Interaction of norbornadiene with allyl acetate in the presence of Ni^0 complexes: a DFT modeling

R. S. Shamsiev★ *and V. R. Flid*

MIREA — Russian Technological University, M. V. Lomonosov Institute of Fine Chemical Technologies,
86 prosp. Vernadskogo, 119571 Moscow, Russian Federation.
Fax: +7 (495) 434 9287. E-mail: Shamsiev.R@gmail.com

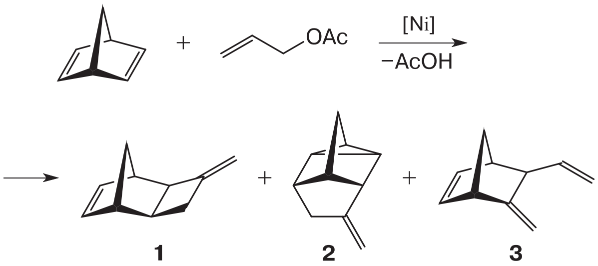
Catalytic allylation of norbornadiene in the presence of Ni^0 phosphite complexes resulting in 3-methylenetricyclo[4.2.1.0^{2,5}]non-7-ene was studied within the framework of the density functional theory using the PBE functional and the L11, L2, and L3 basis sets. According to calculations, the formation of the first C—C bond more likely proceeds involving the η^3-allyl rather than η^1-allyl ligand. The presence of one phosphite ligand favors the formation of the second C—C bond. Hydride transfer from the allyl moiety to the acetate ligand proceeds *via* an intermediate with agostic interaction. The highest energy on the reaction pathway (22.7 kcal mol^{-1}) corresponds to the transition state of the formation of the first C—C bond.

Key words: norbornadiene, allylation, nickel, allyl acetate, reaction mechanism, density functional theory.

Reactions of bicyclo[2.2.1]hepta-2,5-diene (norbornadiene, NBD) with allyl carboxylates occupy a special place in the catalytic chemistry of NBD.[1—7] A feature of such processes is that the addition of allyl moiety can follow a cycloaddition pathway or proceed with cleavage of the carbon—carbon bond. In the former case the allyl fragment becomes part of methylenecyclobutane or methylenecyclopentane ring and loses a hydrogen atom that is removed with the carboxylic acid[3,7] (oxidative allylation).

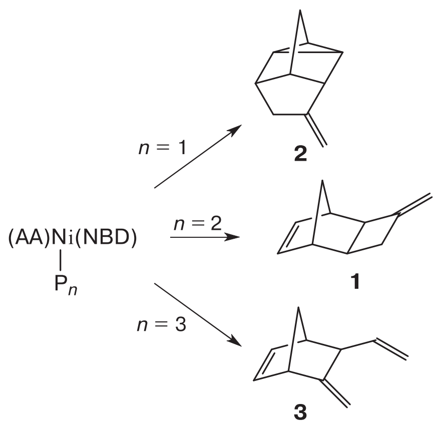
The most selective catalysts include Ni^0 complexes stabilized by phosphite ligands.[1,6] The reaction of NBD with allyl acetate (AA) in the presence of the catalytic system $Ni(C_3H_5)_2$/tertiary phosphites[3,6,7] affords 3-methylenetricyclo[4.2.1.0^{2,5}]non-7-ene (**1**), 8-methylenetetracyclo[4.3.0.0^{2,4}0^{3,7}]-nonane (**2**), and 5-methylene-6-vinylbicyclo[2.2.1]-hept-2-ene (**3**) as major products (Scheme 1).

Scheme 1



The ratio of products **1**—**3** depends on the Ni : phosphite mole ratio (*n*), which is probably due to the formation of intermediates with different number of phosphite ligands[3,7] (Scheme 2).

