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RESEARCH ARTICLE

Palladium-catalyzed allylation of norbornadiene: Experimental and quantum chemical research

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Abstract

Objectives. *Catalytic processes involving norbornadiene (NBD) and norbornene (NBN) derivatives provide exceptional opportunities for the synthesis of a wide range of carbocyclic hydrocarbons. By significantly expanding this range, it becomes possible to obtain materials offering a wide variety of predictable properties. The aim of the present review is to summarize the latest achievements in the creation of novel processes catalyzed by palladium compounds. Considerable attention is paid to the study of the mechanisms of NBD allylation reactions by a combination of experimental and theoretical methods.*

Results. *Various strategies of the molecular design of palladium catalysts for syntheses based on NBN and NBD are considered. The possibility of implementing various directions of NBD allylation is demonstrated. Factors influencing the direction of the reactions, by which means individual products can be selectively obtained, are discussed.*

Conclusions. *The effective development of new catalytic processes involving NBD and NBN derivatives requires the complex application of synthetic, kinetic, isotopic, and quantum chemical approaches. By combining instrumental and theoretical methods with constant feedback, it becomes possible to optimize the search for original catalytic systems, obtain information about the mechanisms of their action, and influence technological parameters in a targeted manner.*

Keywords: *norbornene, norbornadiene, allylation, catalysis, kinetics, quantum chemical calculations, reaction mechanism, transition metals, palladium, strained carbocyclic compounds*

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ОБЗОРНАЯ СТАТЬЯ

Палладий-катализируемое аллилирование норборнадиена: Экспериментальные и квантово-химические исследования

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Аннотация

Цели. *Каталитические процессы с участием норборнадиена (НБД) и производных норборненового (НБН) ряда открывают исключительные возможности для синтеза широкого круга карбоциклических углеводородов. Значительное расширение их ассортимента позволяет впоследствии получать материалы с широким спектром прогнозируемых свойств. Целью обзора является обобщение последних достижений в области создания новых процессов, катализируемых соединениями палладия. Значительное внимание уделено исследованию механизмов группы реакций аллилирования НБД совокупностью экспериментальных и теоретических методов.*

Результаты. *Рассмотрены различные стратегии молекулярного дизайна палладиевых катализаторов для синтезов на основе НБН и НБД. Показана возможность реализации различных направлений аллилирования НБД. Обсуждены факторы, влияющие на направление реакций и позволяющие селективно получать индивидуальные продукты.*

Выводы. *Разработка новых каталитических процессов с участием НБД и НБН-производных требует комплексного применения синтетических, кинетических, изотопных и квантово-химических подходов. Совокупность инструментальных и теоретических методов, имеющих обратные связи, позволяет оптимизировать поиск оригинальных каталитических систем, получать информацию о механизмах их действия и направленно влиять на технологические параметры.*

Ключевые слова: *норборнен, норборнадиен, аллилирование, катализ, кинетика, квантово-химические расчеты, механизм реакции, переходные металлы, палладий, напряженные карбоциклические соединения*

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INTRODUCTION

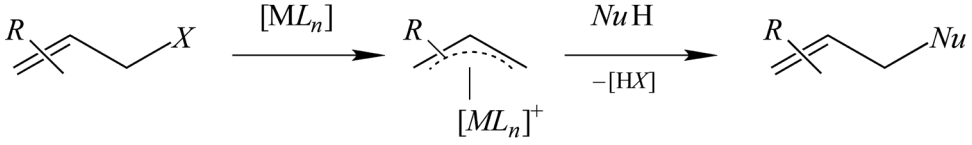
Allyl addition and substitution reactions catalyzed by transition metals attract considerable research attention due to their utility in the synthesis of numerous drugs, semi-product, and materials. Since the pioneering work of Tsuji and Trost in this area, new approaches have been created to form C–C, C–N, C–H, C–O, C–S, C–P, and C–B bonds with high regio- and enantio- control [1, 2]. At the same time, it is worth noting the high functional tolerance of such reactions and the consequent possibility of their implementation under "mild" conditions. Quite typically, the addition of the allyl fragment proceeds without the formation of by-products at high rates of substrate conversion and selectivity for target products.

Such reactions predominantly occur with the participation of allylic substrates (allyl alcohols, allyl carboxylates, allylamines, etc.), a transition metal used as a catalyst (usually nickel or palladium), and a nucleophile attacking allyl complex (Fig. 1). If the substrate is insufficiently reactive, it is possible to provide for its additional activation using the right selection of the metal-catalyst, ligands, solvent and auxiliary activators (for example, Lewis acids).

With the optimal choice of conditions, the possibility of stereoselective allylation of substrates may in some cases arise [3–5]. Compared to most similar reactions catalyzed by metals, asymmetric allyl substitution proceeds at sp^3 rather than sp^2 hybridized centers. Allylation reactions are also used to build cycles, transfer 1,3-chirality, separate racemates, desymmetrize meso substrates, and so on [6].

In recent years, great progress has been achieved in the field of allyl substitution reactions using metal complex catalysts, as summarized in reviews [1–3, 5, 7, 8]. Approaches have been developed for the use of various substrates: allyl ethers, alcohols, and allylamines [1]. Methods for their additional activation along with new generation of ligands for conducting enantioselective synthesis of important natural compounds or drugs have been proposed [9]. Among the various substrates capable of supporting reactions, compounds of the norbornene (NBN) and norbornadiene (NBD) series, representing important objects of organic synthesis, are of particular interest [10–12]. The unconventional nature of the allylation reaction with the participation of these compounds is associated with the structure of the resulting products and the mechanism of their formation. During addition to a nucleophile, the allyl fragment can undergo significant transformations: C–C bond cleavage in the allyl fragment itself with the formation of methylene-vinyl (**1**) and methylenecyclobutane (**2**) derivatives, the formation of methylenecyclopentane cycles (**3**), or addition to the alkene (**4**). In addition, the formation of several isomeric products is possible (Fig. 2).

The possibility of NBN allylation was first demonstrated in 1979 by M. Catellani *et al*. using Ni^0 complexes as catalyst [13]. The reaction products, representing compounds having a type **1** and type **2** *exo* structure, are formed along various routes along which the process conditions are controlled by varying selectivity. Later, along with a demonstration of the universality of the method for NBN substrates, it was shown that effective catalysts for this and related reactions can be formed from various nickel compounds [14, 15]. In the course of further studies, the use of NBD was found to significantly expand the synthetic possibilities of this reaction [16]. The reason of these significant differences lies in the NBD property of chelate-type coordination to the metal, resulted in a more diverse structure of products than for NBN. In addition to compounds of types **1** and **2**, the formation of nortricyclane isomers, compound **3**, is also observed. In addition, double allylation products **6**–**11** and **6'**–**11'** are often observed in the presence of an excess of the allylating agent due to the presence of a second double NBN bond in the NBD molecule.



where *R* is substituent, *M* is transition metal, *L* is ligand, *Nu* is nucleophile, *X* = OAc, OCO_2R, etc.

Fig. 1. Transition metal-catalyzed allylic substitution with activated allylic substrates.

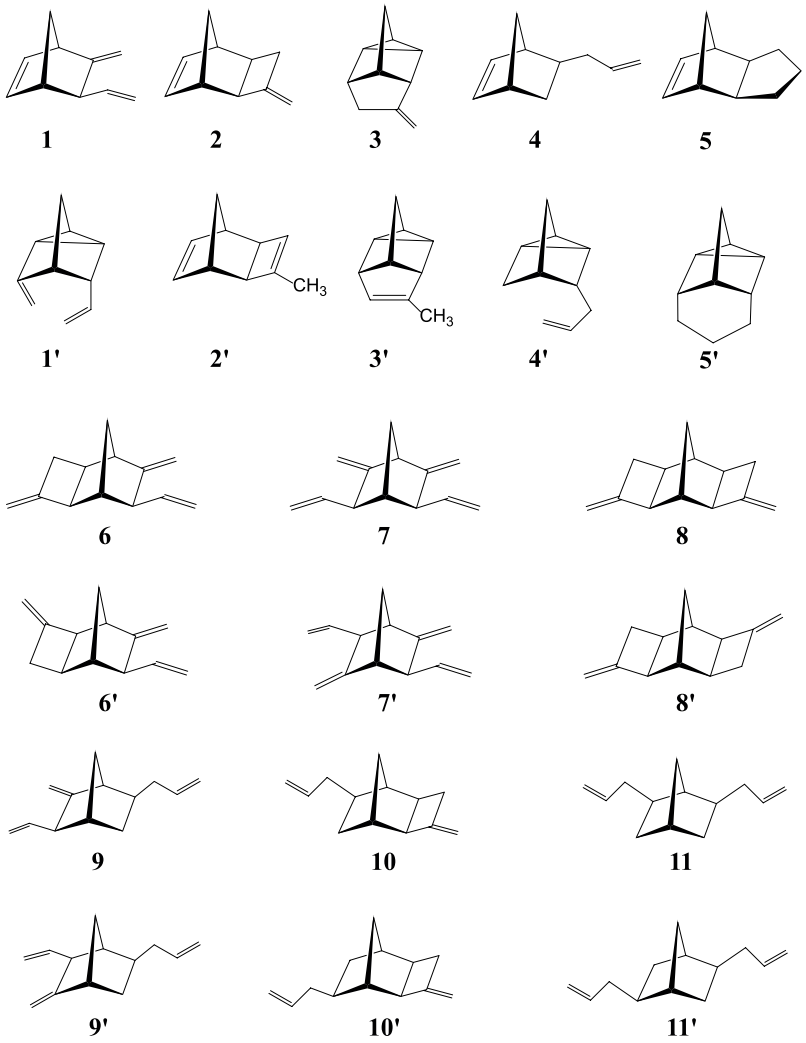


Fig. 2. Products of NBD allylation.

Thus, allylation of NBD leads to a number of products with different structures, which indicates the multipath nature of the process. These compounds have a high potential for use as monomers for obtaining materials with desired properties or components for rubbers of the EPDM type (synthetic ethylene propylene diene monomer rubber). However, the practical use of the NBD allylation reaction is currently quite limited. The structure of the carbocyclic skeleton of the NBD molecule leads to all types of isomerism in the resulting products—regio-, stereo, enantio-, which often produces a mixture that is difficult to separate and adversely affects the selectivity of process. In this regard, it became necessary to conduct regular research to understand the mechanisms of allylation and develop new catalysts. In practical terms, a reasonable selection of a catalyst and reaction conditions is impossible without a deep understanding of the nature of catalytically active particles. An examination of the structure and energy parameters of the intermediates that form the catalytic cycle, informs an understanding of the nature of the rate-determining stages and the roots of different levels of isomerism. The most rational way to solve these key problems of catalysis is associated with the complex application of experimental synthetic, kinetic, isotope, and quantum chemical methods and approaches. Such studies have been carried out for a number of years at the Ya.K. Syrkin Department of Physical Chemistry of the M.V. Lomonosov Institute of Fine Chemical Technologies of RTU MIREA.

Over the past decades, a sufficient amount of kinetic and spectral data has been collected during the research of the stoichiometric and catalytic interaction of NBD with allyl complexes of transition metals and allylcarboxylates. Proposed schemes of mechanisms for these reactions help to qualitatively explain the structure of the resulting products[1]. However, since nickel systems are sensitive even

[1] Flid V.R. *Physical and chemical bases of catalytic syntheses involving norbornadiene and allyl derivatives*. Dr. Sci. Thesis (Chem.). Moscow; 2000. 250 p. (in Russ.).

to trace amounts of oxygen, obtaining accurate information about these transformation mechanisms turned out to be a very difficult task.

In previous work, we have used an integrated approach in the study of various directions of allylation, consisting in the joint application of modern experimental methods, the rational use of physicochemical methods for the analysis of reaction systems, as well as quantum chemistry approaches, in order to obtain elusive information about highly reactive intermediates. The only currently realistic alternative to nickel in NBD allylation reactions takes the form of palladium-based catalyst systems. Due to the special properties of the latter, not only the main intermediates of the process were investigated, but also a new synthetic direction was discovered, leading to the development of the first heterogeneous catalysts.

Thus, the aim of the present review is to summarize the results of recent research in the field of palladium-catalyzed NBD allylation. The important feature of this process approach consists in the unity of theoretical and experimental approaches with constant feedback, which has been successfully used to carry out molecular design of catalysts and develop highly efficient homogeneous and heterogeneous catalytic systems for allylation reactions of NBD and NBN compounds.

