Nonconventional allylation of norbornene and norbornadiene derivatives: stoichiometry and catalysis

E. M. Evstigneeva and V. R. Flid★

M. V. Lomonosov Moscow State Academy of Fine Chemical Technology,
86 prosp. Vernadskogo, 119571 Moscow, Russian Federation.
Fax: +7 (495) 434 7111. E-mail: vitaly-flid@yandex.ru

The key trends for the development of catalytic reactions of allyllic esters of carboxylic acids with norbornene, norbornadiene, and their heterocyclic analogs in the presence of the nickel and palladium complexes are discussed. The main approaches to investigation of the mechanism using model stoichiometric reactions and quantum chemical calculations are described.

Key words: norbornene, norbornadiene, metal complexes, catalysis, palladium complexes, nickel complexes, clusters, allylation, allylic esters, ionic liquids.

The interaction of allylic carboxylates with norbornene (NBN) and norbornadiene (NBD) derivatives catalyzed by transition metal complexes (Scheme 1) has first been described for the reaction of NBN with allyl acetate[1] in the presence of $Ni[(P(OPr^i)_3]_4$.

Scheme 1
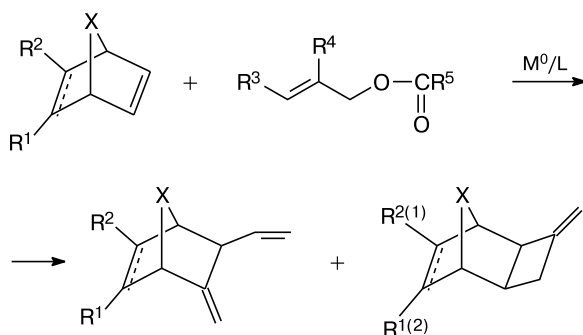
R^1 = H, Me, Me—CH=, H_2C=CH—, HC≡C; R^2 = H;
R^1, R^2 = *endo*-H_2C—CH=CH—, *endo*-C(O)—O—C(O); R^3, R^4 = H;
R^5 = H, Me, Bu^t, Ph, Alk; X = CH_2, O, NR^6, R^6 = H, 4-$MeC_6H_4SO_2$

The unique reaction products, which cannot be prepared using any other method, can contain several double bonds with different reactivities. This makes them valuable organic reagents and efficient additives with special properties. From the viewpoint of the mechanism, the reaction considered is also unusual, because the allylic fragment adds to the strained double bond *via* the nonconventional mode: the C—C bond is cleaved to form a methylidene vinyl derivative, or the product of formal [2+2] cycloaddition is formed.

It should be mentioned that the term "allylation"[1] applied to the given reaction (see Scheme 1) is not un-

questionable. This term does not reflect a diversity of transformations to which the allyl group is subjected during addition to the double bond of NBN or NBD. Nevertheless, the term seems applicable, because the key intermediate responsible for the course of the whole process is of the allylic nature. The term "nonconventional allylation" used in the present work reflects the unusual addition of the allylic group to the double bond.

The recent achievements in the synthetic area using the nonconventional allylation of NBN and NBD and experimental and theoretical studying its mechanism for model objects are reviewed here.

It is doubtless that the initial step of the catalytic cycle of the considered reaction (see Scheme 1) is the insertion of the double bond of an NBN or NBD derivative into the metal—carbon bond (Scheme 2). It has previously[2]

Scheme 2
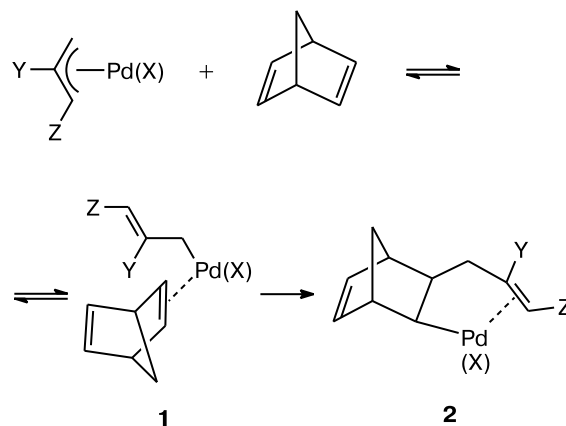
Y = H, Me; Z = H, Me; X is hexafluoroacetylacetonate

been shown that, after alkene was inserted into the bond of the metal with the carbon atom of the aryl or allylic ligand (complex **1**), the latter remained bound with the metal by the η^2-bond (complex **2**). Product **2** was characterized by ^{1}H NMR spectroscopy, mass spectrometry, and elemental analysis. When some ligands X are used, the step of formation of a cyclic complex can be reversible.[3] In the case of X = Hal, this equilibrium shifts toward intermediate σ-allyl complex **1** with π-coordinate NBD.

It is important that the intermolecular character of insertion into the metal—allyl bond appears only for NBN derivatives. Other unstrained olefins manifest intramolecular insertion[4] characterized by the favorable entropy factor[5] (Scheme 3). Many carbo- and heterocy-

Scheme 3

I

II

clic compounds were synthesized using this reaction catalyzed by the palladium, nickel, and rhodium complexes.[6] The substrates were molecules containing a group, being a precursor of the key intermediate, *viz.*, the η^3-allyl complex containing a substituent of three—four atoms with the terminal double bond linked to the terminal (type I) or central (type II) atom of the allyl system.

No β-elimination of hydrogen occurs due to steric factors in the σ,π-metallacycles with the σ-coordinate NBN or NBD fragment, for example, **2**. This process is the major path of decomposition of intermediates of type **3**, which undergo transformations until β-elimination and metal liberation become possible. This ability of the NBN derivatives is used for studying the mechanisms of catalytic reactions[7] and development of new methods for C—C bond formation.

