THEORETICAL BASES OF CHEMICAL TECHNOLOGY

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Dedicated to the 125th birthday of Academician Yakov Kivovich Syrkin

Quantum chemical investigation of the oxidative addition reaction of allyl carboxylates to Ni(0) and Pd(0) complexes

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Objectives. *The first allylpalladium complex was synthesized and characterized 60 years ago at the Department of Physical Chemistry of M.V. Lomonosov Moscow State University of Fine Chemical Technology (MITHT). This discovery was an important stage in the development of a new direction in chemistry – metal complex catalysis, which subsequently led to understanding the strategy for studying the mechanisms of catalysts action, and gave a powerful impetus to the study of intermediates of catalytic reactions. The key stage in many catalytic processes involving transition metal complexes is the oxidative addition stage. The study's aim was the quantum chemical modeling of the oxidative addition stage of allylic carboxylates to the Ni(0) and Pd(0) complexes.*

Methods. *Quantum chemical calculations were carried out under the Kohn-Sham method for the density functional theory using the PBE exchange-correlation functional and all-electron L11 basis set.*

Results. *As a result of theoretical study, we showed that the oxidative addition of allyl acetate to the triisopropylphosphite complex of nickel(0) and allyl formate to the triphenylphosphine complex of palladium(0) can proceed along two routes. In the first of them, in the coordinated breaking of the C–O bond and the formation of the metal–O bond, the same oxygen atom is involved, thus forming a three-center transition state. In the second route, the restructuring of relations is carried out in a five-center transition state. The chelating effect in the five-centered transition state of the second route reduces the reaction's activation barrier by 12.7 kcal/mol for allyl acetate and the nickel(0) triisopropylphosphite complex* $Ni(P(O^iPr)_3)_2$ *and by 9.9 kcal/mol for allyl formate and the palladium(0) triphenylphosphine complex* $Pd(PPh_3)$*. The presence of the second triphenylphosphine ligand in* $Pd(PPh_3)_2$ *reduces the activation barrier by only 2.6 kcal/mol.*

Conclusions. *The quantum chemical modeling performed allowed us to determine the preference for the oxidative addition of allyl carboxylates to the Ni(0) and Pd(0) complexes through a five-center transition state. The reaction's activation barriers through the "classical" three-center interaction are 9.9–12.7 kcal/mol higher, and the chelating effect is more noticeable for the Ni complex. The presence in the coordination sphere of several bulky ligands, such as triphenylphosphine, practically eliminates the chelating effect in the oxidative addition of allyl carboxylates.*

Keywords: *allyl complexes, nickel, palladium, oxidative addition, reaction mechanism, density functional theory, quantum chemical calculation.*

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К 125-летию со дня рождения академика Я.К. Сыркина

Квантово-химическое исследование реакции окислительного присоединения аллилкарбоксилатов к комплексам Ni(0) и Pd(0)

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Цели. *Первый аллильный комплекс палладия был синтезирован и охарактеризован 60 лет назад на кафедре физической химии МИТХТ имени М.В. Ломоносова. Это открытие явилось важнейшим этапом развития нового направления в химии – металлокомплексного катализа, привело к пониманию стратегии изучения механизмов действия катализаторов, дало мощный импульс исследованию интермедиатов каталитических реакций. Ключевой стадией многих каталитических процессов с участием комплексов переходных металлов является стадия окислительного присоединения. Целью работы явилось квантово-химическое моделирование стадии окислительного присоединения аллиликарбоксилатов к комплексам Ni(0) и Pd(0).*

Методы. *Квантово-химические расчеты проведены в рамках метода Кона-Шэма теории функционала плотности с использованием обменно-корреляционного функционала PBE и полноэлектронного базиса L11.*

