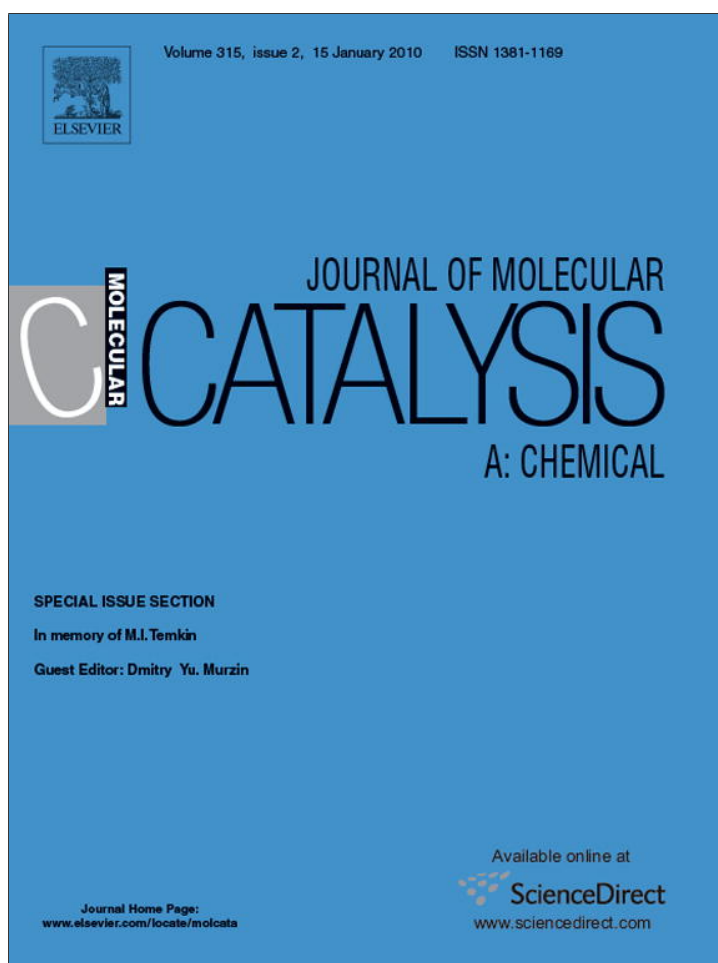


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journal homepage: www.elsevier.com/locate/molcataCycloisomerization and [2 + 2]cycloaddimerization of 1,5-cyclooctadiene catalyzed with the Ni(COD)₂/BF₃·OEt₂ systemV.V. Saraev^a, P.B. Kraikovskii^{a,b,*}, D.A. Matveev^a, V.V. Bocharova^a, S.K. Petrovskii^a, S.N. Zelinskii^c, A.I. Vilms^a, Hans-Friedrich Klein^b^a Department of Chemistry, Irkutsk State University, Str. K. Marx, 1, Irkutsk, 664003, Russia^b Eduard-Zintl-Institut für Anorganische und Physikalische Chemie der Technischen Universität Darmstadt, Petersenstrasse 18, 64287 Darmstadt, Germany^c Limnological Institute SB RAS, Str. Ulan-Batorskaya, 3, Irkutsk, 664033, Russia

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ABSTRACT

The catalytic system Ni(COD)₂/BF₃·OEt₂ 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 cycloaddimers above 70%). It has been shown that the catalytic system Ni(COD)₂/BF₃·OEt₂ 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)₂/BF₃·OEt₂ 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 BF₄⁻ 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].

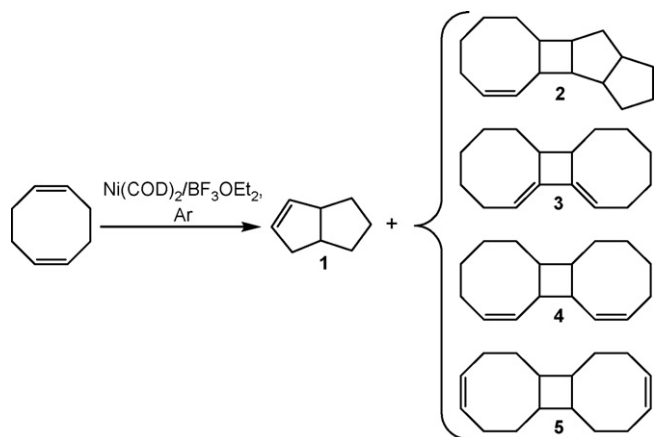
The catalytic cycloisomerization of COD into the bicyclic product, cis-bicyclo-[3.3.0]-octene-2, (**1**) may be carried out on basic

[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].

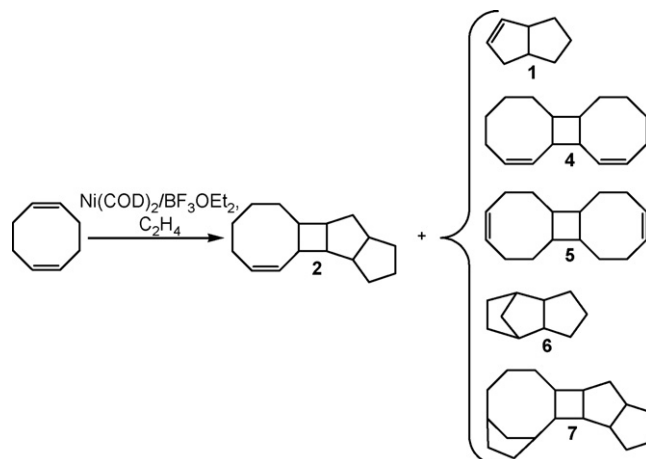
In a recent paper [21] we have shown that the system Ni(COD)₂/BF₃·OEt₂ additionally exhibits a high activity in the COD cycloisomerization. In this respect it proved to be superior to all known catalytic systems. Preliminary studies [22] revealed that the COD cycloisomerization with the catalytic system Ni(COD)₂/BF₃·OEt₂ is accompanied by the [2 + 2]cycloaddimerization 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]cycloaddimerization of COD in the system Ni(COD)₂/BF₃·OEt₂ 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 to 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.

