Russian Chemical Reviews

December 1985

Translated from *Uspekhi Khimii*, 54, 1945-1970 (1985)

U.D.C. 541.128

The Electronic Structure and Reactivity of Palladium Compounds

O.V.Gritsenko, A.A.Bagatur'yants, I.I.Moiseev, and V.B.Kazanskii

The state of the quantum-chemical theory of the electronic structure of palladium compounds has been examined. The results of quantum-chemical calculations for palladium(II) and palladium(0) compounds and palladium clusters, and also of calculations for model reactions of palladium compounds, have been discussed. Methods for analysing the relationship between the electronic structure and reactivity of palladium complexes have been examined.
The bibliography contains 121 references.

CONTENTS

I.	Introduction	1151
II.	General concepts	1152
III.	Quantum-chemical calculations of the electronic structure of palladium compounds	1153
IV.	Quantum-chemical studies of reactions involving palladium compounds	1158

I. INTRODUCTION

The high catalytic activity of metallic palladium in heterogeneous catalysis, for example the hydrogenation of unsatuarated compounds,[1] the catalytic reforming of petroleum,[2] and the conversion of carbon monoxide into methane or methanol,[3] is well known. Interest in the chemistry of palladium has been increasing since the late nineteen-fifties, when it was found that Pd^{II} complexes can oxidise alkenes selectively at low temperatures to give carbonyl compounds,[4,5] vinyl esters, acetals, and ketals.[6] These reactions not only provided a basis for industrial methods for obtaining acetaldehyde and vinyl acetate but also initiated the development of a new field in homogeneous metal-complex catalysis, based on the thermodynamic analysis of possible catalyst–substrate reactions and its use to construct a catalytic cycle.[7]

In the earliest papers by Syrkin and co-workers[5,6] it was suggested that the key compounds in the oxidation of alkenes by palladium complexes are organic derivatives of palladium with a metal–carbon σ-bond, produced by reactions of the initially formed alkene π-complexes of Pd^{II}. This suggestion, which at first appeared unusual and was not immediately accepted by organometallic chemists of the classical school, was subsequently proved by direct synthetic methods[7-9] and confirmed by kinetic studies.[9,10]

The chemistry of organic derivatives of palladium is now among the most well developed fields of the organic chemistry of transition metals.[11,12] It has become clear that the coordination possibilities of Pd compounds, their electronic structure, and their reactivity, which changes with change in the nature of the solvent and the ligands not taking direct part in the reaction, are most important factors which must be taken into account both in the analysis of the mechanism of the action of catalysts and in the prediction of their catalytic effect.

In the present review, the results of the quantum-chemical study of the electronic structure of palladium compounds are discussed. The main aims of the review are to compare the results obtained by different workers and by different

methods, to compare data on the electronic structure and properties of compounds of palladium and other elements of the platinum group, and to find methods for the quantum-chemical analysis of the relationship between the electronic structure of transition metal complexes and their reactivity.

II. GENERAL CONCEPTS

In the nature of the filling of its electron levels, the palladium atom occupies a unique position in the periodic system. Thus it is only for this atom in the ground state ^1S that the valence d-level is completely filled (electron configuration $4d^{10}$) while the outer 5s and 5p atomic orbitals (AO) are unoccupied. It should be noted for comparison that for the other elements of the platinum triad with ten valence electrons, the outer s-level is partly or completely filled: thus for platinum the ground state is the atomic state ^3D (configuration $5d^96s^1$), and for nickel ^3F (configuration $3d^84s^2$). As a result, the ionisation potential of the palladium atom $I_{Pd} = 8.33$ eV[13] corresponds to the ionisation of a 4d AO, whereas in the case of platinum the first ionisation potential $I_{Pt} = 9.0$ eV corresponds to the removal of an electron from the 6s AO. This characteristic feature of the electronic structure is related to the fact that in the Pd atom, the outer 5s and 5p AO have relatively high energies. Table 1 shows that the energies of electron promotion $d^{10} \rightarrow d^9s^1$ and $d^{10} \rightarrow d^9p^1$ increase considerably in the order Ni < Pt < Pd. At the same time, for palladium the outer 5s and 5p AO are much more extended in space (that is more diffuse) than its 4d AO. Thus the average radius of the Hartree–Fock 5s AO of palladium, equal to 0.194 nm for the state $d^9s^1(^3D)$, is more than twice the corresponding radius of the 4d AO (Ref.17, see Table 1), and much greater than the covalent radius of palladium (~0.13 nm).