Scheme 2



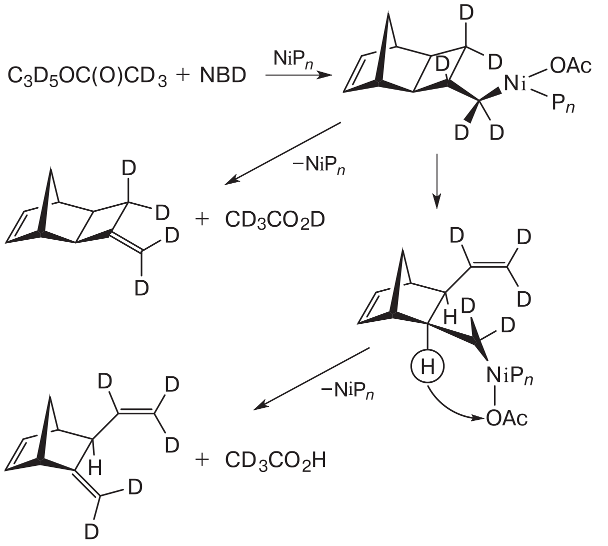
Published experimental data suggest that the mechanism of NBD allylation involves the following sequence of steps[3,7]: coordination of AA and NBD to the phosphite complex of Ni^0, oxidative addition of AA to give the η^3-allyl ligand, a η^3—η^1-allyl rearrangement, the formation of the first and second C—C bonds, and hydride transfers. Clearly, hydride transfer from the organic ligand to the metal is the key step since it is the direction of hydrogen abstraction from the allyl or C^β position of the norbornene moiety that determines the structure of product **1** or **3**. The feasibility of these pathways involv-

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 4, pp. 0653—0659, April, 2020.

1066-5285/20/6904-0653 © 2020 Springer Science+Business Media LLC

ing the C_β atom was confirmed[3] taking the system $C_3D_5OCOCD_3$—NBD (Scheme 3) as an example.

Scheme 3



Detailed information on the molecular mechanism of NBD allylation, which is necessary to optimize the process, can be obtained using quantum chemical calculations. However, no theoretical studies on the interaction of NBD with allyl carboxylates have been reported so far. In this connection the aim of our study was to carry out a quantum chemical modeling of the mechanism of NBD allylation *via* the formation of methylenecyclobutane ring in the presence of triisopropylphosphite complexes of Ni^0.

Calculation Methods

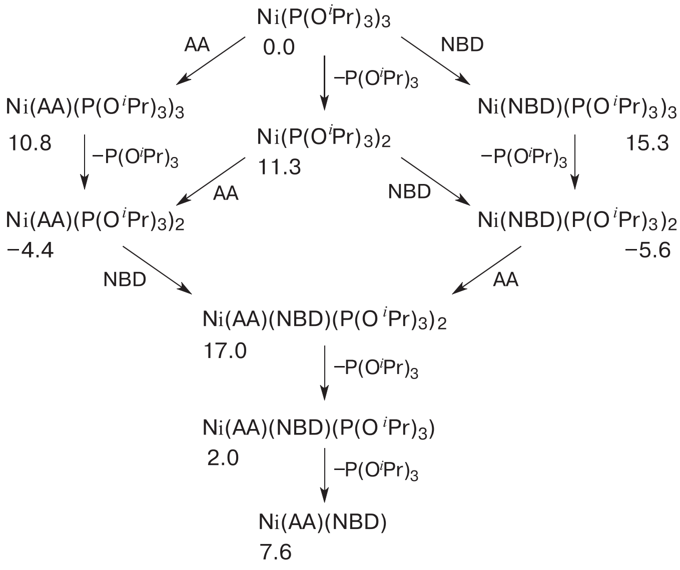
All calculations were carried out within the framework of the density functional theory (DFT) using the Priroda program.[8,9] Main calculations were performed using the PBE exchange-correlation functional[10] and the L11 all-electron basis set[11] with the following orbital contraction scheme: (6s2p)/[2s1p] for H, (10s7p3d)/[4s3p1d] for O and C, (14s11p6d)/[5s4p2d] for P, and (19s15p11d5f)/[6s5p3d1f] for Ni. This computational strategy was previously used in the studies of Ni-catalyzed dimerization of NBD[12,13] and co-dimerization of NBD with alkyl acrylates.[14,15] To assess how the size of the basis set influences the results of calculations, certain structures were calculated with the L2 and L3 basis sets[11] that are analogous to the cc-pVTZ and cc-pVQZ basis sets, respectively.

Correspondence between the optimized structures and the energy minima or transition states (TSs) was confirmed by normal vibrational frequency analysis. Thermodynamic parameters (ΔG_{298}, $\Delta G^{\neq}_{298}$) were calculated for $T = 298$ K. Since the reaction is carried out in *m*-xylene that is characterized by much lower coordination ability compared to NBD and AA, the solvation energy was calculated within the framework of the polarizable continuum model (PCM).