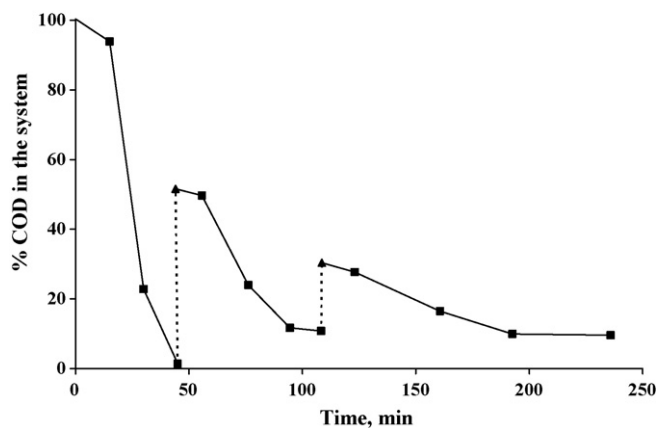


Fig. 1. Content of COD in the system vs. time. Two portions of COD successively introduced into the system $\text{Ni}(\text{COD})_2/5\text{BF}_3\cdot\text{OEt}_2/400\text{COD}$ under argon at 20 °C. One portion increases the ratio COD:Ni by 400.

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 $\text{B:Ni} \geq 15$ 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 $\text{Ni}(\text{COD})_2/\text{HBF}_3\text{OEt}$. The curves of the COD conversion rate vs. the molar ratio B:Ni are given in Fig. 3 for the two systems (COD) $_2/\text{HBF}_3\text{OEt}$ (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.

Table 1
Activity and selectivity of the system $\text{Ni}(\text{COD})_2/n\text{BF}_3 \cdot \text{OEt}_2$ in the conversion of COD under argon.

No	$\text{Ni}(\text{COD})_2:\text{COD}$	Ni:B	COD conversion (%)	TOF ^a	Yields of products (%)				
					1	2	3	4	5
1	1:400	1:15	97.3	657	85.7	8.5	4.8	0.4	0.5
2	1:400	1:10	98.2	680	90.7	7.4	1.3	0.5	
3	1:400	1:5	100 ^b	630	98.4	1.1	0.5 ^{>}	– ^b	– ^b
4	1:400	1:2	100 ^b	540	97.0	1.8	0.5	0.3 ^{>}	0.3
5	1:1000	1:5	98.5	1230	96.4	2.2	0.7	>0.3	0.3
6	1:2000	1:5	57.6	1300	98.0	– ^b	– ^b	– ^b	– ^b
7	1:400 ^c	1:5	100 ^b	650	99.5	– ^b	– ^b	– ^b	– ^b

^a TOF: mol COD/mol Ni h.

^b According to GC.

^c In a toluene solution, molar ratio toluene:COD = 1:1.

Table 2
Activity and selectivity of the system $\text{Ni}(\text{COD})_2/n\text{BF}_3 \cdot \text{OEt}_2$ in the conversion of COD under ethylene atmosphere.

No	$\text{Ni}(\text{COD})_2:\text{COD}$	Ni:B	COD conversion (%)	TOF ^a	Yields of products (%)				
					1	2	6	7	4, 5
1	1:400	1:2	95.6	13,600	20.5	70.2	5.5	2.1	~1.5
2	1:400	1:5	97.2	14,200	58.4	34.7	4.7	1.2	~1
3	1:400	1:10	98.6	14,400	82.6	13.0	4.3	~1	– ^b
4	1:400	1:15	97.8	12,800	90.1	9.6	0.2	– ^b	– ^b
5	1:1000	1:5	56.0	15,200	64.2	33.2	1.4	– ^b	– ^b
6	1:400 ^c	1:5	100 ^b	9,800	30.6	66.1	0.8	– ^b	– ^b

^a TOF: mol COD/mol Ni h.

^b According to GC.

^c In a toluene solution, molar ratio toluene:COD = 1:1.

A flash-up of the activity of the system $\text{Ni}(\text{COD})_2/\text{HBF}_3\text{OEt}$ in the neighborhood of $\text{B}:\text{Ni} \approx 0.5$ seems to be associated with a partial oxidation of Ni(0) to Ni(I). Previously, similar patterns were noted for the catalytic systems $\text{Ni}(\text{PPh}_3)_4/\text{HBF}_3\text{OEt}$ and $\text{Ni}(\text{PPh}_3)_4/\text{BF}_3 \cdot \text{OEt}_2$ in ethylene oligomerization [28,29].

For understanding the origin of the activity of the system $\text{Ni}(\text{COD})_2/\text{BF}_3 \cdot \text{OEt}_2$ the nickel complexes formed in the system under argon and ethylene have been studied with EPR and IR spectroscopy. Unfortunately, ¹H and ¹³C NMR spectroscopy was inapplicable because of the strong paramagnetism of the system.

