



## Cycloisomerization and [2 + 2]cycloaddition of 1,5-cyclooctadiene catalyzed with the Ni(COD)<sub>2</sub>/BF<sub>3</sub>·OEt<sub>2</sub> system

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### ABSTRACT

The catalytic system Ni(COD)<sub>2</sub>/BF<sub>3</sub>·OEt<sub>2</sub> has been studied in conversions of 1,5-cyclooctadiene under argon and ethylene atmosphere. It has been demonstrated that the catalytic system formed under argon exhibits a high effectiveness in cycloisomerization of 1,5-COD surpassing in this characteristic all known nickel complex catalysts (selectivity to bicyclo-[3.3.0]-octene-2 is up to 99.5% at 100% conversion). In the case of ethylene atmosphere the system produces mainly dimers (yield of cycloaddition products above 70%). It has been shown that the catalytic system Ni(COD)<sub>2</sub>/BF<sub>3</sub>·OEt<sub>2</sub> has the feature of “a living catalyst” consisting in resuming the initial activity with a new portion of 1,5-COD added when the monomer was fully exhausted. The main and side products of the 1,5-COD conversion have been identified with GC-MS and preparative liquid chromatography combined with NMR and IR spectroscopy. Based on EPR and IR spectroscopic data a mechanism for the catalytic performance of the Ni(COD)<sub>2</sub>/BF<sub>3</sub>·OEt<sub>2</sub> system in argon or ethylene atmospheres is suggested. It has been shown that Ni(0) is oxidized by the Lewis acid to Ni(I) which is stabilized by substrate molecules in a mononuclear form without involvement of conventional organoelement entities. Three sorts of paramagnetic nickel species have been found: ionic complexes containing π-coordinated COD ligands; ionic complexes σ-bonded to COD; complexes as intimate pairs with BF<sub>4</sub><sup>−</sup> counter ions. A mechanism for the catalytic conversion of 1,5-cyclooctadiene is proposed.

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### 1. Introduction

Polycyclic olefins are valuable products for organic synthesis. Their use comprises manufacture of drugs, biologically active compounds, molecular biology reagents, high molecular weight polyolefins bearing cyclic units and may serve as starting reagents in a number of fine organic syntheses [1,2].

The generation of polycyclic olefins is based on cycloaddition reactions where two interacting molecules or two fragments of a molecule give a new cycle with a general reduction in the bond multiplicity [3–13]. Of particular interest are the reactions of less-reactive non-conjugated cyclic dienes, such as cis-cis-1,5-cyclooctadiene (COD) employed widely in coordination chemistry as a π-ligand [14].

The catalytic cycloisomerization of COD into the bicyclic product, cis-bicyclo-[3.3.0]-octene-2, (**1**) may be carried out on basic

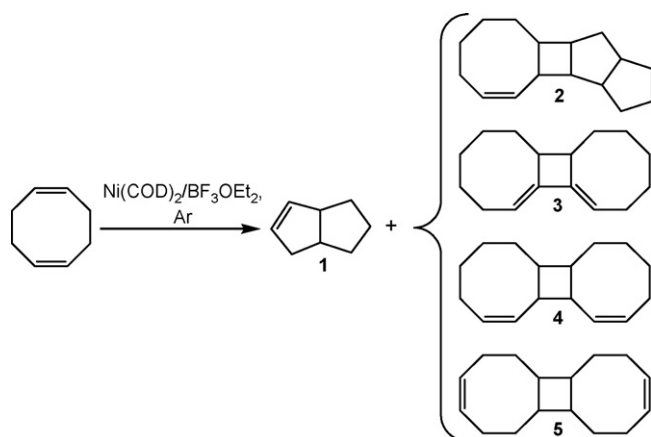
[15], acidic [16], and metal complex catalysts [17–20]. Among them nickel complex catalysts are the best for cycloisomerization of COD in terms of activity, productivity, and selectivity. These nickel complex catalysts are formed in non-aqueous solutions from Ni(II) compounds in combination with aluminium alkyl halides [17,18] as well as from Ni(0) compounds coupled with halide compounds [18] or organic acids [20].

