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Norbornadiene as a Universal Substrate for Organic and Petrochemical Synthesis

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Abstract

A wide range of rare polycyclic hydrocarbons can be obtained through catalytic processes involving norbornadiene (NBD). The problem of selectivity is crucial for such reactions. The feasibility of controlling selectivity and reaction rate has been shown for cyclic dimerization, co-dimerization, isomerization and allylation of NBD. Kinetic rules have been scrutinized. Consistent mechanisms have been proposed. Factors affecting directions of the reactions and allowing us to obtain individual stereoisomers quantitatively, have been established. A series of novel unsaturated compounds has been synthesized; they incorporate a set of double bonds with different reactivity and can find an extremely wide range of applications.

Introduction

The importance of NBD and its derivatives in various fields of human activity is growing. More and more new applications are being discovered for these compounds. Since they were first obtained less than 50 years ago, these substances have been successfully utilized in medicine, agriculture, rocketry, syntheses of polymers with unique properties, microelectronics, and as solar energy converters. The number of patents concerned with synthesis and application of NBD derivatives and norbornene-2 (NBN) had exceeded 100 hundreds by the year 2000. Due to their unique structure, compounds with NBD and NBN-moieties are achieving the leading positions in contemporary chemistry and chemical technology [1-3].

It should be strongly emphasized that NBD itself and some of its simplest derivatives are obtained from chemicals, produced on a large scale during oil processing [4]. They are cyclopenta-1,3-diene (CPD), acetylene, alkenes, and alkadienes with various structures. Production of CPD can easily be combined with synthesis of other petrochemical products, for example ethylene. Today, a large proportion of CPD cannot be duly utilized, so it is very important to search for new ways of its utilization.

Even though NBD has extremely rich synthetic possibilities, its utilization as a universal substrate is rather limited, since NBD-derivatives can form all kinds of isomers: skeleton, regio, stereo, enantio ones. A resultant mixture of isomeric products is often difficult to separate and analyze, and the consumption of reagents may become excessive. All this restricts widespread use of NBD.

Metal-complex catalysis is very interesting and attractive for solving various problems connected with selectivity [5]. By applying its tenets and methods to reactions involving NBD and its derivatives, by scrutinizing mechanisms of reactions, we can control structure and range of regio- and stereo isomers, synthesize new compounds of this type, and can make their production sensible from technological and economical points of view.

The present article bases on several research directions concerned with application of the above-mentioned methods in some of the most promising processes involving NBD.

Experimental

All of the experimental techniques are described in detail in the literature cited. Synthesis of significant quantities of mentioned compounds by means of non-catalytic Diels-Alder reaction needs high pressure and temperature (autoclave etc.). As for cata-

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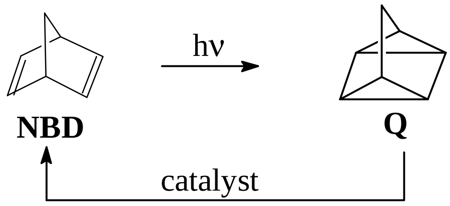
*corresponding authors. E-mail: vflid@cityline.ru lytic methods of their synthesis under homogeneous conditions, they take high-vacuum equipment and usage of purified inert gases. All cited compounds were identified by means of: chromato-mass spectrometry with use of chemical ionization and electron blow as well («Kratos MS-80» and «HP-5989B MS MG»); ^{1}H, ^{13}C and ^{31}P NMR spectroscopy («Bruker WP-250», «Bruker DPX-300», «Bruker MSL-200»); infra-red Fourier-transform spectroscopy («Bruker IFS-113V» supplied with chromatographic device «Karlo-Elba Strumentation 4200»); gas-liquid chromatography («Khrom-5» with a range of capillary and preparative columns). Structure of catalysts was investigated by X-ray photoelectron spectroscopy («Riber LAS-4000») and electron spin resonance spectroscopy («Bruker ER-200»).

Results and discussion

Valence isomerization of NBD

Valence isomerization of NBD into quadricyclane (Q) has a considerable practical importance [6]. This reaction draws attention, since it allows us to accumulate solar energy through a cyclic process (reaction 1).



(1)

In this photoreaction, solar energy is accumulated due to the formation of a methastable structure incorporating highly-strained moieties: one cyclobutane and two cyclopropane rings, which results in an unusually high thermal effect of the reverse dark reaction (110 kJ/mol). This system is also characterized by the following positive qualities:

(i) the direct photochemical reaction can be sensitized;
(ii) the reverse reaction has a high activation barrier (its half-life period is 14 hours at 140°C), but can be accelerated catalytically;
(iii) NBD and Q are liquids, which is convenient from the technological point of view.

The process has some shortcomings, too: NBD adsorbs in the short-wave area (up to 300 nm) and the quantum yield of the direct photoreaction in the absence of a sensitizer is low ($\Phi = 0.05$).

The characteristics of phototransformaiton of NBD into Q can be substantially improved through introduction of substituents into the NBD molecule. For instance, when both an electron donating and an electron withdrawing moieties (C_6H_5 and COC_6H_5 respectively) are simultaneously introduced into one of the double bonds, the limit of adsorption can be moved into the long-wave area up to 350 nm or, if the aryl substituent gets additionally modified, up to 400 nm, with the quantum yield increasing up to 0.3÷0.6 [7].

Further introduction of substituents into different double bonds allows us to vary λ from 350 to 450, with a quantum yield being up to 0.96; the best results were attained when electron-acceptor substituents were introduced into one of the double bonds, and electron-donor ones into the other.

Compounds of the NBD-series with a similar structure are suitable for practical application, even though they have shortcomings. The most serious of them are the decrease in the quantity of accumulated energy per 1 g of compound (due to the increase in the molecular weight of substituted NBD) and complexity of their synthesis.

One more general drawback is side reactions with NBD. Even though the yield of side products is negligible from the conventional point of view (hundredths of one per cent per one working cycle), they accumulate as the cycle NBD↔Q repeats over and over again. This substantially deteriorates the performance of the system.

To increase the number of working cycles, NBD molecules can be covalently bound to a polymeric matrix. For instance, application of polymethylacrylate films increases the number of working cycles up to 10^3-10^4, with λ and Φ remaining high [8].

Phototransformation of unsubstituted NBD into Q features a low quantum yield. This can be considerably increased through applying sensitizers. The best results were obtained for Cu (I) salts (Φ=0.2) and phenylketones (acetophenone, benzophenone Φ=0.5÷0.9). However, even these systems have imperfections. First, they work only in the UV spectrum area. Second, Cu (I) complexes turn into Cu (II) ones, which show no photoactivity. Third, ketones chemically react with NBD to give photo-adducts. All this prevent such stabilizers from practical application. These obstacles may probably be overcome through use of natural or artificial polyheterocyclic sensitizers such as porphyrins[9].

A system for solar energy accumulation can only be created if the product of the photoreaction is chemically stable. The high energy barrier for the thermal transition NBD→Q results from orbital symmetry rule for $[2\sigma+2\sigma]$–addition. This barrier can be made lower through using compounds of transition metal as catalysts.

Of these substances, flat-square cobalt (II) complexes are the most promising. They are more active than compounds of other metals under both heterogeneous and homogenous conditions. Besides, no side reactions occur when Co (II) compounds are used. However, under isomerization conditions, many of Co (II) complexes oxidize easily into Co (III), which in turn leads to formation of NBD dimers and trimers. From this point of view, Co(II) porphyrin complexes are considered the best nowadays. When covalently bonded to a polymeric support or applied to inorganic carriers (activated carbon, alumina), they can easily be regenerated and are suitable for practical use.

The global ecological problem imposes stricter requirements on chemical production processes. Hence photochemical methods can play an important role, since they are able to provide a means to absorb solar energy and utilize it in chemical transformations. Light is a kind of an inertialess chemical reagent creating no wastes. However, photochemical processes only have minor importance now, chiefly because some complicated technical problems have not been solved yet.

All the above-described is completely correct for the NBD-Q system. Its practical significance is obvious. NBD-based pilot power units have already been being developed in several countries.

However, economical obstacles hinder the widespread use of heat energy emitted through the chemical transformation of Q into NBD. At the moment heat (as water steam) generated though this process is 50 to 100 times more expensive than that obtained through conventional methods. The mentioned systems need further improvements: the number of working cycles should be increased up to 10^4 and higher, the quantum yield and conversion of NBD per cycle should be increased, and the cost of synthesis of NBD with required spectral characteristics must be reduced. However, the creation of portable units may be sensible even now: they can be used in sunny regions located far away from other energy sources, or for space satellites.

Catalytic homodimerization of NBD

Norbornadiene dimers are strained hydrocarbons with a high energy content. They can be used as components of high-density jet fuel. Their specific combustion heats and densities are extremely high (up to 11000 kcal/l and 1.1 g/cm^3 respectively). To compound high-quality products of these dimers, synthetic methods are required allowing us to obtain pure substances. Even though this reaction seems to be very simple, it can yield a wide range of isomers (Fig. 1).