When at 0 °C under argon two mole equivalents of $\text{BF}_3 \cdot \text{OEt}_2$ were added to $\text{Ni}(\text{COD})_2$ in toluene, the initial light-yellow coloration of the solution immediately turned bright-red. The process is attended with the appearance of intensive EPR signal 1 (Fig. 4) characteristic for the Ni(I) compounds with the 3d⁹ electron configuration ($g_{\parallel} = 2.38$, $g_{\perp} = 2.05$). Simultaneously an IR spectrum shows

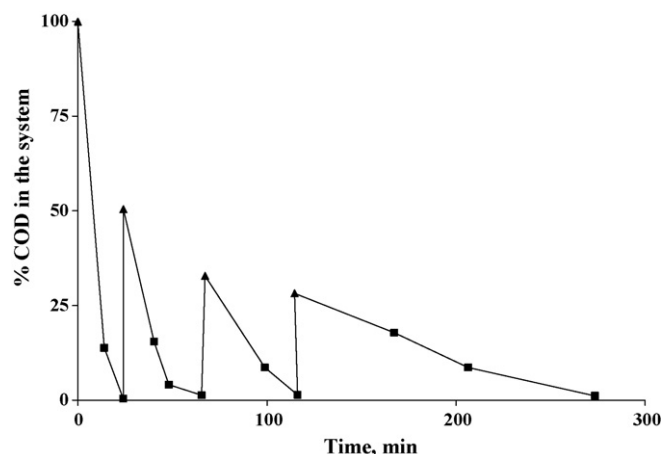


Fig. 2. Content of COD in the system vs. time. Three portions of COD successively introduced into the system $\text{Ni}(\text{COD})_2/5\text{BF}_3 \cdot \text{OEt}_2/400\text{COD}$ in ethylene atmosphere (0.2 MPa) at 20 °C. One portion increases the ratio COD:Ni by 400.

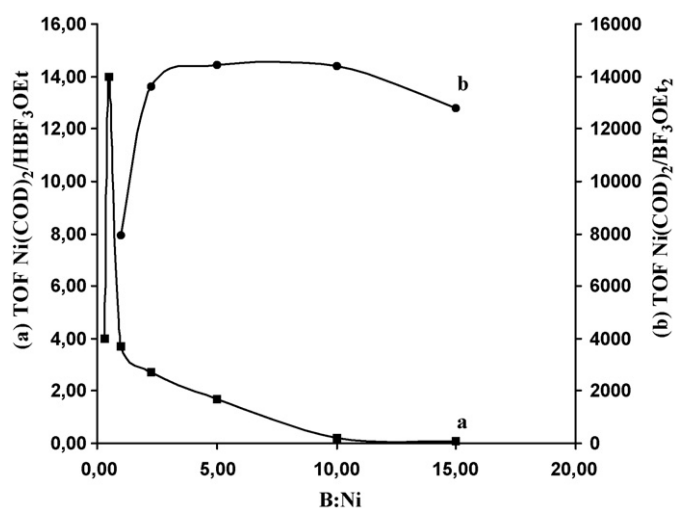


Fig. 3. Initial rate of COD conversion vs. molar ratio B:Ni for the catalytic systems $\text{Ni}(\text{COD})_2/\text{HBF}_3\text{OEt}$ (a) and $\text{Ni}(\text{COD})_2/\text{BF}_3 \cdot \text{OEt}_2$ (b) in ethylene atmosphere (COD:Ni = 400, $t = 20$ °C, $P_{\text{C}_2\text{H}_4} = 0.2$ MPa).

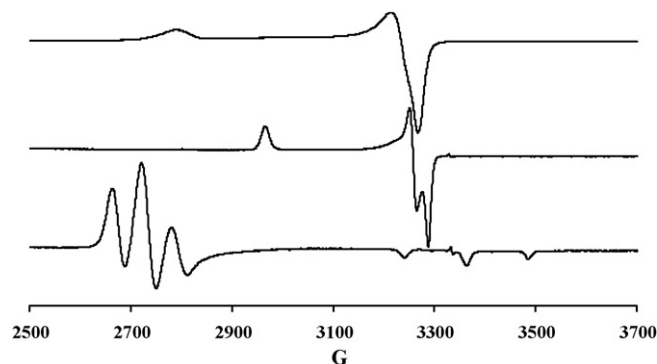


Fig. 4. EPR spectra of paramagnetic nickel complexes in the catalytic $\text{Ni}(\text{COD})_2/\text{BF}_3 \cdot \text{OEt}_2$ ($C_{\text{Ni}} = 10^{-2}$ mol/L, toluene as a solvent, $t = -196$ °C).

new bands at 1122–1050 and 826 cm^{-1} characteristic for the tetrahedral anion BF_4^- having no bridged bonds [30]. Consequently, in the $\text{Ni}(\text{COD})_2/\text{BF}_3\cdot\text{OEt}_2$ system $\text{Ni}(0)$ is oxidized to some $\text{Ni}(\text{I})$ species which appears to be stabilized in solution by cyclooctadiene ligands in the form the cationic complex $[\text{Ni}(\text{COD})_2]\text{BF}_4$.

Within 7–8 min the initial paramagnetic complex is transformed into a stable complex giving EPR signal 2 (Fig. 4). The EPR parameters of this new complex ($g_x = 2.030$, $g_y = 2.048$, $g_z = 2.249$) indicate that its metal–ligand bond is more covalent than that of the initial complex. Concurrently an IR spectrum demonstrates a slip of the BF_4^- anion bands to a region of higher frequencies with peaks at 1210 and 1085 cm^{-1} . In addition, a new band appears in the low frequency region at 577 cm^{-1} , which is characteristic for organometallic complexes with delocalized carbon–metal bonds [30,31]. These spectral data indicate activation of the cyclooctadiene ligand in the $\text{Ni}(\text{I})$ coordination sphere. The amount of $\text{BF}_3\cdot\text{OEt}_2$ introduced into the system does not affect the composition of paramagnetic nickel complexes within the studied limits $\text{B}:\text{Ni} = 2\text{--}30$. For all the intervals only signals 1 and 2 are detected. The introduced amount of $\text{BF}_3\cdot\text{OEt}_2$ reflects only on the time it takes for signal 1 to transform into signal 2 (about 2 min for $\text{B}:\text{Ni} = 30$).