EXPERIMENTAL RESEARCH OF PALLADIUM-CATALYSED ALLYLATION OF NBD

At the first stage of research, in order to identify new—in addition to nickel-based—catalytic systems, the stoichiometric interaction of NBD with homoligand η^3-allyl complexes of other metals, Co, Fe, Ni, Rh, Pd, and Pt, was studied [17]. The reaction was found to proceed quantitatively at 25°C in just a few minutes, yielding a wide range of products. The general nature of the reaction, which is associated with the transfer of hydrogen between η^3-allyl ligands, was established for all metals. When using complexes of nickel, palladium, and platinum, compounds with a double bond in the norbonene ring are predominantly formed. This fact illustrates the monodentate nature of NBD coordination in transition metal complexes of the nickel subgroup. Noting the closeness of the ratio of products for these metals, an assumption was made about the similarity of their coordination capabilities. It is noted that the activity of the metals significantly decreases from nickel to platinum.

Since the stoichiometric model of a single catalytic cycle turned out to be convenient in establishing the main directions of the addition of the allyl fragment to NBD and revealing the details of the mechanism, in 1991 a hypothesis was put forward about the possibility of developing similar catalysts based on other transition metals [17]. However, it was only in 2000 that a catalytic process using palladium compounds could be implemented [18]. When NBD is allylated with allyl acetate, almost the same set of products is formed as for nickel [19]. For various palladium precursors: $Pd(dba)_2$+2PPh_3, $Pd(OAc)_2$+2PPh_3, $PdCl_2(PPh_3)_2$, $[(C_3H_5)Pd]NO_3$+2PPh_3, similar activity values and product ratios are observed. The composition of products is similarly affected by temperatures and the ratio of reagents. Thus, at 25–60°C, compounds **1** and **2** are formed in high yields, while at temperatures above 80°C, the relative amount of compound **3** increases. The selectivity for individual isomers does not exceed 50–60%. With an excess of allyl acetate, as in the case of nickel catalysts, secondary allylation of the unsubstituted NBN double bond in compounds **1** and **2** occurs, leading to a large quantity of isomeric products **6**–**8** and **6'**–**8'**.

Thus, qualitative analogy was established in the behavior of Ni- and Pd-catalytic systems during the allylation of NBN and NBD substrates, on which basis we can assume a similar structure of key intermediates. Despite the fact that the reaction rate for palladium-based systems is somewhat lower than for their nickel-based counterparts, the former tend to be more stable and exhibit activity under normal conditions in air. By greatly simplifying the technological aspects of the process itself, this allows the application of new tools to the study of its mechanism. In this regard, further studies on optimizing the conditions for obtaining individual products were carried out using palladium systems.

Palladium catalysts containing phosphines have a high group selectivity with respect to compounds **1**–**3**; in most cases, however, the yield of individual products does not exceed 50%. An exception is the nanocluster system consisting of $Pd_{55/147}$ and triphenylphosphine in the [bmim][BF_4] ionic liquid medium, when the only product **1** is formed [20]. Apparently, this is one of the few examples of the fact that the Pd_{147} cluster is not destroyed in the medium of an ionic liquid. Indirectly, this experiment anticipated a new direction: the development of heterogeneous catalytic systems for supporting this reaction.

An interesting direction of the reaction was discovered when using a new allylating agent, allyl formate (AF). Although AF is not used for nickel catalysts due to the consequent instability, the same catalytic system is formed in NBD and AF media for ligand-free catalytic systems and various

palladium precursors (Pd^0, Pd^{2+}), heteronuclear carboxylate complexes of the composition $[PdM(\mu\text{-}RCOO)_mL_n]_x$, where *M* = Zn, Co, Ni, Mn, and rare earth elements; *R* = Me, *tert*-Bu; *m* = 4.5; *x* = 1, 2, and $Pd_2Cu(\mu\text{-}OAc)_6$, as well as giant $Pd_{55/147}$ clusters [21]. The main reaction product in all cases is 5-allylnorbornene-2 (5-allylbicyclo[2.2.1]-heptene-2) **4**, which was previously unavailable when using nickel catalysts. Products **1**–**3** under similar conditions are formed only in trace amounts.

Substituted AFs, which also enter the reaction, selectively add to the double bond of NBD with an unsubstituted carbon atom. The differences between the processes described earlier and this reaction are that, in the first case, the allyl group, in adding to NBD, loses the H atom (oxidative allylation), while in the second case, it adds it (reductive allylation). Thus, palladium compounds are catalysts for both oxidative and reductive NBD allylation. Previously, the formation of reductive NBD allylation products was observed only in stoichiometric interactions [22].

It was shown that for Pd^{2+} precursors, the process begins after a long induction period. As a result of kinetic and electrochemical experiments, it was established that Pd^{2+} is reduced to Pd^0 during this period under the action of the components of the reaction mixture. The process can be accelerated by the right choice of base.

The proposed mechanism of NBD hydroallylation is based on the totality of all experimental and spectral data (Fig. 3). After the formation of the Pd^0 complex at the initial stage, AF is oxidatively added to it. This is followed by the insertion of NBD, coordinated in the *trans* position relative to the substituent *R*, at the palladium-allyl bond. The structure of such relatively stable complexes has been studied by X-ray diffraction analysis[2]. As a result of decarboxylation at the subsequent stage, a palladium hydride complex is most likely formed. Although this has not yet been observed directly in this reaction, the possibility of the formation of similar complexes in other catalytic processes has already been experimentally demonstrated [23]. This is followed by the stage of reductive elimination with the formation of compound **4** and regeneration of the original Pd^0 form.

The formation of hydride complexes of palladium as a result of decarboxylation of formate ions has long been known [24]. It can be assumed that NBD and a neutral ligand on palladium, for example, dibenzylideneacetone (dba) or phosphine, play an important role in the stabilization of Pd^0 formed as a result of the reductive elimination of the product at the final stage of the catalytic cycle. Further, due to the greater prevalence and commercial availability, we used palladium acetate as a catalyst precursor.

By analogy with nickel systems, it was assumed that greater selectivity in the formation of products **1**–**3** could be achieved by varying the phosphine/palladium ratio. In the course of the studies, however, we found that varying the amount of the phosphine ligand has practically no effect

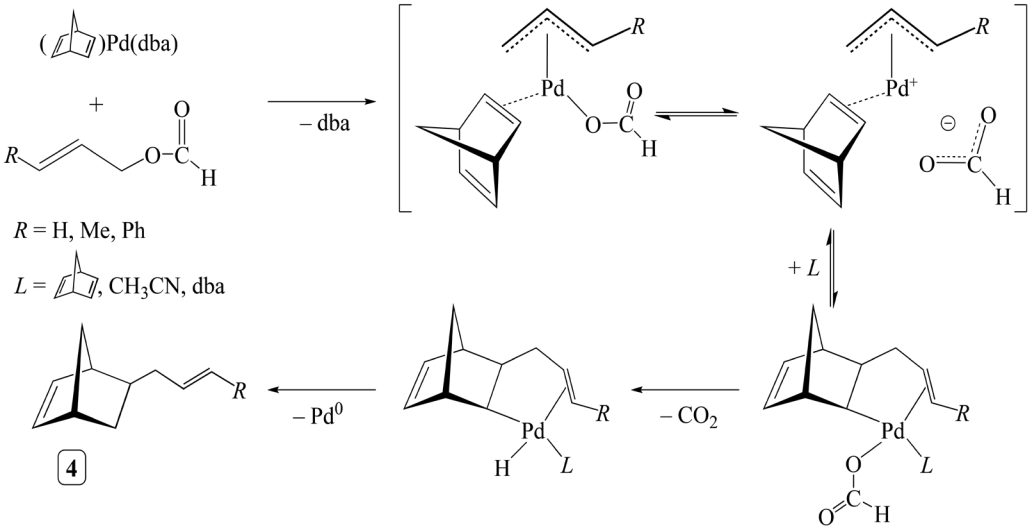


Fig. 3. Mechanism of catalytic hydroallylation of NBD.

[2] Evstigneeva E.M. *Electronic structure, spectral and catalytic properties of allyl complexes of palladium*. Dr. Sci. Thesis (Chem.). Moscow; 2011. 259 p. (in Russ.).

on the ratio between products **1**–**3**. However, in the case of carrying out the reaction in acetonitrile and using AF as an allylating agent, the direction of the process changes with an increase in the amount of phosphine ligand towards an increase in the amount of oxidative allylation products and a decrease in compound **4** [25].

To explain this phenomenon using a combination of physicochemical methods of analysis, we studied the stages of formation of palladium intermediates in solutions of various compositions. The study was carried out using the methods of cyclic voltammetry (CV), high-resolution mass spectrometry, nuclear magnetic resonance spectroscopy (NMR) and by gas chromatography-mass spectrometric (GC-MS) control of products and intermediates in various model systems and in the reaction itself.

The complex formation reactions in solutions necessary for the formation of catalytically active complexes proceed by the substitution mechanism, in which the ligand and/or reagents replace the solvate molecules of the solvent. The nature of the solvent also affects the kinetics and mechanism of such transformations. The rate of its exchange with another ligand depends on the strength of interaction between a metal cation and a coordinated solvent molecule. This means that at each stage of the reaction it is necessary to take into account the role of stabilization of key intermediates by solvent molecules. Solvents with a wide range of physicochemical properties were studied as reaction media. In addition, all components of the catalytic system of the reaction under study should be soluble in them. Although the properties of a solvent are characterized by many parameters, the main contribution is usually determined under conditions of homogeneous metal complex catalysis by the ability of the solvent to form hydrogen bonds with substrates and intermediates, as well as the degree of polarity, polarizability, and coordinating ability with respect to transition metals. The totality of these relative characteristics correlates with the statistical probability of solvent coordination to transition metal complexes and reflects its ability to solvate and stabilize them.

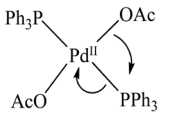
When studying the effect of solvents, two series of experiments were carried out: without additional introduction of ligands and with the use of PPh_3. At the first stage, the interaction of palladium acetate with NBD with AF in a ligand-free system was studied. The data obtained confirmed that the very possibility of a reaction between NBD and AF under the indicated conditions really depends on the solvent used. For a significant number of non-polar or low-polar solvents, the reaction is practically absent. An increase in the conversion of reagents, on the contrary, is observed when using solvents capable of coordination (acetonitrile, dimethyl sulfoxide), and, to a lesser extent, for water and ethanol. The complete absence of reaction when using pyridine, despite its higher ability to coordinate, is obviously associated with the difficulties of replacing it with reagents in palladium complexes during the formation of intermediates. In general, in the medium of coordinating solvents, the reaction proceeds with the predominant formation of **4**, compounds **2'** and **3** are observed in insignificant amounts. In some cases, products of double allylation of NBD **11** and **11'** are formed (Fig. 2).

During the formation of catalytically active complexes from $Pd_3(OAc)_6$ in solutions in the presence of phosphine ligands, it was found that upon addition of PPh_3 (^{31}P = −5.81 ppm), a brown solution becomes yellow. The resulting complex is characterized by the signals E^p_{red} = −1100 mV and ^{31}P = 14.67 ppm. (14.84 ppm in $CDCl_3$), which corresponds to the $Pd(OAc)_2(PPh_3)_2$ compound (1). According to [26–29], this complex undergoes intramolecular rearrangement (2), during which Pd^{2+} is reduced to Pd^0, while PPh_3 (3) is oxidized to triphenylphosphine oxide (O=PPh_3) ^{31}P = 26.41 ppm (29.50 ppm in $CDCl_3$).

In the case of an excess of phosphine, the $Pd^0(PPh_3)(OAc)^-$ complex associated with the acetate ion and characterized by the peak of E^p_{ox} = +190 mV and the signal of ^{31}P = 17.94 ppm (15.95 ppm in $CDCl_3$), in accordance with reactions (4) and (5) forms complexes $Pd(PPh_3)_4$, $Pd(PPh_3)_3$, giving a broadened peak E^p_{ox} = +580 mV, signals ^{31}P = 15.31 ppm (15.39 ppm in $CDCl_3$) and ^{31}P = 20.80 ppm (20.18 ppm in $CDCl_3$). 14-Electron particles of the $Pd(PPh_3)_2$ type are not observed in model systems.

For the ligand-free system, as a result of the CV analysis, the addition of AF to $Pd_3(OAc)_6$ was found to lead to the gradual formation of two Pd^0 complexes. Most likely, these are $Pd(CH_3CN)(OAc)^-$

$$Pd(OAc)_2 + 2PPh_3 \longrightarrow Pd(OAc)_2(PPh_3)_2 \quad (1)$$



$$\longrightarrow Pd^0(PPh_3)(OAc)^- + AcO{-}PPh_3^+ \quad (2)$$

$$AcO{-}PPh_3^+ + H_2O \longrightarrow AcOH + O{=}PPh_3 + H^+ \quad (3)$$

$$Pd^0(PPh_3)(OAc)^- + 2PPh_3 \longrightarrow Pd^0(PPh_3)_3 + OAc^- \quad (4)$$

$$Pd^0(PPh_3)_3 + 2PPh_3 \rightleftharpoons Pd^0(PPh_3)_4 \quad (5)$$

and $Pd(CH_3CN)_2$, which are characterized by broad peaks E^p_{ox} = –20 mV and E^p_{ox} = 700 mV, respectively. In the NBD–$Pd_3(OAc)_6$ system, such interactions are not observed.