Результаты. *В результате теоретического исследования мы показали, что окислительное присоединение аллилацетата к триизопропилфосфитному комплексу никеля(0) и аллилформиата к трифенилфосфиновому комплексу палладия(0) может протекать по двум маршрутам. В первом из них, в согласованном разрыве С–О-связи и формировании связи металл–О участвует один и тот же атом кислорода, таким образом формируется трехцентровое переходное состояние. Во втором маршруте перестройка связей осуществляется в пятицентровом переходном состоянии. Хелатирующий эффект в пятицентровом переходном состоянии второго маршрута уменьшает активационный барьер реакции на 12.7 ккал/моль для аллилацетата и триизопропилфосфитного комплекса никеля(0) $Ni(P(OiPr)_3)_2$ и на 9.9 ккал/моль для аллилформиата и трифенилфосфинового комплекса палладия(0) $Pd(PPh_3)$. Наличие второго трифенилфосфинового лиганда в $Pd(PPh_3)_2$ уменьшает активационный барьер только на 2.6 ккал/моль.*

Заключение. *Проведенное квантово-химическое моделирование позволило определить предпочтительность протекания реакции окислительного присоединения аллилкарбоксилатов к комплексам Ni(0) и Pd(0) через пятицентровое переходное состояние. Активационные барьеры реакции, протекающей через «классическое» трехцентровое взаимодействие, выше на 9.9–12.7 ккал/моль, причем для Ni-комплекса хелатирующий эффект оказывается более заметным. Наличие в координационной сфере нескольких объемных лигандов, таких как трифенилфосфин, практически нивелирует хелатирующий эффект в окислительном присоединении аллилкарбоксилатов.*

Ключевые слова: *аллильные комплексы, никель, палладий, окислительное присоединение, механизм реакции, метод функционала плотности, квантово-химические расчеты.*

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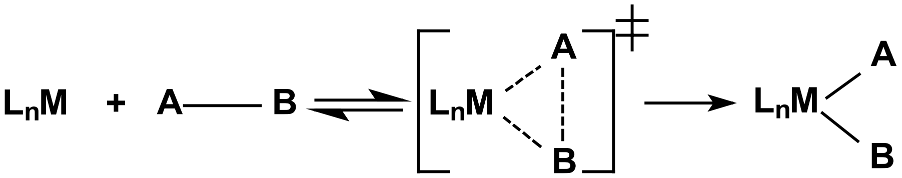
Introduction

The outgoing year 2019 has been a landmark for all chemists, not only because of the 150th anniversary of the opening of D.I. Mendeleev's Periodic Law. This year marks three more anniversary dates. This is the 125th birthday of Academician Yakov Kivovich Syrkin, an outstanding physical chemist and one of the founders of quantum chemistry in Russia, who made a huge contribution to the development of the theory of the structure of molecules and the nature of chemical bonds. His student, an outstanding technologist and catalysis specialist, academician Ilya Iosifovich Moiseev, turned 90 years old this year. The third anniversary is directly related to the names of Y.K. Syrkin and I.I. Moiseev. Sixty years ago at the Department of Physical Chemistry of M.V. Lomonosov Moscow State University of Fine Chemical Technology (MITHT) they synthesized and characterized the first allyl complex of palladium [1]. This discovery was an important stage in the development of a new direction in chemistry – metal complex catalysis, leading to an understanding of the strategy for studying the mechanisms of catalyst actions, and provided a powerful impetus to the study of intermediates of catalytic reactions. In addition, the presence of electron density delocalization in allyl fragments was a brilliant confirmation of resonance theory, actively supported and followed by Y.K. Syrkin.

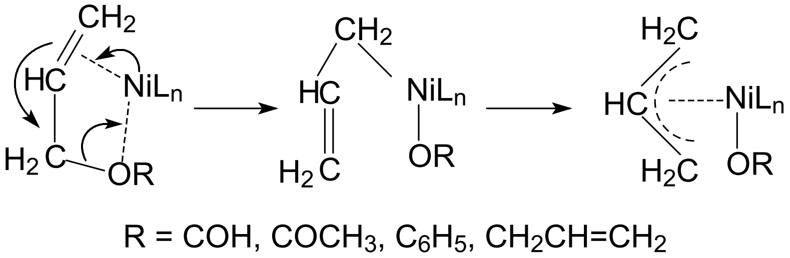
The key stage in many catalytic processes involving transition metal complexes is the oxidative addition stage [2–7]. Oxidative addition can be represented as the addition of substrate AB to a metal complex in such a way that the formal oxidation state and the coordination number of the resulting complex increase by 2 (Scheme 1). The reverse reaction may be considered as a stage of reductive elimination.