Notice that the paramagnetic complex responsible for signal 2 is stable in a toluene solution under argon. Its signal intensity is virtually unchanged during 36 h for $\text{B}:\text{Ni} = 30$. However, contact with air causes EPR signal 2 and the IR band at 577 cm^{-1} to disappear rapidly. If excess COD is added to the system when EPR signal 2 gets maximum, the EPR spectrum starts altering. Signal 2 is initially replaced by signal 1, then, as COD is being converted, the process is reversed. These spectral transformations may be recurred with a next portion of COD.

An entirely different spectral pattern is observed under ethylene atmosphere.

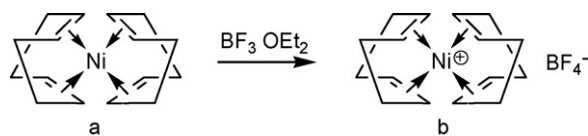
At the beginning of the reaction between $\text{Ni}(\text{COD})_2$ and $\text{BF}_3\cdot\text{OEt}_2$ in toluene under ethylene (within the molar ratio limits $2 < \text{B}:\text{Ni} < 30$), the EPR spectrum shows an intensive signal 1 which further transforms into signal 3 with the well-defined hyperfine structure (HFS) from two equivalent nuclei having spin $I = 1/2$ ($g_{\parallel} = 1.987$, $g_{\perp} = 2.452$, $A_{\parallel} = 122.2$ Gs, $A_{\perp} = 58.8$ Gs). The replacement of EPR signal 1 by signal 3 is attended with the replacement of the IR BF_4^- anion bands by the group of bands peaked at 1224, 1184, 1082, and 1030 cm^{-1} that may be assigned to tetrafluoroborate bridged structures according to published data [30].

Addition of an excess of COD to the system when EPR signal 3 is at maximum intensity replaces signal 3 for signal 1 followed by the reverse transformation as COD is being converted.

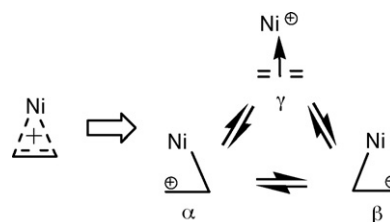
A next portion of COD added in ethylene atmosphere recovers the dynamic spectral pattern.

To find the cause of the HFS in signal 3, runs with perdeuterated ethylene have been carried out. When ordinary ethylene was substituted by C_2D_4 prior to combining the components of the catalytic system, EPR signal 3 underwent no change in form and intensity. Consequently, the HFS in signal 3 bears no relation to ethylene protons but most likely arises from two equivalent nuclei of ^{19}F ($I_F = 1/2$). This assumption is supported by the large value of the HFS constant, it is tenfold as great as the known ^1H HFS constants for $\text{Ni}(\text{I})$ hydride complexes [32].

^2H NMR and GC-MS control of the reaction products of the deuterated ethylene runs have revealed increasing ^2H content in



Scheme 3.



Scheme 4.

codimerization products **6** and **7**, whereas products **1** and **2** had the natural ^2H content. The absence of deuterium exchange for products **1** and **2** serves as an indirect evidence that the catalytic system $\text{Ni}(\text{COD})_2/\text{BF}_3\cdot\text{OEt}_2$ converts COD without participation of nickel hydride complexes.

The presented data allow the following conclusions:

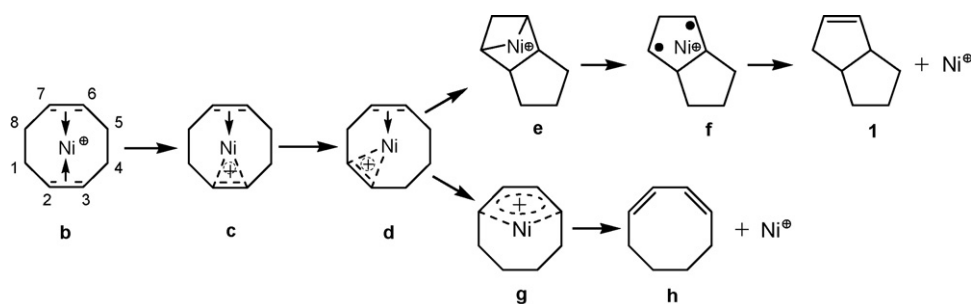
1. The activity of the catalytic system $\text{Ni}(\text{COD})_2/\text{BF}_3\cdot\text{OEt}_2$ for the cycloisomerization and cyclodimerization of COD is associated with the $\text{Ni}(\text{I})$ cations stabilized in solution by molecules of the monomer and its reaction products.
2. The conversion of COD with the catalytic system $\text{Ni}(\text{COD})_2/\text{BF}_3\cdot\text{OEt}_2$ proceeds with no nickel hydride complexes involved.