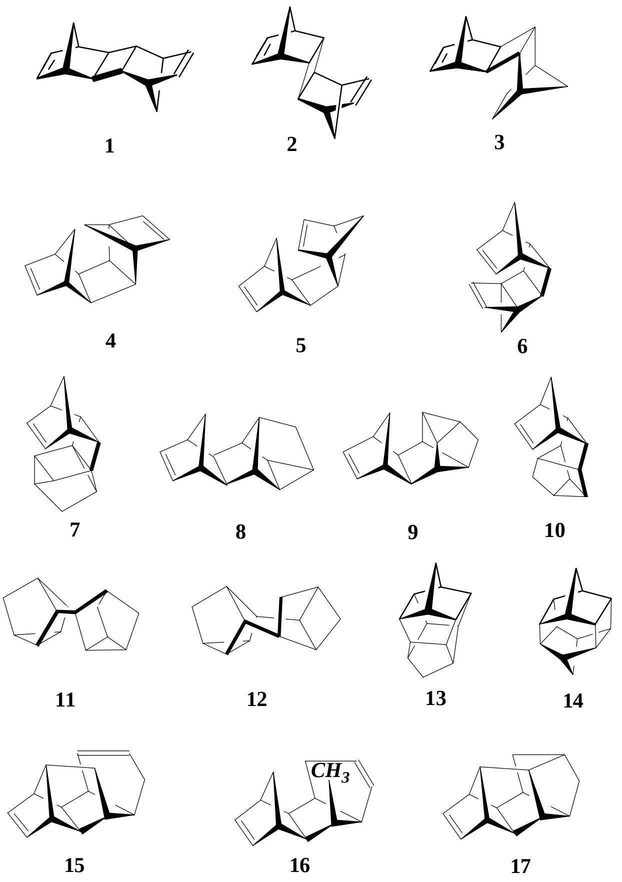


Fig. 1. NBD-dimers. Possible structures.

NBD can participate in various cycle-formation reactions. Products of its cyclodimerization can be categorized into 4 groups. The first three groups correspond to different types of cycloaddition: $[2\pi+2\pi]$, $[2\pi+4\pi]$ and $[4\pi+4\pi]$. The fourth group includes products of subsequent skeletal isomerization of dimers incorporating a strained cyclopropane moiety.

Dimers **1** to **6** of the group I are products of $[2\pi+2\pi]$-cycloaddition. They are pentacyclic compounds incorporating two double bounds and a cyclobutane moiety. Of this group, only *trans*-dimers were separated: *exo-trans-exo-* (**1**), *endo-trans-endo-* (**2**) and *exo-trans-endo-* (**3**) pentacyclo[8.2.1.1.^{4,7}.0^{2,9}.0^{3,8}]-tetradeca-5,11-dienes. *Cis*-isomers have not been described in literature. They probably cannot be formed due to spatial difficulties.

Dimers **7-10** (group II) are products of [2π+4π]-cycloaddition: hexacyclic compounds containing one double bond and a nortricyclyl moiety: *endo-endo-* (**7**), *exo-exo-* (**8**), *exo-endo-* (**9**) and *endo-exo-*(**10**) hexacyclo-$[9.2.1.0^{2,10}.0^{3,7}.0^{4,9}.0^{6,8}.]$tetradec-12-enes.

Saturated heptacyclic dimers **11-14** (group III) results from [4π+4π]-cycloaddition. Of these compounds, *«Binor-S»* (**11**) possesses the most interesting properties.

Dimers of group IV (**15-17**) obtained in the presence of $[Rh(PPh_3)_3Cl]$ are probably derivatives of **9**. We can suppose that they appear due to incorporation of the Rh(I) complex in the cyclopropane ring of the nortricyclyl moiety **9** with a subsequent transfer of a hydrogen atom from the bridge carbon.

Catalysts are necessary for NBD cyclodimerization to take place. They are usually complexes of Ni, Co, Fe and Rh in lower oxidation states. Some examples of utilization of Cr, Ti, Pd and Ir compounds were reported. The type of the central atom substantially influence the direction of cyclodimerization of NBD, i.e. the structural selectivity of the process.

Iron-containing catalytic systems can act in a number of different ways. Various kinds of cycloaddition can be realized through varying ligands, reducing agents, and reaction conditions.

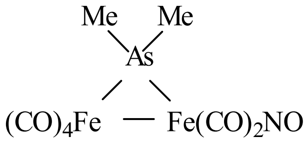
For example, iron carbonyl complexes $Fe(CO)_5$, $Fe_2(CO)_9$, $Fe_3(CO)_{12}$ catalyze all routes of NBD cyclodimerization and give rise to a mixture of products, chiefly isomers **1**, **8** and **9**.

If several nitrosyl ligands are substituted for carbonyls, the activity and selectivity of ferruginous catalysts can be enhanced. For instance, when $Fe(CO)_2(NO)_2$ is used, dimerization only proceeds through the [2π+2π]-direction to give dimers **1** and **3**. The unsaturated complex $Fe(NO)_2$ formed *in situ* via a reaction of nitrosylferrates with NBD or its dimers, is probable the key intermediate through which NBD dimers are formed.

That the moiety $Fe(NO)_2$ is catalytically active is indirectly confirmed by a series of electrochemical experiments where a range of nitrosyl iron salts were reduced. Catalysts generated this way yield dimers **1** and **3** only, independent of the structure and type of the initial complex.

The type of reducing agent almost does not affect the yield of dimers and the selectivity of the process. However, when powdered zinc is used, the conversion of NBD depends on the type of solvent. Acetone and THF are more favorable for the reaction than toluene, methanol or acetonitrile [10].

Cluster complex **18** proved to be a highly active catalyst. It [2π+2π]-dimerizes NBD into **1** almost quantitatively at 60°C in benzene [11].



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It is interesting, that the character of cycloaddition can be changed completely through adding an equimolar quantity of $BF_3{\cdot}OEt_2$: in CH_2Cl_2, the only product is [4π+4π]-isomer **11** (*Binor-S*). When two-component systems like $Fe(acac)_3–AlEt_3$ are used, a mixture of dimers **1**, **3**, **7** и **9** is usually formed [12]. The content of isomers depends on the solvent type and how the catalyst was synthesized [13-14].

The yield of hexacyclic dimers can be increased through adding phosphine ligands to this catalytic system, and substituting reducer $AlEt_2Cl$ for $AlEt_3$. When a chelate *bis*-(diphenylphosphino)ethane (*diphos*) is used, the yield of **9** increases up to 80-90%. In the presence of triphenylphosphine the major product is dimer **7** [15].

[2π+4π]-cycloaddition is also the major reaction route in the presence of other ferruginous systems: $FeCl_3$ – (*i*-Pr)MgCl, $FeCl_3$ – AlR_3, $FeCl_3$ – Na, $Fe(C_8H_8)_2$ etc.

These systems generally manifest a high activity, yield and turnover. Their shortcomings are low selectivity to individual isomers and non-repeatability of results.

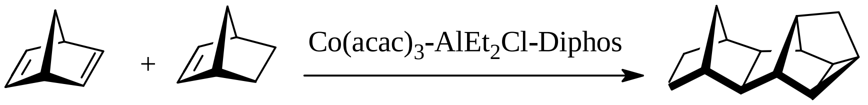
Cobalt systems resemble iron catalysts in a number of ways. NBD cyclodimerization can go through [2π+2π]-, [2π+4π]- and [4π+4π]-directions in their presence.

Binuclear carbonyl complex $Co_2(CO)_8$ augmented with PPh_3 leads NBD dimerization through the [2π+2π]-route. Pentacyclic isomers **1** and **3** are formed. Their ratio is 10 to 1.

The selectivity of nitrosyl Co complexes is lower than that of analogous ferruginous catalysts. Even though $Co(CO)_3NO$ is isoelectronic with $Fe(CO)_2(NO)_2$, NBD cyclodimerization in its presence gives not only **1**, but also a mixture of hexacyclic hydrocarbons. Isomer **1**, however, can be synthesized with a selectivity up to 98% when complexes $Co(NO)_2Cl$ or $Co(NO)_2Br$ promoted with $AgBF_4$ or $NaBPh_4$ are used [16].

A series of catalysts like $M[Co(CO)_4]_n$ (M = Zn, Cd, Hg) can stereospecifically dimerize NBD into *Binor-S* (**11**) with a yield of 95% [17]. These compounds only manifest their catalytic activity in the presence of Lewis acids (BF_3, SbF_3, $AlBr_3$, $BF_3 \cdot OR_2$) as co-catalysts with a ratio of 1 to 8. Lewis bases (pyridine, triethylamine) favor formation penta- and hexacyclic dimers [17].

Acetylacetonate Co systems reduced by organoaluminum compounds demonstrate a high catalytic activity. For example, the system $Co(acac)_2$–$AlEt_3$ yields the following mix of dimers: **1** – 62%, **3** – 29%, hexacyclic dimers 9%. The direction of this reaction can be changed through adding phosphines. When PPh_3 is used, *Binor-S* forms rather selectively. If *diphos* is substituted for PPh_3, hexacyclic dimer **8** is generated almost quantitatively. This system has a unique feature: it catalyzes not only NBD dimerization, but also its co-dimerization with NBN. The yield of the co-dimer is 42%.