Table 1. Ionisation potentials I, promotion energies E, and average radii R_d of the Hartree–Fock d AO of nickel, palladium, and platinum.

Atom	I, eV ($d^{10} \rightarrow d^9$)	E, eV		R_d, nm
		($d^{10} \rightarrow d^9s^1$)	($d^{10} \rightarrow d^9p^1$)	
Ni	5.81 [14]	−1.79 [15]	1.72 [16]	0.055 [17]
Pd	8.33 [14]	0.95 [15]	4.23 [13]	0.076 [17]
Pt	8.20 [14]	−0.76 [16]	3.28 [13]	—

Note. Numbers in square brackets denote references (Ed. of Translation).

Thus quantum-chemical calculations for palladium systems, in particular Pd^0 compounds, are of considerable interest, since the results reveal in purest form the role of the outer s and p orbitals of the transition metal in coordinate bond formation. Thus for example the ability of the Pd atom with its filled d level to undergo Pd ← L donor–acceptor interaction should be determined by the contribution of the unoccupied 5s and 5p AO to bond formation.

In the Ni–Pd–Pt series, the relative energetic and geometric characteristics of the valence d AO of palladium are characteristic of an element of the second transition series. With reference to energy, these orbitals are even more stable than the d AO of elements of the third transition series, whereas with respect to size they are still fairly highly localised.

Most published quantum-chemical studies have been devoted to calculations of the electronic structure of compounds of palladium in its typical formal oxidation states Pd^0 and Pd^{II}. The problem of determining the oxidation state in complexes of metals in low oxidation states is not simple. The formal oxidation state of a metal in a complex compound is defined as the charge produced on the given atom after the removal of the ligands. It is assumed that in the leaving carbon-containing ligands and acido-ligands (for example H^-, Cl^-, OH^-), the electron pair of the M–L bond remains associated with the ligand (that is the ligand is removed as an anion), and that molecular ligands are removed as uncharged species. In view of the variety of electronic characteristics of ligands, the classification of complexes according to the formal oxidation state of the metal is to a large extent arbitrary. The position becomes even more complicated when the ligands (for example the carbon atom in the system PdC examined in Refs.18 and 19) do not exist as free anions in solution.

One way of determining the oxidation state is by analysing the electron densities of the transition metal atom in a complex. Sometimes, the formal oxidation state is related to the effective charges of the atoms in the molecules, calculated by quantum-chemical methods. The charge of a transition metal atom, however, depends to a significant extent on the population of the outer s and p orbitals, and in the case of palladium an appreciable proportion of the electron density of these orbitals is localised outside the sphere of the covalent radius.[20] It seems more justified to relate the oxidation state not to the total charge of the palladium atom but to the total population of its valence d AO, which are localised mainly within the sphere of the covalent radius. If it is assumed that an increase in the oxidation state by one unit corresponds to an increase in the vacancy in the d level by 1 e, then the valence electron configuration of palladium is d^{10} for Pd^0, and d^8 for Pd^{II}.

To conclude this section, the quantum-chemical methods used in the calculations for the specific systems which will subsequently be examined can be considered. The different approaches were analysed in detail in Ref.21. For transition metal compounds, a reliable calculation of the bond strengths and the potential surfaces of reactions requires a non-empirical calculation using a large number of basis AO with subsequent allowance for the effects of electron correlation. A qualitatively reliable picture of the electron density distribution, and the relative energies of coordination for the simplest systems, can also be obtained, however, by non-empirical calculations by the SCF MO LCAO method using small basis sets requiring a much smaller volume of calculations. The volume of non-empirical calculations is often further reduced by using the valence approximation, in which the influence of the core electrons is effectively taken into account using atom pseudo-potentials.[22]

Since for most palladium systems the non-empirical level of calculation remains unattainable, simplified semi-empirical methods involving the complete neglect of differential overlap (CNDO)[23] and incomplete neglect of differential overlap (INDO),[24] and also the extended Hückel method (EHM),[25] are most frequently used. The approximations introduced in these methods lower the reliability of the quantitative results of the calculations. To decrease the error of the approximate methods, their parameters are calibrated using available experimental and theoretical data. The results of the calculations are analysed using different indices of

electronic structure, such as the Wiberg indices W_{AB}, the bond orders, and the two-centre components of the total energies E_{AB}.[26] Comparison of these indices makes it possible to study the regular features of the change in the electronic structure and reactivity in a series of related systems.