The formation of a complex of palladium with NBD and an acetate moiety, solvent, and NBD was registered by high-resolution mass spectrometry with electrospray ionization (ESI-MS). The 14-electron complexes $Pd^0(CH_3CN)_2$ and $Pd^0(CH_3CN)(AcO)^-$ were not found in the solution. The $Pd^0(NBD)_2$ complex, which is responsible for the formation of insignificant amounts of NBD dimerization products, was detected only when AF was depleted [30].

When PPh_3 is added to the system, the situation changes dramatically. The ligand actively competes with the solvent for the coordination site on palladium, as a result of which both reductive and oxidative allylation of NBD becomes possible. For solvents incapable of coordination, the direction of reductive allylation is almost completely suppressed; in this case, compounds **1**, **2**, and **3** become the main reaction products. PPh_3 in the active complex as it is oxidized.

In the presence of PPh_3, in addition to the compounds described above, the solution contained a complex characterized by a signal in the NMR spectrum ^{31}P = 18.58 ppm. Based on the data of works [26–29, 31] and the classical work of Yamomoto [32], an allyl derivative of composition $Pd^{2+}(PPh_3)(OAc)^-(\eta^3\text{-}C_3H_5)(OCOH)$ can be concluded to result from the oxidative addition of AF to the spontaneously formed $Pd^0(PPh_3)(OAc)^-$ complex. Similarly, for a ligand-free system, the formation of the compound $Pd^{2+}(CH_3CN)(OAc)^-(\eta^3\text{-}C_3H_5)(OCOH)$ was assumed.

When PPh_3 is used, NBD allylation occurs in both polar and weakly polar solvents with high polarizability. The GC-MS analysis of the reaction mixtures indicates the presence of 14-electron palladium complexes of the anionic form $(PPh_3)Pd^0(OAc)^-$ and $(PPh_3)_2Pd^0(OAc)^-$, stabilized by induced and permanent dipoles of the solvent. Such interactions have been well studied for the closely related system $Pd_3(OAc)_6$+PPh_3 [28].

In some cases, a small amount of double allylation, hydrogenation, and hydroformylation products accumulate in the system, whose formation was described in our earlier works [21, 25, 30, 35, 36].

Thus, it is experimentally confirmed that (depending on the nature of the solvent and the presence of a ligand) two different types of precursors can form in the system, preceding the stage of oxidative addition of AF to the palladium atom (Fig. 4). In the absence of PPh_3, the role of the ligand is taken simultaneously by NBD and the coordinating solvent.

The presence of anionic palladium complexes during the formation of the catalytic system with PPh_3 and at the first stage of reduction in the ligand-free system is confirmed by the CV data. It is known that the formed anionic complexes of zerovalent palladium are much more active in the oxidative addition of allyl carbonates. If they are not sufficiently stabilized by solvent molecules or if they are strongly coordinated by two solvent molecules (for example, pyridine), the catalytic system is destroyed with the formation of propene observed in some cases.

Evidence of the influence of the proton solvent, which is expressed in the stabilization of palladium intermediates by additional hydrogen bonds, was not found.

The mechanism of the reduction of palladium acetate in a ligand-free system followed by the oxidative addition of AF is still not completely clear. Traces of water present in the solution or formic acid can act as a reducing agent for palladium. The involvement of AF itself cannot be ruled out: the formyl hydrogen atom can transfer to acetate groups from the complex, releasing CO_2 and forming CH_3COOH.

According to the GC analysis, it was found that during the induction period associated with the formation of the active complex, the response of two signals increases, the intensity of which is proportional to the concentration of palladium acetate. It was shown by NMR and GC-MS that they are products of the addition of acetate groups to the NBD **12** and **12'** molecule (Fig. 4). It is important to note that model experiments with acetic acid under conditions of NBD catalytic allylation at T = 20–60°C and in the absence of a catalyst or AF do not lead to the formation of these products, which can be obtained without a catalyst, but only at much higher temperatures [33].

Experiments with the use of deuterated AF indicate the formation of products with a molecular weight of 153. A deuterium atom was found in the norborene ring; it is obvious that it gets there when transferred from the formyl group. This suggests the formation of the

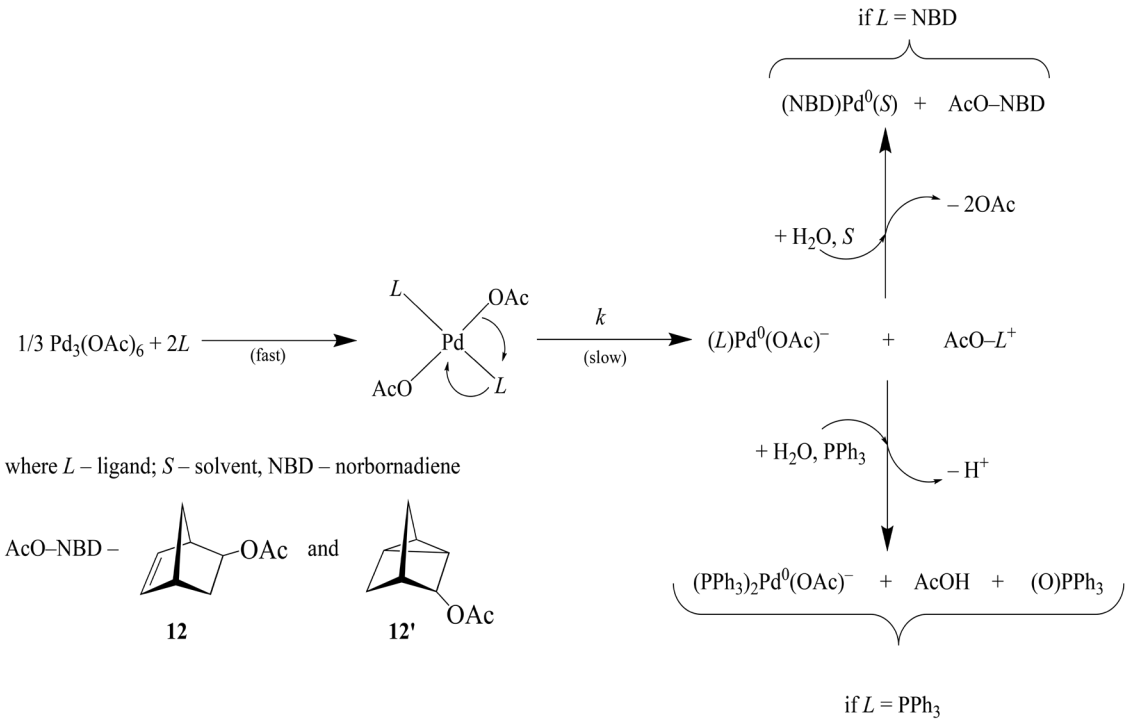


Fig. 4. Scheme of the reduction of palladium acetate to Pd^0 with the formation of active intermediates of neutral and anionic nature.

$Pd^{2+}(\eta^2$-*exo*-NBD$)(OAc)^-(\eta^3$-$C_3H_5)$(OCOH) intermediate. At one of the stages of the mechanism, after coordination of NBD on the Pd complex, theaddition of the acetate ion to NBD occurs, culminating in β-hydride elimination with the formation of compounds **12-D$_1$** and **12'-D$_1$** (Fig. 5).

Following removal of the acetate groups, the interaction of PdL_2 with AF and NBD leads to the Pd(η^2-*exo*-NBD)(η^3-C_3H_5)(OCOH) intermediate. The $Pd^{2+}(PPh^3)(OAc)^-(\eta^3$-$C_3H_5)$(OCOH) complex formed as a result of the oxidative addition of AF is capable of exchanging a phosphine ligand for an *exo*-coordinated NBD molecule. As a result, as in the ligand-free system, the Pd(η^2-*exo*-NBD)(η^3-C_3H_5)(OCOH) complex is formed, whose further transformations lead to NBD allylation products.

During the CV analysis of the NBD+AF+$Pd_3(OAc)_6$+PPh_3 system, not only the $Pd^0(PPh_3)(OAc)^-$ complex is observed, but also a signal in the E^p_{ox} = 0 mV region; this probably belongs to $Pd^0(CH_3CN)(OAc)^-$ formed as a result of stabilization of the system by the solvent.

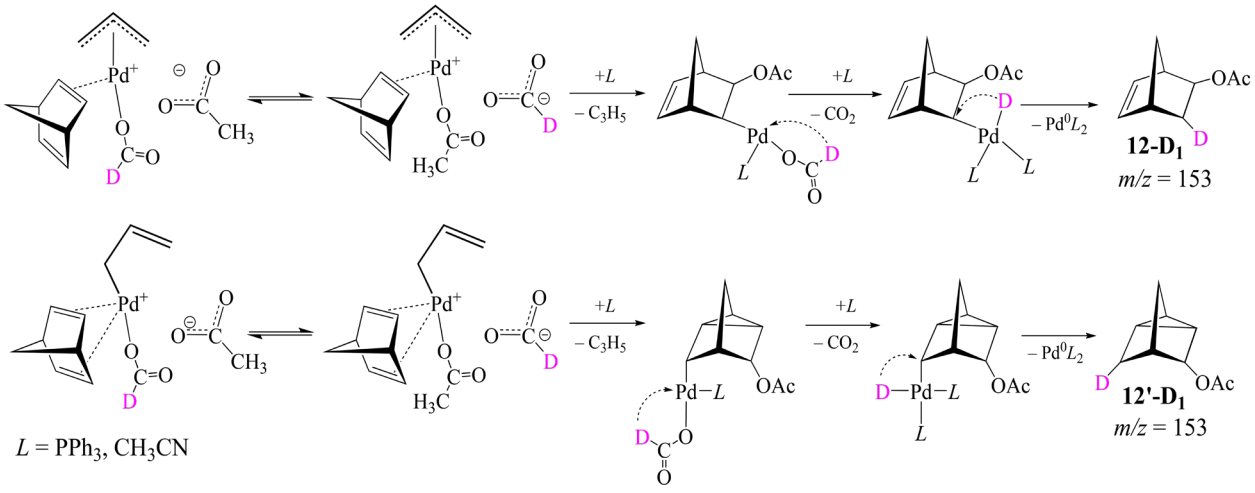


Fig. 5. Mechanism of formation of NBD acetylation products.

Thus, in a catalytic system based on palladium acetate and PPh_3, phosphine molecules, having a higher affinity for palladium, are initially coordinated. After that, intermediates are formed into which the AF molecule is embedded. This is followed by the coordination and implementation of the NBD molecule. The process ends with the transfer of acetyl moieties to NBD. After that, palladium intermediates containing an NBD molecule, as well as allyl and formyl fragments, are again formed.

Acetonitrile or phosphine ligands stabilize the palladium complexes formed after the formation of the C–C bond (^{31}P = 23.14 ppm), occupying the coordination sites released during the reaction. The ligand present in the coordination sphere actively participates in the process. Its properties affect the directions of interaction between AF and NBD, leading to products of various structures.

In the case of η^2-*exo*-coordination of NBD, only one site for the ligand is vacant in the intermediate, which is confirmed by experiments with bi- and tridentate ligands. Thus, when diphenylphosinomethane (dppm), diphenylphosinoethane (dppe), diphenylphosinopropane (dppp), diphenylphosphinobutane (dppb), and terpyridine (terpy) are used, only the corresponding palladium complexes are formed regardless of the temperature and type of solvent [34]. Although these reactions are accompanied by a color change and/or precipitation, no catalytic transformations are observed (Fig. 6).

The described facts confirm the square-planar configuration of palladium complexes throughout the entire reaction, indicating that the chelate ligand, occupying two coordination sites on the palladium atom, blocks the further course of the reaction.

The catalytic cycle is accompanied by the regeneration of various Pd^0 complexes with phosphine or NBD in the coordination sphere. As the reagents are consumed, they are accumulated. With an excess of NBD at the end of the process, its cyclodimerization is possible.

From the obtained data, it becomes clear why it is not possible to radically change the ratio of products **1**–**3** in nonpolar media by varying the amount of PPh_3 in the allylation reaction of NBD with AF. Based on the available ideas, for this purpose, an approach was taken to use sterically bulky tertiary phosphines. Such phosphines can facilitate the oxidative addition of the substrate to palladium, which, due to their structure, then affects other stages. Oxidative addition is accelerated by ligands with strong electron-donating properties, which increase the electron density at the metal center. This effect is clearly manifested in reactions involving allylcarboxylates. Smaller ligands, such as PPh_3, can form active diphosphine complexes ($Pd(PR_3)_2$). In some cases, sterically bulky ligands promote β-hydride elimination, especially when this step is limiting.