In a recent paper [21] we have shown that the system Ni(COD)<sub>2</sub>/BF<sub>3</sub>·OEt<sub>2</sub> additionally exhibits a high activity in the COD cycloisomerization. In this respect it proved to be superior to all known catalytic systems. Preliminary studies [22] revealed that the COD cycloisomerization with the catalytic system Ni(COD)<sub>2</sub>/BF<sub>3</sub>·OEt<sub>2</sub> is accompanied by the [2 + 2]cycloaddition of the monomer. A relative contribution from the latter reaction to the COD conversion depends on the conditions of the catalyst formation.

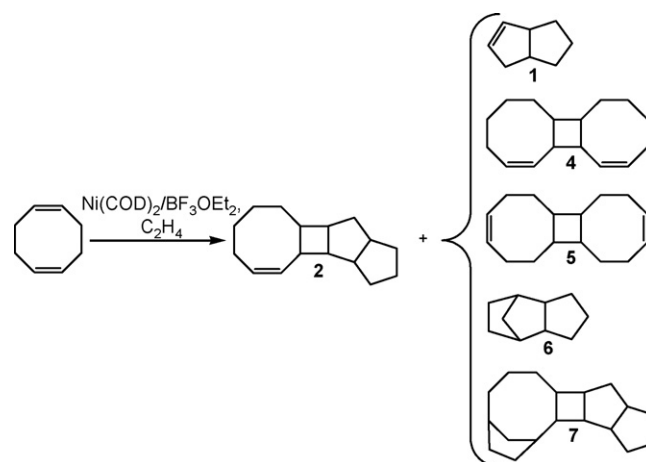
To elucidate the mechanism of the cis-cis-1,5-cyclooctadiene conversion the catalytic cycloisomerization and [2 + 2]cycloaddition of COD in the system Ni(COD)<sub>2</sub>/BF<sub>3</sub>·OEt<sub>2</sub> as well as the nickel complexes formed therein have been studied in this work.

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Scheme 1.



Scheme 2.

## 2. Results and discussion

According to GC the  $\text{Ni}(\text{COD})_2$  complex dissolved in cis-cis-1,5-cyclooctadiene does not react with the diene at 0–40 °C under argon. When two mole equivalents of  $\text{BF}_3\cdot\text{OEt}_2$  are added to a light-yellow solution of  $\text{Ni}(\text{COD})_2$  the coloration rapidly turns bright-red, and a catalytic conversion of COD commences. The main product is the isomer bicyclo-[3,3,0]-octene-2 (1, Scheme 1). The cycloisomerization of cis-cis-1,5-cyclooctadiene is accompanied by the [2+2]cycloaddition of COD and its cycloaddition with the products of the cycloisomerization. Using GC-MS and preparative chromatography combined with NMR and IR spectroscopy tetracyclic a cyclobutane dimer of COD, 2, and tricyclic dimers, 3, 4, and 5 (Scheme 1) have been identified. Table 1 shows how the conditions of formation of the catalytic system  $\text{Ni}(\text{COD})_2/\text{BF}_3\cdot\text{OEt}_2$  influence on the catalytic activity and the yields of the products.

The data of Table 1 allow the conclusion that the catalytic system  $\text{Ni}(\text{COD})_2/\text{BF}_3\cdot\text{OEt}_2$  prepared in the mixture toluene/COD (run #7) surpasses all known catalysts of the COD cycloisomerization with respect to activity and selectivity [7].

When in the reaction mixture the COD supply is completely exhausted, the reaction may be resumed by a fresh portion of COD. This is peculiar to “living” catalytic reactions [23]. The COD expenditure curve for three consecutive cycles is given in Fig. 1.

Noteworthy, the ratio between the COD reaction products remains constant for the subsequent cycles that may be indicative of an unchanged active species.