Therefore, the unique cascade process[8] is worth of special mentioning (Scheme 4). Complex **4**, which is different from **2** mainly by the fact that the π-coordinate double bond belongs to the aryl rather than allyl fragment, undergoes a long sequence of transformations (change in the coordination mode of aryl, oxidative addition to form Pd^{IV}, reductive elimination, *etc.*) up to the formation of aryl complex **5** capable of reacting in various cross-coupling processes. As a result, palladium and NBN act consistently, being the inorganic and organic components of the catalytic system.

The transformations inside the coordination sphere of the metal were studied for the model stoichiometric reaction of bis(allyl)nickel $(\eta^3\text{-}C_3H_5)_2Ni$ with NBD affording all possible allylation products[9] (Scheme 5).

During the reaction of $(\eta^3\text{-}C_3H_5)_2Ni$ with NBD hydrogen is redistributed between the allyl ligands and NBD molecules to form a mixture of oxidative allylation products **6**—**9** with the $C_{10}H_{12}$ composition and reductive allylation products **10** of the $C_{10}H_{14}$ and C_3H_6 compositions. Note that the ratio of the $C_{10}H_{12}$ products is temperature-independent in the interval from −10 to 80 °C. The yield of 5-allyl-2-norbornene **10** increases linearly with an increase in the NBD/$(\eta^3\text{-}C_3H_5)_2Ni$ ratio, which agrees completely with the scheme proposed for the mechanism. In addition, the yield of the reductive allylation product similar to **10** decreases in the series $Ni(2\text{-}CH_3C_3H_4)_2 > Ni(C_3H_5)_2 > Ni(1\text{-}CH_3C_3H_4)_2$, which correlates with the effective positive charge on the metal.[9] The key step is the β-hydride transfer confirmed by the GC-MS study of the products of the $Ni(C_3D_5)_2$—NBD and $Ni(C_3H_5)_2$—NBD-d$_8$ systems (Scheme 6). The composition of the products indicates that the hydrogen atoms belonging to both NBD and the allyl fragment and occupying the β-position toward the metal are involved in the process.

The stoichiometric interaction of NBD with the homoligand allyl complexes of other metals $(Pd(C_3H_5)_2$, $Fe(C_3H_5)_3$, $Co(C_3H_5)_3$, $Rh(C_3H_5)_3$, $Pt(C_3H_5)_2)$ gives

Scheme 4

4

5
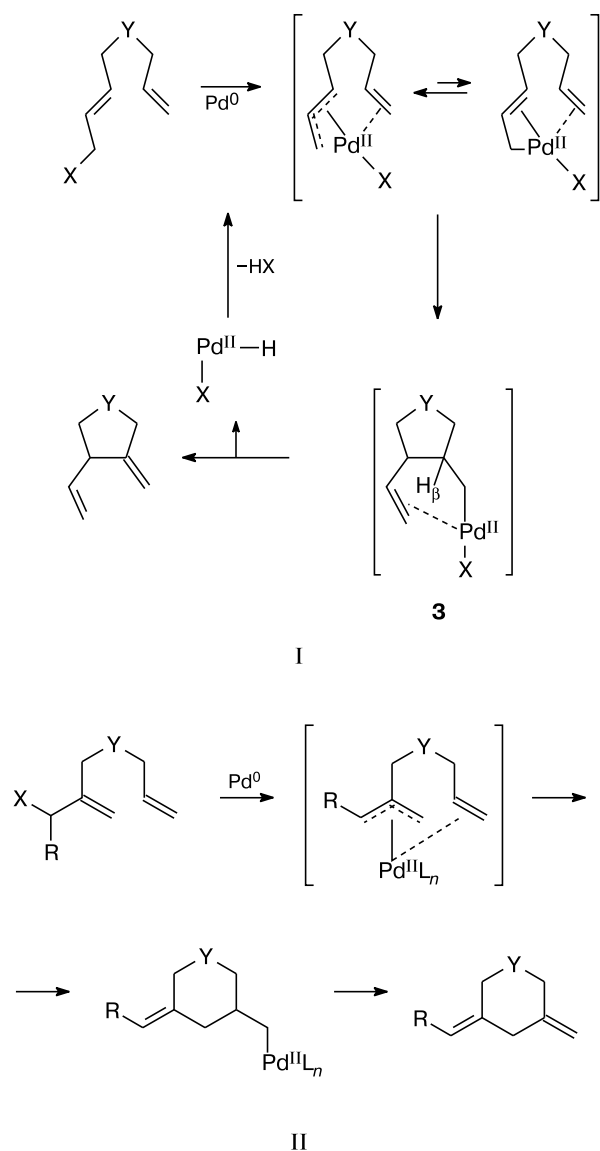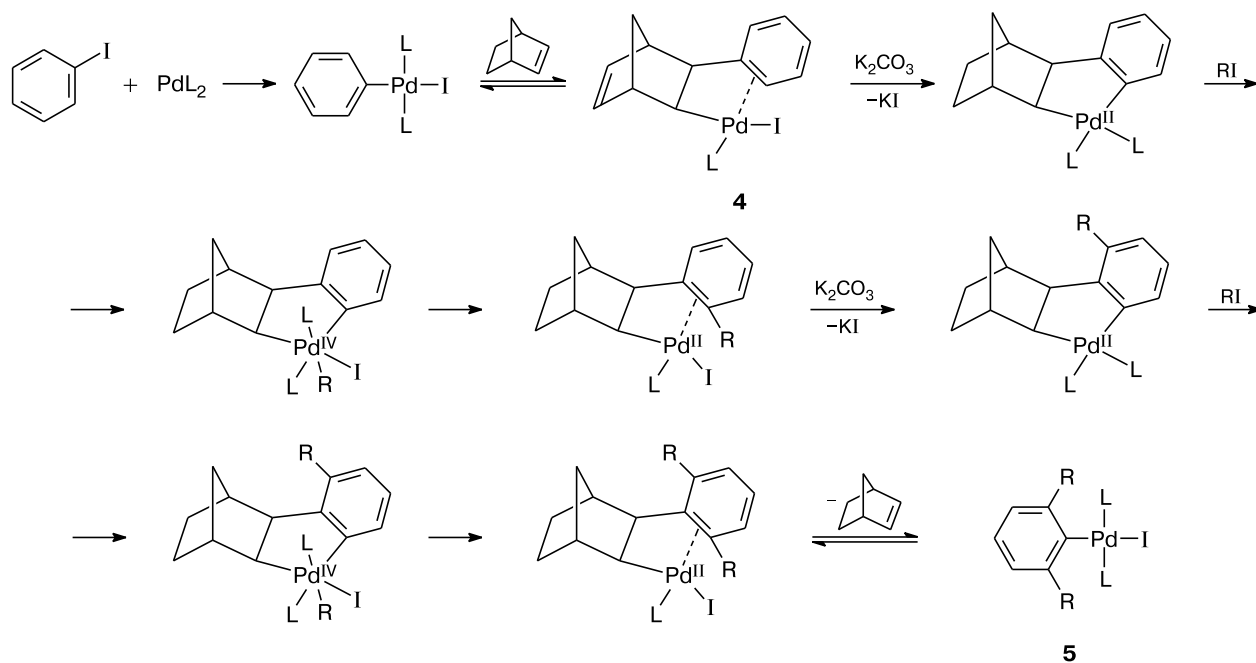
the same product as in the case of $(\eta^3\text{-}C_3H_5)_2Ni$, indicating the similarity of the mechanisms and a principal possibility of catalysis by other metals. Nevertheless, the studies were performed exclusively for the nickel complex during twenty years after the reaction had been discovered. Details of the earlier[1] proposed mechanism were also found, and synthetic possibilities were considerably extended.

