Di- and trinuclear iron/titanium and iron/zirconium complexes with heterocyclic ligands as catalysts for ethylene polymerization

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ABSTRACT

The properties of polyolefin resins depend very much on their molecular weights, the amount of side chain branchings and molecular weight distributions. One way to obtain such tailored products in only one reaction step consists in the application of dissymmetric multi nuclear catalysts with different active sites. Since every active site is producing its own polymer, a "molecular blending" is the result. In order to reach this goal, a variety of mono, di- and trinuclear complexes of iron, titanium and zirconium, containing 2,6-bis(aryliminoethyl)pyridine and phenoxyimine building blocks have been synthesized and characterized. The reaction of iodo functionalized 2,6-bis(arylimino-ethyl)pyridine derivatives with alkyne functionalized phenoxyimine compounds via Sonogashira cross-coupling reactions results in ligand precursors that can provide coordination sites for two different metals. Trinuclear complexes with the combinations Ti/Fe and Zr/Fe, each molecule containing two iron atoms in two 2,6-bis(aryliminoethyl) pyridine units, gave the best ethylene polymerization results. Due to fast ligand exchange reactions, dinuclear iron/titanium complexes could not be isolated from reactions of mono(phenoxyimine) titanium complexes and the coupled bis(chelate) ligand precursor. Since the metal centers show their best performances at different polymerization temperatures, the compositions (and, therefore, the molecular weight distributions) of the desired polyethylenes may be adjusted by a simple change of the reaction temperature.

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1. Introduction

Even after 60 years of its beginning, the field of catalytic olefin polymerization did not lose its attraction. A series of reviews describes the situation [1–5] and it is fascinating to see the catalytic potential of a variety of transition metal complexes. In the 1990s metallocene complexes with group IV metals proved as very efficient homogeneous catalysts for ethylene and propylene polymerization [6–15] and references therein. Ziegler et al. [16,17] reported already in 1955 that traces of nickel inhibited ethylene insertion into aluminium alkyl bonds. In spite of this negative "nickel effect" Ostoja Starzewski showed in the 1980s that nickel ylide complexes can polymerize ethylene very efficiently without any cocatalysts [18] to give polyethylenes with high molecular weights. The breakthrough for late transition metal complexes as catalysts for olefin polymerization came later: in 1995, Brookhart et al. [19–21] described nickel complexes with α,α′-diimine ligands as highly reactive ethylene polymerization catalysts. Depending on the substitution pattern at the imino moieties, these complexes

either oligomerized ethylene to give higher olefins (terminal, internal, and branched) or produced high molecular weight polyethylenes. In 1998, Gibson [22–25] and Brookhart [26–28] independently reported the application of 2,6-bis(aryliminoethyl) pyridine iron complexes as efficient catalysts for the polymerization and oligomerization of ethylene with a comparable potential. Structure–property-relationship studies allowed the tailoring of polyolefin resins [22–45]. In the course of designing and improving new types of transition metal catalysts, the research group of Fujita presented bis(phenoxyimine) complexes of group IV and group V metals in 1998 [46–63]. Due to their simple preparation and a wide variety of possible ligand structures, these complexes have gained a lot of attraction. The fast growth of the polyolefin industry was possible because the properties of the produced polyolefins could be modified by the molecular weight, the density and the branching of the resins to give high density polyethylene (HDPE), "linear low density polyethylene" (LLDPE) [64] and other "new materials". In addition, copolymerization of two or more olefinic monomers allowed to modify the properties of polyolefins [65–70]. Catalyst compositions usually produce unimodal polyethylenes while mixtures of two different polymerization catalysts (for instance, a bis (aryliminoethyl)pyridine iron complex and a zirconium based