Scheme 1. Oxidative addition of AB molecule to L_nM complex (L – ligand, M – metal).

Due to the fact that in the stage of oxidative addition, the formal oxidation state of the metal increases by two, ligands that increase the electron density in the metal center will contribute to lowering the activation barrier and increasing the rate of the process. At the same time, bulky ligands, which create steric hindrances in the metal center, contribute to a decrease in the rate of oxidative addition due to an increase in the activation barrier, since they hinder the increase in the coordination number. It is assumed that the reacting system passes through a three-center transition state (Scheme 1).

Experimental studies of such reactions have been carried out since the middle of the 20th century. Of particular interest are the stages in which the C–O bond undergoes breaking. In the works of Yamamoto et al. the interaction of nickel [8] and palladium complexes [9, 10] with allyl carboxylates, allyl ethers and allyl alcohols was studied. Because of this interaction and the breaking of the C–O bond, an η^3- allyl complex is formed. Based on spectral data, a reaction mechanism has been proposed, which is shown in Scheme 2.



Scheme 2. Hypothetical mechanism of the oxidative addition of allyl containing compounds to the nickel complex (0).

Scheme 2 shows that the C−O bond cleavage in the Ni(η^2-C_3H_5OR)L_n complex initiates the η^2–η^1-rearrangement of the allyl fragment. As a result of the η^1–η^3-isomerization of the allyl fragment during the next stage, an η^3-allyl complex of Ni(II) is formed. The reaction proceeds in a similar manner on Pd(0) complexes. The interaction of allyl carboxylates with nickel and palladium complexes is an important stage in the mechanism of allylation of norbornadiene [11–14].

With the development of calculation methods, it became possible to theoretically explain the process's mechanism, revealing the structural and energy characteristics of short-lived intermediates. Therefore, it seems relevant to apply the methods of modern quantum chemistry in the study of the oxidative addition for allyl carboxylates to transition metal complexes. This study's aim was a quantum chemical modeling of the oxidative addition of allyl acetate to the triisopropylphosphite complex of nickel(0) and allyl formate to the triphenylphosphine complex of palladium(0). The modeling of these stages is also important to understand the mechanism of the allylation of norbornadiene catalyzed by systems based on $Ni(C_3H_5)_2/P(OiPr)3/$*m*-xylene [13, 14] and $Pd_3(OAc)_6/PPh_3/$ acetonitrile [11].

Materials and Methods

Quantum chemical calculations were performed in the "Priroda" program [15] using the Kohn–Sham method for the density functional theory via the PBE exchange-correlation functional [16] and the all-electron L11 basis set [17]. The contraction schemes for orbital basis sets are given in Table 1. In view of the importance of taking into account relativistic effects for palladium, the calculations of palladium complexes were carried out in scalar-relativistic approximation. This calculation technique was earlier used successfully to model reactions involving nickel and palladium complexes [18–20]. The influence of the solvent was taken into account within the framework of the polarized continuum model (PCM). For the nickel-containing system, the medium's dielectric constant was taken to be 2.35 (*m*-xylene solvent), and for the palladium-containing system – 36 (acetonitrile).

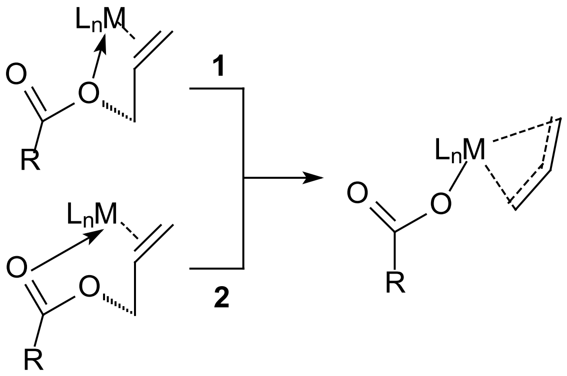
Geometry optimization was carried out without restrictions on the symmetry of the molecule. The type of critical points on the potential energy surface (minima or saddle points) was determined based on analytically calculated second derivatives of energy with regard to all coordinates. To verify the evolutionary relationship of the transition states found with local minima, a procedure to calculate the intrinsic reaction coordinate (IRC) was performed.