The catalytic allylation of NBN[10] and NBD[11] for the Ni(acac)$_2$—P(OR)$_3$—Et$_3$Al (1 : 4 : 3) systems was studied in detail. The dependences of the rate and yield of the products on the nature of the phosphite ligand, solvent, temperature, and ligand to metal ratio were studied. The nature of the reducing agent exerts a slight effect on the product composition; AlEt$_3$, Al(Bu^i)$_3$, MgBu$_2$, and LiAlH$_4$ turned out to be the most efficient reducing agents. The reaction rate involving NBD is substantially higher than that involving NBN. The substituted double bond in the NBD derivatives is not subjected to allylation.

The study of a wide range of the NBN derivatives showed that nonconventional allylation is versatile.[12] The broad screening of unsaturated compounds of various classes made it possible to reveal several common regularities that should be taken as a guide for the selection of an appropriate substrate. Compounds containing the intracyclic unsaturated and strained carbon—carbon double bond are involved in the process. The strain energy values are certainly restricted: from 15 to 30 kJ mol^{-1}. In this respect, the NBN (25.1 kJ mol^{-1}) and NBD (58.2 kJ mol^{-1} based on two bonds) compounds are rather suitable substrates.

Under the conditions of excess allyl acetate, each double bond of NBD is allylated[11] (Scheme 7). The kinetic curves characteristic of consecutive reactions have been obtained later for the $(\eta^3\text{-}C_3H_5)_2Ni$—P(OPr^i)$_3$ systems.[12] For these curves, the concentrations of the primary allylation products passed through a maximum and then decreased with a simultaneous increase in the concentration of the double allylation products. Thus, the allylation products are less reactive than NBD. This could be expected, because the reactivity of NBN is lower than that of NBD.

A comparison of the catalytic activity of the Ni(acac)$_2$—AlEt$_3$—P(OPr^i)$_3$ system and individual Ni[P(OPr^i)$_3$]$_4$ complex revealed substantial distinctions in their behavior. In the first case, most likely, a complicated chain of transformations involving the hydride and cluster nickel complexes is observed.

The use of the $(\eta^3\text{-}C_3H_5)_2Ni$—P(OPr^i)$_3$ catalytic system made it possible to study the kinetics of nonconventional allylation.[12] For NBN and NBD and all products of their interaction with allyl acetate, we obtained the kinetic curves indicating that the phosphite to nickel ratio decreases in a static reactor during the reaction and simultaneously the rate of formation of product **7** decreases and that of **8** increases (Fig. 1). On the one hand, these data suggest that intermediates with different numbers of the phosphite ligands precede these products.

On the other hand, the instability of the catalytic system related to an inconstant phosphite to nickel ratio results in the nonstationary occurrence of the reaction. It is found that the consumption of noncoordinated trialkyl