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metallocene complex) may also produce bimodal molecular weight distributions [71]. In order to avoid disadvantages of heterogeneous catalyst mixtures, like non-uniform distribution of the different catalyst molecules on the support surface or leaching tendencies to give reactor fouling, multinuclear complexes containing differently coordinated metal centers as catalyst precursors [72–80] can solve the problem. Each metal center of such complexes is supposed to produce its own type of polymer but additional blending becomes unnecessary due to the immediate vicinity of the active centers (molecular blending). Covalently bridged, combined ligand systems are required assuring an equal distribution of the different active sites in both homogeneous and heterogeneous polymerization reactions. Dinuclear zirconocene complexes as well as zirconium complexes containing a metallocene moiety and an indenylsilylamido function (based on the "constrained geometry catalysts") have been described by our group [76–84]. Combinations of bis(aryliminoethyl)pyridine iron and zirconium based metallocene complexes have been described by Pronko in 2004 [85]. Metallocene type ligand frameworks have also been coupled with α,α′-diimines yielding dinuclear nickel/zirconium complexes [86], or Fujita's phenoxyimine compounds yielding trinuclear zirconium complexes [87–90]. Another type of early/late heterobinuclear complexes was described by Bianchini et al. [91]. It consists of a palladium, cobalt, or nickel pyridyl imine moiety which is linked to a bridged, substituted bis(cyclopentadienyl) zirconium complex. More recent papers depict the synthesis of dinuclear α,α′-diimine nickel/bis (aryliminoethyl)pyridine iron complexes [92] or α,α′-diimine nickel/bis(aryliminoethyl)pyridine cobalt complexes [93].

Due to the simple synthesis of phenoxyimine compounds, we first laid our focus on coupling reactions of phenoxyimines with metallocene type ligand precursors and obtained trinuclear zirconium complexes [82] which gave polyethylenes with broad or bimodal molecular weight distributions (see Fig. 1).

In this paper, we present a strategy to connect phenoxyimine and bis(aryliminoethyl)pyridine compounds. The behavior of the resulting trinuclear iron/titanium and iron/zirconium complexes in ethylene polymerization reactions is described, and the results are compared with the data obtained for the corresponding mononuclear complexes.

2. Experimental

2.1. General remarks

All experimental work was routinely carried out using Schlenk technique. Anhydrous and purified argon was used as inert gas. The solvents n-pentane, diethyl ether, toluene und tetrahydrofuran were purified by distillation over Na/K alloy. Diethyl ether was
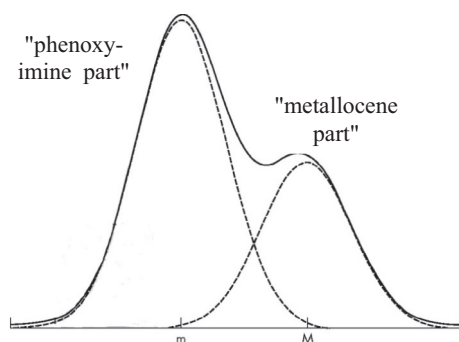

Fig. 1. Bimodal molecular weight distribution of a polyethylene sample obtained with a trinuclear zirconium complex [82].

additionally distilled over lithium aluminum hydride, toluene was additionally distilled over phosphorus pentoxide. Methanol was distilled over magnesium filings, ethanol over pieces of sodium sand. 1-Butanol (p.a.) was purchased from Merck and used without prior distillation. Methylaluminoxane was purchased from Crompton (Bergkamen) as a 10 wt.% solution in toluene. Ethylene (3.0) and argon (4.8/5.0) were supplied by Rießner Company (Lichtenfels). All other starting materials were commercially available and were used without further purification.

NMR spectra were recorded at 25 °C on a Varian Inova 400 spectrometer. The chemical shifts in the ^{1}H NMR spectra are referred to the residual proton signal of the solvent (δ = 7.24 ppm for CDCl$_3$) and in ^{13}C NMR spectra to the solvent signal (δ = 77.0 ppm for CDCl$_3$). EI mass spectra were routinely recorded with a VARIAN MAT CH-7 instrument (direct inlet, E = 70 eV) and a VARIAN MAT 8500 spectrometer. MALDI-TOF MS measurements were performed on a Bruker Daltonic Reflex TOF using graphite as the matrix. The laser intensity was set to 60–70%. GC/MS spectra were recorded with a Thermo Focus gas chromatograph in combination with a Thermo DSQ mass detector (EI, 70 eV) using a HP-5MS GC column (length: 30 m, film thickness: 0.25 μm, flow: 1.5 ml/min, split ratio: 1:50) and helium as the carrier gas. The routinely used temperature program contained a starting phase (2 min at 50 °C), a heating period (10 K/min for 24 min) and a plateau phase (15 min at 290 °C) resulting in a run length of 41 min. GC/MS spectra were recorded with a HP5890 gas chromatograph in combination with a MAT 95 mass detector. GPC measurements were performed on a HT-GPC PL-220 device (RI detector; T = 150 °C). Elemental analyses were conducted with a VarioEl III CHN instrument using acetanilide for calibration.