The SCF Xα scattered wave (SCF-Xα-SW) method[27] has also been used to study the electronic structure of Pd compounds. This method makes it possible to calculate satisfactorily the electronic spectra of transition metal compounds. At the same time, the approximations introduced in the SCF-Xα-SW method do not make it possible to calculate reliably the coordination energies and potential energy surfaces, and the specific form of representation of the wavefunction creates certain difficulties in the interpretation of the results of the calculations, in particular in the determination of the different indices of the electronic structure.

III. QUANTUM-CHEMICAL CALCULATIONS OF THE ELECTRONIC STRUCTURE OF PALLADIUM COMPOUNDS

1. The Electronic Structure of Pd^{II} Compounds

Typical palladium(II) compounds are square-planar complexes, for example K_2PdCl_4, and also the mixed complexes PdX_nY_{4-n} (where X represents an acido-ligand, Y a neutral donor ligand, and $n = 2$).[13] Calculations for the anionic complex $PdCl_4^{2-}$ have been carried out by the non-empirical SCF MO LCAO method,[28,29] the SCF-Xα-SW method,[30] and the semi-empirical INDO[31,32] and CNDO[33,34] methods.

The results of the calculations at first sight are inconsistent with the view that in the $PdCl_4^{2-}$ anion the oxidation state of palladium is +2. Thus according to the results of a non-empirical pseudo-potential calculation in the valence approximation in a minimum basis set[28] and INDO calculations,[31,32] the charge of the Pd atom is only 0.5e. If the total population of the 4*d* AO is considered, however, the electron distribution within the sphere of the covalent radius of the Pd atom is close to that expected for a Pd^{II} complex. The value obtained for the vacancy in the *d* level (~1.5e) is only 0.5e lower than that formally assigned to Pd^{II} (see section I).

As noted above, the low effective charge of Pd is due to the appreciable population of the diffuse outer 5*s* and 5*p* AO (their total population is close to 1e[31,32]). Their diffuse character is responsible for the appreciable contribution of these partly filled Pd orbitals to the Pd–Cl covalent bonding as a result of their extensive overlap with the orbitals of the Cl atom. Thus the overlap integrals of the 5*s* and $5p_x$ AO of palladium with the $3p_x$ AO of chlorine are $S(5s3p_x) = 0.23$ and $S(5p_x3p_x) = 0.32$, whereas $S(4d_{x^2-y^2}3p_x) = 0.10$.[32] Thus the outer 5*s* and 5*p* AO of palladium, together with the valence 4*d* AO, play an important part in the Pd^{II}–L bonding interaction.

Although expansion of the basis set in a non-empirical calculation for $PdCl_4^{2-}$ [28] has a marked influence on the effective charges of the atoms obtained by a Mulliken population analysis, the picture of the electron density distribution changes little, and the reported change in the effective charges is related to the arbitrary nature of the Mulliken procedure. Thus the negative charge of Pd, obtained in the non-empirical calculation in a two-exponent basis set,[28] is due to the assignment to the Pd atom of electron density associated with the polarisation *p* functions, which are much more diffuse than the 5*s* and 5*p* AO of palladium, corresponding to the bound atomic states. In fact, however, an appreciable proportion of this electron density should have been assigned to the ligands.

Thus to determine whether the charges obtained by semi-empirical methods are reasonable, they must be compared with the charges obtained by the non-empirical SCF MO LCAO method in a comparable minimum basis set. In this case the INDO parametrisation schemes[31,32] apparently give a reasonable electron distribution picture, whereas the CNDO parametrisation scheme[33] gives an unrealistic electron distribution.

Different methods give different relative distributions of the energies of the MO of the $PdCl_4^{2-}$ ion. Thus for the energies of the *d* levels (more accurately the energies of the MO consisting chiefly of the *d* AO of Pd), the following relationships have been obtained: $d_{x^2-y^2} > d_{xy} > d_{xz} \cong d_{yz} > d_{z^2}$,[30] $d_{x^2-y^2} > d_{xz} \cong d_{yz} > d_{xy} > d_{z^2}$,[32] and $d_{x^2-y^2} > d_{z^2} > d_{xz} \cong d_{yz} > d_{xy}$.[28,31]

