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Bis(arylimino)pyridine iron(III) complexes as catalyst precursors for the oligomerization and polymerization of ethylene

Christian Görl*, Tanja Englmann, Helmut G. Alt

Laboratorium für Makromolekulare Chemie, Universität Bayreuth, Universitätsstraße 30, Bayreuth D-95447, Germany

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ABSTRACT

A series of 26 bis(arylimino)pyridine iron(III) complexes containing either electron withdrawing or electron donating substituents in their ligand frameworks was synthesized and characterized. After activation with methylaluminoxane (MAO), these catalysts oligomerize or polymerize ethylene to give both linear and branched products. In contrast to iron(II) complexes, the presence of at least one ortho-substituent at the iminophenyl rings is not obligative for catalytic activities of the iron(III) complexes. A couple of such iron(III) complexes containing meta- and para-substituted bis(arylimino)pyridine compounds were accessible and their oligomerization behaviour revealed interesting differences to the well known iron(II) analogues since both internal and branched olefins were found in the product mixtures beside the expected linear α-olefins. The widths of the resulting molecular weight distributions and the degrees of isomerization of the resulting oligomers strongly depend on the substitution pattern at the ligand frameworks.

1. Introduction

Gibson [1–4] and Brookhart [5–7] independently reported the application of 2,6-bis(arylimino) pyridine iron complexes as effective catalysts for the polymerization and oligomerization of ethylene leading to highly linear products. Especially the substitution pattern of the iminophenyl rings has a great influence on the polymerization activities and the product compositions [1–17]. Iron complexes bearing small substituents (alkyl or halogene) at the 2-positions of the iminophenyl rings proved to be excellent catalyst precursors for the oligomerization of ethylene to give low molecular weight α-olefins. These α-olefins are industrially highly desired compounds which are useful, e.g., for copolymerization reactions with ethylene to give linear low density polyethylene (LLDPE). In this context, halogenated 2,6-bis(arylimino)pyridine compounds play an important role as valuable ligand precursors and some of their transition metal complexes are known in the literature [1,5,18–25]. In the past five years, 2,6-bis(arylimino)pyridine iron complexes with halogen substituted iminophenyl rings were reported by Qian et al. and Ionkin et al. [8,9,14]. While fluoro, chloro, and bromo substituted compounds are known for a longer time [8–10,26–28], the analogous iodo substituted compounds were described by our group in 2007 [29]. As demonstrated by Ionkin et al. [14], bromo substituents at the iminophenyl rings can be exchanged with aryl groups applying Suzuki coupling reactions. As an alternative method, Sonogashira coupling reactions of terminal alkynes with 2,6-bis(arylimino)pyridine compounds containing para-bromo and para-iodo substituted iminophenyl rings proved to be a successful pathway to give 2,6-bis(arylimino)pyridine compounds with extended ligand frameworks [29]. The vast majority of these literature known complexes rely on iron(II) compounds. One of the characteristics of 2,6-bis(arylimino)pyridine iron(II) complexes is the fact that the iminophenyl rings of the ligand frameworks must contain at least one substituent at the *ortho*-position to the iminophenyl nitrogen atoms to be stable against ligand transfer reactions. Although the synthesis of the iron(II) complex with the tridentate ligand precursor 2,6-bis(1-(phenylimino)ethyl)pyridine, a ligand without any substituents at the iminophenyl rings, was described by Abu-Surrah et al. [30], this complex does not exist in the common form (L)$FeCl_2$ (L = bis(arylimino)pyridine ligand) but can be isolated as an air stable ionic compound of the composition $[(L)_2Fe]^{2+}[FeCl_4]^{2-}$. Analogous ion-pair complexes were described for 2,6-bis(1-(2-fluorophenyl)ethyl)pyridine [28], 2,6-bis(1-(3,5-dibromo-4-methylphenyl)ethyl)pyridine [14], 2,6-bis(1-(2,6-dibromophenyl)ethyl)pyridine [31], and 2,6-bis(1-(4-nitrophenyl)ethyl)pyridine [13]. According to these results, methyl groups seem to be the smallest ortho-substituents that prevent this ligand transfer reaction. While a great deal of work has been spent on bis(arylimino)pyridine iron(II) complexes, only a few publications report about the corresponding iron(III) complexes despite their higher catalytic activities towards olefin

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* Corresponding author. Tel.: +49 921 55 2993; fax: +49 921 55 3206.
E-mail address: christian.goerl@uni-bayreuth.de (C. Görl).