Analysis of the obtained data leads us to propose the following mechanism of the catalytic conversion of COD (Schemes 3–8):

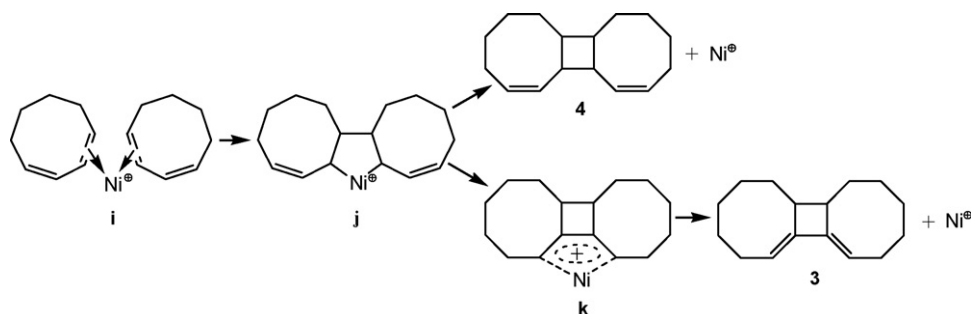
Under the action of $\text{BF}_3\cdot\text{OEt}_2$ $\text{Ni}(0)$ the starting material $\text{Ni}(\text{COD})_2$ is oxidized to the cationic complex $[\text{Ni}(\text{COD})_2]\text{BF}_4$ (**b**, Scheme 3) which seems to be responsible for EPR signal 1. The oxidation is likely to proceed through the mechanism we previously proposed for the system $\text{Ni}(\text{PPh}_3)_4/\text{BF}_3\cdot\text{OEt}_2$ [33]. It contains the steps of oxidative addition and subsequent dismutation to $\text{Ni}(\text{II})$ and $\text{Ni}(0)$.

The most important point in the conversion of COD is activation of the multiple bond. Taking into account catalytic passivity of $\text{Ni}(0)$ and a high activity of nickel arising after the oxidation, one should accept that the positive charge plays an important role in polarization and activation of the multiple bond. It seems likely that the positive charge of the Ni ion migrates to the hydrocarbon with formation of a Ni–C covalent bond (formation of a carbocationic complex). A similar activation mechanism was systematically studied for $\text{Fe}(\text{II})$ cationic complexes [34–42] and applied to explain conversion of hydrocarbons with cationic complexes of $\text{Pt}(\text{II})$ and $\text{Pd}(\text{II})$ [43,44], $\text{Pt}(\text{II})$ [45], $\text{Zr}(\text{IV})$ [46], $\text{Cu}(\text{I})$ [47] and $\text{Ni}(\text{I})$ [48,49]. The carbocationic activated complex may be conceived as a metal-cyclopropane (Scheme 4) having delocalized positive charge, its resonance forms (α , β and γ) are shown in Scheme 4.

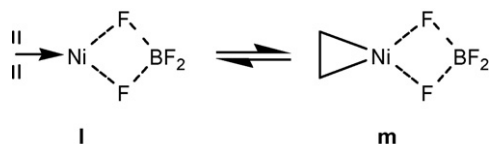
Scheme 5 displays reactions of 1,5-COD in an argon atmosphere: the main cycloisomerization to **1** and the side position isomerization to 1,3-COD (**h**). According to Scheme 5 activated complex **c** undergoes a hydride transfer and position isomerization of 1,5-COD to 1,4-COD (**d**) which has a geometry favorable for forming the C2–C6 bond synchronous with the oxidative addition of nickel (C1–Ni–C7). In intermediate **e** nickel is in 3+ oxidation state. The reductive elimination $\text{Ni}(\text{III}) \rightarrow \text{Ni}(\text{I})$ gives the main product cycloisomer **1**. This process is attended by formation of biradical **f**. Its existence is substantiated by the formation of **6** through the [2+3]cycloaddition of C_2H_4 to the cycloisomers in ethylene atmosphere. When the C2–C6 bond is not formed, then the position isomerization goes on to give metalcyclopentadiene **g**. This is evidently the most stable compound among the nickel species involved and appears to exhibit EPR signal 2.



Scheme 5.



Scheme 6.



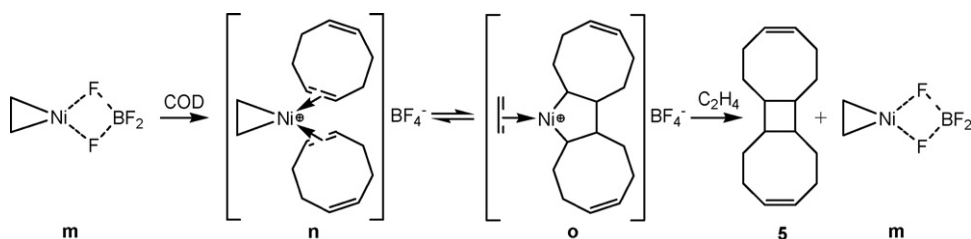
Scheme 7.

Scheme 6 illustrates the cyclodimerization of 1,3-COD through the oxidative addition of Ni(I) to two COD molecules resulting in metalocyclopentane intermediate **j** containing nickel in the oxidation state 3+. A similar scheme for the formation of cyclobutane structures was thoroughly studied for systems containing Ni(0) and Ni(II) [50–52]. According to Scheme 6 the reductive elimination gives cyclobutane **4**, or, alternatively, the position cycloisomerization results in cyclobutane **3**. The complex of Ni⁺ with conjugated dimer (**k**) is qualitatively similar to complex **g** in Scheme 5. Therefore, signal 2 assigned to complex **g** may likewise refer to complex **k**.