It was concluded that phosphines with electron-withdrawing substituents promote the formation of NBD **1**–**3** oxidative allylation products. Such ligands facilitate β-hydride elimination involving the hydrogen atom of the NBN ring. The steric factor also plays an important role in the process. Thus, the use of ligands with a small cone angle ($\theta < 145°$) causes β-hydride elimination in the formyl fragment with the formation of propene. Bulky ligands direct the process towards the production of NBD allylation products. However, it should be taken into account that an excessively large value of the phosphine cone angle, for example, in the case of trimesitylphosphine ($P(Mes)_3$) with $\theta > 212°$, leads to inhibition of the reaction, probably due to steric hindrances arising in the coordination of substrates.

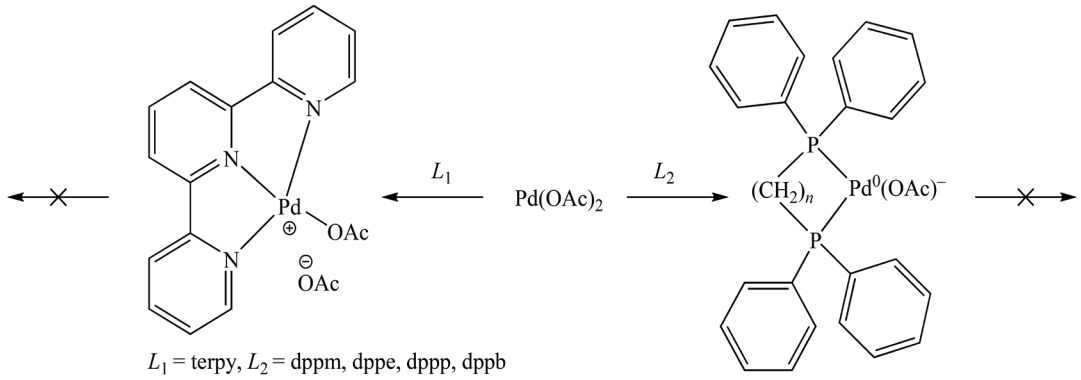


Fig. 6. Palladium complexes with polydentate ligands.

Thus, the best rates of conversion and selectivity for products **1**–**3** are achieved when using phosphines with a conical angle θ close to 145°, whose electronic parameters are higher than 2065 cm^{-1}, to achieve a selectivity of more than 65% in obtaining isomer **1** and maintaining a high catalyst activity.

Interesting information was obtained using isotopically substituted AFs with different degrees of substitution of protium for deuterium [35] (Fig. 7).

An analysis of the mass spectra of the products showed that the use of AF with a deuterated label in the formyl group resulted in the formation of allylation products **1**–**3**, **4**, and **4-D$_1$** with molecular weights of 132, 134, and 135, respectively. For AF deuterated at the allyl moiety, the masses of products **1-D$_5$**, **2-D$_4$**, **3-D$_4$**, and **4-D$_5$** of single allylation are 137, 136, 136, and 139. Using fully deuterated AF gives products **1-D$_5$**, **2-D$_4$**, **3-D$_4$**, and **4-D$_6$** with molecular weights 137, 136, 136, and 140. Depending on the composition of the deuterated AF, isomers of compounds **1** and **4** are formed in small amounts, namely: **1'**, **1'-D$_5$**, **4'**, **4'-D$_1$**, **4'-D$_5$**, **4'-D$_6$**. For compound **2**, these are derivatives **2'** and **2'-D$_4$**, probably formed as a result of double bond migration. Compound **15** and its deuterated analogues **5-D$_1$**, **5-D$_5$**, and **5-D$_6$** were discovered for the first time (Fig. 8). Small amounts of C_3H_6, C_3H_5D, C_3HD_5, and C_3D_6 propene are also formed, whose composition depends on the AF structure.

A number of important conclusions can be formulated according to a structural analysis of the products as follows:

1. The products of catalytic reactions and the position of deuterium atoms in them are similar to the compounds obtained by the stoichiometric interaction of NBD with deuterium-substituted bis(η^3-allyl)nickel.

2. The structure of all NBD **1**–**3** oxidative allylation products is the same for various allylating agents, as well as for nickel and palladium.

3. The reductive NBD allylation product **4** in the catalytic version is formed only when AF and palladium complexes are used. This compound

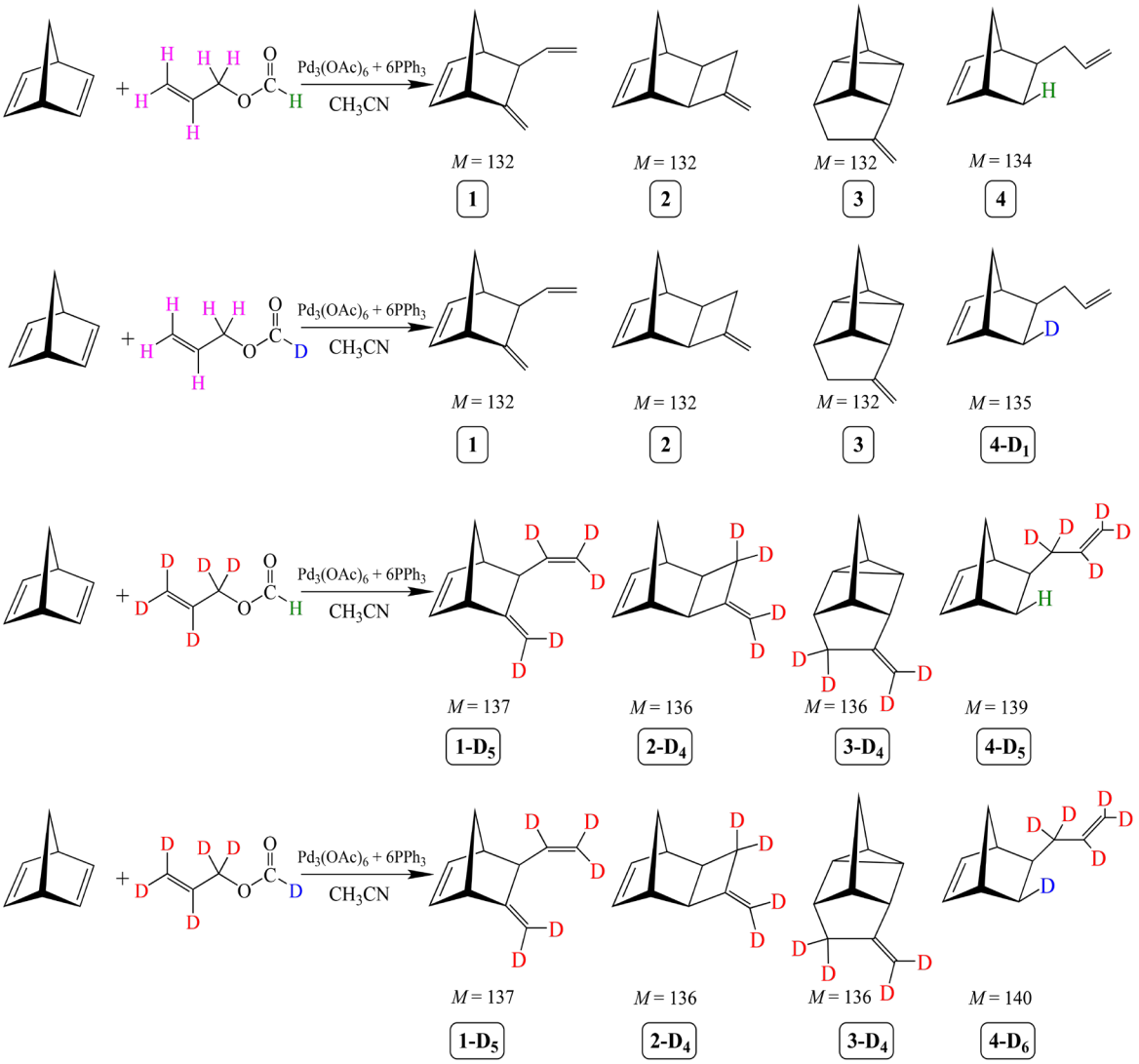


Fig. 7. Catalytic NBD allylation under the action of the $Pd_3(OAc)_6$+6PPh_3 system using a series of isotopically substituted allyl formats.

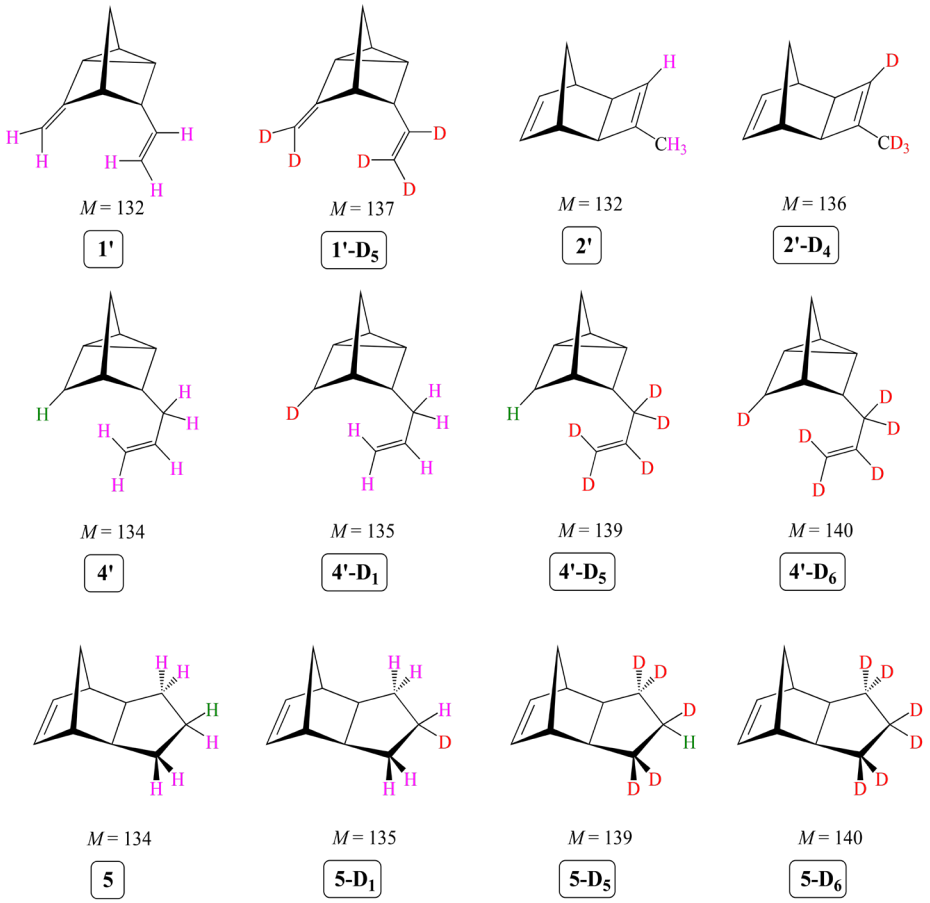


Fig. 8. Structure of side-produced analogs of NBD allylation products.

is also observed in the stoichiometric interaction of NBD with homoligand allyl complexes of transition metals. The stereochemistry of compound **4** is determined by the *exo* direction of attack of the hydride transfer and allyl with respect to the NBN ring.

4. The direction of hydride transfer for all products, which is of a general nature, is associated with the breaking of the C–H β-bond with respect to the metal atom. This stage can proceed with the participation of allyl, norbornenyl, or formyl fragments.

5. The formation of products **1** and **5** suggests the formation of an intermediate with the cyclopentane fragment and the presence of formyl hydrogen in the palladium complex.

6. Compounds **1'**, **3**, **3'**, **4'**, and their deuterated analogs are formed as a result of η^4-coordination of NBD on the palladium atom, which activates the second double bond in the molecule and leads to nortricyclane products.

7. Compounds **2** and **3** are formed as a result of the rearrangement of the allyl fragment at the stages of [2+2]- or [2+4]-addition.

8. The formation of isomers **2'** and **3'** occurs as a result of double-bond migration in the allyl fragment coordinated on the palladium atom at the stage of β-hydride transfer.

9. The formyl fragment is retained in the coordination sphere of the palladium complex throughout the entire catalytic cycle up to the stage of β-hydride transfer, whose direction determines the structure and ratio of products (Fig. 9).