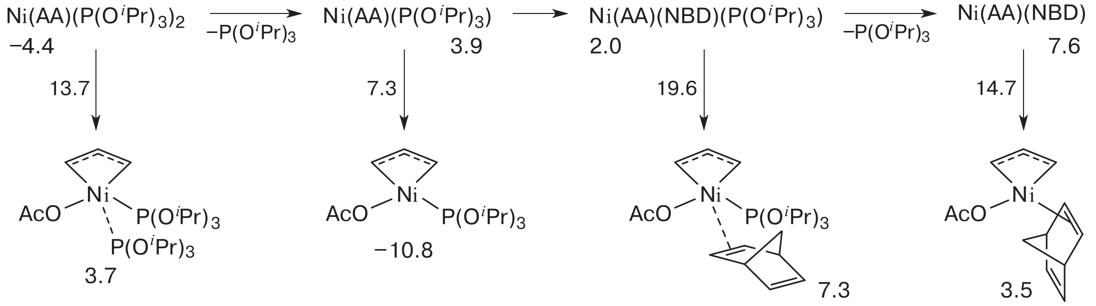
Results and Discussion

To find the most probable catalytically active complexes in the system containing the triisopropylphosphite complex of Ni^0, $Ni(P(O^iPr)_3)_3$, as well as NBD and AA, we calculated thermodynamic effects of the possible reactions leading to their coordination and elimination of $P(O^iPr)_3$ from the initial nickel complex. Since the methylenecyclobutane ring in product **1** has *exo*-orientation relative to the norbornene bridge, only the *exo*-coordination of NBD was considered.

