



# Nickel catalyzed dimerization reactions of vinylidene compounds: Head-to-head couplings and catalyst stabilization



Arno Behr<sup>a,\*</sup>, Nils Rentmeister<sup>a</sup>, Thomas Seidensticker<sup>a</sup>, Thiemo A. Faßbach<sup>a</sup>,  
Stephan Peitz<sup>b</sup>, Dietrich Maschmeyer<sup>b</sup>

<sup>a</sup> Technische Universität Dortmund, Lehrstuhl für Technische Chemie, Emil-Figge-Str. 66, D-44227 Dortmund, Germany

<sup>b</sup> Evonik Industries AG, Paul-Baumann-Str. 1, 45772 Marl, Germany

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## ABSTRACT

Co-dimers of the vinylidene compound isobutene with different 1-alkenes as well as homo-dimers from other vinylidene compounds are generated in high selectivities using (4-cyclooctene-1-yl)(1,1,1,5,5,5-hexafluoro-2,4-acetylacetonato)nickel as a catalyst. Regarding co-dimerization reactions very high selectivities for head-to-head couplings of up to 99% are achieved. Beside co-dimers as main products, homo-dimers of both substrates are obtained as relevant by-products. By careful variation of the initial proportion of substrates the distribution of co-dimers and homo-dimers can effectively be adjusted. Depending on shifts in product selectivity a deeper insight into the insertion mechanism is concluded. Although head-to-head couplings of other vinylidene compounds are also feasible with very high selectivities of >99%, different limitations for the catalytic system are shown. Subsequent considerations result in an extension of catalyst lifetime applying additives with internal electron-poor double bonds.

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## 1. Introduction

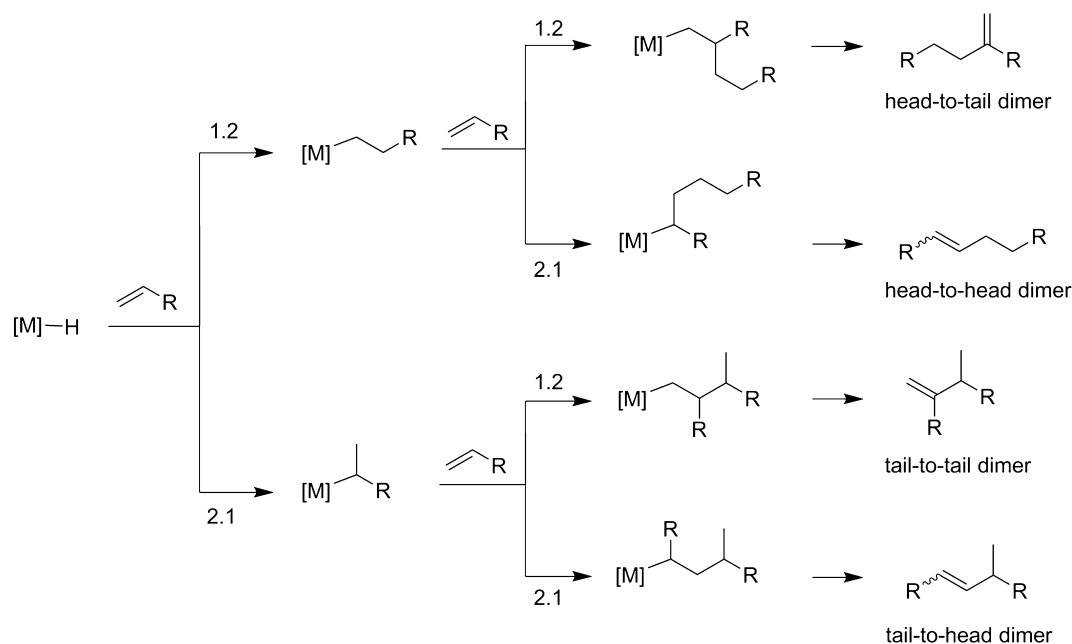
The dimerization of alkenes by transition metal complexes is of considerable industrial interest [1]. Although several catalysts are known to generate dimers from 1-alkenes, only a few catalysts are capable of producing head-to-head dimers in high selectivities [2–7]. In most cases, alkenes such as propene and 1-butene are dimerized on large scale to give mainly head-to-tail or tail-to-tail products which are used, e.g., as feedstocks for gasoline blending or alcohol production [8,9]. To obtain 1-alkene dimers for advanced applications a control of product selectivity is crucial. Following the pathways of insertion various isomers are possible (Scheme 1).