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oligomerization and polymerization [14,24,29,32–39]. Although both iron(II) and iron(III) complexes can be undoubtedly characterized, the oxidation state of the iron centers (Fe(II) or Fe(III)) after activation with aluminoxane cocatalysts and the nature of the active species still remains unclear [4,36,40]. Actual DFT calculations by Cruz et al. [41,42] and Raucoules et al. [43] give strong evidence for the enhanced oligomerization/polymerization ability of active iron(III) species compared with iron(II) species. However, iron centers in both oxidation states may be present in the same catalyst system ("multicentered catalysts") and lead, e.g., to polyethylenes with broad or even bimodal molecular weight distributions [41,44]. The increased activities of the bis(arylimino)pyridine iron(III) complexes can be explained with the stronger Lewis acidic character of iron(III) centers compared with iron(II) centers and, therefore, an enhanced affinity to coordinate electron rich olefin molecules. Lopez Reyes [24], Devore [35], Bryliakov [36], and Prades [37] describe some bis(arylimino)pyridine iron(III) complexes with ortho-disubstituted iminophenyl rings useful for ethylene polymerization reactions. As mentioned above, Ionkin et al. [14,19] explored the reactivity of halogen substituted bis(arylimino)pyridine compounds towards Suzuki coupling. During these studies, three iron(III) complexes were described along with a huge number of iron(II) complexes which were applied for ethylene oligomerization. The synthesis of ω-alkenyl substituted bis(arylimino)pyridine compounds and their corresponding iron(II) and iron(III) complexes was described by our group [33]. While their ethylene oligomerization and polymerization behaviour was superior compared with analogous alkyl substituted bis(arylimino)pyridine iron complexes, self-immobilization [45] as described for metallocene complexes was not observed during the oligomerization/polymerization runs. Due to the extreme preference of the iron centers to ethylene molecules compared with higher α-olefins, the incorporation rates of such higher olefins are very low [46–48]. While the early literature mainly emphasizes the influence of substituents at the ortho-positions of the iminophenyl rings, more actual publications laid the focus on the meta- and para-substituents [13,14,24,29]. The introduction of electron withdrawing substituents into the ligand backbones resulted in an enhanced temperature stability and, therefore, lead to higher activities. According to Gong [38], bis(arylimino)pyridine transition metal complexes without any substituents at the iminophenyl rings can be applied for the polymerization of 1,3-butadiene. These results engaged us to synthesize bis(arylimino)pyridine iron(III) complexes containing halogen or other electron withdrawing substituents on the iminophenyl rings and to investigate their abilities towards selective ethylene oligomerization/polymerization including the question if catalytic activities are also observed when the iminophenyl rings of the ligand frameworks do not contain substituents in ortho-positions to the former amino groups.

2. Experimental

2.1. General considerations

All experimental work was routinely carried out using Schlenk technique. Dried 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 additionally distilled over lithium aluminum hydride, toluene was additionally dried over phosphorus pentoxide. Methylene chloride was dried over phosphorus pentoxide and calcium hydride. Methanol and ethanol were dried over magnesium. 1-Butanol (p.a.) was purchased from Merck and used without prior distillation. Methylalumoxane was purchased from Crompton (Bergkamen; 30% in toluene) and Albemarle (Baton Rouge, USA/Louvain – La Neuve, Belgium; 10% 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 at the Zentrale Analytik of the University of Bayreuth 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 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. At the Zentrale Analytik of the University of Bayreuth, GC/MS spectra were routinely recorded with a HP5890 gas chromatograph in combination with a MAT 95 mass detector. For the analysis of oligomer mixtures, GC spectra were obtained with an Agilent 6890N gas chromatograph equipped with a HP-5 column (length: 30 m, film thickness: 1.5 μm, flow: 150 ml/min, split ratio: 1:50). The temperature program included a starting phase (6 min at 35 °C), two heating ramps (1 K/min up to 55 °C, then 20 K/min up to 250 °C) and a plateau phase (20 min at 250 °C) resulting in a run length of 55.75 min. This temperature program allowed the separation of most of the hexene isomers. GPC measurements were routinely performed by SABIC Company (Riyadh, Saudi Arabia). Elemental analyses were performed with a VarioEl III CHN instrument using acetanilide for calibration.

2.2. Synthesis of 2,6-bis(arylimino)pyridine compounds applying molecular sieves and a heterogeneous SiO_2/Al_2O_3 catalyst (Method A)

To a solution of 2.6-diacetylpyridine (0.49 g; 3 mmol) in toluene (20 ml) were added molecular sieves (4 Å or 3 Å; 15 g), the corresponding amine or aniline compound (7 mmol), and the silica/alumina catalyst (0.5 g). The reaction mixture was heated to 45–50 °C for 24 h. If the reactions were not completed (according to GC/MS analyses), the heating period was prolonged till completion. After cooling to room temperature, the mixture was filtered over sodium sulfate, and the residue was washed several times with toluene. After removal of the solvent, methanol was added for precipitation. After storage at −20 °C for 24 h, the precipitated bis(imino)pyridine compounds were isolated and dried in vacuo (yields: 40–90%). Their spectroscopical data are given in the Supporting Information (Tables A1 and A2).

2.3. Synthesis of 2,6-bis(arylimino)pyridine compounds applying a Dean-Stark trap (Method B)

To a solution of 2,6-diacetylpyridine (0.82 g; 5 mmol) in 150 ml of toluene were added a substituted aniline (12.5 mmol; 2.5 equivs.) and a few milligrams of para-toluenesulfonic acid. The reaction mixture was heated under reflux for 8–48 h applying a Dean-Stark-trap. After cooling to room temperature, a saturated sodium hydrogencarbonate solution (200 ml) was added. The organic phase was separated and filtered over sodium sulfate and silica. The solvent was removed and methanol (20 ml) was added. The imino compounds precipitated when stored at −20 °C for some days