Scheme 4



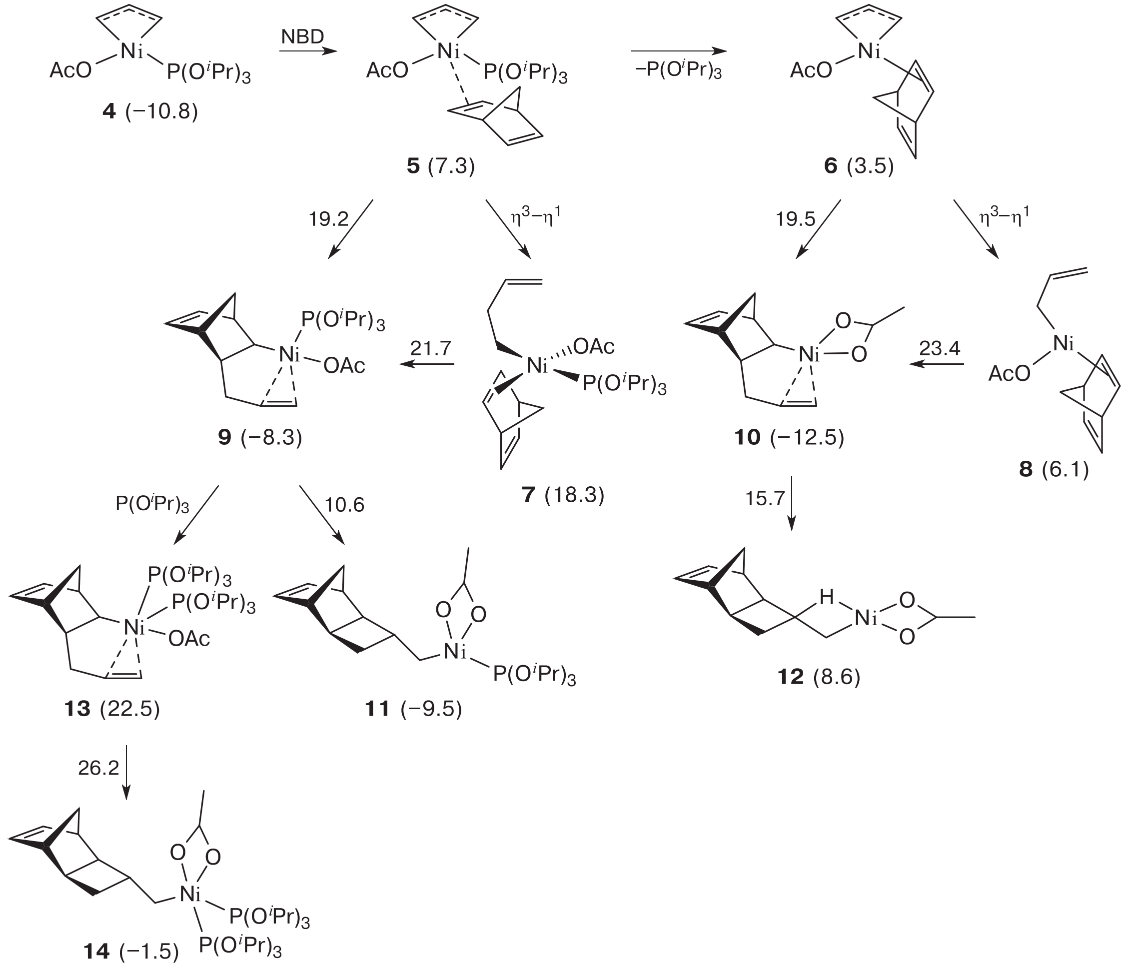
Scheme 5



From this point on numbers near structures denote the Gibbs energies of intermediates, while numbers near arrows denote the Gibbs activation energies (in kcal mol^{-1}) calculated relative to the sum of the energies of Ni(P(O^{i}Pr)$_3$)$_3$ and the reactants.

From Scheme 4 plotted using the results of calculations it follows that the most stable species are the three-ligand diphosphite complexes Ni(AA)(P(O^{i}Pr)$_3$)$_2$ and Ni(NBD)(P(O^{i}Pr)$_3$)$_2$ characterized by close Gibbs energy values (ΔG_{298} = –4.4 and –5.6 kcal mol^{-1}, respectively). The formation of monophosphite complex with the AA and NBD ligands is much less probable (ΔG_{298} = 2.0 kcal mol^{-1}). Nevertheless, the subsequent oxidative addition step was modeled for both the stable complex Ni(AA)(P(O^{i}Pr)$_3$)$_2$ and the complexes Ni(AA)(P(O^{i}Pr)$_3$), Ni(AA)(NBD)-

Scheme 6



($P(O^iPr)_3$), and Ni(AA)(NBD) (Scheme 5) characterized by positive Gibbs energies (calculated relative to the sums of the energies of free reactants) assuming that cleavage of the C—O bond in AA mainly proceeds *via* the five-center TS.**16** In all cases, products formed in this step contain an allyl ligand that is η^3-coordinated to nickel.

According to calculations (см. Scheme 5), oxidative addition of AA requires the overcoming of high activation barriers for NBD-containing complexes. It follows that the NBD molecule is coordinated to nickel only upon completion of this reaction step. The formation of the C—C bond in the complex Ni(AA)(NBD)($P(O^iPr)_3$) can also be ruled out due to the high activation energy ($\Delta G^{\neq}{}_{298}$ = = 34.1 kcal mol^{-1}).