(2)

Rhodium complexes probably manifest the most versatile synthetic possibilities as compared with other catalysts of NBD cyclodimerization. They can catalyze all the above-described types of cycloaddition and also give new dimers **15-17**.

Nickel catalysts are the best for [2π+2π]-cycloaddition. The ratio of isomers depends on the type of ligands in nickel complex, temperature, solvent and other conditions [18].

To discover general features and individual peculiarities of nickel catalysts, kinetic studies were carried out for the following initial compounds: $Ni(1,5\text{-}C_8H_{12})_2$, $Ni(CH_2{=}CHCN)_2$, $Ni(CO)_4$, $Ni(\eta^3\text{-}C_3H_5)_2$, $Ni(\eta^5\text{-}C_5H_5)_2$, and a catalytic system obtained through diffusing metal nickel on a frozen NBD-matrix under vacuum.

NBD cyclodimerization was found to begin with an induction period, the length whereof depends on the complex type and temperature. The reason for this phenomenon is that the NBD-nickel catalyst forms through substituting initial ligands, and this process is different for each system (3-5) [19].

$$NiL_n \overset{NBD}{\rightleftharpoons} NiL_{n-1}(NBD) + L \overset{NBD}{\rightleftharpoons} NiL_{n-2}(NBD)_2 + 2L \overset{NBD}{\rightleftharpoons} \cdots\cdots \qquad (3)$$

$$NiL_2 + 2\,NBD \longrightarrow Ni(NBD)_2 + L\text{–}L \qquad (4)$$

$$NiL_2 + 4\,NBD \longrightarrow Ni(NBD)_2 + [NBD + L - H] + [NBD + L + H] \qquad (5)$$

Direction (3) is characteristic of complexes with ligands stable in the free state: $Ni(CO)_4$, $Ni(1,5\text{-}C_8H_{12})_2$ and $Ni(CH_2{=}CHCN)_2$. The second direction takes place for compounds containing unstable moieties. They can decompose through ligand coupling (4) or intramolecular disproportionation (5).

Intermediates $Ni(NBD)_n$ were separated at different stages of the catalytic process with various initial nickel compounds. The molar ratio of NBD to Ni proved to be 2.07 (±0.03) in all these cases, which testifies that one the same catalyst forms *in situ* in all the systems: it is an equilibrium mix of complexes $Ni(NBD)_2$ and $Ni(NBD)_3$ at a ratio of 12÷14 to 1.

Kinetic studies showed that the formation rate of dimers **1, 3** and **8** (with taking into consideration that Ni complexes with different number of NBD ligands exist simultaneously in the reaction mass) are described by the following kinetic equations:

$$W_1 = k_1 \cdot C_{Ni} \cdot C_{NBD}^2$$

$$W_3 = k_3 \cdot C_{Ni} \cdot C_{NBD}$$

$$W_8 = k_8 \cdot C_{Ni} \cdot C_{NBD,}$$

where k_1, k_3, и k_8 are observed cyclodimerization rate constants.

Even though these equations retain the same form for different solvents, the type of medium influences the ratio of products and the general rate of the process. It should be emphasized, that dimers **1**, **3** and **8** have different kinetic orders with respect to NBD, which is quite unusual for concurrent formation of isomers with a similar structure.

Observed rate constants k_1, k_3, and k_8 are in a satisfactory agreement with the Arrhenius equation. Activation parameters are presented in Table 1.

Phosphine nickel complexes where at least two places are blocked with ligands are not active in NBD cyclodimerization. When the ratio of PR_3 to Ni is equimolar, dimers **1**, **3** and **8** are formed in accordance with a common kinetic equation, which is right for various phosphines:

$$W_i = k_i^{obs} \cdot C_{Ni} \cdot C_{NBD}$$

The mutual ratio of resulting cyclodimers of NBD depends on the steric characteristics of the phosphine, which probably influence the mutual orientation of NBD molecules coordinated in the complex. The proportion of dimer **1** is growing with an increase in the conical angle of phosphine.

The catalytic action mechanism of nickel complexes was scrutinized.

An NBD molecule can be either a η^2- or a η^4-coordinated ligand. A bidentate coordination of NBD is thermodynamically more favorable than a monodentate one. The difference between these two states equals to the homoconjugation energy of double bonds (about 8.0 kJ/mol), which can contribute to the stability of the resultant complex. Kinetic data testify that three different π-complexes of Ni and NBD are formed (**19-21**); there is an equilibrium between them (Fig. 2) [20].

When considering the stereochemistry of cycload-

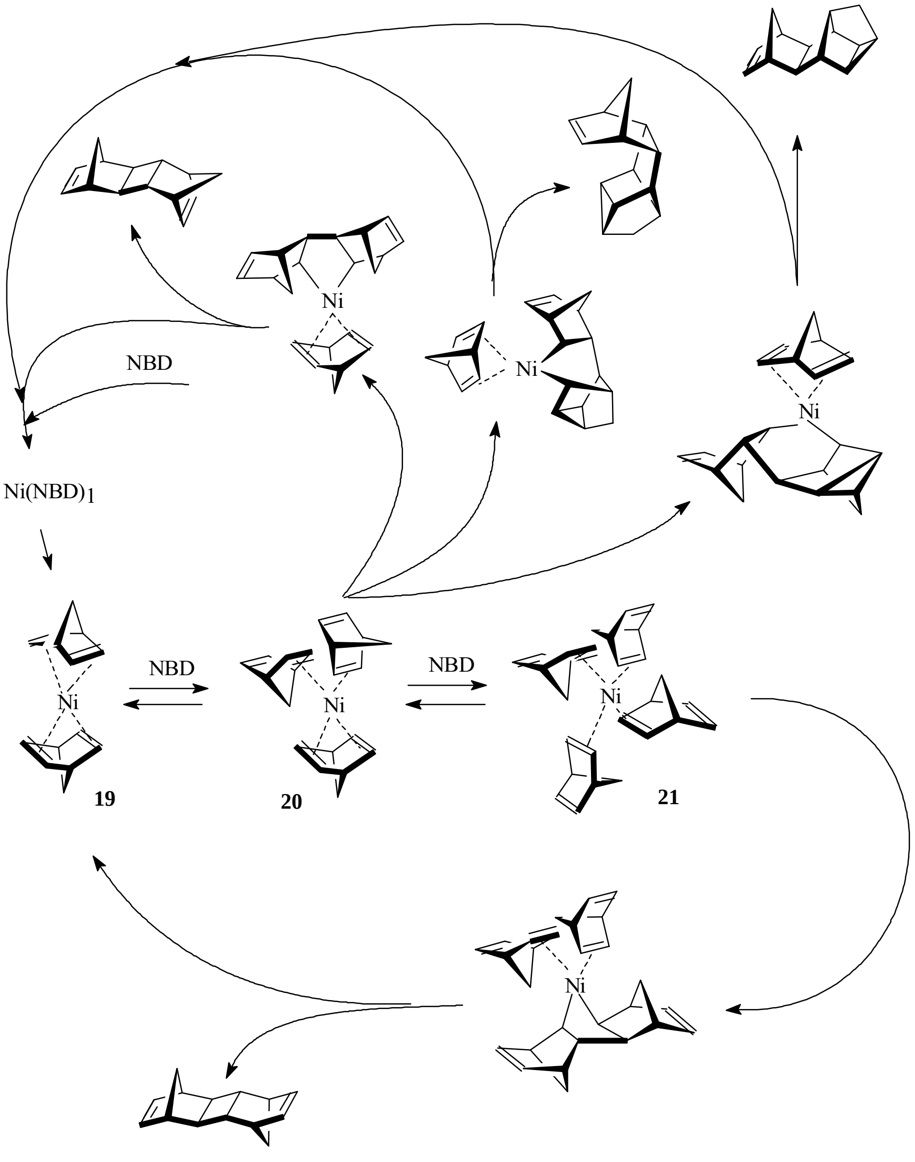


Fig. 2. Mechanism of NBD catalytic cyclodimerization.

Table 1

Activation parameters of NBD cyclodimerizaton

Product	Solvent	Activation energy E_{act}, kJ/mol	Preexponential factor, $M^{-1}\cdot c^{-1}$	Activation enthalpy, kJ/mol	Entropy, J/(mol·K)
1$^{*)}$	*n*-nonane	33±4	$1{,}3\cdot10^{2}$	30±4	-209±23
	THF	44±5	$1{,}0\cdot10^{3}$	41±5	-187±10
3	*n*-nonane	70±7	$5{,}6\cdot10^{7}$	68±7	-97±10
	THF	51±6	$7{,}1\cdot10^{3}$	49±6	-171±20
8	*n*-nonane	55±5	$1{,}2\cdot10^{4}$	52±5	-168±16

$^{*)}$ dimension of preexponential factor is c^{-1}

dition, we must take into account not only the coordination type of an NBD molecule on a nickel atom (monodentate or chelate), but also its *exo*/*endo*-orientation. When an NBD is coordinated monodentately, its *exo*-coordination is preferable from both sterical and thermodynamic points of view. A stereochemical analysis of various possible orientations of NBD-moieties in complex Ni(NBD)$_4$ testifies that four NBD ligands can only be *exo*-coordinated there. A dimer molecule is formed already in the intermediate π-complex, and the NBD-nickel system is a matrix predetermining the structure of the product.