Results and Discussion

The results of this study showed that the oxidative addition stage of allyl carboxylates to nickel and palladium complexes can proceed along two possible routes, presented in Scheme 3. The main difference between them is the structure of the transition state. If the same oxygen atom is involved in the coordinated breaking of the C–O bond and the formation of the O–M bond, then Route 1 is realized through a three-center transition state.

Table 1. Orbital contraction schemes in L11 basis set

Element	Basis sets (contracted/uncontracted)
	L11
Pd	[26s23p16d5f]/{7s6p4d1f}
Ni	[19s15p11d5f]/{6s5p3d1f}
P	[14s11p6d]/{5s4p2d}
O	[10s7p3d]/{4s3p1d}
C	[10s7p3d]/{4s3p1d}
H	[6s2p]/{2s1p}



Scheme 3. Two possible routes for the oxidative addition of the allyl carboxylate to the transition metal complex.

If different oxygen atoms participate in the breaking of the C–O bond and the formation of the O–M bond, then Route 2 is implemented. In this case, the reacting system passes through a transition state in which five atoms participate in the coordinated stage: C–O–C–O–M. From the standpoint of the balance of bond energy, the more atoms involved in a concerted elementary act during the breaking of old and the formation of new bonds, the lower the activation barrier should be. Thus, the five-center interaction should contribute to lowering the activation barrier. However, in order to the entropy factor in the formation of the transition state of a complex structure was taken into account, conclusions about the preference of a particular route must be made based on the calculation of the Gibbs energy.

We note that at the stage of coordination of the allyl carboxylate molecule, a structure is possible in which the terminal oxygen atom of the carboxylate fragment bonds to the metal atom (Fig. 1). The resulting structure has structural prerequisites to achieve a five-center transition state and the occurrence of a chelating effect.

Oxidative addition of allyl acetate to the nickel(0) triisopropyl phosphite complex. A complex of the composition $Ni(P(O^iPr)_3)_3$ was chosen as the initial one. Since the process of oxidative addition increases the number of ligands by 2, we simulated the substitution stage of one phosphite ligand for allyl carboxylate with the formation of structures **Ni_R1** and **Ni_R2** (Scheme 4). The optimized structures of the reagents **Ni_R1** and **Ni_R2**, the transition states **Ni_TS1** and **Ni_TS2** and the products **Ni_P1** and **Ni_P2** of allyl acetate oxidative addition to $Ni(P(O^iPr)_3)_2$ stage are presented in Fig. 2.