Scheme 5

6
+ Ni⁰ + C₃H₆

7 + Ni⁰ + C₃H₆

8
+ Ni⁰ + C₃H₆

9
+ Ni⁰ + C₃H₆

7   **10**   + Ni⁰
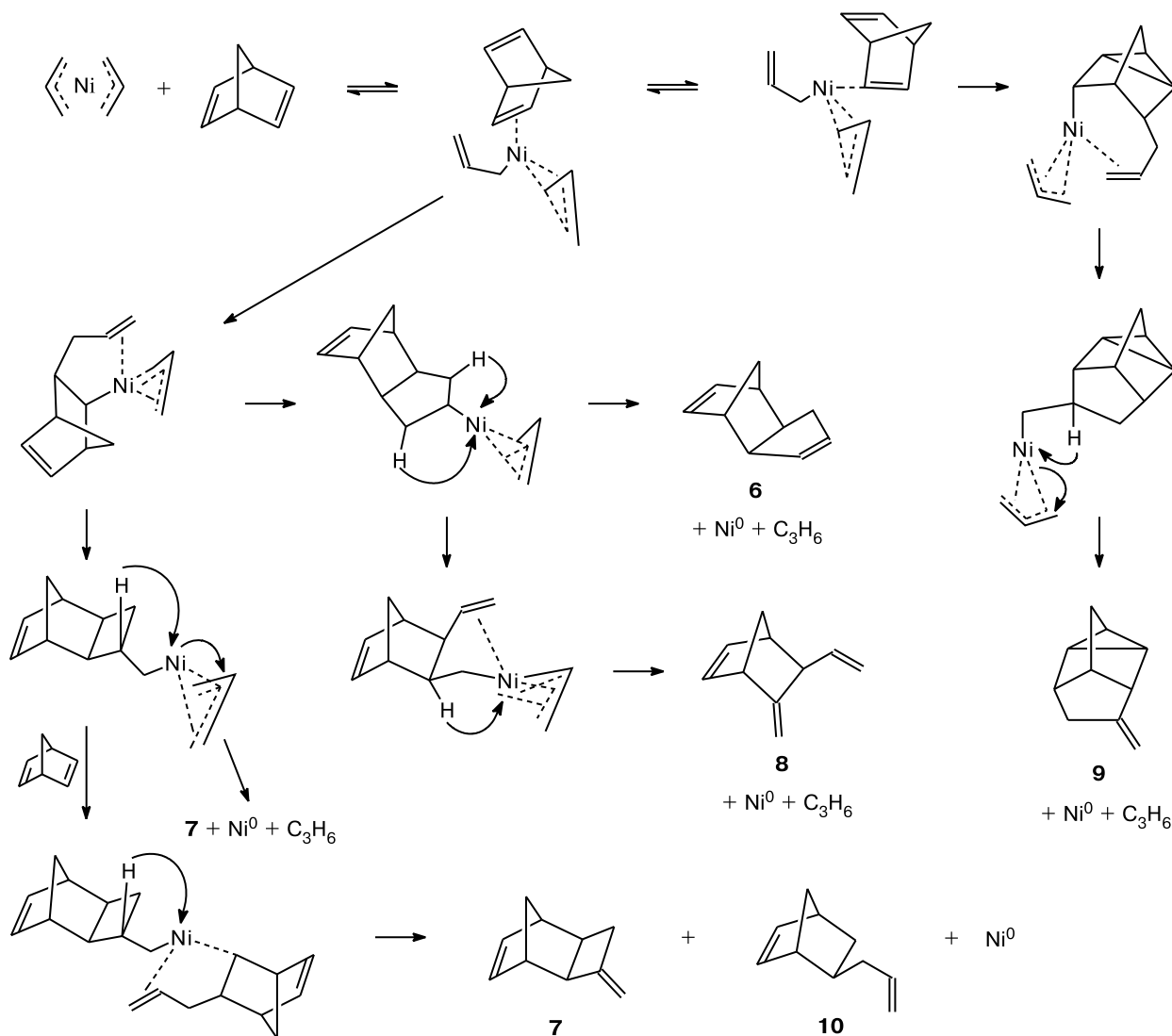
phosphite is due to ester interchange in the presence of one of the products, namely, carboxylic acid[13] (Scheme 8).

The use of zeolite additives to the catalytic system (molecular sieves 3 Å) made it possible to increase the number of catalytic cycles to 2000 and selectively (85—90%) synthesize individual products under specified unchanged conditions.
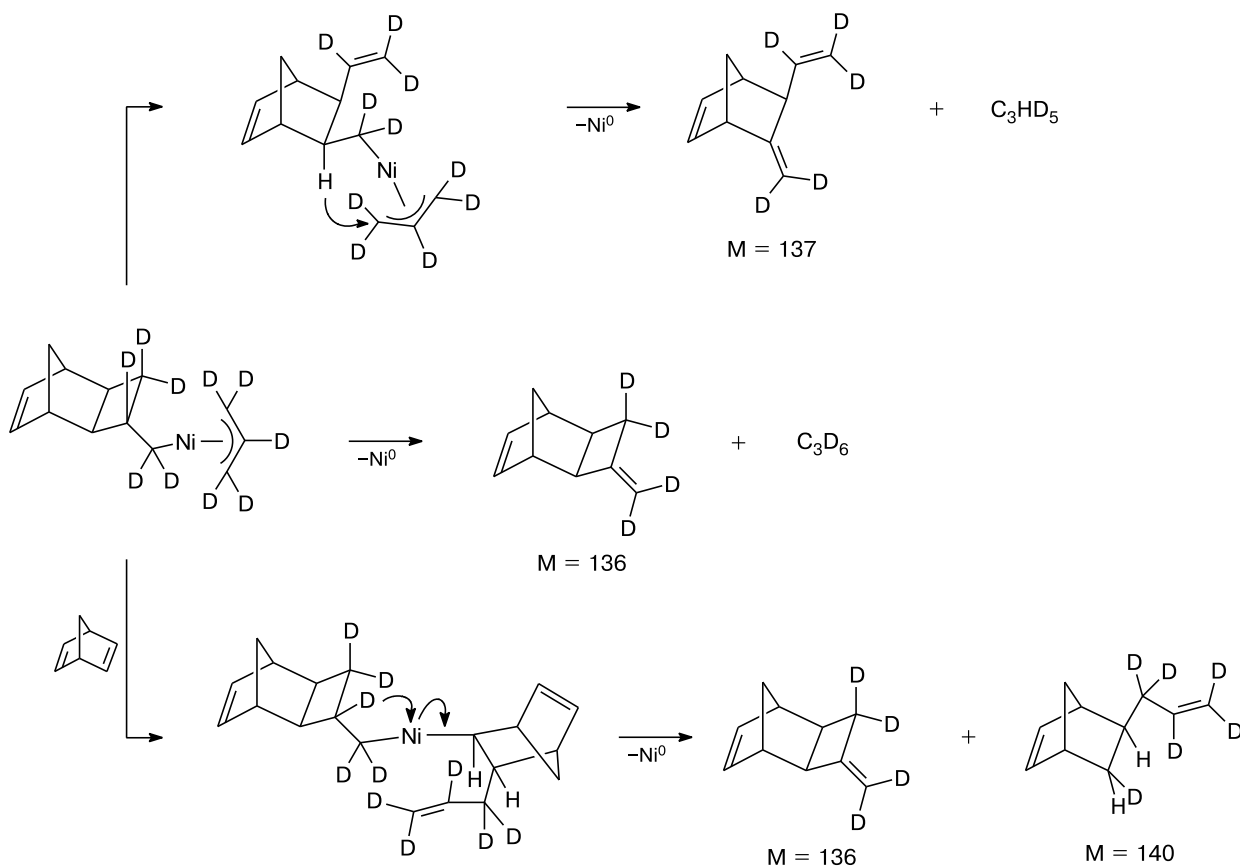
The detailed study[12] of the kinetics and mechanism of the reaction in the presence of the $(\eta^3\text{-}C_3H_5)_2Ni\text{—}P(OPr^i)_3$ catalytic system made it possible to develop conditions for the quantitative synthesis of valuable additives to ethylene-propylene rubbers, namely, 3-methylidene-2-*exo*-5-*exo*(*endo*)-divinylnorbornane,[14] 2-methylidene-3-*exo*-vinyl-5(6)-ethylidenenorbornene,[15] 5-methylidene-6-isopropenyl-2-norbornene,[16] and 5-methylidene-6-alkenyl-2-norbornene derivatives.[17]