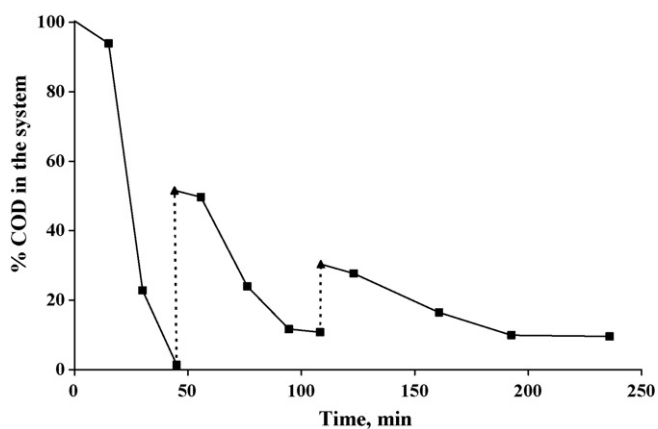


Fig. 1. Content of COD in the system vs. time. Two portions of COD successively introduced into the system  $\text{Ni}(\text{COD})_2/5\text{BF}_3\cdot\text{OEt}_2/400\text{COD}$  under argon at 20 °C. One portion increases the ratio COD:Ni by 400.

It is known that the polymerization of norbornene with nickel complex catalysts in ethylene atmosphere produces not only co-polymers [24], the presence of ethylene facilitates homopolymerization of norbornene as well [25,26]. This phenomenon is attributable to altering the active species. Therefore, to improve the catalytic system  $\text{Ni}(\text{COD})_2/\text{BF}_3\cdot\text{OEt}_2$  in COD dimerizing the catalysis in ethylene atmosphere ( $P=0.2$  MPa) has been studied.

$\text{Ni}(\text{COD})_2$  when dissolved in COD under ethylene is inactive at 0–40 °C according to GC. When  $\text{BF}_3\cdot\text{OEt}_2$  is added to the solution 1,5-cyclooctadiene undergoes a catalytic conversion. If the molar ratio B:Ni is equal to 2, the tetracyclic dimer 2 is the main COD product (>70%) for more than 95% monomer conversion. In addition to products 1 and 2 together with side products 4 and 5, unsaturated hydrocarbons 6 and 7 resulted from the [2+3]cycloaddition of ethylene and the products of COD cycloisomerization and cycloaddition have been identified with GC-MS, preparative chromatography combined with NMR and IR spectroscopy. It is noteworthy that not even a trace of compound 3 was found among the side products (Scheme 2). Table 2 shows how the conditions of formation of the catalytic system  $\text{Ni}(\text{COD})_2/\text{BF}_3\cdot\text{OEt}_2$  influence on its activity and the distribution of the COD conversion products in an ethylene atmosphere.

The data in Table 2 suggest that with an increasing molar ratio B:Ni the yield of cycloaddition 2 decreases, whereas the yield of cycloisomer 1 increases. At the ratio B:Ni  $\geq 15$  the ethylene influence on the ratio of products 1 and 2 becomes negligible.

As soon as COD is introduced to the COD-depleted system, the reaction is resumed as under an argon atmosphere (Fig. 2). The ratio between products 1 and 2 in the consequent cycles remains almost constant.

In papers [20,27] a hydride mechanism for the COD cycloisomerization on nickel complex catalysts was proposed. This concept was based on the fact that the  $\text{Ni}(\text{COD})_2$  complex was activated with Brønsted acids for the catalytic reaction. In our studies the Lewis acid  $\text{BF}_3\cdot\text{OEt}_2$  acts as an activator. To estimate the influence of contaminating proton acids on the activation of  $\text{Ni}(\text{COD})_2$  we have studied the conversion of COD with the catalytic system  $\text{Ni}(\text{COD})_2/\text{HBF}_3\cdot\text{OEt}$ . The curves of the COD conversion rate vs. the molar ratio B:Ni are given in Fig. 3 for the two systems (COD) $_2/\text{HBF}_3\cdot\text{OEt}$  (a) and  $\text{Ni}(\text{COD})_2/\text{BF}_3\cdot\text{OEt}_2$  (b) under comparable conditions. According to Fig. 3 the system with the Brønsted acid is less active by a factor of  $10^3$  than the system with the Lewis acid. Consequently, uncontrolled contamination of  $\text{BF}_3\cdot\text{OEt}_2$  with proton acids plays no fundamental role in the formation of the nickel complex catalyst.

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