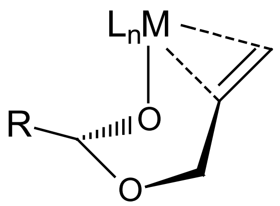
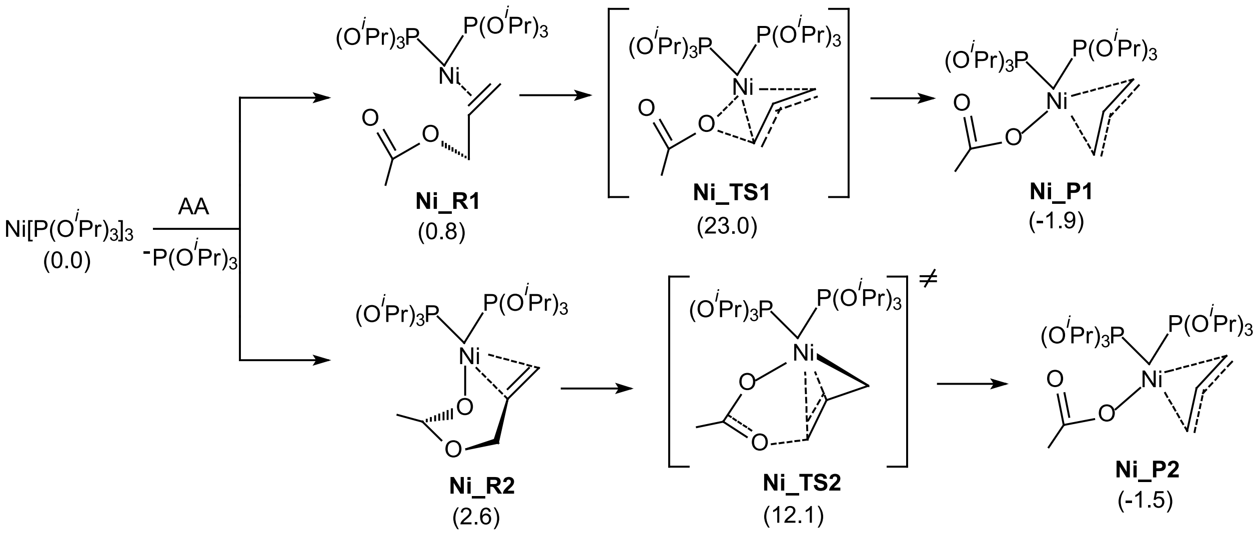
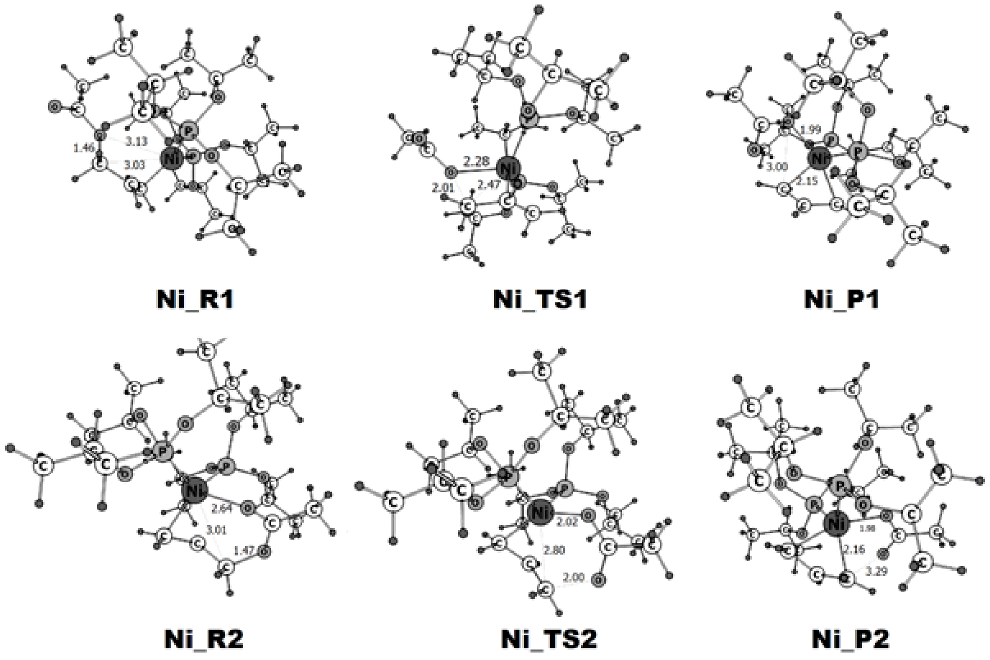


Fig. 1. Structure of the intermediate formed along Route 2, where M – Ni, Pd; L – PPh_3, $P(O^iPr)_3$; R – H; CH_3.



Scheme 4. Coordination and oxidative addition stages of allyl acetate (AA) to the $Ni(P(O^iPr)_3)_2$ involving three- and five-center interactions. The values of ΔG_{298} are given in kcal/mol.