The palladium-based catalytic systems have been proposed only recently for NBN[18] and NBD.[19] The Pd(PPh₃)₄, Pd(OAc)₂—PPh₃, and other complexes are much less active than the Ni⁰ complexes and do not allow one to perform the reaction at room temperature. However, their important advantages are the lower sensitivity to oxygen and moisture and the tolerance to various functional groups.
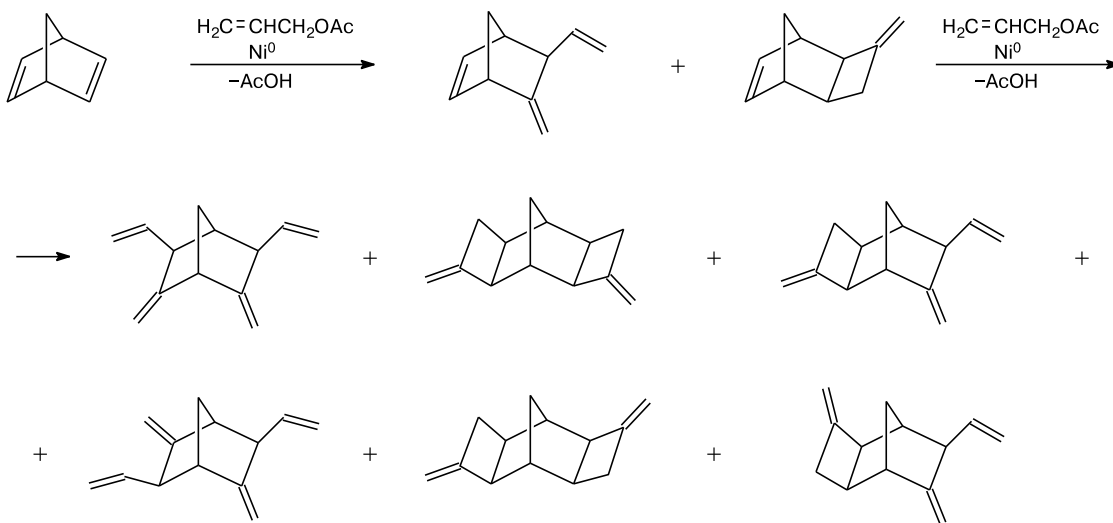
The influence of the nature of substituents in the allylic component on the ratio of the products was observed (see Scheme 1): in the case of the aryl substituent (R³ = Ph, R⁴ = H) the major product is a methylidenecyclobutane derivative, whereas alkyl-substituted allyl esters (R³ = Alk, R⁴ = H), under the same conditions, mainly give a methylidene vinyl derivative.[18]

The high selectivity with respect to the methylidene vinyl derivative is also observed for the use of the

Scheme 6

M = 137

M = 136

M = 136   M = 140

Scheme 7

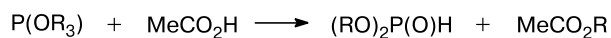
Scheme 8

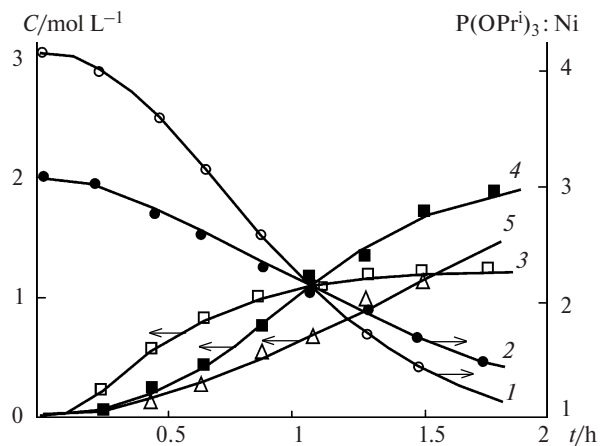$$P(OR_3) + MeCO_2H \longrightarrow (RO)_2P(O)H + MeCO_2R$$

Fig. 1. Change in the phosphite/Ni ratio (*1, 2*) at the initial phosphite/Ni ratio 3 : 1 (*1*) and 2 : 1 (*2*) and in the concentration of the products of NBD allylation (*3—5*) during the kinetic experiment ($C^0_{NBD} = C^0_{AA} = 3.0$ mol L^{-1}, $C^0_{Ni} = 0.02$ mol L^{-1}, 25 °C, *m*-xylene): *3*, 3-methylidenetricyclo[4.2.1.0^{2,5}]non-7-ene (**7**); *4*, 5-vinyl-6-methylidene-2-norbornene (**8**); *5*, 2-methylidene-tetracyclo[4.2.1.0^{4,8}.0^{5,9}]nonane (**9**).