The information obtained with the use of deutero-substituted AFs is still insufficient for discussing the nature of the rate-limiting step. Given the variability of hydride transfer, the rate-determining steps may differ for products **1**–**4**. Therefore, additional kinetic studies were carried out with AF-D_1 deuterated at the formyl group. The first series of experiments consisted of the combined use of AF and AF-D_1 to create competitive conditions. The kinetic isotope effect (KIE) was estimated by comparing the concentrations of products **4** and its deuterated analog **4-D_1**, which are formed in parallel using the $Pd_3(OAc)_6$ catalytic system and using the same amounts of AF and AF-D_1. Assuming that the reaction mechanism does not change for different isotopes, the formation of products **4** and **4-D_1** should

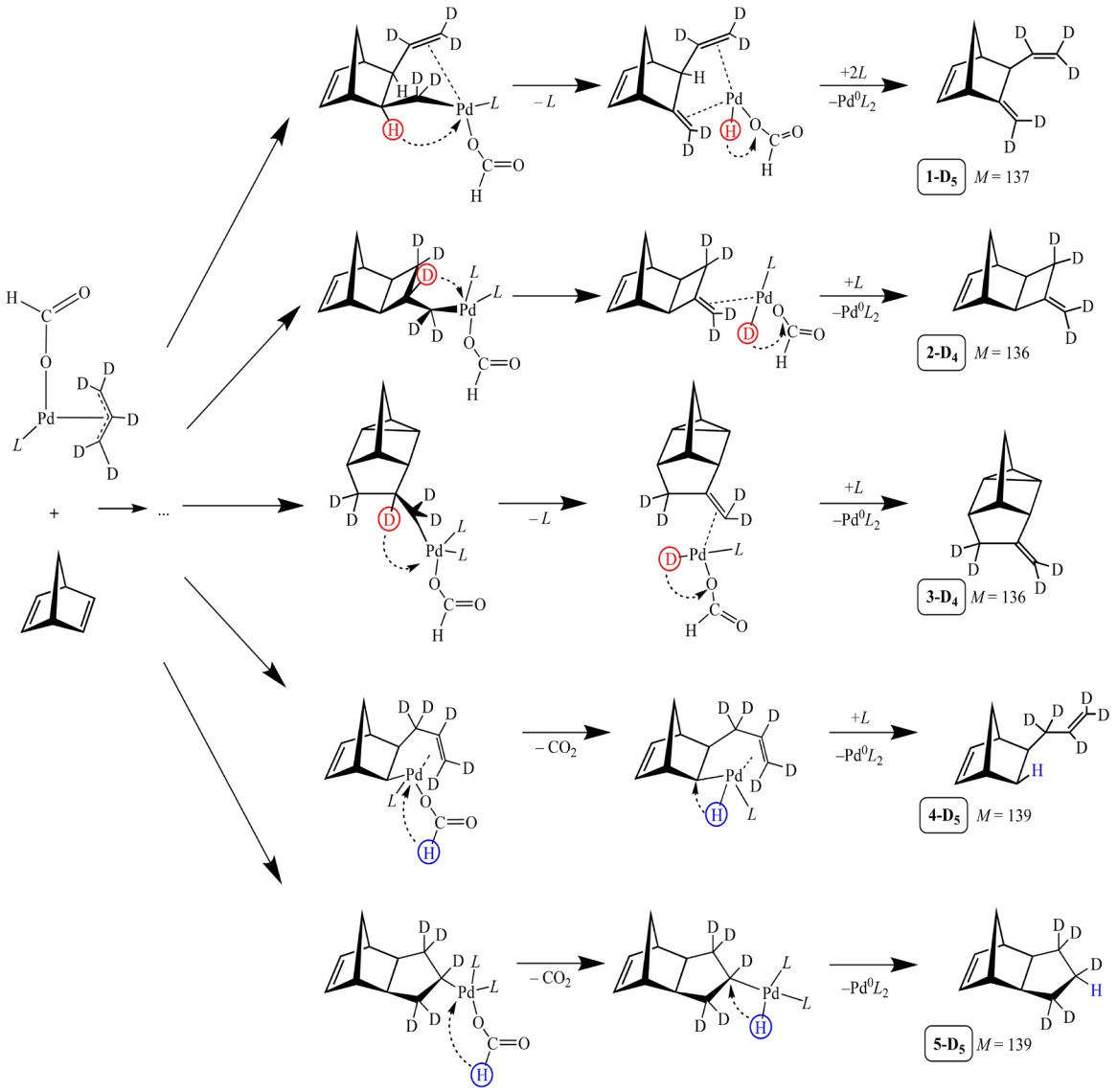


Fig. 9. Options for the direction of the β-hydride transfer step for key intermediates in the catalytic NBD allylation reaction.

have the same kinetic description. Then the ratio of the concentrations of the products will be constant in time and equal to the ratio of the observed rate constants.

The second series of experiments involving AF and AF-D_1 was carried out separately under identical conditions, minimizing the formation of by-products. For this, AF was taken in deficiency (10%) in relation to NBD. Taking into account the low reaction rate at 25°C, the concentrations of the products were similarly determined at low conversions of the reagents (not higher than 5%). The time was counted after the end of the induction period (Fig. 10).

The KIE values obtained in two series of experiments completely coincide: $K_{KIE} = 2.2 \pm 0.2$. A rather high KIE value excludes isotope insensitive steps, such as trans-metalation and product dissociation, from consideration [36]. It is very likely that the formation of a C–H bond (β-hydride transfer or reductive elimination) occurs at the limiting stage of the process. The assumption of β-hydride transfer as a limiting step in the catalytic cycle of the NBD hydroallylation mechanism was also considered in our theoretical works [37].

Thus, all compounds formed during NBD allylation can formally be considered as NBD adducts with [C_3H_4], [C_3H_6], [H], and [COOH] fragments. The source of these hypothetical particles or molecules are the allyl fragments and the formyl group, which are originally part of the AF. For the reaction to proceed, it is necessary that allyl derivatives (All–*X*) with an activated All–*X* bond oxidatively add to Pd^0 complexes to form an

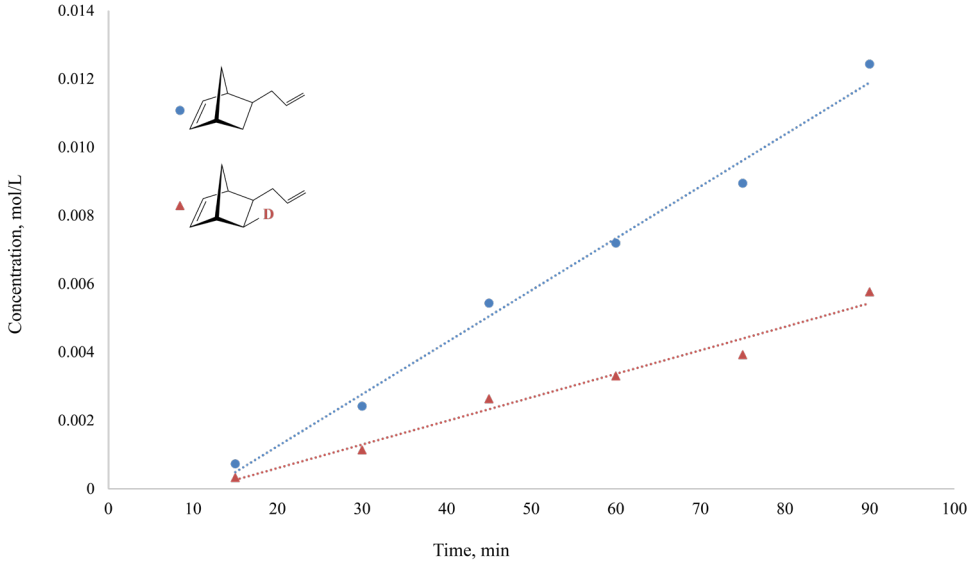


Fig. 10. Time dependence of the ratio of NBD **4** and **4-D**$_1$ hydroallylation products.

allyl-palladium intermediate. Then the NBD molecule is coordinated on the metal atom, causing η^3–η^1 isomerization of the allyl ligand, and is introduced into the η^1-allyl–metal bond. The different directions of cyclization occurring in the resulting intermediate depend on the type of the ligand coordinated on the palladium atom. The catalytic cycle is completed with β-hydride transfer, product formation, and regeneration of Pd^0L_2 particles. Here, hydride transfer can proceed in different directions.

The totality of our experimental data suggests a consistent mechanism of the process that explains the formation of all NBD allylation products when AF is used as an allylating agent (Figs. 11 and 12).

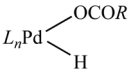
The formation of secondary NBD allylation products occurs according to a similar mechanism. The substrates are mono-adducts containing an active intracyclic NBN bond capable of being coordinated on the palladium atom in the allyl complex (Fig. 12). The yield of products depends on the activity of the double bond in the corresponding mono-adduct. Since in this case the η^4-coordination of the reagents is impossible, no products having a nortricyclane structure are formed.

The reduction of double bonds is probably associated with the formation of formic acid, which acts as a hydrogenating agent in the reaction mixture. One of the possible ways of its decomposition in the presence of a palladium catalyst is associated with the formation of carbon dioxide and hydrogen. These assumptions were confirmed by an analysis of the gas phase in the reactor attesting to the formation of carbon dioxide. Additional experiments testify to the stability of the catalytic system under study. The resulting formic acid enters into further transformations without having a deactivating effect, probably due to its decomposition on palladium (6).

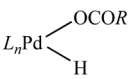
$$HCOOH \xrightarrow{[Pd]} CO_2 + 2[H] \qquad (6)$$

This transformation is associated with the formation of a certain amount of NBD hydrogenation products. Thus, under the conditions of the process, AF simultaneously acts as an allylating and hydrogenating agent.

In accordance with the mechanism (Fig. 12), the formation of compounds **1**–**3** in the presence of AF proceeds similarly to other allyl ethers. The key role in the formation of hydrogenation and hydroformylation products of NBD and compounds **1**–**4** is played by the hydride complex formed at the stage



of β-hydride transfer. For all *R* that are alkyl or aryl radicals, the decomposition of this intermediate as a result of reductive elimination leads to the formation of the acid *R*COOH. In the case of *R* = H, however, the situation is fundamentally different. All directions are implemented simultaneously, their ratio depends on many factors, including NBD conversion. It can be assumed that the complex



is involved in the following transformations (Fig. 13 and 14).

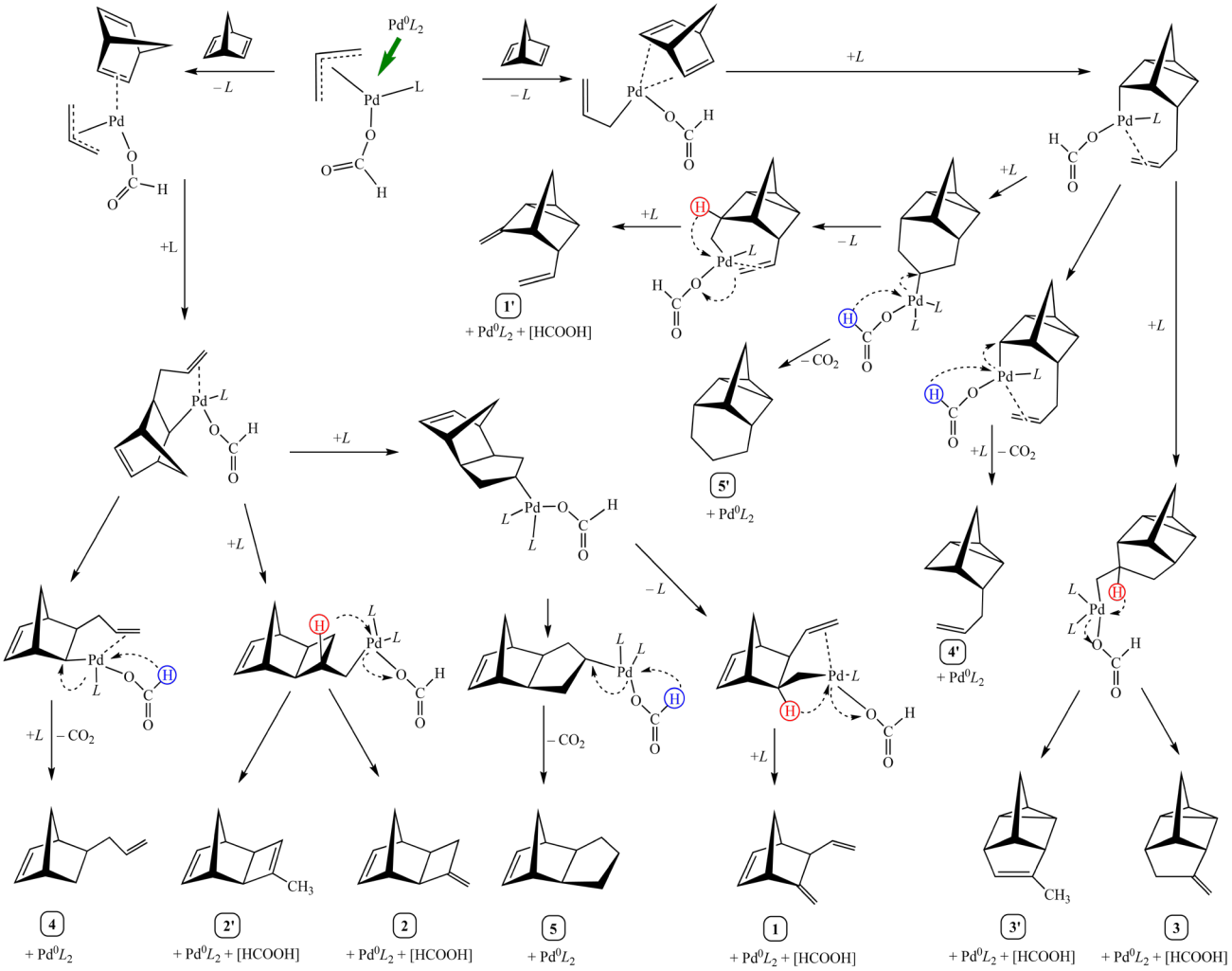


Fig. 11. Mechanism of catalytic NBD allylation with allyl formate on palladium catalysts.

