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Di- and trinuclear zirconium complexes as catalysts for ethylene polymerization

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ABSTRACT

Bimodal and multimodal molecular weight distributions of polyethylenes can be achieved with di- or trinuclear zirconium catalysts in homogeneous solution. In order to prepare such complexes, bis(phenoxyimine) zirconium complexes and zirconocene complexes were coupled in Sonogashira reactions. Hydrosilylation reactions were applied for the combination of metallocene complexes with silane substituted N-heterocyclic compounds, such as 3,5-dimethylpyrazoles. The resulting di- and trinuclear complexes were activated with methylaluminoxane (MAO) and applied as catalysts for ethylene polymerization. The catalytic performances of these complexes and their applications in olefin polymerization reactions are discussed.

1. Introduction

One of the most intriguing properties of mono- and dinuclear homogeneous olefin polymerization catalysts is the fact that tiny differences in the molecular structure of the catalyst precursors can have a tremendous influence on their performances [1–10]. This is the main reason for the preparation of thousands of such complexes to study structure-property-relationships empirically and to prepare tailored polyolefins [11–15]. Polyolefins with a broad or bimodal molecular weight distribution (MWD) show an advantageous processability and therefore it is very attractive to prepare catalysts that are able to produce polyolefins with a desired molecular weight distribution. Attempts to obtain bimodal molecular weight distributions of polyethylenes by mixing mononuclear di(arylimino)pyridine iron complexes and metallocene complexes in homogeneous and heterogeneous systems failed in most cases because of averaging effects of different active sites leading to balanced molecular weights of the resulting polymer [16–18]. In order to avoid uncontrolled interactions of different active sites, different metal centers must be held at a certain distance to each other. A concept to reach this goal is the synthesis of di- or multinuclear complexes where the metal centers are far enough away from each other. In the literature only a few examples for multinuclear polymerization catalysts are known [19–25]. Since there exists a pool of more than 1500 mononuclear complexes as potential catalyst precursors in our research group, we had excellent starting conditions for this project. We picked metallocene complexes [26–29] as promising candidates for high molecular weight polymers and bis(phenoxyimine) [30–36], α-di(imine) [37–43] and 2,6-bis(arylimino)pyridine [44–48] complexes for polymers with low molecular weights Scheme 1.

The best way to couple these complexes depends on the complex type. Complex types with different metal centers, i.e. metallocene zirconium complexes and α-di(imine) chromium complexes need to be combined after the metal centers are introduced. Donor/acceptor interactions are also a suitable synthesis pathway. For complexes with the same metal center like metallocene zirconium complexes and bis(phenoxyimine) zirconium complexes, C–C coupling reactions can be performed before the complexation is carried out. The combination of phenoxyimine complexes and metallocene complexes works with palladium catalysed Sonogashira reactions [49,50].

Another method for combining ligand precursors are hydrosilylation reactions. Silicon compounds with a silicon-hydrogen bond and ω-alkenyl substituted ligand precursors are required.

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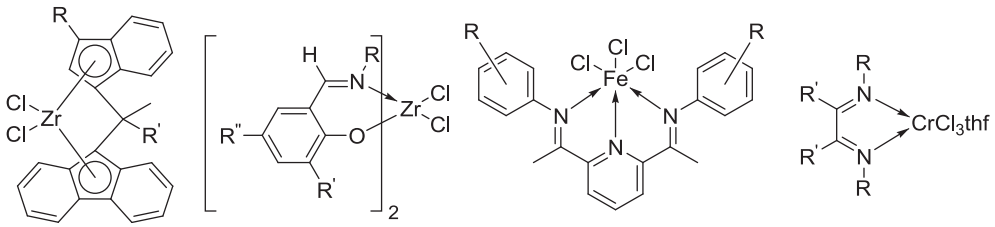
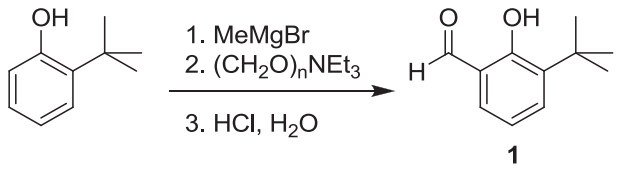


Scheme 1. Some complexes suitable for combination reactions: Metallocene complexes, bis(phenoxyimine complexes, 2,6-bis(arylimino)pyridine complexes, α-di(imine) complexes.