Pd$_{147}$Phen$_{32}$O$_{60}$(OCOBu^t)$_{30}$ cluster catalyst (Phen is 1,10-phenanthroline) in a medium of the ionic liquid [bmim][BF$_4$] (1-butyl-3-methylimidazolium tetrafluoroborate).[20] A specific feature of the latter reaction is the unexpected stability of the giant palladium clusters in the presence of phosphines, which is due, most likely, to specific properties of the medium.[21]

An important trend of extension of synthetic possibilities of the reaction (see Scheme 1) is the involvement of the NBN analogs with bridging heteroatoms,[22] which can easily be synthesized using the Diels—Alder reaction, into a range of substrates.

The study of the effect of the nature of the leaving allylic group performed for the Ni and Pd catalysts showed[12] some difference in the rate and selectivity for allyl acetate, benzoate, and pivalate and allyl alkyl carbonates. The variation of the acid nature can be useful for controlling the selectivity and solubility of participants of the reaction.

Allyl formates represent a special group in the list of allylating agents. They are considerably more reactive but less selective. The latter is related, most likely, to the fact that the formate leaving group coordinated to the transition metal is readily decarboxylated to form the hydride complex,[5] and a complicated mixture of the hydrogenation products is formed due to the decomposition of these intermediates in the presence of the phosphine and phosphite ligands.

One of the methods for formate stabilization is the reaction in a medium of ionic liquids.[20] Perhaps, the formate ions are stabilized due to the formation of a hydrogen bond between the carbonyl group and acidic hydrogen atom of the imidazolium cation (Scheme 9).
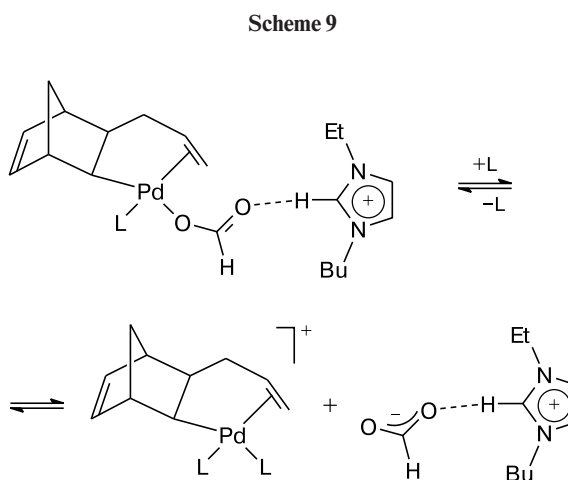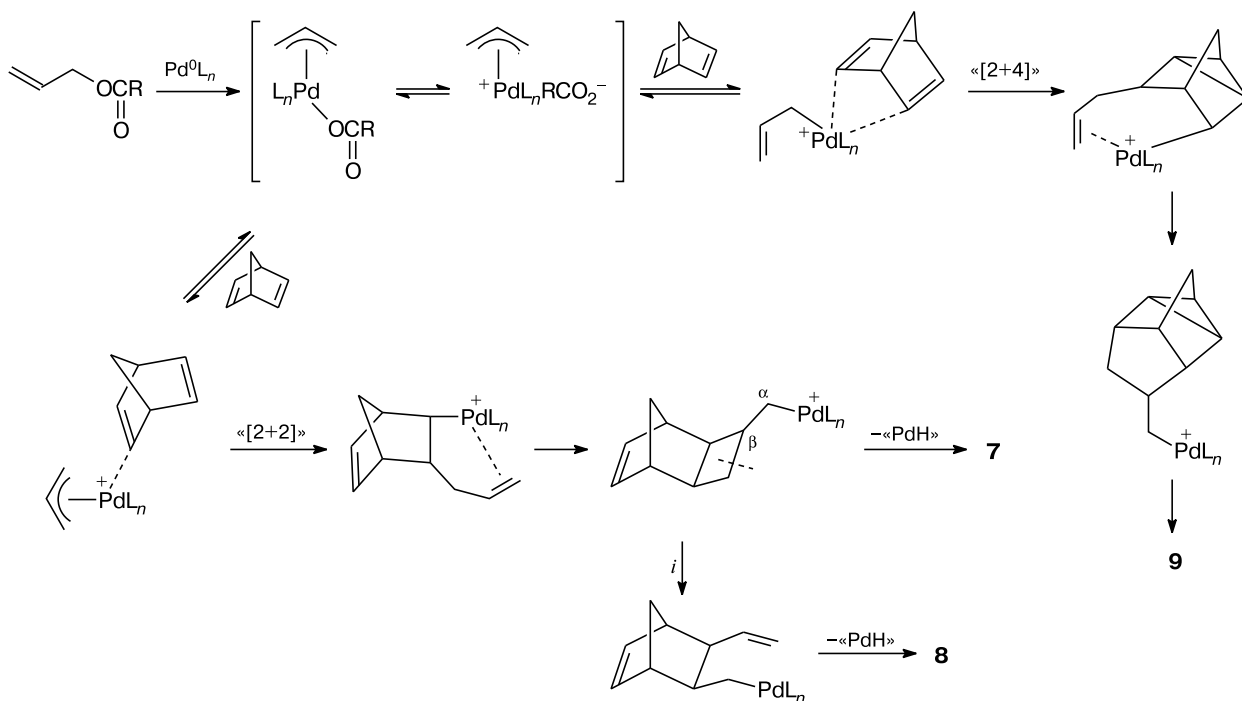
Scheme 9