Based on the totality of the data obtained, and taking into account the previously proposed reaction mechanisms for palladium and nickel catalytic systems, it is shown that palladium complexes can be effectively used to develop and vary the composition of a catalytic system, as well as the conditions of its operation, to achieve high values of the conversion of the reagents for the selective preparation of compounds **1** and **4**. At the same time, the efficient preparation of products **2** and **3** is possible only in the case of the use of nickel catalysts having a different coordination polyhedron and broader possibilities for coordinating additional molecules of phosphorus-containing ligands. This understanding of the catalytic NBD allylation mechanism was used to inform the first successful prototypes of heterogeneous catalysts based on the immobilization of metal complexes on various supports with the preservation of the structure of active sites in the selective preparation of products **1**–**4** [38].

QUANTUM-CHEMICAL SIMULATION OF NBD ALLYLATION

In addition to experimental research carried out at the Ya.K. Syrkin Department of Physical Chemistry, theoretical studies of reactions involving NBD have been undertaken, in particular, concerning oxidative and reductive NBD allylation with AF. Quantum-chemical modeling was used in a number of cases to explain the experimental facts, clarify the reaction mechanism, identify key stages and intermediates, as well as to predict the effect of chiral ligands on the enantioselectivity of NBD allylation.

The calculations were performed in the scalar-relativistic approximation of the density functional theory (DFT) using the Priroda [39, 40] and ORCA 5.0.3 [41, 42] programs. Geometry optimization of all reactants, products, transition states (TS), and intermediates was carried out in the

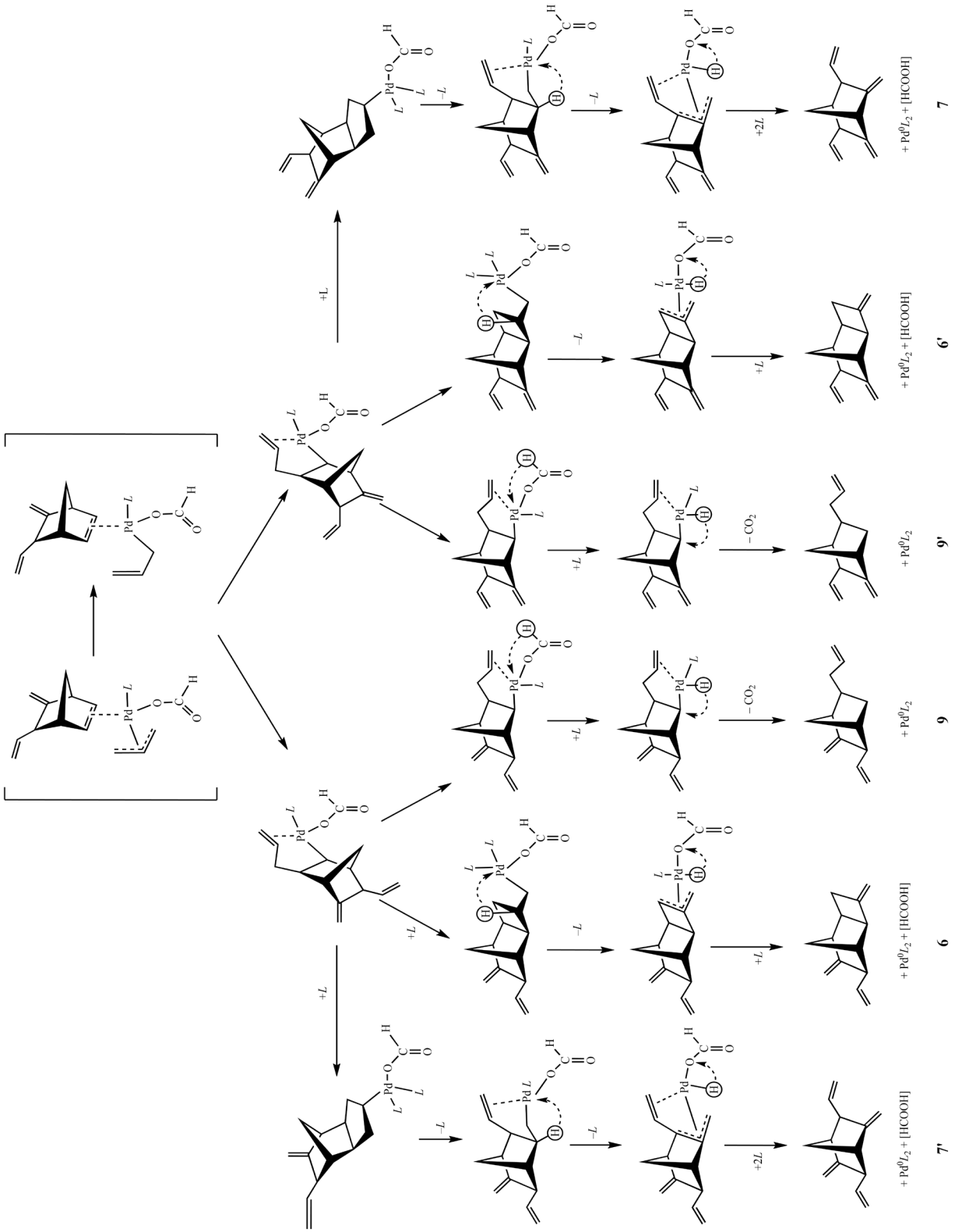


Fig. 12. Mechanism of formation of double NBD allylation products.

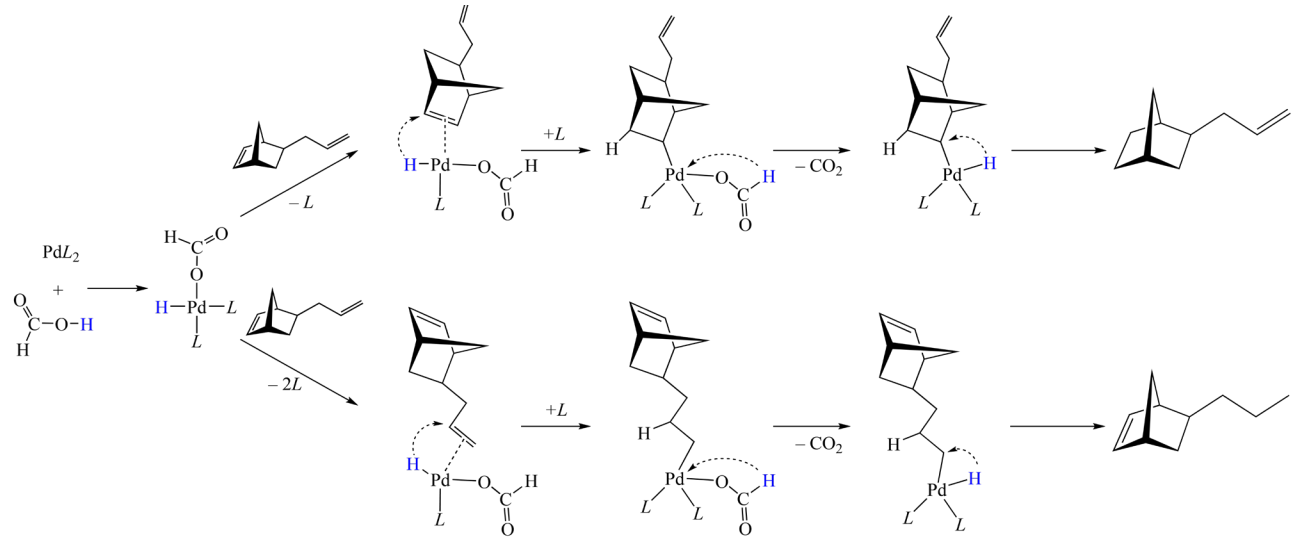


Fig. 13. Mechanism of formation of NBD allylation product with simultaneous hydrogenation.

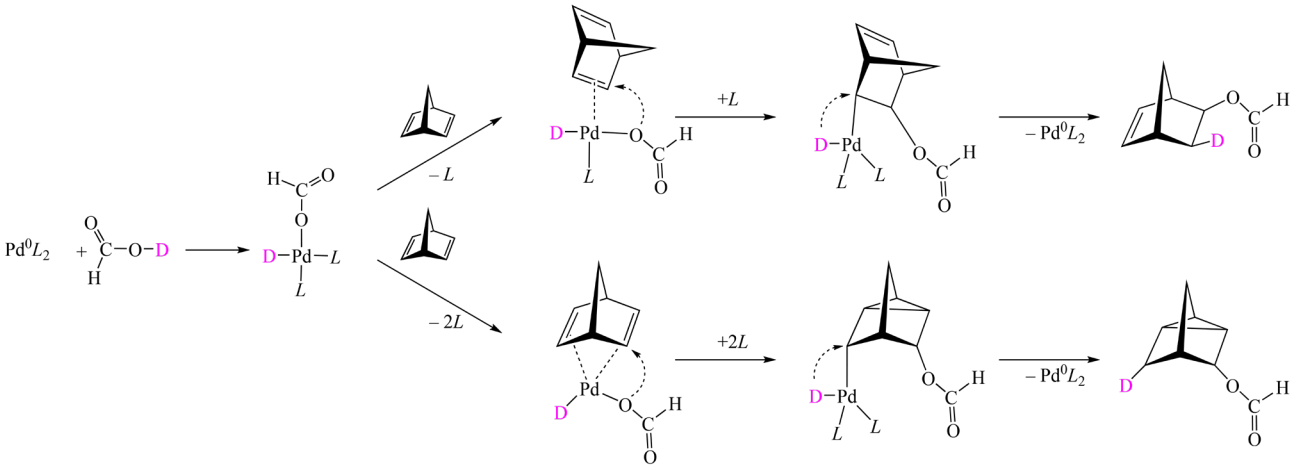


Fig. 14. Mechanism of formation of NBD hydroformylation products.

PBE[3] exchange-correlation functional [43] to set the full-electron L11[4] basis [44]. The calculations described in the section on evaluating enantioselectivity were further refined in the ωB97X-D3(BJ)[5] long-range-corrected hybrid functional [45] and the ZORA-def2-TZVP[6] all-electron basis [46] for P, O, C, H, and SARC-ZORA-TZVP[7] [47] for Pd. The correspondence of the optimized structures to minima or TS was confirmed by analysis of vibration frequencies. To check the relationship of localized TSs with the products and reagents of the stage, the internal reaction coordinate (IRC) was calculated. Thermodynamic parameters were calculated for 25°C. Corrections to solvation energies were obtained within the PCM-SMD[8] model [48] for acetonitrile (ε = 35.7).

[3] PBE is Perdew-Burke-Ernzerhof exchange-correlation functional.

[4] L11 is all electron double zeta basis set, built according to the type of correlation-consistent polarization valence-split Dunning basis set cc-pCVDZ.

[5] ωB97X-D3(BJ) is hybrid exchange-correlation functional corrected for long-range interaction with the inclusion of Grimme dispersion corrections.

[6] ZORA-def2-TZVP is valence triple zeta polarization basis set for calculations in zero regular approximation (ZORA).

[7] SARC-ZORA-TZVP is valence triple zeta polarization basis set for calculations in zero regular approximation (ZORA) taking into account relativistic corrections for heavy elements.

[8] PCM-SMD is Polarizable Continuum Model and Solvation Model of Density.

In a phosphine-free catalytic system with a high selectivity of up to 95% [21], the product of reductive NBD allylation with 5-allyl-2-norbornene AF (**4**) is formed. Quantum-chemical calculations made it possible to identify two most probable routes for the formation of product **4**. Figure 15 shows the results of modeling the mechanism of reductive allylation for two types of NBD coordination aimed at elucidating the stereostructure of the product.