The reaction is catalysed by hexachloro platinum acid. In the literature, coupled binuclear metallocene complexes are described [19,20,51,52] as well as amido functionalized half sandwich complexes [53,54]. The idea is to mix these complex types and functionalize metallocene ligand precursors with amino groups by hydrosilylation reactions Scheme 2.



Scheme 3. Synthesis of substituted salicylaldehydes.

2. Results and discussion

2.1. Coupling of phenoxyimine ligand precursors and metallocene type ligand precursors using Sonogashira reactions

2.1.1. Synthesis of substituted salicylaldehydes

To obtain 3-substituted salicylaldehydes, phenols containing one unsubstituted ortho-position, are deprotonated in tetrahydrofuran with a Grignard reagent. The following reaction with para formaldehyde in toluene and subsequent acidic hydrolysis leads to salicylaldehydes Scheme 3 [34].

2.1.2. Introduction of iodo substituents

For introducing an iodine substituent in the para-position to the hydroxyl group, 3-*tert*-butylsalicylaldehyde is treated with benzyltrimethylammonium dichloroiodate in methanol/dichloromethane to give 3-*tert*-butyl-5-iodo-salicylaldehyde Scheme 4 [55].

2.1.3. Synthesis of phenoxyimine compounds

The synthesis of phenoxyimine compounds was achieved following two different routes:

a) The condensation reaction of a substituted salicylaldehyde with an aliphatic or aromatic amine in toluene at reflux temperatures gives the phenoxyimine compound under azeotropic water separation [56].
b) The substituted salicylaldehyde is reacted with a small excess of an aliphatic or aromatic amine in the presence of molecular sieves (3 Å) in toluene at room temperature.

The second method is milder and produces less undesired side products.

As starting material either compound **1** or **2** can be used since the iodo substituent can be located either in the 5-position of the salicylaldehyde or anywhere in the used amine Scheme 5.

The preparation of the phenoxyimine part requires two, respectively three steps depending where the iodo substituent is introduced.

2.1.4. Synthesis of ω-alkenyl and ω-alkynyl substituted indenyl derivatives

The synthesis of ω-alkynyl and ω-alkenyl substituted indenyl compounds is carried out in toluene at room temperature adding ω-alkynyl bromides to indenyl lithium Scheme 6.

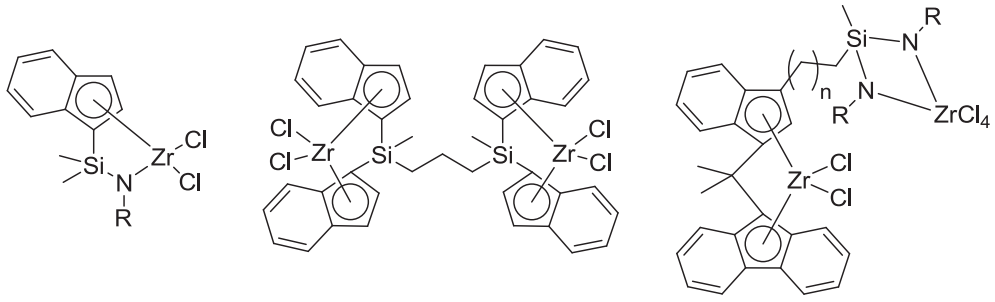
These compounds could be used for the next reaction without further purification.

2.1.5. Synthesis of fulvene derivatives

Fulvene derivatives can be obtained by base catalysed condensation reactions of indenes and ketones [57,58] The substituted indenyl derivatives were dissolved in methanol. The addition of a ketone and pyrrolidine as a base to the reaction mixture resulted in 3-substituted fulvene derivatives Scheme 7.

2.1.6. C_1-bridged ligand precursors containing an ω-alkynyl or ω-alkenyl substituent

The synthesis of C_1-bridged ligand precursors follows the fulvene method [59,60]. This method makes use of the fact that fluorenyl or indenyl anions can act as nucleophils and add to exocyclic double bonds. An anion is formed that gives the C_1-bridged ligand



Scheme 2. Amido functionalized half sandwich complexes, binuclear silicon bridged metallocene complexes and the combination of both types.