Signal 3, registered only in runs under ethylene atmosphere when the load of COD was completely exhausted, uniquely points to the formation of an intimate ion pair consisting of a nickel cation and the BF₄⁻ anion. The ratio between the components of the *g*-factor (*g*_⊥ > *g*_∥ ≈ 2) is characteristic of Ni(I) ions with 3d⁹ electron configuration in a trigonal field of ligands [53] and Ni(III) ions with 3d⁷ electron configuration in a tetragonal field of ligands [54,55]

as well. The rigorous axial anisotropy of the *g*-factor is feasible only when the ligands are equivalent in an equatorial plane. The exceptions are flat tetracoordinate cis-complexes with equivalent ligands arranged in pairs [56]. Considering the fact that only two equivalent fluorine atoms are within the first coordination sphere of nickel, signal 3 should be ascribed to a flat tetracoordinate cis-complex of Ni(III). Scheme 7 displays a cyclopropane Ni(III) complex as intimate ion pair **m**: equilibrium biased aside Ni(III).

The transformation of the free (solvated by COD molecules) ions into intimate ion pairs in ethylene atmosphere evidently results in a reduced delocalization of the positive charge to the hydrocarbon and, consequently, reduces the rate of the position isomerization and cycloisomerization of COD. The absence of cyclobutane **3** among products of the COD conversion in ethylene atmosphere also points to a reduction in activity of the catalytic system in the isomerization of COD under these conditions. A mechanism for the cyclodimerization of COD in ethylene atmosphere is proposed in Scheme 8. When a more basic hydrocarbon donor is coordinated in complex **m** the intimate ion pair dissociates. The formed metalocyclopropane complex rearranges to give a metalocyclopentane intermediate **o**. The latter decomposes into cyclobutane **5** and the initial Ni(III) complex (**m**). A relative rise of the rate of the COD cyclodimerization in ethylene atmosphere is attributable to the fact that the nickel(III) oxidation state stays intact during the formation of the cyclobutane structures.



Scheme 8.

3. Experimental

3.1. General procedures and materials

Standard vacuum techniques were used in manipulations of volatile and air-sensitive materials. All the prepared and synthesized reagents were kept under argon in sealed ampoules.

1,5-Cyclooctadiene, toluene, hexane (Merck) were additionally dried with 3A molecular sieves (Aldrich) and degassed. Boron etherate trifluoride (Merck) was distilled over lithium hydride prior to use. Preparative chromatography separations were carried out with a 600 mm × 20 mm column filled with a 60 Merck silica, hexane-ether (95:5).

Mass spectra were obtained on a Varian MAT spectrometer. GC-MS spectra were obtained on an Agilent 5973N-6890 mass spectrometer with electron impact and chemical ionization coupled with a gas chromatograph (GC-MS). Mass spectra were identified using a database from the NIST Library of Mass Spectra and Subsets.

^1H , ^{13}C and ^{31}P NMR spectra were obtained from BRUKER AVANCE 500, AVANCE DRX-700 spectrometers. ^{13}C and ^{31}P NMR resonances were obtained with broad-band proton decoupling. Assignment of ^{13}C signals was supported by APT, DEPT, COSY, NOESY, TOCSY, HMQC, HSQC, HMBC.

EPR spectra were recorded with a CMS-8400 spectrometer (operating frequency 9.6 GHz) at the temperature of boiling nitrogen. The free radical diphenylpicrylhydrazyl (DPPH) and Mn^{2+} in MgO were used for the calibration of the spectrometer.

IR spectra were recorded in KBr cuvettes in argon with an Infracum FT-801 Fourier spectrometer.

Perdeuterated ethylene was synthesized from deuterio-ethanol according to [57].

Bis[1,2:5,6- η -cyclooctadiene-1,5]nickel was synthesized according to [58].

Product 1: NMR C^{13} (100.61 MHz, CDCl_3 , 203 K): δ = 50.90 (d, $^1J_{\text{C,H}}$ = 132.85 Hz, C1), 134.68 (d, $^1J_{\text{C,H}}$ = 160.68 Hz, C2), 129.55 (d, $^1J_{\text{C,H}}$ = 160.92 Hz, C3), 41.25 (t, $^1J_{\text{C,H}}$ = 130.80 Hz, C4), 40.40 (d, $^1J_{\text{C,H}}$ = 139.46 Hz, C5), 35.92 (t, $^1J_{\text{C,H}}$ = 128.32 Hz, C6), 25.46 (t, $^1J_{\text{C,H}}$ = 128.09 Hz, C7), 32.56 (d, $^1J_{\text{C,H}}$ = 127.41 Hz, C8) ppm. NMR H^1 (400.13 MHz, CDCl_3 , 203 K): δ = 3.15 (m, 1H1); 5.55 (m, 1H2); 5.49 (m, 1H3); 2.58–2.63 (m, 2H4); 1.90–2.02 (m, 1H5); 1.65–1.69 (m, 2H6); 1.29–1.39 (m, 2H7); 1.42–1.46 (m, 2H8) ppm [59,60].

MS (70 eV): m/z (%) = 51(15.3), 65(15.9), 66(44.2), 67(43.1), 79(100), 80(86.9), 93(31.8), 108(37.6) [61].

Product 2: Since data bases [61] have no information about product 2, we may assert that 2 was first obtained by us. For structure studies product 2 was isolated with vacuum fractionation followed by preparative liquid column chromatography. According to GC-MS a fraction within 95–100 °C/5 × 10⁻² Hg mm had the maximum content of product 2. It was chromatographed through a silica column to crop product 2 ($\geq 97\%$ purity) consisting of the mixture of two isomers 2A and 2B (the ratio of 3:2) according to GC-MS. Attempts to separate these isomers applying preparative liquid column chromatography failed. Mass spectra of the individual isomers A and B recovered from GC-MS. It is noteworthy that these spectra moderately vary only in the relative intensities of the peaks. This observation, in the case of saturated cycloalkanes, generally points to a stereoisomerism of the molecules having several cycles equal in size. MS clearly displays a molecular ion with m/z = 216. The most intensive ion peak has m/z = 175 (relative intensity 100%), whereas the relative intensity of the peak at m/z = 108 was about 28%. So, product 2 is assignable to none of the known dimers of cyclooctadiene [4–13]. The recorded mass spectrum failed to be found neither in a commercial data base nor in a free one [61].