The initial stages of the mechanism are associated with the formation of catalytically active Pd(AF)(CH_3CN) (**H1**) and Pd(AF)(NBD) (**H2**, **H3**) complexes from Pd(CH_3CN)$_3$ and AF and NBD molecules. This is followed by the stage of oxidative addition (**H2→H4**, **H3→H5**), which, as shown by calculations [49], can have two TSs. The difference between them lies in the number of atoms involved in the TS formation. In one TS, one O atom is involved, while in the other, more preferably, both O atoms are involved.

Since an intramolecular change in the η^2-*exo*/η^2-*endo* orientation of the NBD ligand is impossible, the stereostructure of the product is predetermined at the stage of NBD coordination on the Pd atom: *exo* (**4**) or *endo* (**4'**).

This is followed by the formation of a C–C bond between the allyl ligand and NBD (**H4→H6**, **H5→H7**), which is associated with a noticeable decrease in the Gibbs free energy of the system. This stage is also characterized by the highest activation energy over the entire reaction path: 22.1 and 23.9 kcal/mol, respectively, for the routes of formation of products **4'** and **4**. Taking into account the possibility of isomerizing the **H5** complex into the more stable **H5.1**, the activation energy of the route of product **4'** formation will be equal to 24.8 kcal/mol, which exceeds the energy for **4** by 0.9 kcal/mol. Taking into account the solvation energy, the energy difference between the energies of the rate-determining TSs decreases to 0.1 kcal/mol, indicating the possibility of observing a mixture of stereoisomers **4** and **4'**.

Subsequent steps involve hydride transfers (**H8→H10→H12** and **H9→H11→H13**) from the formate ligand to the Pd atom and back from the Pd atom to the allylnorbornene derivative. As in the case of the stage of C–C bond formation, the stages of hydride transfer involving the *exo*- and *endo*- NBN fragment have similar activation energies. At the final stage, the formed product is

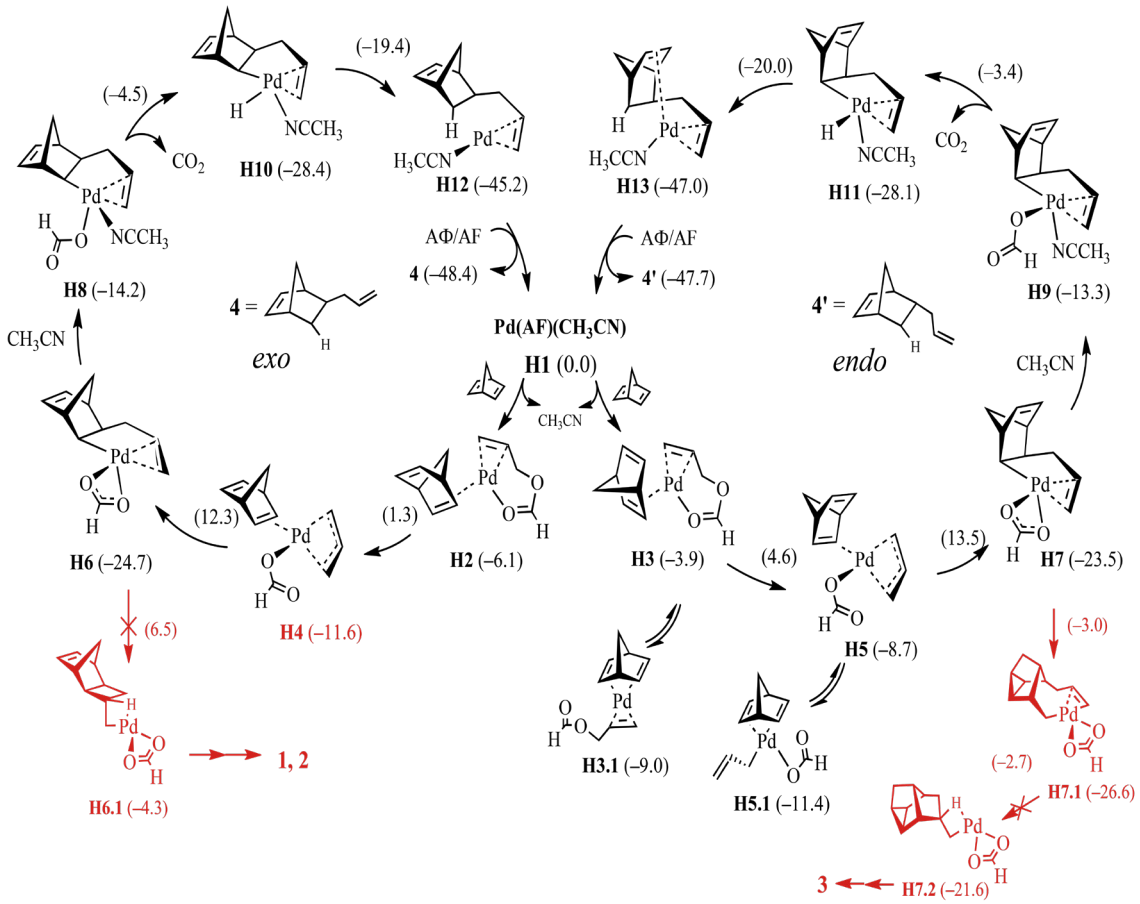


Fig. 15. Catalytic cycles for the formation of stereoisomers of 5-allyl-2-norbornene **4** and **4'**. Gibbs energies are indicated in parentheses (ΔG_{298}, $\Delta G^{\neq}_{298}$, kcal/mol).

replaced by an AF molecule to form a catalytically active complex **H1**, which is returned to the next catalytic cycle.

Detailed quantum chemical calculations do not rule out an alternative route for the formation of *exo*-product **4**, in which β-hydride elimination precedes the stage of C–C bond formation (mechanism **B**, Fig. 16). Mechanism **B** branches off immediately after the oxidative addition step. As a result of the C–H bond cleavage in the formate ligand in **H14**, a hydride intermediate **H15** is formed, which can be converted along the following route: first, the C–C bond is formed (**H15→H16**), then the CH_3CN molecule is added (**H16→H10**), then hydride transfer occurs with a Pd atom to the NBD fragment (**H10→H12**) and, finally, the product is cleaved off.

As in the case of mechanism **A**, the maximum activation barrier to the reaction proceeding via mechanism **B** is at the stage of C–C bond formation. Allowing for solvation within the framework of SMD and the inclusion of two solvent molecules (acetonitrile) leads to activation energies of this stage equal to 21.0 and 20.8 kcal/mol for routes **A** and **B**, respectively. Thus, according to the results of theoretical studies, product **4** is formed via two routes with almost equal contributions to the reaction mechanism (Fig. 16).

Quantum-chemical calculations were carried out to clarify the nature of the KIE manifested in this reaction. The experimental estimate of the KIE [36] of allylation is 2.2, possibly indicating that the stage of C–H bond cleavage during hydride transfer is rate-determining. However, according to the quantum chemical calculation data [50], the KIE should be significantly larger than 4.7 in this case. The difference is explained by the fact that, according to [51], the KIE depends not only on the rate constant (k) of the rate-determining stage (which, according to calculations, is the C–C bond cleavage stage, but in this case, KIE = ~1), but also on k stage preceding or following the rate-determining. In both mechanisms, the stage of hydride transfer from the formyl ligand is irreversible; in this case, the experimentally observed value of KIE is an average value determined by k stages of C–H and C–C bond cleavage.

The high selectivity for product **4** in the phosphine-free system can be explained by kinetic obstacles ($\Delta\Delta G^{\neq}_{298}$ = 24–31 kcal/mol) during the formation of subsequent C–C bonds (**H6→H6.1** and **H7→H7.1→H7.2**) required to obtain allylation products **1**–**3**. In the presence of phosphines, in particular PPh_3, the activation barriers of this stage are noticeably lowered to form all possible products **1**–**4**.

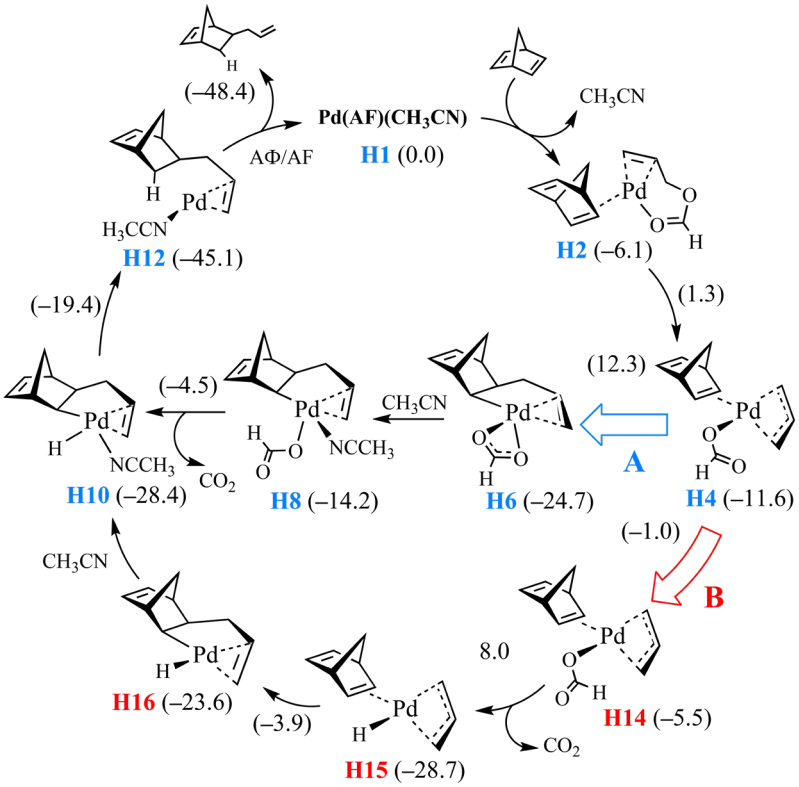


Fig. 16. Routes of formation of *exo*-5-allyl-2-norbornene (**4**) according to mechanisms **A** and **B**. Gibbs energies (ΔG_{298}, $\Delta G^{\neq}_{298}$, kcal/mol) relative to **H1** are given in parentheses.

The performed quantum-mechanical calculations of the stability of compounds **2** and **3** and their isomeric analogs show that isomer **2'** is thermodynamically preferable to isomer **2** by 0.73 kcal/mol ($\Delta G°_{298}$). Isomer **3** is thermodynamically preferable to **3'** by 1.27 kcal/mol ($\Delta G°_{298}$). This conclusion is in complete agreement with the yields of these isomers for phosphine-free systems. However, the real yield of compound **2** increases with the introduction of phosphine into the system, which indicates the influence of kinetic factors.

Figure 17 shows the mechanism of formation of product **3**. $Pd(\eta^2\text{-}C_3H_5COOH)(PPh_3)_2$ (**A1**) can be considered as a catalytically active complex. As a result of the oxidative addition steps (**A2→A3**) and NBD coordination, the key intermediate $Pd(\eta^2\text{-}endo\text{-}NBD)(C_3H_5)(OCOH)$ (**A4**) is formed. Since NBD coordination predetermines the stereostructure of the product, further transformations of intermediate **A4** lead to *endo*-structure product **3**.

The structure of product **3** suggests the sequential formation of three C–C bonds. Various routes of formation of the first and subsequent carbon bonds are considered. In the case of preliminary η^2/η^4 isomerization of the NBD ligand and addition of the PPh_3 ligand, the activation energy for the formation of the first C–C bond turns out to be the lowest possible (**A5→A6**, $\Delta G^{\neq}_{298}$ = 25.4 kcal/mol). Alternative routes for the formation of the first C–C bond are associated with overcoming much higher activation barriers. Therefore, the C–C bond between the allyl and NBD ligands is formed first.

The lowest energy, and therefore the most probable route for the formation of the second C–C bond is associated with the formation of a cyclopropane fragment in the NBN derivative (**A6→A7**). The stage is characterized by a noticeable activation barrier ($\Delta\Delta G^{\neq}_{298}$) of 18.7 kcal/mol, but also accompanied by a noticeable decrease in energy. The presence of the PPh_3 ligand in the Pd coordination sphere noticeably lowers the activation barrier during the formation of the third C–C bond, which leads to the formation of the cyclopentane fragment (**A7→A8**). For example, this stage for the phosphine and phosphine-free systems is characterized by an activation barrier of 14.0 and 23.9 kcal/mol, respectively [52].

An interesting feature of this route is the formation of intermediate **A9** with C–H agostic interaction with Pd. At the final stages, the *endo*-allylation product **3** and the HCOOH molecule are eliminated by adding PPh_3 and AF molecules. Thus, the **A1** complex is returned to the catalytic cycle.

Figure 18 shows the mechanism of formation of the reductive allylation product **4** in the presence of phosphines. Of the allylation mechanisms in the presence of PPh_3, mechanism **A** is the most probable. However, in contrast to the previously described mechanism **A**, the formation of a C–C bond occurs in the presence of phosphine between the η^1-allylic and NBD ligands. This is facilitated by the preliminary coordination of PPh_3 and $\eta^3\text{-}\eta^1$ isomerization of the allyl groups (**A11→A12→A13**). Further hydride transfers (**A13→A17→A18**) proceed with sufficiently low activation barriers to form product **4** and CO_2.