Ni_R1 Ni_TS1 Ni_P1

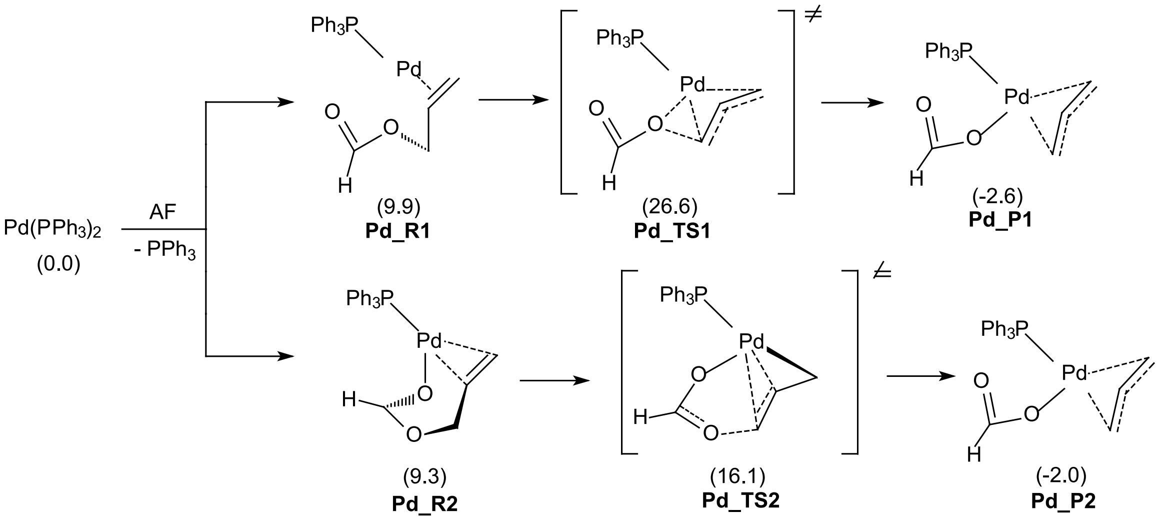
Ni_R2 Ni_TS2 Ni_P2

Fig. 2. Optimized structures of reagents (R), transition states (TS), and products (P) of the oxidation addition stage of $C_3H_5OCOCH_3$ to the $Ni(P(O^iPr)_3)_2$. Interatomic distances are given in Å.

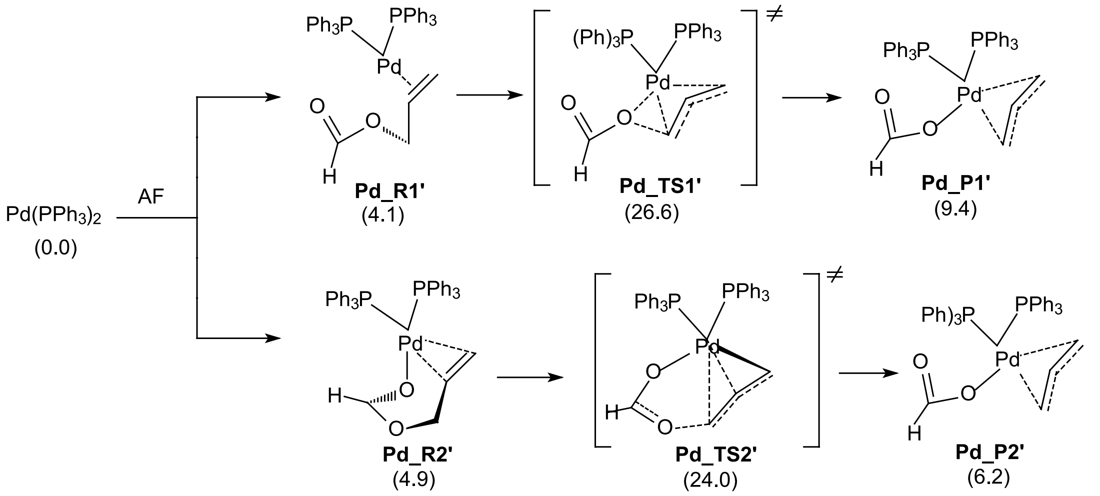
According to the calculations, despite the appearance of an additional Ni–O interaction, the Gibbs energy of the **Ni_R2** complex is 1.8 kcal/mol higher than the energy of the **Ni_R1** complex. In this case, the formation of the three-centered transition state **Ni_TS1** upon breaking the C–O bond is characterized by a higher activation Gibbs energy ($\Delta^{\neq}G_{298}$ = 22.2 kcal/mol) compared with the five-centered transition state **Ni_TS2** ($\Delta^{\neq}G_{298}$ = 9.5 kcal/mol). Figure 2 shows that the length of the formed Ni–O bond in the structure of **Ni_TS2** is noticeably shorter than that of **Ni_TS1**. Therefore, the chelating effect in the transition state of **Ni_TS2** favors the occurrence of oxidative addition.