The comparison of the results of calculations by the MO LCAO and Xα methods is somewhat arbitrary, since the energies of the MO have a different physical significance in these methods. The highest occupied MO were found to be those consisting chiefly of the *d* AO of the Pd atom in Ref.30, or the AO of the Cl atom in Refs.28, 31, and 32. The energies of the electron transitions were estimated in Refs.29 and 32 by independent SCF calculations for the ground and excited states; in Ref.34 by the SCF method with allowance for electron correlation within the framework of configuration interaction; and in Ref.30 by the transition state method.[27] The calculated energies of the lowest *d*–*d* transition and the lowest allowed charge-transfer transition L → Pd agree with the experimental data[35] in the case of the CNDO method.[34] This agreement may be accidental, however, since the energies of the subsequent *d*–*d* transitions show less satisfactory agreement with the experimental data.

The dependence of the electronic structure of square Pd^{II} complexes on the type of ligand has been studied.[33,36,37] CNDO calculations for the complexes PdX_4^{2-},[33] $PdX_3(C_2H_4)^-$ [36] (X = F, Cl, Br), and $Pd(PH_3)_2XY$ (X, Y = H, Cl, $OCOCH_3$, OH)[37] showed that in all cases the electron density on the Pd atom increases with decrease in the electronegativity of the ligands. For example, the effective charge of Pd calculated for the complexes *trans*-$XYPd(PH_3)_2$ increases from 0.51e for X, Y = H to 0.67e for X, Y = OR.[37] As in the case of $PdCl_4^{2-}$ examined above, the magnitude of the vacancy in the 4*d* level of Pd correlates with the formal oxidation state of palladium, that is in all cases it is close to 2e. An important role in the bonding interaction is played by the outer 5*s* and 5*p* AO of the Pd atom, which, in accordance with the calculated[37] covalent components of the Pd–L bond energy (E_{PdL}^{cov}), makes a significant contribution to the Pd–L covalent bonding. The observed increase in the charge of Pd with increase in the electronegativity of the ligands agrees with published data on the X-ray electron spectra[38–40] of Pd^{II} complexes.

A comparative estimation of the strength of the Pd–X bond in the complexes PdX_4^{2-} and the Pd^{IV} complexes PdX_6^{2-} showed[33] that the strength of the Pd–X bond increases with increase in the electronegativity of X and the coordination number of Pd. The regular features observed agree with conclusions[41] based on the experimental determination of the vibrational wavenumbers and force constants for the complexes $M_2[PdX_4]$ and $M_2[PdX_6]$.

The static *trans*-influence (and also *cis*-influence), revealed by the dependence of the strength of a palladium–ligand bond on the nature of the ligand in the *trans* (or *cis*) position, has been studied.[37,42,43] The stronger the *trans*

(or *cis*) influence of a ligand, the weaker the bond formed by its *trans* (or *cis*) partner in the square complex. Calculations have been carried out for the complexes $[PdCl_3L]^q$,[42] *trans*-$X_2Pd(NH_3)_2$ and *cis*-$X_2Pd(NH_3)_2$,[43] and *trans*-$XYPd(PH_3)_2$.[37] Series giving the order of the static influence of ligands have been constructed by analysing the two-centre components of the total energy E_{AB} and the Wiberg indices W_{AB}, which correlate with the strengths of the corresponding bonds.

The calculations for the complexes $[PdCl_3L]^q$ by the CNDO method[42] showed that the *trans*-influence of the ligand L decreases (and the strength of the Pd–Cl bond correspondingly increases) in the order $CN^- > CH_3^- > NO_2^- > H^- > Cl^- > SCH_3^- > NH_3 \cong CO \cong C_2H_4 > (CH_3)_2S > (CH_3)_2SO > H_2O$. Exactly the same series was obtained for the corresponding platinum complexes. From these and published data it was concluded that the position of a ligand in the order of the static *trans*-influence in palladium and platinum complexes is determined by its donor–acceptor properties; with increase in the donor power of the ligand, its *trans*-influence generally increases.

The calculations by the INDO method for the complexes *cis*-$PdX_2(NH_3)_2$[43] gave the following order of the *trans*-influence: $H^- > SCN^- > NCS^- > Cl^- > NH_3 > H_2O$. The *cis*-influence in the complexes *trans*-$PdX_2(NH_3)_2$ increases in the same order as the *trans*-influence in the corresponding *cis*-complexes, but the range of change in the values of E_{PdN}^{cov} with change in the nature of the *cis*-ligands is smaller by a factor of approximately 3.