Intermediate **A13**, which is formed in the route of formation of product **4**, is the key one in relation to the regioselectivity of the allylation reaction. Its various transformations lead either to the reductive allylation product **4** or to the oxidative

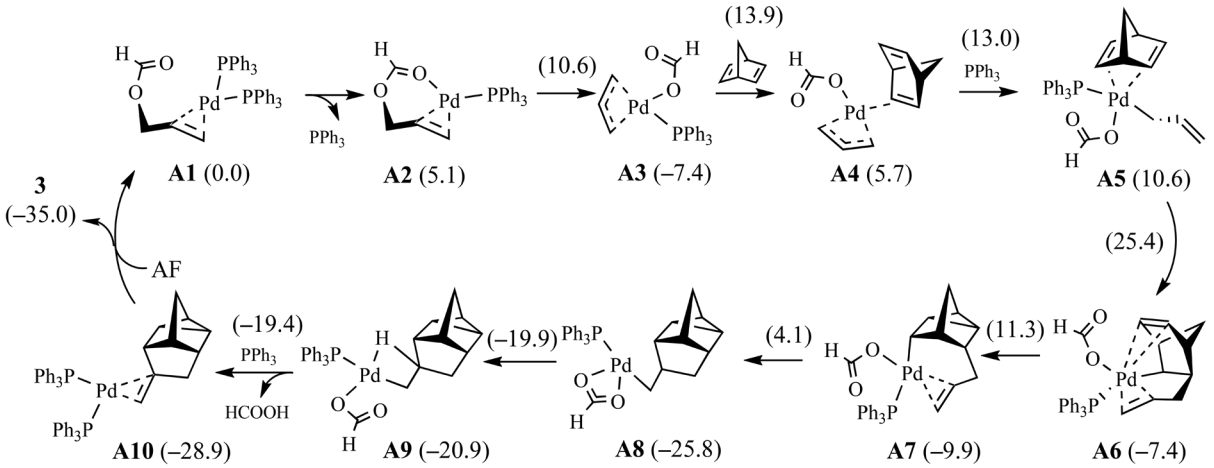


Fig. 17. Mechanism of formation of NBD *endo*-allylation product with indication of key intermediates. The Gibbs energies (ΔG_{298}, $\Delta G^{\neq}_{298}$, kcal/mol) relative to **A1** are given in parentheses.

allylation products **1** and **2**. The latter are obtained during the formation of the second C–C bond with the formation of an NBN derivative with a four-membered cyclic fragment (**A14**). Thus, it is due to the presence of phosphine that the activation barrier of this transformation noticeably decreases ($\Delta G^{\neq}_{298}$ = 12.6 kcal/mol).

Another important key intermediate, **A14**, determines the selectivity of the reaction with respect to products **1** and **2**. Depending on the bond being broken, C–H or C–C, product **1** or **2** is formed, respectively, ($\Delta\Delta G^{\neq}_{298}$ = 4.5 kcal/mol), but subject to the preliminary formation of the **A15** agostic complex.

An additional route for **A14** transformation leads to product **1**. A specific feature of the formation of **1** is the need to break the C–C bond in the $C_7H_8C_3H_5$ fragment. Detailed quantum chemical calculations made it possible to explain the mechanism of this transformation, which proceeds via the mechanism of β-carbon elimination. The most probable cause is the cleavage of the bond in the methylenecyclobutane fragment of intermediate **A14**. In this case, C–C cleavage and the formation of new Pd–C bonds occur in one stage, i.e., consistent with an activation barrier of 20.0 kcal/mol. The subsequent stages of the mechanism for the formation of product **1** are associated with intramolecular isomerization and hydride transfer from the NBN derivative to the formate ligand without the direct involvement of the Pd atom (**A19→A20**). Closing of the catalytic cycle occurs when the reaction products are replaced by PPh_3 and AF molecules.

At all key stages of the reaction, the coordination sphere of the metal contains no more than one PPh_3 molecule. This is due to a significant increase in the Gibbs energy of the system upon coordination of the second phosphine molecule due to steric repulsions within the complex. Therefore, there will be no direct correlation between the ratio of phosphines and the selectivity of the formation of allylation products. This explains the weaker effect of the P/Pd molar ratio on the reaction selectivity compared to the Ni-containing catalytic system [25].

In the final part, we present the results of theoretical modeling of the enantioselective sensitivity of NBD allylation. Each of products **1**–**4** has enantiomers due to the presence of chiral centers. Due to the fact that one of the coordination sites in the reagent of the stage of formation of the first C–C bond (Fig. 19) is occupied by a phosphine ligand, it is logical to assume that the structure of this phosphine affects the enantioselectivity of allylation.

Our calculations [53] used four model phosphines: methylisopropylphenylphosphine PPh(*i*Pr)(Me), isopropylisobutylphenylphosphine PPh(*i*Bu)(*i*Pr), methylisopropylisobutylphosphine P(*i*Bu)(*i*Pr)(Me), and cyclohexylphenyl(*p*-tolyl)phosphine P(*p*-Tol)(Cy)(Ph).

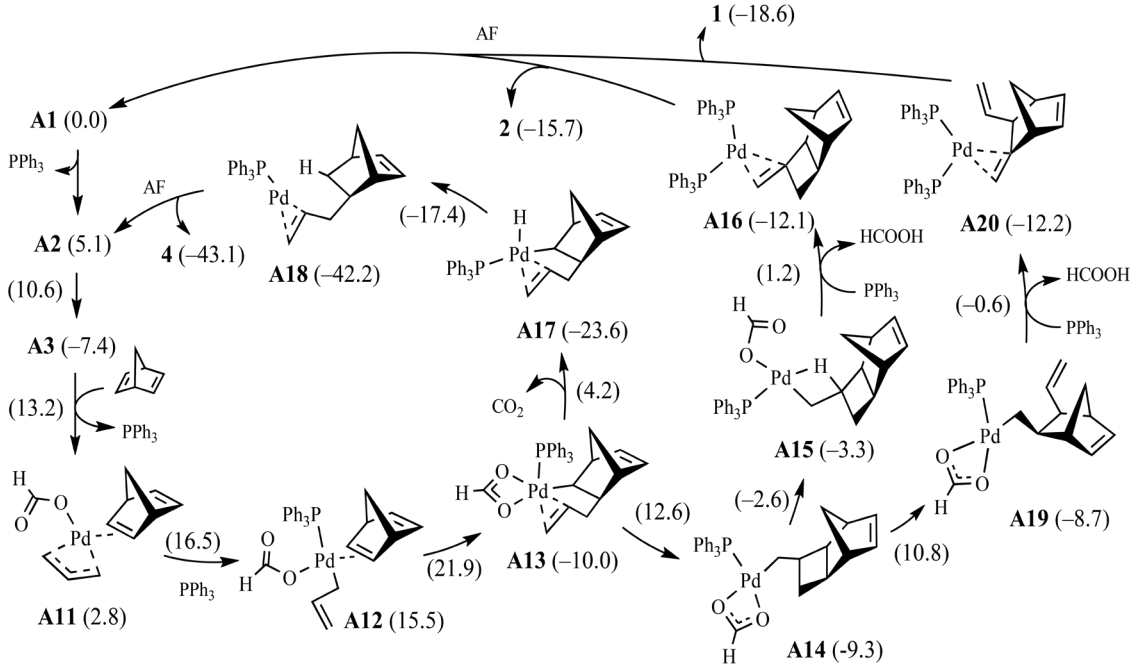


Fig. 18. Mechanism of formation of NBD *exo*-allylation product with indication of key intermediates. he Gibbs energies (ΔG_{298}, $\Delta G^{\neq}_{298}$, kcal/mol) relative to **A1** are given in parentheses.

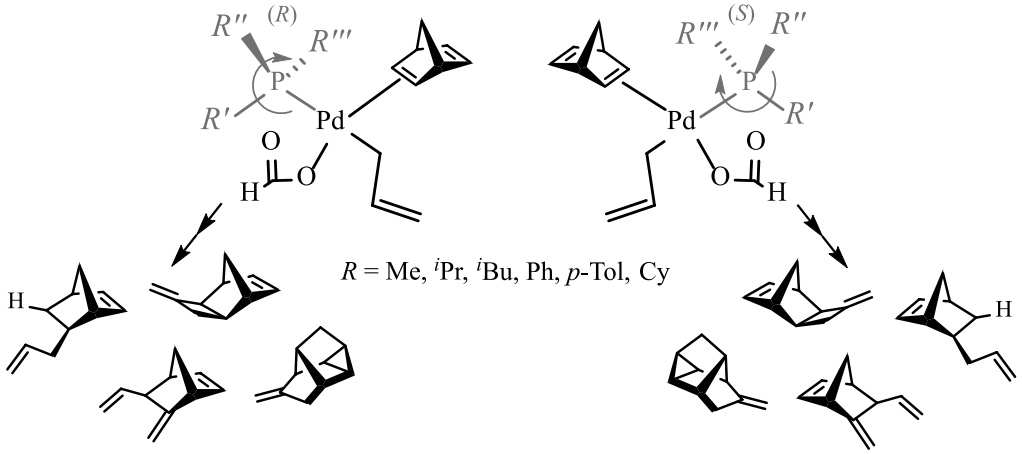


Fig. 19. Structure of enantiomers of allylation products (**1–4**) depending on the nature of the phosphine ligand in the reagent of the stage of formation of the first C–C bond.

Table. Theoretical evaluation of the regio- and enantioselectivity of NBD allylation in the presence of chiral phosphines

Phosphine	Ratio of regioisomers, %		Ratio of enantiomers, %	
	exo	*endo*	*exo*	*endo*
PPh_3	81	19	50:50	50:50
PPh(^{t}Bu)(^{i}Pr)	99.7	0.3	91:9	91:9
PPh(^{i}Pr)Me	99	1	98:2	98:2
P(^{t}Bu)(^{i}Pr)Me	93/99.9*	7/0.1*	19:81	94:6
P(*p*-Tol)(Cy)(Ph)	18/80*	82/20*	96:4	60:40

*depending on the configuration of the initial phosphine.

Since the enantiomeric excess is associated with the difference in the energies of TSs with different (*R*/*S*) configurations of the phosphine, the presence of only one aryl group in the chiral phosphine is desirable. According to the table, two aryl groups or their absence leads to a decrease in the enantiomeric excess. The calculations performed predict the fundamental possibility of obtaining enantiomerically pure NBN derivatives.

CONCLUSIONS

Until recently, the synthesis of carbocyclic compounds based on NBN and NBD was mainly carried out empirically by intuitive iterating of catalysts, ligand environment, and reaction conditions. Over the last 15–20 years, however, systematic studies of the kinetics and mechanisms of reactions involving NBN and NBD have begun, as well as the application of quantum chemistry methods for such objects and processes. The synergy between these intensively developing areas already now allows targeted development and optimization of reaction conditions to obtain individual products and materials having valuable properties. On the example of our research of the NBD allylation reaction, carried out in recent years at the Ya.K. Syrkin Department of Physical Chemistry of the M.V. Lomonosov Institute of Fine Chemical Technologies of RTU MIREA, the advantages

of the constant feedback between theoretical and experimental approaches have been demonstrated. We believe that the further development of such strategy will not only reduce the total cost and complexity of research into optimizing the total experimental cycle, but also help to develop a better and deeper understanding of the mechanisms of the investigating reactions. Using this strategy, for example, new homogeneous and heterogeneous catalytic systems based on nickel and palladium complexes have been already developed for the reactions of NBD allylation and hydroallylation, on which basis the conditions for the selective production of 5-allylnorbornene-2 and 5-methylene-6-vinylnorbornene-2 have been optimized. All the necessary prerequisites have been also created for optimization of methods and approaches in the direction of carrying out enantioselective syntheses of NBN derivatives. Obtaining compounds with enantiomeric purity will open up new possibilities for their application in medicine and polymer chemistry through the development of materials offering valuable properties. It also seems promising to continue research on the development of new heterogeneous catalytic systems that have undoubted technological advantages over homogeneous one.

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Authors' contributions

Sergey A. Durakov – search for publications on the topic of the review, analysis of literary sources, writing the text of the review on experimental studies of norbornadiene allylation;

Karen T. Egiazaryan – search for publications on the topic of the review, analysis of literary sources, writing the text of the review on quantum chemical studies of norbornadiene allylation;

Ravshan S. Shamsiev – systematization of publications, scientific and technical editing, design of bibliography and illustrative materials;

Vitaly R. Flid – conceptualization of the idea of the review, scientific editing of the work, critical evaluation of the article materials, formulation of conclusions.

The authors declare no conflicts of interest.

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