Oxidative addition of allyl formate to the palladium(0) triphenylphosphine complex. To study the effect of the number of ligands on the activation parameters of the oxidative addition stage, quantum chemical modeling of the oxidative addition of allyl formate to the $Pd(PPh_3)_n$ was carried out for $n = 1$ and 2. According to our calculations, the reaction mechanism (Schemes 5 and 6) is similar to the Ni-containing system.

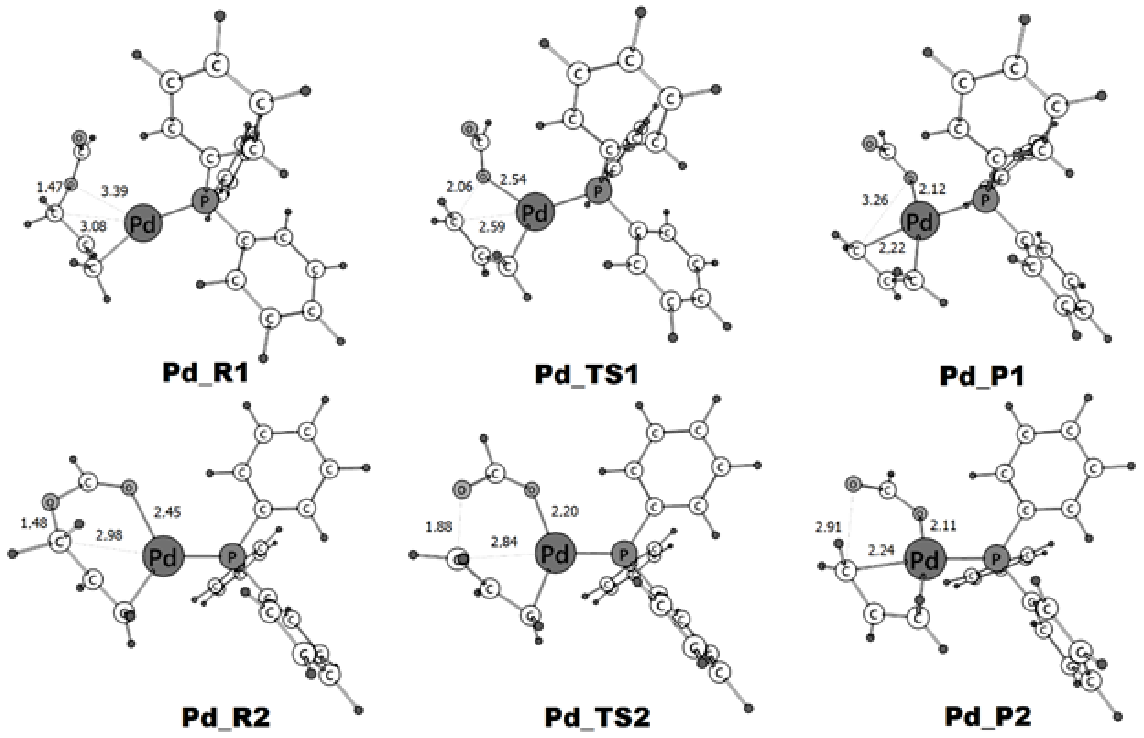
A comparison of the energy parameters of 4 routes (Schemes 5 and 6) showed that from the point of view of thermodynamics, the replacement of one phosphine ligand with allyl formate is not beneficial, since it leads to an increase in energy by 4.4–5.8 kcal/mol. However, from the point of view of kinetics, it is obvious that the oxidative addition of allyl acetate can proceed only to the coordination-unsaturated complex $Pd(PPh_3)$. In this case, as in the case with the nickel complex, the formation of a five-center transition state (**Pd_TS2**) leads to a significant reduction in the activation barrier (by 10.5 kcal/mol) compared to a three-center interaction (**Pd_TS1**). The optimized structures of the reagents **Pd_R1** and **Pd_R2**, the transition states **Pd_TS1** and **Pd_TS2** and the products **Pd_P1** and **Pd_P2** of the reaction of the oxidative addition of allyl formate to the $Pd(PPh_3)$ complex are presented in Fig. 3.