Oxidative addition of coordinated NBD molecules to the Ni center results in the creation of metallocyclic intermediates. Decomposition of the latter is the limiting stage. Monodentate NBD-molecules remaining in the coordination sphere after the complex has decomposed transform into chelate ligands and stabilize Ni(0).

The results of our studies of the kinetics and the mechanism of the process allow us to forecast the behavior of the system in various conditions. For examples, if one coordination vacancy is blocked on the Ni atom (the ratio of PR_3 to Ni = 1:1), kinetic regularities of the process change. Use of phosphines with large conical angles is favorable for the more compact *exo*-coordination of NBD molecules and, consequently, results in an increased content of dimer **1**.

The difference in kinetic orders with respect to NBD in the above equations testifies that the formation rate of isomer **1** depends on NBD concentration more strongly than that of isomer **3**. Analysis of the activation parameters of the process indicates that the yield of *exo-trans-endo* isomer **3** is growing dramatically as temperature is increasing (Fig.3).

Isomer **1** is formed quantitatively in the temperature range from 10 to 30°C in non-polar media at NBD concentrations above 3 mol/l. As reaction temperature is growing and NBD concentration is decreasing, the relative amount of *exo-trans-endo* isomer is increasing; its yield reaches 95% at 100°C and an NBD concentration of 0.5 mol/l. Virtually any required ratio of **1** and **3** can be achieved through varying these parameters.

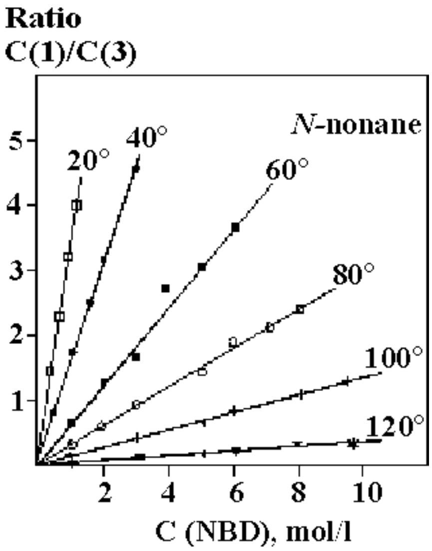


Fig.3. Ratio of dimers **1** and **3** *vs.* temperature and NBD concentration; a – *n*-nonane, b – THF

The process rate decreases in the presence of phosphines. Besides, the selectivity cannot any longer be controlled through NBD concentration in phosphine-containing systems [21].

Co-dimerization of NBD with unsaturated compounds.

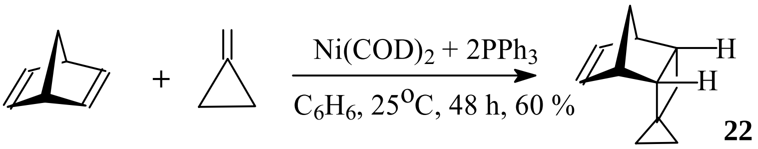
Co-dimerization with NBD is a very versatile and prospective way of synthesizing polycyclic compounds. It often is an alternative to diene syntheses based on cyclopentadiene. Sometimes co-dimerization is preferable.

The range of substrates suitable for catalytic co-dimerization with NBD is rather narrow. It is obviously stipulated by the peculiarities of complex-forming by NBD and the second substrate on a metal atom. To form a mixed hetero-substrate complex, the second co-monomer and NBD must have comparable abilities to coordinate on the metal atom. Ankynes, a range of alkenes with highly-reactive double bonds, and some oxygen- and nitrogen-containing compounds are suitable for this process. Co-dimerization of NBD with unsaturated compounds results in products of [2π+2π] and [2π+4π]–cycloaddition; each direction of such a reaction can give a range of spatial and optical isomers.

[2π+2π]-cycloadducts retain an intra-cyclic norbornene double bound. They can be used for further transformations, for example in methathesis oligomerizaitoin or polymerization. When NBD co-dimerize with some dienes or alkynes, the resulting product has several double bonds with different reactivity, which is rather attractive for manufacturing of special-purpose rubbers.

All the above-mentioned confirms that such compounds can be used as semiproducts in medicine, microelectronics, perfumery etc. The range of application of NBD co-dimerization-based processes is limited for some reasons. They are possible homodimerization of NBD or the second substrate; formation of side products through consecutive cycloaddition to both the double bonds of NBD; formation of isomers of all kinds: skeletal, spatial (*exo*/*endo*, *cis*/*trans*, *enantio*) ones. Hence it is extremely important to develop highly active and selective catalytic systems for the aforementioned processes.

In the presence of Ni(0)-catalysts, alkenes with electron withdrawing substituents usually react with NBD to give [2π+4π]-adducts. However, strained alkenes like methylenecyclopropane (MCP) react with NBD to yield [2π+2π]-cycloadducts with chiefly *endo*-structure (reaction 6).



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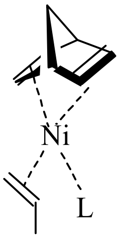
(6)

Such a spatial structure of **22** is mostly predetermined by the combination of ligands in the key intermediate **23** where NBD is bonded to nickel as an *endo*-chelate ligand.



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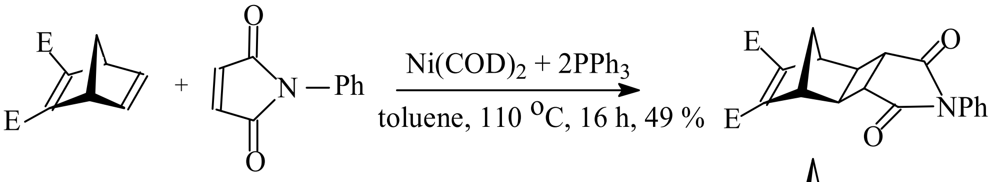
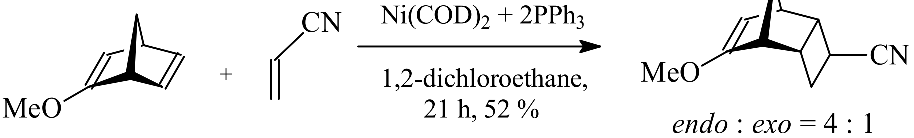
Attempts to perform enantioselective cycloaddition of NBD and MCP through use of chiral phosphine ligands were not successful. Substitution of Pd(0) for Ni(0) results in formation of [3π+2π]-cycloadducts [22].

Even though unsaturated NBD-derivatives usually react with alkenes with acceptor substituents to give [2π+4π]-cycloadducts, sometimes we can observe [2π+2π]-cycloaddition with a high regio- and even stereo-selectivity. These reactions usually proceed through the unsubstituted double bound of NBD, and substituents in locations 2 and 3 can favor one direction of the reaction or the other, *exo*- or *endo*-.

Electron-acceptor substituents promotes *exo*-cycloaddition, while donor-substituents shift the reaction toward *endo*-adducts (reactions 21-23):

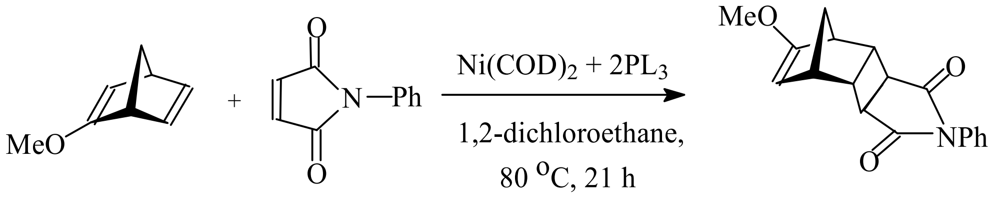


(7)



endo : *exo* = 4 : 1

(8)

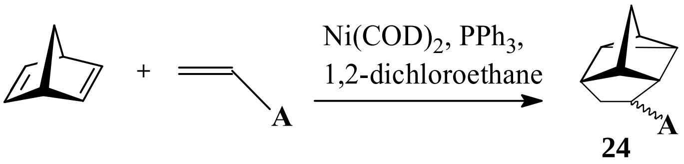


(9)

L = PPh$_3$: 69% (5:1)
L = P(OPh)$_3$: 34% (12:1)

Stereoselectivity to the *endo*-isomer in reaction (9) increases if a phosphite is substituted for a phosphine ligand.

Unsubstituted NBD usually reacts to give [2π+4π]-adducts. These reactions proceed far easier in the presence of transition metals, and their stereoselectivity changes, too. For example, if the thermal process mostly gives *endo*-adducts, a catalyst promotes formation of *exo*-cyclic compounds [23-24] (reaction 10 and Table 2):



(10)

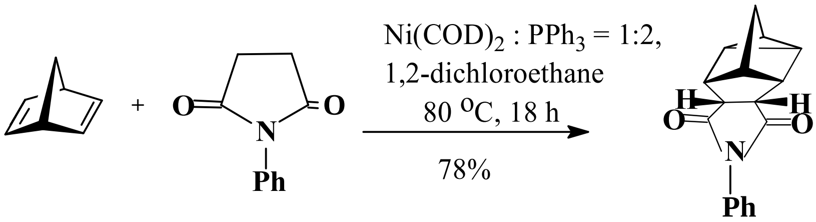
Table 2

Effect of the type of acceptor (A) and temperature of the yield of co-dimer **24** and stereoselectivity.

