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Short Communication

Dimerization reactions with iron and cobalt bis(imino)pyridine catalysts: A substrate based approach☆

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ABSTRACT

Herein, we present a substrate based approach to gain insight into effects on reactivity as well as selectivity of dimerization reactions using bis(imino)pyridine catalysts. Common iron and cobalt systems show several limitations applying sterically demanding alkenes. Systematic substrate alterations reveal that structural properties are able to influence reactivity and dimer selectivity whereas electronic properties have an impact on insertion selectivity. Finally, successful conversion of the simplest vinylidene compound isobutene is achieved by catalyst variation.

1. Introduction

Oligomerization reactions of alkenes by transition metal complexes are of considerable industrial interest [1–3]. For example, alkenes such as propene and 1-butene are dimerized on large scale to give mainly branched products which are used e.g. as feedstocks for gasoline blending or alcohol production [4,5]. While highly branched products are favored in fuels, products with higher linearities are more desirable as precursors for plasticizers. Although several catalysts are known to generate branched dimers, only a few catalysts are capable of producing linear dimers from 1-alkenes [6,7].

One strategy to generate linearly linked products from 1-alkenes is the use of bis(imino)pyridine ligated iron or cobalt complexes using aluminum alkyls like methylaluminoxane (MAO) as activation agents [8–10]. Initially, these bis(imino)pyridine complexes were introduced as a promising alternative to commonly used Ziegler–Natta catalysts of early transition metals in the polymerization of ethene. By applying linear aliphatic 1-alkenes, for example using an iron-based catalyst, dimers were generated with linearities of up to 80% [11]. By using analogous cobalt catalysts even higher product linearities of over 97% were achieved [12]. High selectivity towards these head-to-head dimers is caused by the change from 1.2 to 2.1 insertion between the first and the second step [13,14]. Since a variation of the ligand backbone is easy to achieve, many different substitutions of the ligand have been conducted. In this manner, significant effects on elimination rate, overall activity and product linearity were observed [15,16].

Besides the catalytic system, the choice of the substrate plays a key role for the product formation in oligomerization reactions. While ethene can be applied in most cases, the use of propene and higher 1-alkenes often leads to lower reactivities as well as lower linearities. Although in comparison to ethene 1-alkenes reveal lower reactivities in oligomerization reactions, higher dimer selectivities can be achieved. In this context, the application of vinylidene compounds must be considered separately. Isobutene, for example, differs significantly from linear aliphatic 1-alkenes and usually shows no reactivity for a linear linkage. Due to the two methyl substituents, the double-bond of isobutene possesses higher electron density and shows stronger polarization compared to other aliphatic 1-alkenes. However, we recently showed a novel approach towards head-to-head homo-dimers from isobutene using nickel catalysts [17]. Although, selectivity for the linear linkage was very high (98%) only moderate reaction rates and a poor stability of the catalyst were observed.

Since bis(imino)pyridine catalysts are known to be highly active in different dimerization reactions of linear aliphatic 1-alkenes, we aimed for the successful transformation of isobutene. Our target reaction was the head-to-head linkage of isobutene producing homodimers as well as codimers with propene (Scheme 1), since these compounds are considered as highly valuable precursors for plasticizers.

☆ Dedicated to Professor Wilhelm Keim on the occasion of his 80th birthday.
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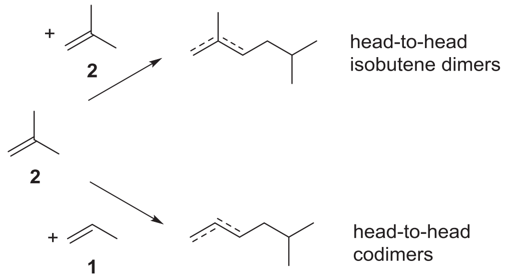


Scheme 1. Head-to-head dimerization reactions of isobutene.

Aside from previous studies, our work on bis(imino)pyridine catalysts was therefore focused on substrate effects rather than ligand effects. Product linearity and substrate reactivity were examined using different bis(imino)pyridine-metal and related catalytic systems. Several substrate limitations were discovered. Furthermore, investigations provided an improved understanding concerning the product formation with these types of catalysts. Finally, linear linkage of isobutene was realized by ligand modifications.

2. Experimental

2.1. Reagents

All preparations and manipulations were performed under a dry, oxygen-free argon atmosphere using standard Schlenk techniques. Argon gas (99.998%, AIR LIQUIDE, Düsseldorf, Germany) was passed through a P_2O_5 column and an OXISORB® cartridge (Messer, Bad Soden, Germany). Chemicals were purchased from Acros Organics (Geel, Belgium) and Sigma Aldrich (Steinheim, Germany) and dried over 4 Å molecular sieves. Isobutene, received from Evonik Industries AG (Marl, Germany), as well as propene, obtained from Messer (Bad Soden, Germany), were used without further purification. Axion® CA 1310 (Methylalumoxane, 10 wt.% solution in toluene) was provided by Chemtura Organometallics GmbH (Bergkamen, Germany). Ligands and catalyst precursors were synthesized according to the literature [16,18,19].

