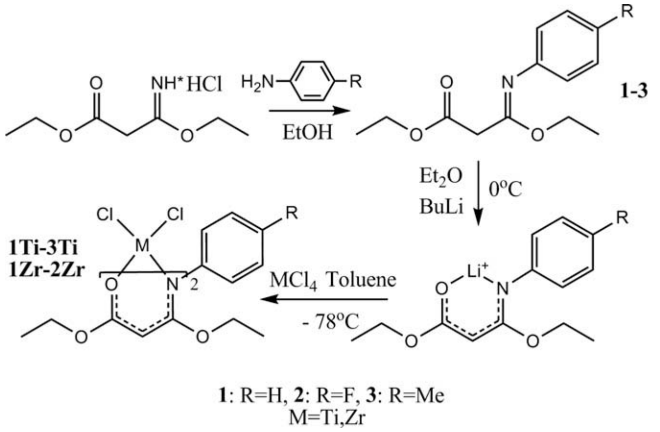


Scheme 1. Synthetic route for the complexes **1Ti–3Ti** and **1Zr–2Zr**.

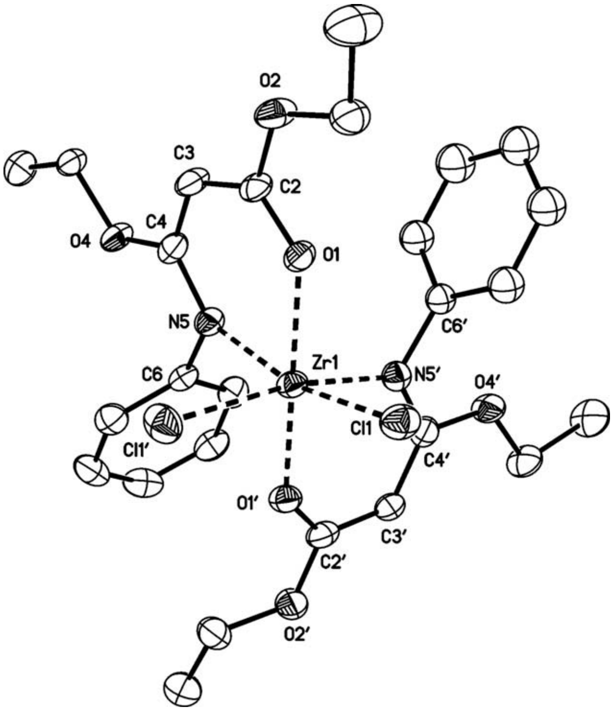
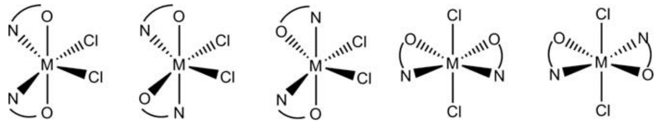


Fig. 1. Molecular structure of complex **1Zr** with thermal ellipsoids at 50% probability level. The solvent and all hydrogen atoms are omitted for clarity.

Table 1
Selected bond lengths and angles for complex **1Zr.**

Bond distances (Å)		Bond angles (°)	
Zr1–Cl1′	2.446(1)	O1–Zr–N5′	78.4(1)
Zr1–Cl1	2.463(1)	O1–Zr–N5′	95.5(1)
Zr1–N5′	2.235(3)	O1′–Zr–N5′	94.4(1)
Zr1–N5′	2.248(3)	O1′–Zr–N5′	78.52(1)
Zr1–O1’	2.072(3)	N5′–Zr–Cl1′	167.9(1)
Zr1–O1	2.069(3)	N5–Zr1–Cl1′	89.7(9)
O1′–C2′	1.288(5)	O1′–Zr1–Cl1	99.0(1)
O1–C2	1.285(5)	O1–Zr1–Cl1	88.0(1)
N5–C4	1.341(5)	N5′–Zr1–Cl1	88.9(1)
N5′–C4′	1.330(5)	Cl1–Zr1–Cl1′	93.75(4)
N5–C6	1.455(5)	O1–Zr1–O1′	170.6(1)
N5′–C6′	1.451(5)	N5–Zr1–N5′	90.5(1)



Scheme 2. Five different configurational isomers of (N,O)-type complexes.

Scheme 2. According to ^{1}H NMR the complexes have two different configurational isomeric structures in $CDCl_3$-solution, which can be seen from ^{1}H NMR spectrum of complex **1Zr** displayed in Fig. 2. These two isomers can be indentified from the two distinctive singlets, attributed to the CH-group in the molecule. Intensity ratios of these singlets are close to 1:2 favoring the isomer having CH-signal at lower field. Both configurational isomers have also two sets of CH_2 and CH_3 protons uprising from the ethoxide groups. With one of the isomers of complex **1Zr**, the rotation of phenyl ring is not hindered and CH_2-protons display clear quartet structures. In the other isomer structure the rotations of phenyl groups are hindered revealing complex set of aromatic proton signals and splitted metheine signals. ^{1}H-NMR of **1Zr** was measured also in a different, less polar, solvent d^{8}-toluene. Then the intensity ratio of the CH-signals was changed close to 1:4 again favoring the isomer having CH-signal at lower field. This phenomenon can be seen from the spectrum displayed in Fig. 3. These results underline the dynamic behavior of the complex in solution and dependence of balance between the isomers in different solvents.

To gain a more detailed understanding of the fluxional behavior of the complexes dynamic ^{1}H NMR (d^{8}-toluene) measurements were carried out. From Fig. 4 it can be seen that upon heating the two sets of peaks from CH_2 protons in the upper field become equivalent and also coalescence for the CH_2 protons in the lower field can be observed. The coalescence temperatures for the CH_2-protons are 25 °C and 5 °C and the corresponding energies for activation of rotation process are $\Delta G \neq (300.5\ K) = 14.8 \pm 0.9\ kcal\ mol^{-1}$ and $\Delta G \neq (288.2\ K) = 14.3 \pm 0.9\ kcal\ mol^{-1}$. All the spectra are reversible within the studied temperature range. It should also be noted that the second isomeric structure of the complex, where the rotation of the phenyl ring is not hindered, is not affected by the temperature change.

The fluxuation phenomenon of the herein studied malonate based enaminoketonato complexes is noticeably different than some of the other (N,O)-type complexes published before [20,24,35]. With the complexes studied here no coalescence of chelating proton was observed. These results suggest that different isomers of malonate based enaminoketonato dichloro complexes are fairly stable in solution under the applied temperature scale. To verify that the isomers arise from different configurational structures and not from various intra- or intermolecular hydrogen bonding, NMR measurements in d-THF were carried out with complex **1Zr**. Presence of different isomers was observed also in these experiments, thus excluding plausible intra- or intermolecular hydrogen bonding [36].

2.3. Ethylene polymerization

Synthesized complexes were activated with MAO and used as catalysts for ethylene polymerization. The results of these experiments are listed in Table 2. Electron-withdrawing or -donating *para*-substituents were introduced onto coordinating imino group to study how the electronic properties influence the catalytic activities of the complexes. However, these substituents revealed only minor changes in polymerization activities of the catalysts. Of the five catalyst system studied, *para*-F substituted **2Zr**/MAO exhibited the highest catalytic activity of 104 kg PE/(mol_{Zr} h bar). Correspondingly in the series of the titanium catalyst the *para*-F