№	A	Temperature, °C	Yield **24**, %	exo/endo
1	COMe	80	99	20 : 1
2	CHO	20	58	3 : 1
3	CN	80	82	4 : 1
4	SO_2Ph	20	75	1 : 1
5*	SOPh	20	73	19 : 1

*$P(OPh)_3$ was used instead of PPh_3.

The indicated regularities, however, do not work for cyclic dienophiles: enones, lactones and imides of maleic acid (reactions 11, 12 and Table 3):



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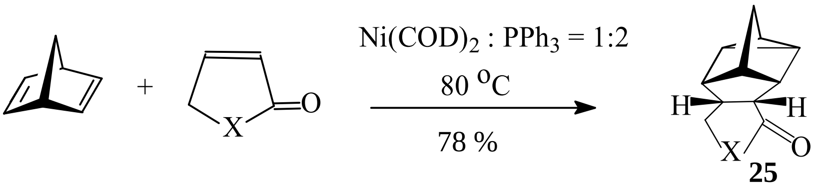


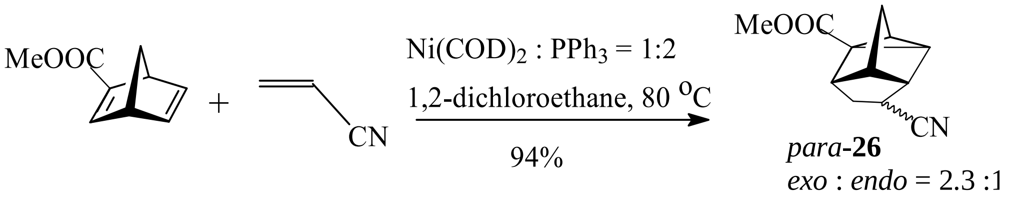
(12)

Table 3

Product type vs. substituent type X

X	O	CH_2	CH_2CH_2
Yield **25**, %	58	56	23

Interesting regularities concerned with regio- and stereo-selectivity of cycloaddition were established for reactions of unsymmetrical NBDs. Addition rules vary considerably for NBD molecules with different substituents in location 2 (reactions 13–15):



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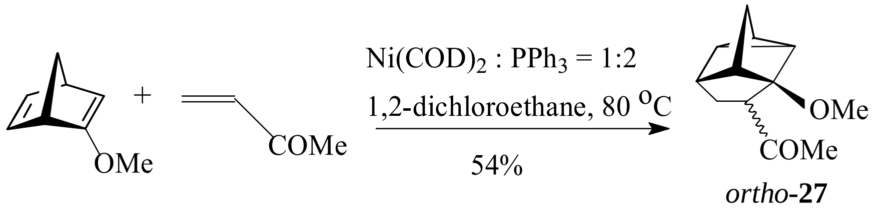

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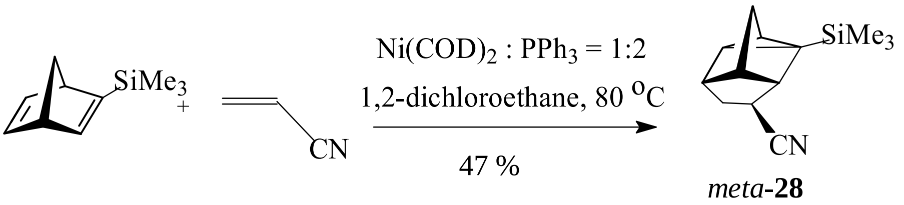
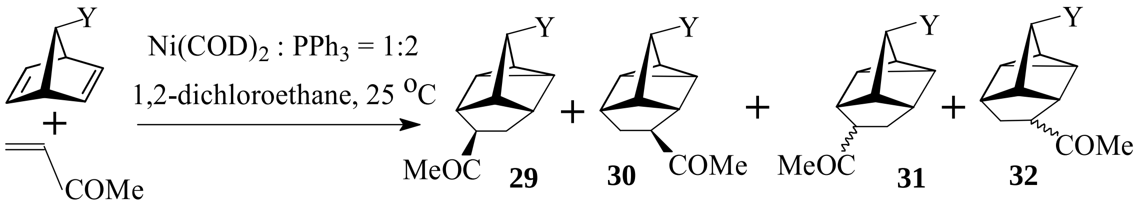


(15)

Para-cycloadduct *26* is the major product for electron-acceptor substituents, ortho-isomer **27** is for electron-donor ones, while a CN-moiety promotes formation of metha-isomer **28**. So, the type of the substituent in diene and dienophile can affect the selectivity of [2π+4π]-cycloaddition.

A substituent in position 7 in the NBD-ring also influences the regio-selectivity of the process. An extremely high *exo*-selectivity of cycloaddition is characteristic of such reactions, independent of the type of the substituent. However, *syn/anti*-isomerism becomes possible in this case. The yield of anti-isomer is growing with an increase in the electronegativity of substituent 7 [25] (reaction 16 and Table 4):



(16)

Table 4

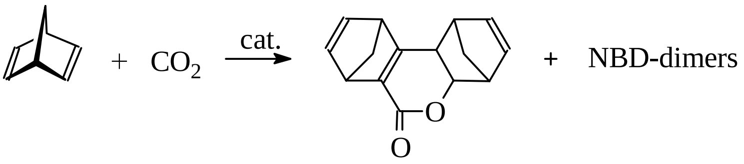
Selectivity of reaction (16) vs. type of substituent Y in position 7 of the NBD ring.

№	Y	Yield, %	**29:30:31:32**	*anti : syn*	*exo : endo*
1	*n*-hexyl	83	40:58:1,6:0,4	42:58	98:2
2	Ph	84	54:45:0,8:0,2	55:45	99:1
3	Cl	60	71:28:0,8:0,2	72:28	99:1
4	OCOPh	97	80:20:0:0	80:20	100:0
5	O-*t*-C_4H_9	95	95:5:0:0	95:5	100:0

Changes in reaction temperature or substitution of phosphite for phosphine influence selectivity of such cycloadditions weakly.

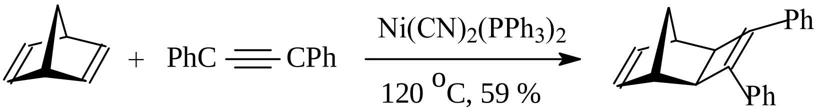
These data agree completely with the results of quantum-chemical *ab initio* calculations of 7 substituted NBDs carried out in the basis STO-3G·[26-27]

A bimetallic system capable of catalyzing reaction between CO_2 and NBD under mild conditions was synthesized from bis-π-allyl nickel and cationic π-allyl palladium complexes [31].



As a result of the reaction, isomeric pentacyclic lactones form.

Acetylenes usually add to NBD through the [2π+4π]-route [29] (reaction 17). There are only rare examples of [2π+2π]-cycloaddition. Some iron and cobalt compounds also induce [2π+2π]-addition with a low yield; only *exo*-adducts form in the latter case (reaction 18):



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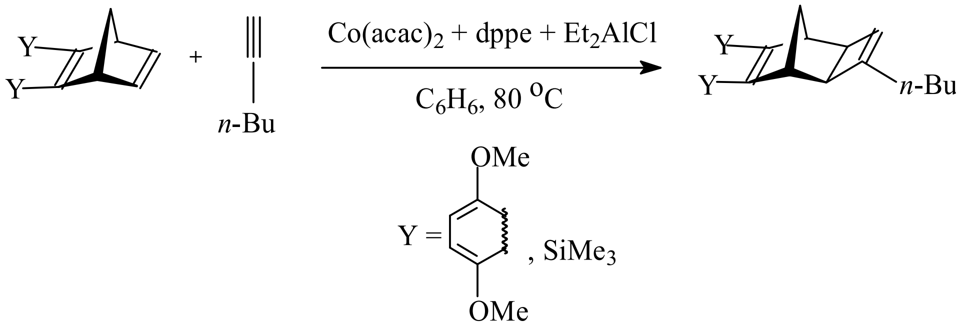
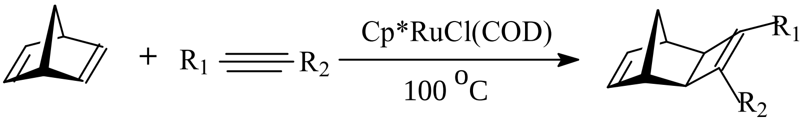


(18)

Low-valence ruthenium complexes also catalyze [2π+2π]-cycloaddition of various acetylenes to NBD and NBD [30] (reaction 19):



(19)

The type of substituents affects the reaction rate considerably (Table 5)

It should be emphasized that [2π+2π]-cycloaddition of alkenes to NBD yields *endo*-adducts chiefly, while reactions with acetylenes result in *exo*-adducts only.

[2π+4π]-Cycloaddition is more characteristic of NBD in reactions with alkynes.