2.2. Dimerization experiments

All reactions were performed in a 25 mL custom-made stainless steel autoclave. [20] In a typical experiment, the catalyst precursor was transferred to the reactor. Alkenes were added sequentially as required. At room temperature liquid alkenes were transferred to the reactor with a syringe. Gaseous alkenes were added volumetrically as a liquid with a transparent pressure resistant tube (Tecalan GmbH, Grünberg, Germany). After addition of the substrates, the reactor was sealed and placed in an ice bath. Subsequently, methylalumoxane was injected in a by-pass of the pressure resistant tube under argon flow. The by-pass was closed and the tube was pressurized with a small amount of isobutene or propene (in the case of codimerization experiments). Under stirring of the substrates, methylalumoxane was transferred to the reactor by opening the reactor valve. The autoclave was placed in a preheated oil bath at the desired temperature. The magnetic stirrer was accelerated to 500 rpm. After 2 h, the reaction was stopped by rapidly cooling to room temperature using an ice bath. Reaction mixture was slowly degassed by stirring at room temperature. Then, excess of methylaluminoxane was neutralized with 20 mL of a solution of hydrochloric acid (0.5 M). The organic layer was separated and analyzed by gas chromatography using dodecane as an internal standard.

2.3. Product analysis

Standard gas chromatographic analyses were performed on a HP 6890 instrument (Hewlett-Packard GmbH, Waldbronn, Germany) equipped with a flame ionization detector (FID) and a HP5 capillary column (30 m, diameter 0.25 mm, film thickness 0.25 μm) connected to an auto sampler. GC–MS analyses were carried out on a Hewlett-Packard 5973 (70 eV). Initial product formations were obtained from GC-FID-analyses of the alkene mixture. GC-FID and GC–MS analyses of the hydrogenated products were carried out in order to determine product selectivities. Hydrogenation was achieved using 10% Pd/C catalyst applying 20 atm of hydrogen. Total conversion to alkanes was accomplished after 16 h at 80 °C using 10 mg Pd/C and 2 mL of the alkene mixture.

3. Results and discussion

3.1. Reactions with common bis(imino)pyridine catalysts

In the course of our investigations on linear dimerization of isobutene we applied several common bis(imino)pyridine metal complexes (Fig. 1) [21].

With these systems, in contrast to the already described conversion of linear aliphatic 1-alkenes, conversion of isobutene (**2**) could not be achieved. We assumed that a metal-isobutyl complex, formed by an insertion of isobutene in the first step, is sterically hindered which prevented a second insertion of isobutene. In order to enable an alkene insertion in the assumed metal-isobutyl complex, further experiments were conducted using propene (**1**) as a cosubstrate. Previous studies on ethene oligomerization by Small and Marcucci showed that a less reactive substrate is able to compete with highly reactive ethene in the first insertion step, but an insertion of the less reactive substrate in the second step is almost excluded [11].

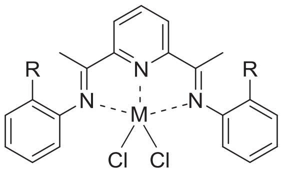
Thus, the addition of the more reactive cosubstrate propene seemed promising in order to achieve an insertion and subsequent product formation. In these codimerization experiments, propene dimers and oligomers were formed, but again no products including isobutene were detected.

With the aim of understanding the observed limitation for isobutene, further experiments were conducted. To investigate substrate effects on both reactivity and selectivity, different aliphatic 1-alkenes were selected. Applied substrates are shown in Fig. 2.

Complexes **Fe-1** and **Fe-2** were chosen as model catalysts since these show very different product linearities in the dimerization of linear aliphatic 1-alkenes [11]. Results are given in Table 1.

Initial experiments were carried out using linear aliphatic 1-alkenes (entries 1–6). In accordance with the literature, higher proportions of branched products are favored with catalyst **Fe-1** whereas with **Fe-2** linear dimers are observed as main products. For example, dimerization of 1-butene (**3**) with **Fe-1** resulted in a l:b ratio of 30:70 while using **Fe-2** the l:b ratio was 65:35 (entry 1 and entry 2).

In comparison to 1-butene (**3**), by applying 1-pentene (**7**) and 1-hexene (**12**), similar product selectivities were achieved (entries 3–6). An attachment of a methyl group along the chain of **3** and **7** showed



Fe-1: R = H, M = Fe
Fe-2: R = Me, M = Fe
Fe-3: R = Et, M = Fe
Co-1: R = H, M = Co
Co-2: R = Me, M = Co
Co-3: R = Et, M = Co

Fig. 1. Applied bis(imino)pyridine metal complexes.