In contrast to linear aliphatic 1-alkenes, similar vinylidene compounds usually show no reactivity for a head-to-head linkage. Due to the twofold alkyl substitution in beta position, the double-bond of aliphatic vinylidene compounds possesses a higher electron density and shows stronger polarization compared to

linear aliphatic 1-alkenes. In consequence, the reactivity of vinylidene compounds strongly depends on the ready formation of a carbocation by either Lewis or Brønsted-acids. Considering isobutene, the simplest representative of aliphatic vinylidene compounds, many transformations such as the conversion to methyl *tert*-butyl ether, isooctene, polyisobutene and butyl rubber have been industrially established [10]. Owing to the reaction pathway, the resulting products are always highly branched. However, we very recently showed a novel approach towards head-to-head homo-dimers from isobutene using (4-cyclooctene-1-yl)(1,1,1,5,5,5-hexafluoro-2,4-acetylacetonato)nickel **1** as well as analogous aluminum activated nickel catalysts [11]. The one component catalyst **1** was investigated in detail for oligomerization reactions with different 1-alkenes before but reactions of vinylidene compounds were not covered [12–21].

In this work, the nickel catalyzed head-to-head coupling is widened to co-dimerization experiments with isobutene as well as homo-dimerization reactions with other vinylidene substrates. Investigations on co-dimerization have led to an improved understanding regarding the ways of insertion. Additionally, substrate limitations of the catalyst as well as a novel approach for catalyst stabilization have been found.

\* Corresponding author. Tel.: +49 231 755 2310; fax: +49 231 755 2311.  
E-mail address: [behr@bci.tu-dortmund.de](mailto:behr@bci.tu-dortmund.de) (A. Behr).



**Scheme 1.** Pathways of insertion for dimerization reactions.

## 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<sup>®</sup> 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 (Marl, Germany), as well as propene, obtained from Messer (Bad Soden, Germany), were used without further purification.

Catalyst (4-cyclooctene-1-yl)(1,1,1,5,5,5-hexafluoro-2,4-acetylacetonato)nickel (**1**) was synthesized as described and stored as a *m*-xylene solution at  $-20^\circ\text{C}$  [11].

### 2.2. Oligomerization experiments

All reactions were performed in a 25 mL custom-made stainless steel autoclave [22]. In a typical experiment under inert conditions, complex **1** was transferred to the reactor as a *m*-xylene solution. Solvent was removed in vacuum ( $10^{-3}$  mbar); additives and alkenes were added sequentially as required. Gaseous alkenes (isobutene, propene) were added volumetrically as a liquid with a pressure resistant tube. 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. The conversion of isobutene was determined by analyzing the gas phase using a mixture of the internal standard isobutane and the substrate isobutene (20/80 wt%). A sample was taken from the autoclave by shortly opening the valve connected to a gas tight sample bag (SKC, Valley View Road, USA) equipped with a septum. The collected gas-sample was injected manually to the gas chromatograph by a gas syringe. The conversions were determined comparing the area of the inert standard isobutane and the remaining isobutene. After degassing, a sample of the liquid phase was taken and analyzed by gas chromatography with *n*-dodecane as internal standard.

### 2.3. Product analysis

Routine 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  $\mu\text{m}$ ) connected to an auto sampler. GC-MS analyses of the hydrogenated products were carried out on a Hewlett-Packard 5973 (70 eV). Hydrogenation was achieved using 10% Pd/C catalyst applying 20 atm of hydrogen. Total conversion to alkanes was accomplished after 16 h at  $80^\circ\text{C}$  using 10 mg Pd/C and 2 mL of the alkene mixture.

## 3. Results and discussion

### 3.1. Co-dimerization of isobutene with different 1-alkenes

Due to the high selectivity of catalyst **1** for the insertion sequence 1,2 in the first step and 2,1 in the second step, linearly linked products are observed as main products using aliphatic 1-alkenes. A catalytic cycle for the generation of head-to-head dimers from isobutene is given in Scheme 2.

In co-dimerization reactions of isobutene with different 1-alkenes, beside co-dimers, homo-dimers of both substrates were expected as relevant by-products, since **1** is active in homo-dimerization reactions of each substrate. Scheme 3 shows a schematic summary of the structural isomers that were expected as products.

Beside linearly linked head-to-head products, the formation of branched dimers as well as higher oligomers must be taken into consideration, since linearity and dimer selectivity for most alkenes are significantly lower than for isobutene (Table 1).

In the homo-dimerization of ethene, 1-butene is formed rapidly. Since 1-butene is highly reactive itself, higher oligomers were formed from further additions of ethene to 1-butene resulting in 1-hexene formation. Additionally, formed 1-alkenes are able to react with one another to create higher alkenes. Consequently, dimer selectivity is very low when ethene is applied. Using propene, dimer selectivity is also low, due to the formation of 1-hexene during the reaction. In comparison to reactions of ethene higher propene dimer selectivity can be easily explained since 2-hexene is the main

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