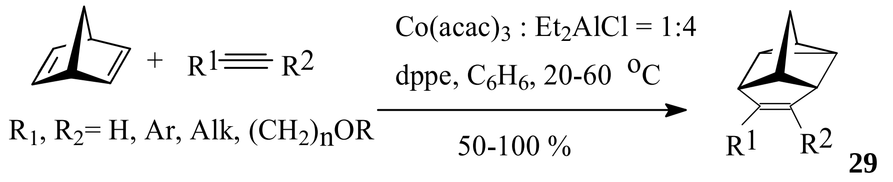
In such systems even non-activated alkynes react

Table 5

Effect of the substituent type in alkyne on regularities of reaction (19)

R^1	R^2	Time, hours	Yield, %
COOMe	COOMe	24	37
Me	COOMe	24	87
Ph	Ph	120	23

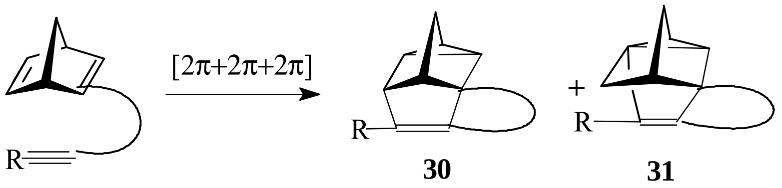
easier than alkenes with electron-acceptor substituents (reaction 20):



(20)

First publications have appeared recently where enantio-selective cyclocodimerization of NBD and alkynes is described. The system $Co(acac)_2$ – Et_2AlCl with chiral diphosphines was used as a catalyst. The regioselectivity of these processes with the participation of substituted NBDs is low (50÷70%), the enantioselectivity reaches 85÷90%.

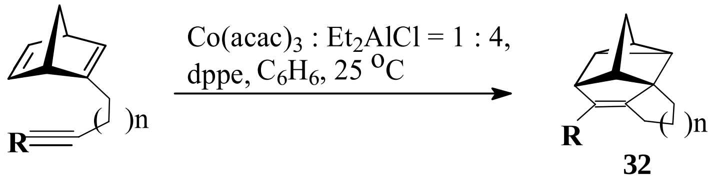
Very interesting examples of intramolecular cycloaddition with the participation of 2-alkenyl-substituted NBD with various lengths of the hydrocarbon bridge were described [28] (reaction 21):



(21)

The aklyne moiety has two possible ways of attachig to NBD. However, only direction **30** takes place at any bridge length. The last characteristics influences the yield of **32** (reaction 22):

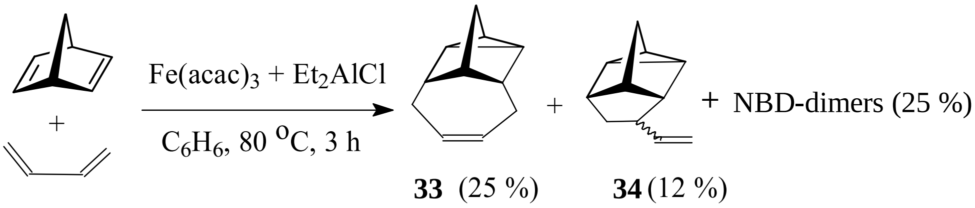
R	Yield	
	n=1	n=2
H	78	64
Me	69	43
$SiMe_3$	63	48
Ph	70	-



(22)

Formation of 8-membered cycles was also described for reactions of NBD with conjugated dienes. Metal complexes play the major role in these processes.

An example of this type of cyclization is co-dimerization of NBD and 1,3-butadiene in the presence of iron complexes [32] (reaction 23):



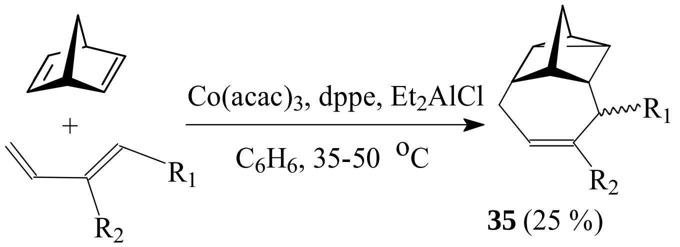
(23)

In addition to [4+2+2]-cycloaddition, [2π+4π]-cyclization also proceeds to give **34** during this reaction, and so does formation of NBD dimers with different structures.

If a cobalt catalyst ($CoCl_2$-*diphos*) is substituted for ferruginous one in similar conditions, the yield of

33 increases up to 68 %, and product **34** virtually ceases forming [33].

When system $Co(acac)_3$-dppe-Et_2AllCl in benzene is used, NBD can dimerize not only with 1,3-butadiene, but with its derivatives as well [34] (reaction 24):

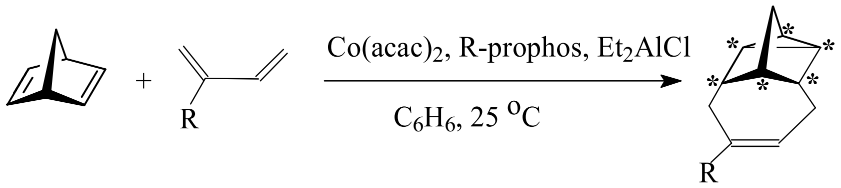


35 (25 %)

$R_1 = R_2 = H$ 89%
$R_1 = H$, $R_2 = CH_3$ 40%
$R_1 = CH_3$, $R_2 = H$ 38%

(24)

Lautens and his colleagues performed this reaction enantioselectively recently [35]. $Co(acac)_2$ or $Co(acac)_3$ can be used for the initial cobalt compound, and a chiral diphosphine can be applied as the ligand. The best results were obtained for R-diphenylphosphinepropane (*R-Propos*), where the selectivity to ee-isomer exceeded 70% (reaction 25 and Table 6):



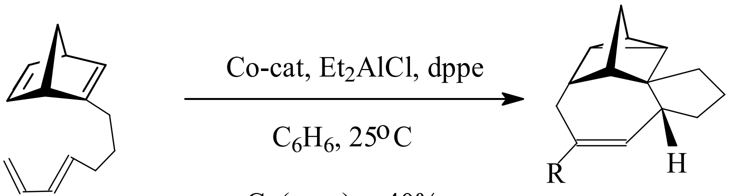
(25)

Table 6

Effect of the phosphine type on the reaction yield and stereoselectivity in reaction 25.

R	yield, %	ee,%
CH_3	66	72
$(CH_2)_8CH_3$	40	74
$CH_2CH_2CH{=}C(CH_3)_2$	49	79
$(CH_2)_3OAc$	52	73
$CH_2Si(CH_3)_3$	49	71

The first example of intramolecular cycloaddition was described; the yield of the adduct was not high, however (reaction 26):



$Co(acac)_2$: 40%
$Co(acac)_2$: 32%

(26)

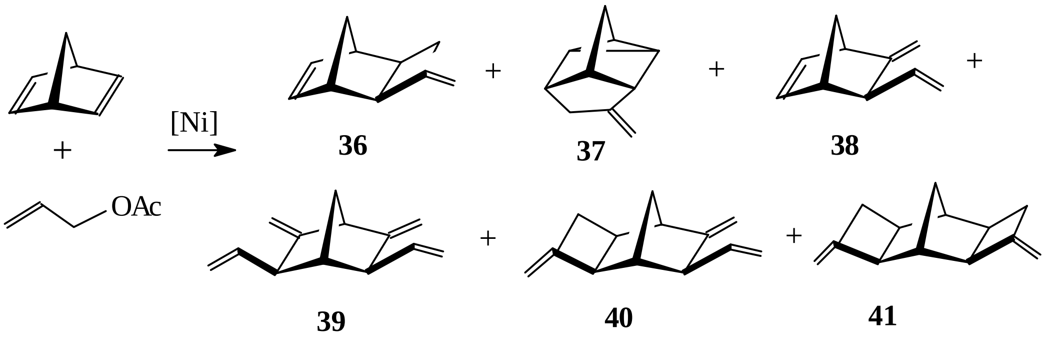
All examples of such addition were described for a very restricted number of catalytic systems with a rather low yield of [4π+2π+2π]-adducts. In addition to them, NBD dimers and products of polymerization form.

The codimerization processes involving NBD have a range of qualitative analogies. Intramolecular type of co-dimer formation implies formation of heteroligand π-complexes of nickel; the ability of the substrate to co-coordinate has to be between that of the mono- and bidentated NBD molecule. One must know these regularities to obtain individual products with a high yield and selectivity.

Catalytic allylation of NBD.

Catalytic allylation of the strained double bond in NBD-derivatives is a promising way to obtain compounds with unique structures. It was first described by M. Catellani and G. Chiusoli in 1979 [36]. This method was substantially developed in studies by [37-39]. A series of NBD-derivatives incorporating two or more double bonds with different reactivity can be obtained in one technological stage through this reaction. The various reactivity of the double bonds is rather valuable when these compound are used as co-monomers for special-purpose synthetic rubbers.

Allylic esters of organic acids are the source of allyl moieties. The most unusual feature of this reaction is the character of addition, which can be not only linear (the conventional type), but cyclic as well, or even proceed with breaking a C-C bond.