The calculations for the complexes *trans*-$PdXY(PH_3)_2$ by the CNDO method[37] showed that for all ligands Y the *trans*-influence of X decreases in the order $X = H^- > Cl^- > OCOCH_3^- > OH^-$. The decrease in the *trans*-influence of the ligands in this series correlates with the increase in the negative charge on the ligand (more accurately on the atom of the ligand closest to palladium). This agrees with the published conclusion[42] that the *trans*-influence of a ligand increases with increase in its donor power. The hydride ligand, which shows the strongest *trans*-influence in the series studied, also forms the most covalent bond with palladium (judging from the values of the effective charges on X or from the Wiberg indices W_{PdX}). The highly covalent nature of the Pd–H bond is due to the lower electronegativity of H compared with other anionic ligands, and to the better ability of the 1*s* AO of the H atom to overlap with the diffuse 5*s* and 5*p* AO of the Pd atom.

The published quantum-chemical data on the *trans*-influence of the ligands in square Pd^{II} complexes[37,42,43] agree with one another. The *trans*-influence is revealed thermodynamically by the dependence of the instability constants k_{Cl} for the reaction

$$trans\text{-}[LMCl_3]^- + H_2O \rightleftharpoons [L(H_2O)MCl_2] + Cl^-$$

on the nature of L.

The order of the change in k_{Cl} agrees with the theoretical order of the *trans*-influence,[42] although the quantum-chemical calculation did not take account of the influence of solvation on this reaction. The conclusion that H has a strong *trans*-influence in Pd^{II} complexes is confirmed by the results of an X-ray diffraction study of the complex *trans*-$ClPd(H)(PPh_3)_2$, for which the bond length $R(Pd–Cl) = 0.247$ nm is much greater than the average value for Pd^{II} complexes, $R(Pd–Cl) = 0.223$ nm.[45] Thus the available experimental data confirm the regular features of the change in the *trans*-influence obtained theoretically.

A comparative study of the electronic structure of related complexes of Pd^{II}, Ni^{II}, and Pt^{II} has been carried out.[34,46–48] The complexes MCl_4^{2-}, $M_2Cl_6^{2-}$, $[MCl_3(C_2H_4)]^-$, and ML_2 with σ-donor ligands show an increase in the covalent character of the M–X bonds in the order Ni < Pd < Pt, revealed by a decrease in the effective charge of the central atom. A comparative non-empirical pseudo-potential calculation for the anion of Zeise's salt $[PtCl_3(C_2H_4)]^-$ and its palladium analogue[46] showed that on going from Pd to Pt the strength of the M–C_2H_4 bond increases: thus the calculated energy of the dissociation $[Cl_3M(C_2H_4)]^- \rightarrow [Cl_3M]^- + C_2H_4$ is 25 kcal mole^{-1} for Pt, and only 12 kcal mole^{-1} for Pd. In both cases the structures of $[Cl_3M(C_2H_4)]^-$ with ethylene arranged at right angles to the plane of the complex are energetically more favourable than those with the equatorial arrangement of the alkene molecule. The barrier to the rotation of ethylene about the M–C_2H_4 bond is low, and is to a large extent due to the increase in the C–Cl repulsion interaction on going to the planar structure. An estimate of the strength of the bonds in the complexes ML_2 by the CNDO method[48] also indicates that the strength of the M–L bond increases with increase in its covalent character in the order Ni < Pd < Pt. These results agree with the experimental estimation of the strengths of the M–C_2H_4 and M–L bonds in the complexes $[Cl_3M(C_2H_4)]^-$ and ML_2.[49]

The results are determined by the general regular features, noted above, in the change in the electronic structure of the transition elements, namely the increase in the diffuse character and simultaneous stabilisation of the valence *d* orbitals on going from the elements of the first transition series to the elements of the second and third series. The energy of interaction of orbitals *i* and *j* can be estimated in second-order perturbation theory using the expression[50]

$$E_{ij} = -\frac{H_{ij}}{\varepsilon_i - \varepsilon_j} \qquad (1)$$

where H_{ij} is the integral of the resonance interaction of the orbitals, which increases with increase in the degree of overlap of the orbitals, and ε_i and ε_j are the orbital energies. The more diffuse character of the 4*d* AO of the Pd atom and the 5*d* AO of the Pt atom compared with the 3*d* AO of the Ni atom is responsible for their greater overlap with the ligand orbitals, and hence for the higher value of E_{ij}. Moreover, for Pd and Pt, the lower-lying 4*d* and 5*d* AO are closer in energy to the ligand orbitals involved in the M–L bonds, compared with the 3*d* AO of the Ni atom. This also leads to an increase in E_{ij} as a consequence of the decrease in the difference $\varepsilon_i - \varepsilon_j$. Thus the electronic characteristics of the *nd* AO are responsible for the increase in the covalent bonding M–L in the order Ni < Pd < Pt.