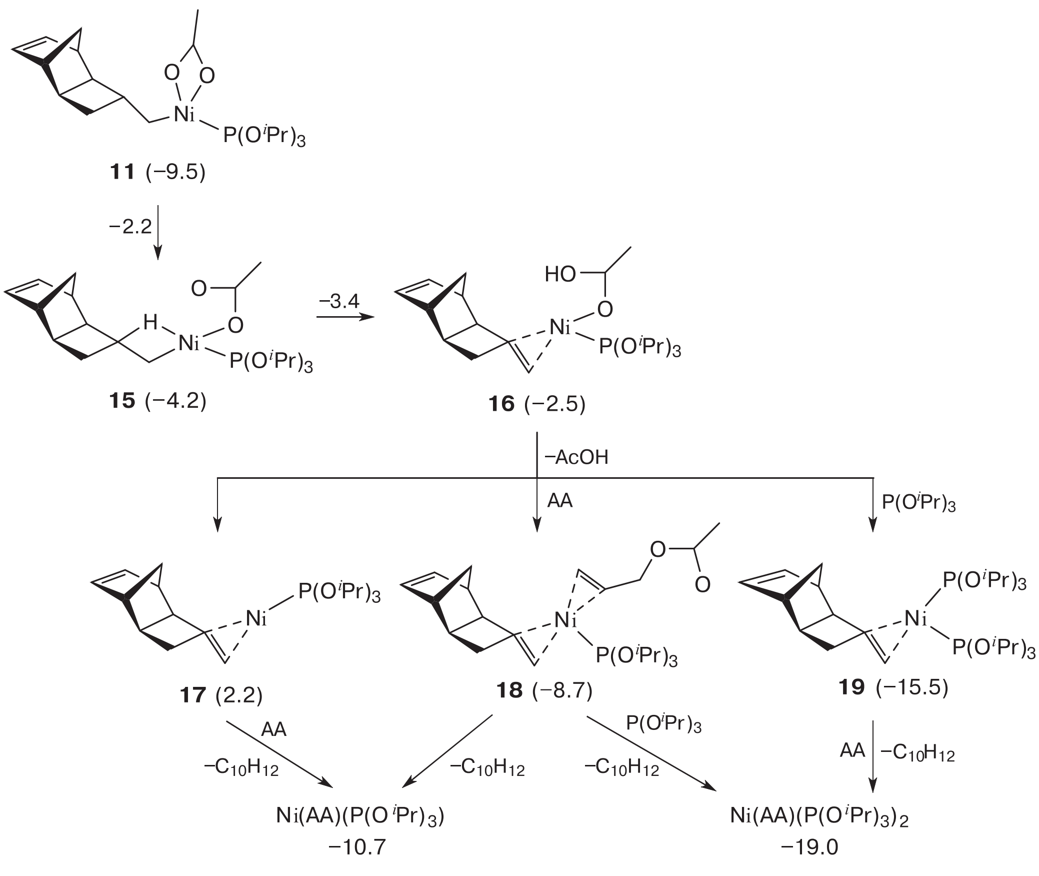
Oxidative addition in the complex Ni(AA)($P(O^iPr)_3$) results in thermodynamically stable monophosphite intermediate Ni($P(O^iPr)_3$)(η^3-C_3H_5)(η^1-OAc) (**4**, ΔG_{298} = = −10.8 kcal mol^{-1}). Thus, from the standpoint of kinetics and thermodynamics, this step apparently proceeds *via* the complex Ni(AA)($P(O^iPr)_3$).

The addition of NBD molecule to complex **4** in η^2-*exo* fashion is followed by a noticeable increase in energy (ΔG_{298} (**5**) = 7.3 kcal mol^{-1}) due to steric repulsion in the coordination sphere of nickel. In the absence of phosphite ligands, the coordination of NBD is more feasible. Considering the formation of complex Ni(η^3-C_3H_5)(OAc)-(η^2-*exo*-NBD) (**6**), the Gibbs energy is 3.5 kcal mol^{-1}. The Gibbs energy for coordination of solvent molecule (*m*-xylene) to the double bond even in the most sterically accessible complex Ni(η^3-C_3H_5)(OAc) is high and positive (ΔG_{298} = 13.7 kcal mol^{-1}) owing to the presence of weak Ni—*m*-xylene bond (ΔE < 1 kcal mol^{-1}).

Modeling of the formation of the first C—C bond in complexes **5** and **6** (Scheme 6) showed that approach of the η^1-allyl ligand to the NBD ligand in complexes **7** and **8** is difficult ($\Delta G^{\neq}{}_{298}$ = 21.7 and 23.4 kcal mol^{-1}, respectively) compared to the η^3-allyl intermediates ($\Delta G^{\neq}{}_{298}$ = 19.2 and 19.5 kcal mol^{-1} for **9** and **10**, respectively). The main reason is that the η^1-allyl intermediates are less stable than their η^3-allyl analogues. Although intermediate **5** is characterized by a higher Gibbs energy than the phosphite-free intermediate **6**, transformation of the former to **9** proceeds with a slightly lower (by 0.3 kcal mol^{-1}) activation energy.