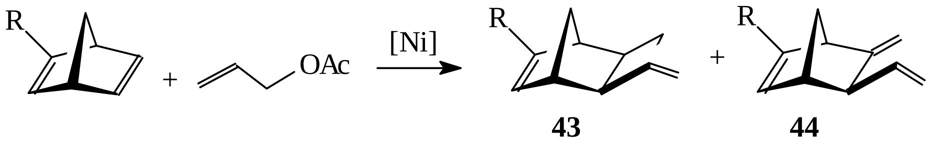


(27)

Catalytic system – Ni(acac)$_2$–AlEt$_3$–P(OR)$_3$ is very active and sufficiently selective when used to obtain *exo*-methylenecyclobutane derivatives. Sterical features of substrates incorporating *exo*-substituents in positions 5 and 6 with respect to the intracyclic double bond do not exert a substantial effect on the rate of cycloaddition. Quite the opposite, the reactions slows down considerably in the case of *endo*-substituents. The structure of allylating agent (allylic ester) is not decisive. For example, you can use not only allylacetate (AA), but allylpropoinate, allylbenzoate and allylformate as well. However, you will not be able to attain a high conversion of reagents due to decomposition of the catalytic system in the last case.

The shares of individual isomers among the oligomeric products depend of temperature, the type and structure of the organophosphous ligand. At 25°C, major products are methylenecyclobutane derivatives.

The structure of substituents in location 7 of the NBD molecule exerts little influence on co-oligomerization catalysts. However, substituents in positions 2 and 3 of the NBD-moiety can block this reaction route (reaction 28)



(28)

Catalytic allylation of NBD and NBD derivatives is an extremely complicated multiparameter process, which proceeds unconventionally. Different factors affect its rate, yield, turnover, and selectivity.

The kinetics and mechanism of the process were scrutinized through a complex of physical and chemical methods for catalytic system Ni(C$_3$H$_5$)$_2$(P(O-iC$_3$H$_7$)$_3$)$_n$. Its results indicate that there are equilibrium stages like:

$$NiL_n \rightleftharpoons NiL_{n-1} + L \qquad (29)$$

Complexes with different number of phosphite ligands were detected through ^{31}P NMR in model systems and in conditions of a catalytic process. Phosphite gets re-esterified by acetic acid, one of the reaction products. This leads to the formation of a mix of phosphonates and deactivates the catalytic system. That NBD molecules can coordinate in the complex in different ways makes the process more complicated, and so does the successive allylation of two double bonds (Fig. 4).

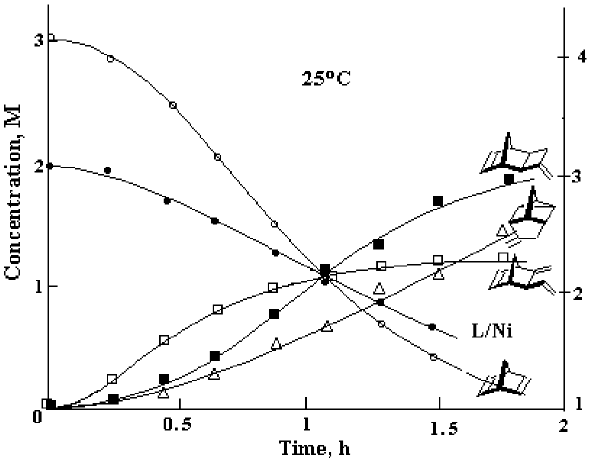


Fig. 4. Changes in concentrations of NBD, products of its allylation, and in the ratio P/Ni during a kinetic experiment.

Analysis of the kinetic data let us assert that individual products **45-47** form due to the presence of nickel complexes with different number of phosphite ligands in the catalytic system (Fig. 5).

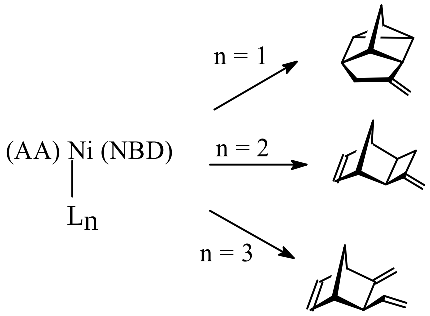


Fig. 5. Possible routes of the intermediates destruction.

The experimental data allow us to propose a mechanism of catalytic allylation of NBD (Fig. 6). In accordance with it, complexes all NiL_nOAc dominate in the reaction media. An NBD molecule co-ordinates on a nickel atom, which induces η^3-η^1-isomerization of the allyl ligand, and then inserts into the η^1-allyl-metal bond. Then, depending on «n», cyclization proceeds in one route or another. It finishes with a β-hydride transfer, formation of products and regeneration of NiL_n (a quick oxidative addition of an allylacetate molecule to NiL_n from solution). When n = 1, NBD coordinates chelately in the complex, which gives rise to product **47** that has a nortricyclene structure.

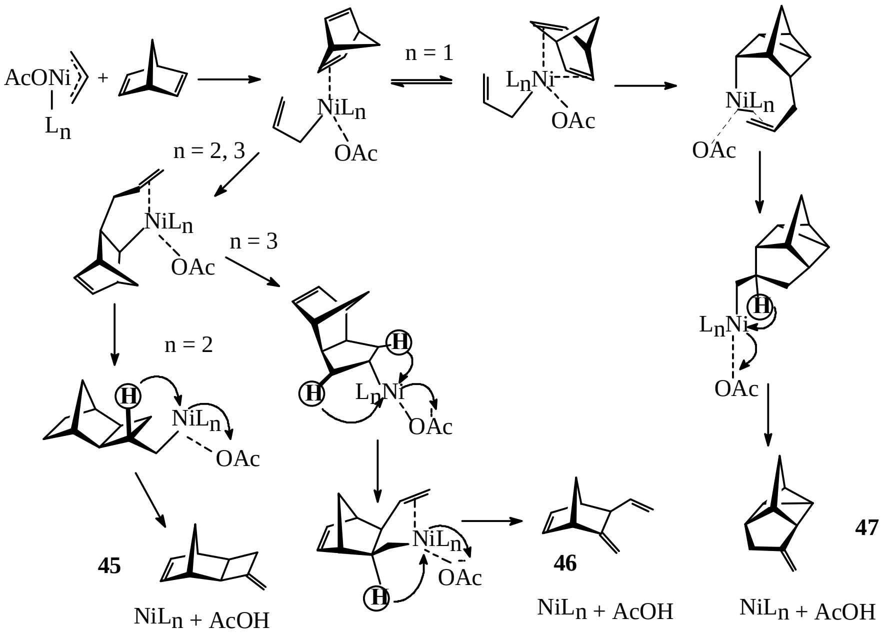


Fig. 6. Catalytic allylation of NBD with allylacetate.

Hydrid transfer is probably the limiting step of the process. This step proceeds with the participation of a β-carbon, which was confirmed through using model system $C_3D_5OCOCD_3$ – NBD (Fig. 7).

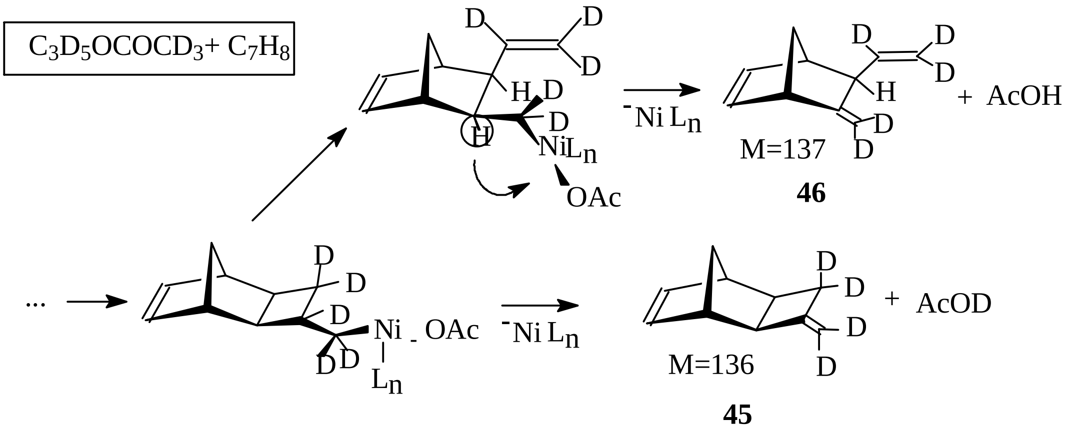


Fig. 7 A mechanism fragment for catalytic allylation of NBD with allylacetate in model system $C_3D_5OCOCD_3$ – NBD

Molecular weights of products **46** and **45** are different. This confirms that hydrogen can be torn from either the NBD-ring, or the allyl moiety.