The mechanism proposed for the palladium complexes (Scheme 10) is analogous to that of catalysis by the nickel complexes[1] and even to the mechanism of the stoichiometric reaction (see Scheme 5). In the latter case, the allylic ligand rather than the carboxylate anion acts as a hydrogen acceptor, which is observed in the catalytic reaction with the ester. Two major reaction products are formed involving the same cyclobutane intermediate for which two decomposition routes are possible: β-elimination of hydrogen to form product **7** and (at elevated temperature) β-elimination of carbon leading to product **8**. It should be mentioned that the latter reaction is not a rare direction for the decomposition of cyclic intermediates with three- and four-component rings, mainly cyclobutanol derivatives.[23]

The phosphorus-containing ligand : metal ratio exerts a determining effect on both the selectivity and mechanism of the reaction. In the absence of phosphines, the reaction of NBD with allyl formate catalyzed by Pd(dba)$_2$ (dba is *trans,trans*-dibenzylideneacetone) and Pd(^{t}dba)$_2$ (^{t}dba is (4-Bu^{t}C$_6$H$_4$CH=CH)$_2$CO) under mild conditions (25 °C) selectively (93—95%) affords compound **10** due to the hydroallylation of one of the double bonds of NBD[24] (Scheme 11). The [PdM(μ-RCOO)$_m$]$_x$ heteronuclear carboxylate complexes (M = Zn, Co, Ni, Mn, rare-earth metals; R = Me, Bu^t; m = 4, 5; x = 1, 2) also catalyze the reaction but in a lower yield and in the presence of formic acid as the cocatalyst. The role of the latter is the reduction of Pd^{II} to Pd^0. Evidently, the role of stabilizing ligands, under the reaction conditions, belongs to dba, ^{t}dba, and NBD. Note that compound **10** is the major product of the stoichiometric reaction of (η^3-C$_3$H$_5$)$_2$Ni with NBD (see Scheme 5) involving no phosphines, which additionally confirms the proposed mechanism.
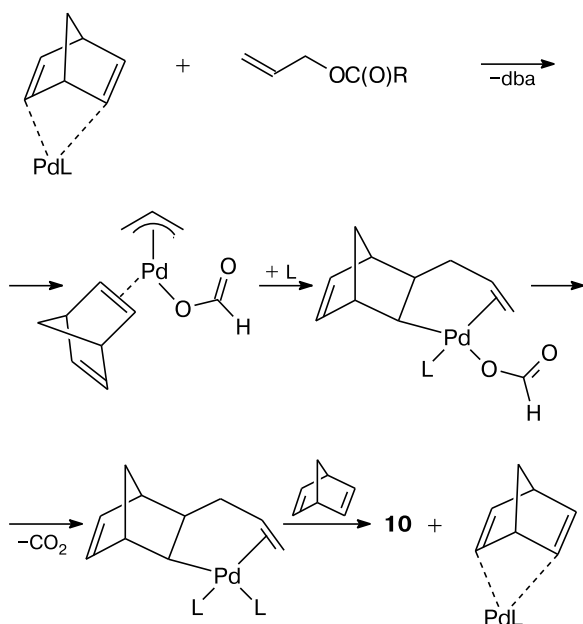
Some details of the mechanism for nonconventional alkylation remain presently unclear. In particular, it was not found to which position olefin inserted: into the η^1- or η^3-bonded ligand. The modern quantum chemical meth-

Scheme 10

*i*. β-Elimination of carbon.

Scheme 11

L = dba, MeCN, NBD

ods are widely used for the elucidation of details of the mechanism of catalytic reactions involving transition metal complexes. The recent DFT calculations of the insertion mechanism with allowance for the solvent effect showed that the cyclic transition state in the ene reaction was energetically unfavorable.[25] Two other most probable mechanisms for the insertion of the double bond of coordinated ethylene in complexes **11** $[PdL(\eta^2\text{-}C_2H_4)(\eta^3\text{-}C_3H_5)]^+$ (L = H_2O, PH_3, Cl, $H_2C=CH_2$) were studied by the DFT method taking into account the solvent. It was concluded that an olefin inserts directly into the η^3-allyl complex[26] (Scheme 12, steps *a* and *b*) without a preliminary formation of the η^1-complex[27] (Scheme 12, steps *c* and *d*).

Scheme 12
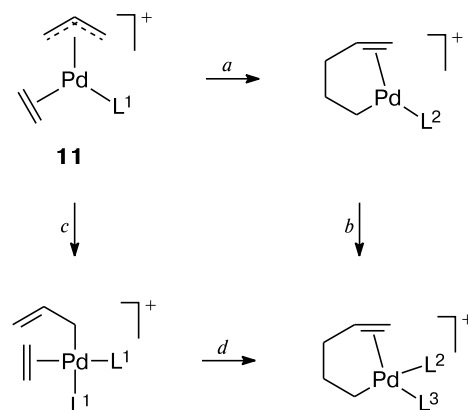
Later a possibility of the alternative route of the outer-sphere attack of olefin to the σ-allyl intermediate[28] has been shown (Scheme 13). However, it should be expected that the calculated data obtained to presently will considerably be corrected after a possibility would appear to calculate at a high theoretical level the energy barriers of reactions that are more real and involve a considerably more strongly coordinating NBD molecule and alkyl- or arylphosphines.