The presence of a phosphite ligand in the nickel complex causes a decrease in the activation energy of the formation of the second C—C bond from 28.2 kcal mol^{-1} (**10**→**12**) to 18.9 kcal mol^{-1} (**9**→**11**). Besides, the formation of intermediate **11** is characterized by a decrease rather

Scheme 7

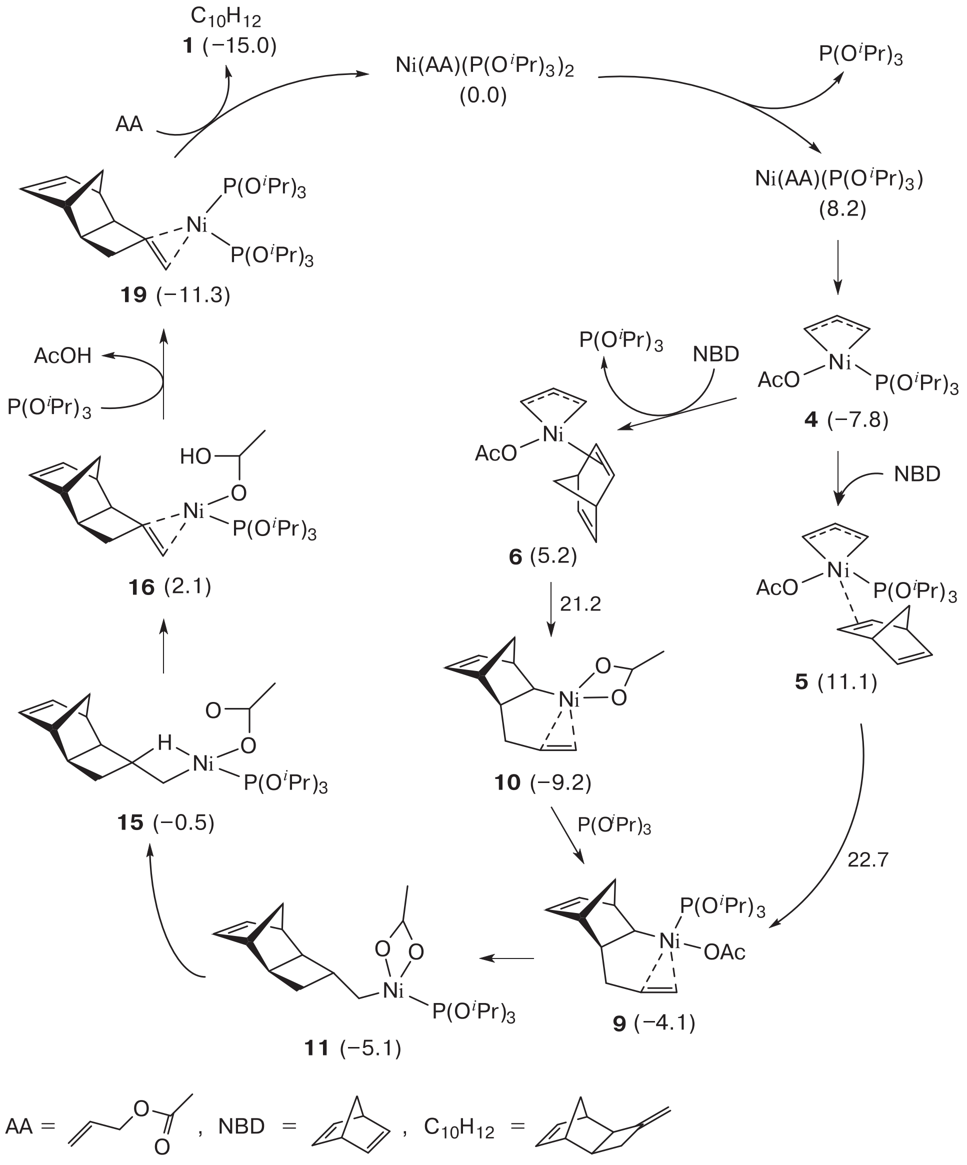


than noticeable increase in the Gibbs energy, as in the case of **12**. Two phosphite ligands in the coordination sphere of nickel (**13**) cause the activation energy to increase substantially to $\Delta G^{\neq}_{298}$ = 26.2 kcal mol^{-1}. Thus, subsequent steps of the reaction mechanism are only possible if the monophosphite intermediate **11** is involved.