2.2. Synthesis of 2-acetyl-6-(arylimino)pyridine compounds ("mono-imino compounds")

At 0 °C, formic acid (50 μl) was added dropwise to a solution of 2,6-diacetylpyridine (1.63 g; 10 mmol) and the appropriate aniline derivative (9 mmol) in methanol (15 ml). The mixture was kept at 0 °C for 24 h without stirring. The desired mono-imino compounds precipitated as bright yellow crystals which were separated by filtration, washed with cold methanol (0 °C), and finally dried in vacuo. Second crops of crystals could be obtained after prolonged storage of the mother liquor at −20 °C.

2.2.1. 2-Acetyl-6-[1-(2,6-diisopropylphenyl)iminoethyl]pyridine (2)
^{1}H NMR (400 MHz, CDCl$_3$): δ [ppm] = 8.35 (d, 1H, Py-H), 7.93 (d, 1H, Py-H), 7.73 (t, 1H, Py-H), 6.97 (d, 2H, Ar-H), 6.90 (t, 1H, Ar-H), 2.58 (s, 3H, O=C-CH$_3$), 2.52 (sept, 2H, ^{i}Pr-CH), 2.06 (s, 3H, N=C-CH$_3$), 0.95 (s, 6H, ^{i}Pr-CH$_3$), 0.94 (s, 6H, ^{i}Pr-CH$_3$).
^{13}C{1H} NMR (100 MHz, CDCl$_3$): ä [ppm] = 200.1 (1C, C$_q$, O=C-CH$_3$), 166.4 (1C, C$_q$, (ArN)=C-CH$_3$), 155.5 (1C, C$_q$, Py), 152.5 (1C, C$_q$, Py), 146.2 (1C, C$_q$, Ar-C-N), 137.3 (1C, Py-CH), 135.7 (2C, Ar-C$_q$), 124.5 (1C, Ar-CH), 123.7 (1C, Py-CH), 123.0 (2C, Ar-CH), 122.6 (1C, Py-CH), 28.3 (2C, ^{i}Pr-CH), 25.6 (1C, O=C-CH$_3$), 23.2 (1C, ^{i}Pr-CH$_3$), 22.9 (1C, ^{i}Pr-CH$_3$), 17.0 (1C, (ArN)=C-CH$_3$).
MS [m/z] (rel. intensity in brackets): 322 M$^+$ (38), 307 M-Me (100). Yield: 91%.

2.2.2. 2-Acetyl-6-[1-(2,6-dimethylphenyl)iminoethyl]pyridine (3)
^{1}H NMR (400 MHz, CDCl$_3$): δ [ppm] = 8.57 (d, 1H, Py-H), 8.12 (d, 1H, Py-H), 7.92 (t, 1H, Py-H), 7.07 (d, 2H, Ar-H), 6.94 (t, 1H, Ar-H), 2.78 (s, 3H, O=C-CH$_3$), 2.23 (s, 3H, N=C-CH$_3$), 2.03 (s, 6H, Ar-CH$_3$).
^{13}C{1H} NMR (100 MHz, CDCl$_3$): ä [ppm] = 200.1 (1C, C$_q$, O=C-CH$_3$), 166.6 (1C, C$_q$, (ArN)=C-CH$_3$), 155.5 (1C, C$_q$, Py), 152.4 (1C, C$_q$, Py), 148.5 (1C, C$_q$, Ar-C-N), 137.3 (1C, Py-CH), 127.9 (2C, Ar-CH), 125.3 (2C, Ar-C$_q$), 124.5 (1C, Ar-CH), 123.2 (1C, Py-CH),