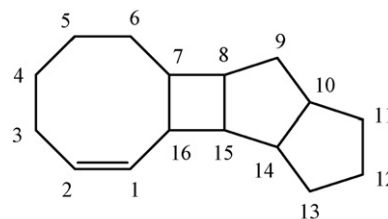


Fig. 5. Assignment of ^{13}C signals in 2.

From the mass spectrum of the product one can see that fragmentation occurs at the tertiary carbon atoms of cyclopentane moieties of the molecule followed by cleaving alkyl groups and alkenes. This pattern is characteristic of polycyclic unsaturated compounds with cycles of a C4–C8 size [62,63]. To arrive at the structure of compound 2 the obtained MS data were complemented with NMR spectroscopy using DEPT, COSY, NOESY, TOCSY, HMQC, HSQC, and HMBC.

The C^{13} spectrum has two groups of resolved signals with relative intensities 3:2; this ratio corresponds to the contents of isomers 2A and 2B in the analyzed mixture according to GC. So, the intensity difference allowed us to distinguish two groups of signals in NMR spectra and attribute each group to a particular isomer. To assign the signals of heteronuclear correlation NMR spectra we relied on signals of carbon and hydrogen atoms at the double bond and the C16 carbon (numeration of atoms in Fig. 5). The analysis of combined DEPT, COSY, NOESY, TOCSY, HMQC, HSQC, HMBC spectra made possible the unambiguous assignment of the signals of the mentioned carbons and the hydrogen atoms joined to them. Following interpretation of the spectra was carried out in the conventional manner. Constants of spin–spin interaction were determined from the HMQC spectrum without heteronuclear resolution.

IR spectrum of compound 2 displays a group of weak bands in the region of 900–923 cm^{-1} , they are attributable to skeleton vibrations of the cyclobutane ring [64,65].

2A: NMR C^{13} (176 MHz, CDCl_3 , 203 K): δ = 128.19 (d, $^1J_{\text{C,H}}$ = 156 Hz, C1), 135.17 (d, $^1J_{\text{C,H}}$ = 155 Hz, C2), 39.76 (dd, $^1J_{\text{C,H}}$ = 131 Hz, $^1J_{\text{C,H'}}$ = 129 Hz, C3), 32.58 (dd, $^1J_{\text{C,H}}$ = 130 Hz, $^1J_{\text{C,H'}}$ = 124 Hz, C4), 25.81 (dd, $^1J_{\text{C,H}}$ = 132 Hz, $^1J_{\text{C,H'}}$ = 109 Hz, C5), 32.13 (dd, $^1J_{\text{C,H}}$ = 131 Hz, $^1J_{\text{C,H'}}$ = 129 Hz, C6), 45.96 (d, $^1J_{\text{C,H}}$ = 132 Hz, C7), 52.93 (d, $^1J_{\text{C,H}}$ = 132 Hz, C8), 33.71 (m, C9), 44.25 (d, $^1J_{\text{C,H}}$ = 131 Hz, C10), 33.56 (dd, $^1J_{\text{C,H}}$ = 133 Hz, $^1J_{\text{C,H'}}$ = 121 Hz, C11), 33.47 (dd, $^1J_{\text{C,H}}$ = 125 Hz, $^1J_{\text{C,H'}}$ = 126 Hz, C12), 33.65 (m, C13), 48.30 (d, $^1J_{\text{C,H}}$ = 131 Hz, C14), 53.89 (d, $^1J_{\text{C,H}}$ = 129 Hz, C15), 51.65 (d, $^1J_{\text{C,H}}$ = 132.5 Hz, C16) ppm.

NMR H^1 (700 MHz, CDCl_3 , 203 K): δ = 5.50 (m, H1); 5.60 (m, H2); 2.54 (m, H3), 2.14 (m, H3'); 1.69 (m, H4), 1.17 (m, H4'); 1.50 (m, H5); 1.90 (m, H6); 1.16 (m, H'6), 2.34 (m, H7); 1.27 (m, H8); 1.52 (m, H9), 1.31 (m, H'9); 2.39 (m, H10); 1.72 (m, H11), 1.11 (m, H'11); 1.82 (m, H12), 1.00 (m, H'12); 1.50 (m, H13), 1.32 (m, H'13); 2.1 (m, H14), 1.35 (m, H15), 3.1 (m, H16) ppm.

MS (70 eV): m/z (%) = 55(12.5), 67(68.2), 80(71.8), 91(30.5), 93(31.3), 107(27.8), 119(7.56), 134(17.3), 147(5.9), 175(100), 187(3.2), 216(12.9).

HRMS $\text{C}_{16}\text{H}_{24}$: Calculated—216.1878, Measured—216.18726.