Scheme 7 describes two steps, *viz.*, hydride transfer and elimination of the reaction product. According to calculations, as a hydrogen atom attached to the C$^{\beta}$ atom approaches the metal atom, an unstable intermediate **15** with agostic interaction (Ni—H and Ni—C$^{\beta}$ distances of 1.72 and 2.15 Å, respectively) is formed. Subsequent hydrogen transfer to the acetate ligand with the formation of intermediate **16** proceeds with a low activation barrier of 0.8 kcal mol^{-1} and does not involve intermediate formation of nickel hydride.

Elimination of acetic acid molecule with the formation of intermediate **17** is thermodynamically unfavorable since this leads to an increase in the Gibbs energy by 4.7 kcal mol^{-1}. However, if the acetic acid molecule is displaced by a new AA molecule (**16→18**) or by the P(O^{i}Pr)$_3$ ligand (**16→19**), the Gibbs energy of the system decreases considerably, the latter reaction being thermodynamically more favorable. The addition of the new AA molecule to the inter-

Scheme 8



Gibbs energies corrected for solvation energy ($\Delta G_{298,\mathrm{PCM}}$) are given relative to the sum of the energies of the catalytically active complex Ni(AA)(P(O^{i}Pr)$_3$)$_2$ and reactants.

Table 1. Gibbs energies[a] (kcal mol^{-1}) of the intermediate Ni(P(O^{i}Pr)$_3$)(η^3-C_3H_5)-(η^1-OAc) (**4**) and transition states of the stages of the formation of C—C bond (TS **5**→**9** and TS **6**→**10**) calculated using different methods

Basis set	$\Delta G_{298,PCM}$ (**4**)	$\Delta G^{\neq}_{298,PCM}$		$\Delta\Delta G^{\neq}_{298,PCM}$	
		(TS **5**→**9**)	(TS **6**→**10**)	(**4**→**5**→**9**)	(**4**→**6**→**10**)
L11	−12.55	17.89	16.47	30.44	29.02
L2	−14.85	14.27	11.23	29.12	26.09
L3	−13.86	15.92	13.37	29.77	27.23
L2[b]	−16.26	13.18	10.87	29.44	27.12

[a] Calculated relative to the sum of the energies of isolated Ni(P(O^{i}Pr)$_3$)$_3$ and reactants.

[b] Calculated in the scalar relativistic approximation.

mediates **18** or **19** returns the complex Ni(AA)(P(O^{i}Pr)$_3$)$_2$ to the new catalytic cycle.

Thus, the results of quantum chemical modeling of the mechanism of the interaction between AA and NBD allow one to propose the catalytic cycle shown in Scheme 8 assuming the complex Ni(AA)(P(O^{i}Pr)$_3$)$_2$ as the catalytically active species. The presence of two phosphite ligands in the complex offers an explanation for the optimum Ni/P(O^{i}Pr)$_3$ ratio (Ni/P(O^{i}Pr)$_3$ = 1 : 2) for the reaction pathway associated with the formation of product **1** (see Scheme 2).

Since the intermediate Ni(P(O^{i}Pr)$_3$)(η^3-C_3H_5)(η^1-OAc) (**4**) has the lowest energy ($\Delta G_{298,PCM} = -8.1$ kcal mol^{-1} relative to the catalytically active complex), almost all nickel atoms in the reaction mixture are bound in the complex in intermediate **4**. The maximum energies were found for the TSs of the formation of the first C—C bond **5**→**9** and **6**→**10** ($\Delta G^{\neq}_{298,PCM}$ = 22.7 and 21.2 kcal mol^{-1}, respectively). Taking account of the solvation energy leads to a slight decrease in the TS energy of the **6**→**10** step compared to that of the TS of the **5**→**9** step. The energies of intermediate **4** and TS **5**→**9** or TS **6**→**10** determine the Gibbs activation energy of the overall process, *viz.*, $\Delta\Delta G^{\neq}_{298,PCM}$ = 30.4 (**4**→**5**→**9**) and 29.0 kcal mol^{-1} (**4**→**6**→**10**). This value seems to be somewhat overestimated since the process can actually proceed at moderate temperatures (25—40 °C). A possible reason is the overestimation of the activation entropy of the reaction since the enthalpy of activation determined at the same points is two times lower, *viz.*, 14.8 kcal mol^{-1} for the pathway **4**→**5**→**9**.