Scheme 5. Coordination and oxidative addition stages of allyl formate (AF) to the $Pd(PPh_3)$ involving three- and five-center interactions. The values of ΔG_{298} are given in kcal/mol.



Scheme 6. Coordination and oxidative addition stages of allyl formate (AF) to the $Pd(PPh_3)_2$ involving three- and five-center interactions. The values of ΔG_{298} are given in kcal/mol.



Pd_R1 **Pd_TS1** **Pd_P1**

Pd_R2 **Pd_TS2** **Pd_P2**

Fig. 3. Optimized structures of reagents (R), transition states (TS), and products (P) of the oxidation addition stage of C_3H_5OCOH to the $Pd(PPh_3)$. Interatomic distances are given in Å.

Table 2. Energy and structural parameters for the three- (**M_TS1**) and five-center transition states (**M_TS2**) of the oxidative addition stage of allyl acetate to the Ni(0) and allyl formate to the Pd(0)

	$\Delta E^{\neq}$, kcal/mol	$\Delta G^{\neq}_{298}$, kcal/mol	$\Delta G^{\neq}_{298,PCM}$, kcal/mol	R(M–O), Å	ν*, cm^{-1}
Ni_TS1	25.2	22.2	22.3	2.28	260.9
Ni_TS2	14.1	9.5	9.3	2.02	195.2
Pd_TS1	19.5	16.7	14.1	2.54	254.8
Pd_TS2	6.7	6.8	6.1	2.20	249.0
Pd_TS1´	25.0	22.5	18.4	2.91	141.4
Pd_TS2´	23.4	19.1	19.3	2.31	255.5

* imaginary frequency

Table 2 presents the energy, spectral, and structural characteristics of the three-center (**M_TS1**) and five-center (**M_TS2**) transition states of the oxidative addition stage of allyl acetate to the Ni(0) complex and allyl formate to the Pd(0) complex. The calculation results confirm the experimental facts about a decrease in the rate of oxidative addition in the presence of bulky ligands in the coordination sphere of the metal that create steric hindrances. Even the presence of a five-center interaction in the diphosphine transition state does not lead to a noticeable decrease in the activation barrier (**Pd_TS2´** and **Pd_TS1´**, Scheme 6). The energy gained from the chelating effect is only 2.6 kcal/mol.

The inclusion of nonspecific solvation in the calculation of the Gibbs activation energy (Table 2, $\Delta G^{\neq}_{298,\ PCM}$) leads to an insignificant correction in the results of the gas-phase calculation in the case of a nickel-containing system in *m*-xylene medium (~0.2 kcal/mol). The polarity of acetonitrile and the significant dipole moment of the three-center transition state of **Pd_TS1´** (6.9 D) lead to the greatest solvent effect for the oxidative addition stage of allyl formate to the **Pd_R1´** diphosphine complex ($\Delta G^{\neq}_{298} - \Delta G^{\neq}_{298,\ PCM}$ = 4.1 kcal/mol). Therefore, the chelating effect has a noticeable effect in coordination-unsaturated complexes and is almost imperceptible in coordination-saturated diphosphine complexes of Pd (0).

Conclusions

The quantum chemical modeling performed made it possible to determine the preferability of the oxidative addition of allyl carboxylates to the Ni(0) and Pd(0) complexes through a five-center transition state. The reaction's activation barriers through the "classical" three-center interaction are 8.0–13.0 kcal/mol higher, and the chelating effect is more noticeable for the nickel complex. The presence in the coordination sphere of several bulky ligands, such as PPh_3, completely eliminates the chelating effect in the oxidative addition of allyl carboxylates.

The authors declare no conflicts of interest.

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