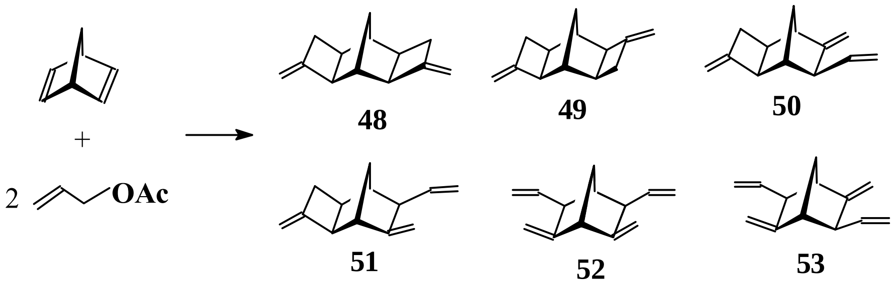
Acetic acid destabilizes the catalytic system. This is why the number of catalyst turnovers does not exceed 150-200 in a static reactor.

The lifetime of the catalyst and the number of its turnovers can be increased up to 2000 through use of zeolites adsorbing acetic acid selectively.

Applying the regularities found, we can obtain product **45** with a yield up to 85% and an output of 350 g/(l·hour) at 80°C and a L/Ni ratio of 3. The product **46** forms with a selectivity of 95% and an output of 220 g/(l·hour) at 25°C and a P/Ni ratio of 2.

The product **47** can be obtained with a selectivity up to 70% at a L/Ni ratio equal to and a temperature of 50 to 70°C.

A very interesting situation exists when a double excess of allylacetate over NBD is used. Secondary allylation of norbornene-type compounds **45** and **46** yields a wide range of isomeric products (reaction 30).



Structures and proportions of double allylation products depends on conditions (the temperature and P/Ni ratio). Allylation of a double bound in NBD is several times faster than the second stage, so the kinetic curves depicting accumulation of products **45** and **46** have pronounced maximums (Fig. 8).

Hence NBD allylation has a general character. It can be used as a promising method for obtaining rare polycyclic hydrocarbons.

Conclusion

Synthetic possibilities of NBD and its derivatives are extremely versatile. However, this positive factor gives rise to problems caused by simultaneous realization of several reactions in a single system. Large-scale use of NBD is substantially limited through difficulties connected with separation and analysis of isomeric products, problems of sensible utilization of

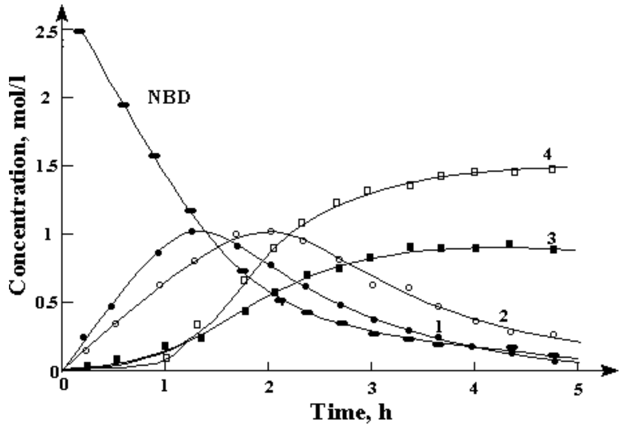


Fig. 8. Kinetic curves of catalytic allylation of NBD with allylacetate. 1 – compound **45**, 2 – compound **46**, 3 – compound **47**, 4 – sum of NBD double allylation products. A static reactor, 40°C; allylacetate:NBD = 2:1; concentration of $Ni(C_3H_5)_2$=0.05 mol/l, initial ratio L/Ni=3; *m*-xylene.

reagents and insufficient catalyst activity. Metal-complex catalysts provide unique opportunities for obtaining various polycyclic hydrocarbons. Use of these complexes is the most promising way of developing this synthetic direction. Transition metals possess the basic ability to influence selectivity to any degree; however, a thorough information about the mechanism of their action is necessary to implement these possibilities. Unfortunately, relevant data are badly scarce in literature.

To find a decent place for NBD among principal substrates in organic and petrochemical synthesis we need deeply understand the basis of NBD-involving processes, which in turn requires us to use a complex of various physical and chemical methods and synthetic techniques, as well as scrutinize the kinetic regularities in the relevant systems.

Acknowledgements

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References

1. Feldblum V.Sh. Synthesis and application of unsaturated cyclic hydrocarbons. (rus.) Moscow, Khimia, 1982, p. 207.
2. Bolshakov G.F. Chemistry and technology of components of liquid rocket fuel. (rus.) Leningrad, Khimia, 1983, 248 pp.
3. Schrauzer G.N. On Transition Metal-Catalyzed Reactions of Norbornadiene and the Concept of π-Complex Multicenter Processes. Advances in Catalysis and related Subjects.,N.-Y.,London, Academic Press, 1968, 9, p.373-396.
4. Smagin V.M., Ioffe F.E., Grigoriev A.A. Chemical Industry (Khemicheskaya Promyshlennost, rus.), 1983, No.4, p.198-201
5. Jemilev U.M., Podpodko N.R., Kozova E.V. Metal-complex catalysis in organic synthesis. (rus.) M., Khimia, 1999, 648 pp.
6. Bren B.A., Dubonosov A.D., Minkin V.I., Chernoivanov V.A. Uspekhi Khimii (rus.), 1991, issue 60, p. 913-948.
7. Franceschi F., Floriani C. Inorganic Chemistry; 1999, 38, No.7, p.1520-1522.
8. Nishikudo T. Macromolecules, 1998, 31, No.9, p.2789-2796.
9. Flid V.R., Aranson M.V., Kozyrev A.N. Journal of general chemistry (rus.). 1992. V.62, issue 11. p.2636-2637.
10. Ballivet D., Billard C., Tkatchenko I. Inorg. Chim. Acta, 1977, 25, p.L58.
11. Langenbach H.J., Keller E., Vahrenkamp H. J. Organometal. Chem., 1979, 171, p.259.
12. Scharf H.D., Weisgerber G., Höver H. Tetrahedron Lett., 1967, N43, p.4227.
13. BRD patent 1239304 (1967); C.A., 1967, 67, 53780.
14. US Patent 3377398, 1968; U.S.C1 260-266.
15. US Patent 4094917 (1978); C.A., 1978, 89, P197060.
16. Ballivet D., Tkatchenko I. J. Mol. Catal., 1975, p.319.
17. Schrauzer G. N., Bastian B.N., Fosselius G.A. J. Amer. Chem. Soc., 1966, 88, p.4890.
18. US Patent N 3329732 (1967); Cl 260-666; C.A., 1967, 67, 90467.
19. Flid V.R., Manulik O.S., Grigor’ev A.A., Belov A.P. Kinetics and Catalysis, 1998, 39, №1, p. 51-55
20. Flid V.R., Manulik O.S., Grigor’ev A.A., Belov A.P. Kinetics and Catalysis, 2000, 41, №5, p. 597-603
21. Flid V.R., Kuznetsov V.B., Grigor’ev A.A., Belov A.P. Kinetics and Catalysis, 2000, 41, №5, p. 604-611
22. Binger P., Schuchardt U. Angew. Chem., 1977, 89, N4, p.254-255.
23. Lucchi O.D., Licini G., Pasquato L., Senta M. Tetrahedron Lett., 1988, 29, p.831.

24. Furukawa J., Kobuke Y., Sigumoto T., Fueno T. J. Am. Chem. Soc., 1972, 94, p.3633.
25. Lautens M., Tam W., Edwards L.G. J. Chem. Soc., Perkin Trans. 1, 1994, p.2143-2144.
26. Lautens M., Tam W. Advances in Metal-Organic Chemistry, Liebeskind L.S., Ed.; JAI Press: Greenwich, 1996, p. 125-168.
27. Gugelchuk M.M., Wisner J. Organometallics, 1995, 14, p.1834-1839.
28. Flid V.R., Kuznetsov V.B., Dmitriev D.V. Kinetics and Catalysis, 1999, 40, №3, p. 301-306
29. Heimbach P., Meyer R.V., Wilke G. Liebigs Ann. Chem., 1975, p.743-748.
30. Misudo T., Naruse H., Kondo T., Ozaki Y., Watanabe Y. Angew. Chem., Int. Ed. Engl., 1994, 33, 580.
31. Lautens M., Tam W., Edwards L.G. J. Org. Chem., 1992, 57, p.8-9.
32. Greco A., Carbonaro A., Dall'Asta G. J. Org. Chem. 1970, 35, p.271-274.
33. Carbonaro A., Cambisi F., Dall'Asta G. J. Org. Chem., 1971, 36, p.1443-1445.
34. Doyle M.P. Chem. Rev., 1986, 86, p.919-939
35. Lautens M., Tam W., Sood C. J. Org. Chem., 1993, 58, p.4513-4515.
36. Catellani M., Chiusoli G.P., Dradi E., Salerno G. J. Organomet. Chem., 1979, 177, p.C29-C31.
37. Jemilev U.M.,Khusnutdinov R.I., Galeev D.K., Nefedov O.M.,Tolstikov G.A. Izv. Akad. Nauk SSSR, Ser. Khim., 1987, N1, p.138-148.
38. Flid V.R., Manulik O.S., Grigor'ev A.A., Belov A.P. Metalloorganicheskaya chimiya, 1991, №4, p. 864-871
39. Flid V.R., Ivanov A.V., Manulik O.S., Belov A.P. Kinetika i Cataliz, 1994, 35, №5, p. 774-775

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