2B: NMR C^{13} (176 MHz, CDCl_3 , 203 K): δ = 128.26 (d, $^1J_{\text{C,H}}$ = 156 Hz, C1), 135.02 (d, $^1J_{\text{C,H}}$ = 155 Hz, C2), 39.99 (dd, $^1J_{\text{C,H}}$ = 129 Hz, $^1J_{\text{C,H'}}$ = 129 Hz, C3), 32.53 (dd, $^1J_{\text{C,H}}$ = 142 Hz, $^1J_{\text{C,H'}}$ = 126 Hz, C4), 25.93 (dd, $^1J_{\text{C,H}}$ = 129 Hz, $^1J_{\text{C,H'}}$ = 109 Hz, C5), 32.53 (dd, $^1J_{\text{C,H}}$ = 120 Hz, $^1J_{\text{C,H'}}$ = 125 Hz, C6), 45.76 (dd, $^1J_{\text{C,H}}$ = 133 Hz, C7), 53.59 (d, $^1J_{\text{C,H}}$ = 132 Hz, C8), 34.24 (m, C9) 44.29 (d, $^1J_{\text{C,H}}$ = 133 Hz, C10), 33.86 (dd, $^1J_{\text{C,H}}$ = 130 Hz, $^1J_{\text{C,H'}}$ = 124 Hz, C11) 33.62 (m, C12), 34.00 (m, C13), 49.05 (d, $^1J_{\text{C,H}}$ = 130 Hz, C14), 54.68 (d, $^1J_{\text{C,H}}$ = 120 Hz, C15), 51.63 (d, $^1J_{\text{C,H}}$ = 132.5 Hz, C16) ppm. NMR H^1 (700 MHz, CDCl_3 ,

203 K): δ = 5.50 (m, H1); 5.59 (m, H2); 2.53 (m, H3), 2.08 (m, H₃′); 1.69 (m, H4), 1.17 (m, H4′); 1.51 (m, H5); 1.92 (m, H6), 1.17 (m, H6′); 2.26 (m, H7); 1.25 (m, H8); 1.77 (m, H9), 1.19 (m, H9′); 2.36 (m, H10); 1.84 (m, H11), 1.02 (m, H11′); 1.58 (m, H12), 1.41 (m, H12′); 1.57 (m, H13), 1.36 (m, H13′); 2.00 (m, H14); 1.33 (m, H15); 3.1 (m, H16) ppm.

MS (70 eV): m/z (%) = 55(12.9), 67(70.9), 80(70.9), 91(30.5), 93(31.1), 107(27.5), 119(7.25), 134(15.8), 147(5.3), 175(100), 187(2.8), 216(11.0).

HRMS C₁₆H₂₄: Calculated—216.1878, Measured—216.18693.

For the mixture of **A** and **B**.

IR (film): ν (=C–H st) = 3045 cm⁻¹, ν (C–H st) = 2940 cm⁻¹, 2858 cm⁻¹, ν (C=C st) = 1614 cm⁻¹, ν (CH₂ δ) = 3045 cm⁻¹, ν (C–C γ) = 925 cm⁻¹, ν (CH₂ γ) = 712 cm⁻¹.

3.1.1. Product (3) as a mixture of isomers

NMR C¹³ (176 MHz, CDCl₃, 203 K): δ = 139.17, 137.79, 135.06, 132.7 (s, quaternary carbon atoms), 127.71, 126.07, 125.84, 124.33 (d) ppm [6,14].

MS (70 eV): m/z (%) = 44(8.6), 55(15.7), 67(34.4), 79(61.4), 91(57.5), 107(34.0), 119(25.1), 134(100.0), 173(9.9), 175(10.4), 216(25.3) [6,14].

Product (4): NMR C¹³ (176 MHz, CDCl₃, 203 K): δ = 26.24, 26.42, 27.14, 27.95, 28.45, 29.32, 30.96, 32.34 (8CH₂), 37.78, 41.84, 48.16, 48.9, 127.9, 128.02, 131.06, 133.9 (8CH) ppm.

NMR H¹ (700 MHz, CDCl₃, 203 K): δ = 5.57 (m, H6); 5.67 (m, H11); 5.72 (m, H7), 5.81 (m, H10); 1.69 (m, H4), 1.17 (m, H4′); 1.51 (m, H5); 1.92 (m, H6), 1.17 (m, H6′); 2.26 (m, H7); 1.25 (m, H8); 1.77 (m, H9), 1.19 (m, H9′); 2.36 (m, H10); 1.84 (m, H11), 1.02 (m, H11′); 1.58 (m, H12), 1.41 (m, H12′); 1.57 (m, H13), 1.36 (m, H13′); 2.00 (m, H14); 1.33 (m, H15); 3.1 (m, H16) ppm [4–9].

MS (70 eV): m/z (%) = 44(6.6), 67(11.6), 99(50.1), 91(17.2), 107(100), 216(9.2) [4–9,61].

Product (5): GC-MS (70 eV): m/z (%) = 53(21.3), 67(71.7), 79(100.0), 91(44.9), 107(24.9), 119(17.5), 134(63.1), 135(43.4), 173(8.4), 187(5.8), 216(20.9) [12,61].

Product (6): GC-MS (70 eV): m/z (%) = 43(7.1), 51(13.1), 53(14.2), 66(88.2), 67(42.4), 77(38.8), 79(100.0), 80(72.5), 91(28.5), 95(94.7), 107(61.1), 121(9.9), 136(19.5) [61,66].

Product (7): GC-MS (70 eV): m/z (%) = 43(7.6), 55(31.8), 67(83.6), 79(86.9), 91(41.3), 107(24.0), 135(21.9), 162(5.7), 203(100.0), 215(13.9), 244(12.4).

GC-MS (70 eV): m/z (%) = 44(11.6), 53(8.3), 67(21.1), 79(58.5), 91(32.2), 107(100), 117(6.9), 134(17.1), 173(11.5), 187(4.6), 216(18.4) [61].

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