Scheme 13
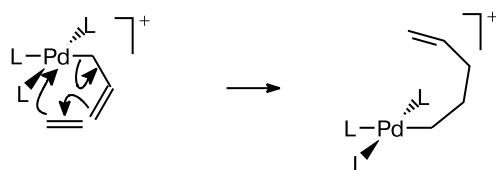
It would be noted in conclusion that synthetic potentialities of the reactions considered in the present review are far from exhaustion. A very large field of activities for the design of new catalytic systems, methods for the synthesis of novel products, and development of calculation and analytical methods is still retained.

References

1. M. Catellani, G. P. Chiusoli, E. Dradi, G. Salerno, *J. Organomet. Chem.*, 1979, **177**, C29.
2. R. P. Hughes, J. Powell, *J. Organomet. Chem.*, 1971, **30**, C45.
3. M. C. Gallazzi, L. Porrim, G. Vitulli, *J. Organomet. Chem.*, 1975, **97**, 131.
4. W. Oppolzer, in *Comprehensive Organometallic Chemistry II*, Eds E. W. Abel, F. G. A. Stone, G. Wilkinson, Pergamon Press, Oxford, UK, 1995, Vol. **9**, p. 905.
5. J. Tsuji, *Palladium Reagents and Catalysts: Innovations in Organic Synthesis*, John Wiley and Sons, Chichester, 1995.
6. W. Oppolzer, *Pure Appl. Chem.*, 1990, **62**, 1941.
7. E. M. Evstigneeva, R. S. Shamsiev, V. R. Flid, *Vestn. MITKhT* [*Bulletin of Moscow Institute of Fine Chemical Technology*], 2006, **1**, No. 3, 3 (in Russian).
8. M. Catellani, E. Motti, F. Faccini, R. Ferraccioli, *Pure Appl. Chem.*, 2005, **77**, No. 7, 243.
9. V. R. Flid, O. S. Manulik, A. P. Belov, A. A. Grigor´ev, *Metalloorg. Khim.*, 1991, **4**, 864 [*Organomet. Chem.*, 1991, **4** (Engl. Transl.).
10. U. M. Dzhemilev, R. I. Khusnutdinov, D. K. Galeev, O. M. Nefedov, G. A. Tolstikov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1987, 138 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1987, **36**, 122 (Engl. Transl.)].
11. U. M. Dzhemilev, R. I. Khusnutdinov, D. K. Galeev, G. A. Tolstikov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1987, 154 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1987, **36**, 137 (Engl. Transl.)].
12. V. R. Flid, O. S. Manulik, D. V. Dmitriev, V. B. Kouznetsov, E. M. Evstigneeva, A. P. Belov, A. A. Grigor´ev, *Eurasian ChemTech J.*, 2001, **3**, 201.
13. V. R. Flid, Yu. G. Shestakova, E. A. Katsman, *Kinet. Katal.*, 1992, **33**, 223 [*Kinet. Catal.*, 1992, **33** (Engl. Transl.).
14. Pat. RF No. 1 796 605; *Byul. Izobret.* [*Invention Bulletin*], 1993, No. 7, p. 76 (in Russian).
15. Pat. RF No. 1 796 606; *Byul. Izobret.* [*Invention Bulletin*], 1993, No. 7, p. 76 (in Russian).
16. Pat. RF No. 1 796 608; *Byul. Izobret.* [*Invention Bulletin*], 1993, No. 7, p. 77 (in Russian).
17. Author´s Certificate. 1 148 269 USSR; *Byul. Izobret.* [*Invention Bulletin*], 1984, No. 3, p. 38 (in Russian).
18. N. Tsukada, T. Sato, Y. Inoue, *Tetrahedron Lett.*, 2000, **41**, 4181.
19. E. M. Evstigneeva, O. S. Manulik, V. R. Flid, *Kinet. Katal.*, 2004, **45**, 188 [*Kinet. Catal.*, 2004, **45**, 172 (Engl. Transl.)].
20. E. M. Evstigneeva, O. S. Manulik, V. R. Flid, I. P. Stolyarov, N. Yu. Kozitsina, M. N. Vargaftik, I. I. Moiseev, *Izv. Akad. Nauk, Ser. Khim.*, 2004, 1292 [*Russ. Chem. Bull., Int. Ed.*, 2004, **53**, 1345].
21. S. Gao, H. Zhang, X. Wang, X. Wang, W. Mai, C. Peng, L. Ge, *Nanotechnology*, 2005, **16,** 1234.
22. S. V. Leont´eva, O. S. Manulik, E. M. Evstigneeva, E. N. Bobkova, V. R. Flid, *Kinet. Katal.*, 2006, **47**, 391 [*Kinet. Catal.*, 2006, **47**, 172 (Engl. Transl.)].
23. T. Satoh, M. Miura, *Top. Organomet. Chem.*, 2005, **14**, 1.
24. I. P. Stolyarov, A. E. Gekhman, I. I. Moiseev, A. Yu. Kolesnikov, E. M. Evstigneeva, V. R. Flid, *Izv. Akad. Nauk, Ser. Khim.*, 2007, 309 [*Russ. Chem. Bull., Int. Ed.*, 2007, **56**, 320].
25. D. J. Gárdenas, M. Alcamí, M. Méndez, A. M. Echavarren, *Chem. Eur. J.*, 2003, **9**, 96.
26. E. Gomez-Bengoa, J. M. Cuerva, A. M. Echavarren, G. Martorell, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 767.
27. D. J. Cárdenas, A. M. Echavarren, *New J. Chem.*, 2004, **28**, 338.
28. M. Garsía-Iglesias, E. Buñuel, D. J. Cárdenas, *Organometallics*, 2006, **25**, 3620.