To improve the results of modeling, we carried out additional calculations using extended basis sets, the scalar relativistic approximation, and the four-component Dirac—Coulomb Hamiltonian.[17] According to calculations (Table 1), extension of the basis set to L3 allowed one to decrease the activation energy for the reaction by 0.7—1.8 kcal mol^{-1}, the decrease being more pronounced for the pathway **4**→**6**→**10**. Relativistic effects only slightly influence the $\Delta\Delta G^{\neq}_{298,PCM}$ value.

Summing up, we for the first time carried out a quantum chemical study of catalytic allylation of NBD affording a product with methylenecyclobutane moiety (**1**) and clarified the reaction mechanism based on experimental data, as well as established the nature of the rate-limiting step and revealed the role of phosphite ligands. According to calculations, the catalytically active species is the complex Ni(AA)(P(O^{i}Pr)$_3$)$_2$. The NBD molecule is added to nickel only as the oxidative addition of AA is completed. The formation of the first C—C bond more likely proceeds involving the η^3-allyl rather than η^1-allyl ligand. The presence of phosphite ligand favors a significant decrease in the activation energy of the formation of the second C—C bond. Hydride transfer from the allyl moiety to the acetate ligand proceeds *via* the intermediate with agostic interaction. The highest energy on the reaction pathway (22.7 kcal mol^{-1}) was found for the TS of the formation of the first C—C bond.

Calculations were carried out on computational facilities at the Joint Supercomputer Center of the Russian Academy of Sciences and at the Center for Collective Use of Super High Performance Computing Resources at the Lomonosov Moscow State University.

This work was financially supported by the Russian Science Foundation (Project No. 18-13-00415).

References

1. V. R. Flid, M. L. Gringolts, R. S. Shamsiev, E. Sh. Finkelshtein, *Russ. Chem. Rev.*, 2018, **87**, 1169.
2. M. Catellani, G. Chiusoli, E. Dradi, G. Salerno, *J. Organomet. Chem.*, 1979, **177**, 29.
3. E. M. Evstigneeva, V. R. Flid, *Russ. Chem. Bull.*, 2008, **57**, 837.
4. E. M. Evstigneeva. R. S. Shamsiev, V. R. Flid, *Vestn. MITHT* [*Bull. Moscow Inst. Fine Chem. Technol.*], 2006, Iss. 3, 3 (in Russian).
5. U. M. Dzhemilev, R. I. Khusnutdinov, G. A. Tolstikov, *Russ. Chem. Rev.*, 1987, **56**, 36.
6. U. M. Dzhemilev, R. I. Khusnutdinov, D. K. Galeev, O. M. Nefedov, G. A. Tolstikov, *Bull. Acad. Sci. USSR*, *Div. Chem. Sci.*, 1987, **36**, 122.
7. V. R. Flid, O. S. Manulik, D. V. Dmitriev, V. B. Kouznetsov, E. M. Evstigneeva, A. P. Belov, A. A. Grigor′ev, *Eurasian Chem.-Tech. J.*, 2001, **3**, 73.

8. D. N. Laikov, *Chem. Phys. Lett.*, 1997, **281**, 151.
9. D. N. Laikov, Yu. A. Ustynyuk, *Russ. Chem. Bull.*, 2005, **54**, 820.
10. J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865.
11. D. N. Laikov, *Chem. Phys. Lett.*, 2005, **416**, 116.
12. R. S. Shamsiev, A. V. Drobyshev, V. R. Flid, *Russ. J. Org. Chem.*, 2013, **49**, 345.
13. R. S. Shamsiev, Ha Ngok Thien, V. R. Flid, *Russ. Chem. Bull.*, 2013, **62**, 1553.
14. R. S. Shamsiev, V. R. Flid, *Russ. Chem. Bull.*, 2013, **62**, 2301.
15. D. V. Dmitriev, R. S. Shamsiev, Ha Ngok Thien, V. R. Flid, *Russ. Chem. Bull.*, 2013, **62**, 2385.
16. K. T. Egiazaryan, R. S. Shamsiev, V. R. Flid, *Tonkie Khim. Tekhnol.* [*Fine Chem. Technol.*], 2019, **14**, No. 6, 56 (in Russian).
17. K. G. Dyall, *J. Chem. Phys.,* 1994, **100**, 2118.

Received December 2, 2019;
in revised form December 9, 2019;
accepted January 9, 2020