The decrease in the polarity of the M–Cl bonds is also responsible for the observed[30,34] closer relative positions of the non-bonding levels of the M and Cl atoms for $PdCl_4^{2-}$ and $Pd_2Cl_6^{2-}$, compared with the corresponding Pt complexes. The highest occupied MO of the $PtCl_4^{2-}$ and $Pt_2Cl_6^{2-}$ ions consist chiefly of the *d* AO of the Pt atom, and lie appreciably higher than the other occupied MO. In the case of the Pd complexes, the relatively high effective charges of Pd and Cl stabilise the non-bonding MO consisting chiefly of the *d* AO of palladium, and destabilise the non-bonding MO localised on Cl (ϕ_{Cl}). This leads to the observed[30,34] approach of the energies of ϕ_{Cl} and the highest occupied molecular orbitals (HOMO) of the $PdCl_4^{2-}$ and $Pd_2Cl_6^{2-}$ ions.

This review of the results of quantum-chemical calculations for Pd^{II} complexes reveals the following regular features of their electronic structure: 1) the electronic characteristic correlating with the formal oxidation state of palladium in

Pd^{II} complexes is the magnitude of the vacancy in the valence 4*d* level of the Pd atom, which is close to 2e for the complexes for which calculations have been carried out; an important role in the Pd–L bonding interaction is played not only by the valence 4*d* AO but also by the outer 5*s* and 5*p* AO of palladium; 2) the electron density at the palladium atom decreases with increase in the electronegativity of the ligands; 3) the static *trans*-influence of the ligand generally increases with increase in its donor power; and 4) in a series of related compounds of Ni^{II}, Pd^{II}, and Pt^{II}, the strength of the M–L bonds increases with increase in their covalent character in the order Ni < Pd < Pt.

2. The Electronic Structure of Pd^0 and Pd^I Compounds

Compounds of zero-valent palladium (formal oxidation state 0) have been the subject of more non-empirical calculations than other palladium systems. The only Pd^I compound for which quantum-chemical studies have been carried out is apparently PdH.[17,18,51] The reason is probably that Pd^I compounds began to attract the attention of chemists only comparatively recently.[52–54] Calculations have been carried out[55] for the hydride complex of Pd^I $Pd_2(PH_3)_2H_2$. The study of the electronic structure of this complex, however, was not the aim of this work,[55] and its results will be discussed below (section V) in relation to the problem of the dissociative reaction of molecular hydrogen with palladium systems.

Following the principle formulated above, the oxidation state of palladium will be related to the magnitude of the vacancy in its valence *d* level. The data given in Table 2 show that, in agreement with the above conclusion, the magnitude of the *d* vacancy correlates with the formal oxidation state. Thus for the Pd^0 complexes $Pd(H_2)$, Pd(CO), and $Pd(C_2H_4)$, the electron configuration of the *d* AO is close to d^{10} (the values of the populations were not given for $Pd(C_2H_4)$, but the electron configuration of Pd is close to d^{10} [58,59]). On the other hand, for Pd^I hydride, the configuration of the *d* AO is close to d^9. It is also shown below that the magnitude of the *d* vacancy is one of the important electronic factors determining the relative strength of Pd–L bonds.

Comparison of the results of calculations for the PdCO, PdH, and PdC systems,[18] carried out in the same pseudopotential scheme, also makes it possible to estimate the oxidation state of Pd in palladium carbide. Table 2 shows that the magnitude of the *d* vacancy for palladium in PdC (~0.5e) is approximately equal to the average of the values for zero-valent palladium in PdCO and univalent palladium in PdH. Thus if the above criterion is applicable, the oxidation state of palladium in PdC is intermediate between 0 and +1. Unfortunately, there are no published data on the electron distribution in alkylpalladium systems, in particular for the important model system $PdCH_3$. It would also be of interest to estimate the change in the actual oxidation state of palladium in complexes with increase in its coordination number. In Refs.59 and 60–62, however, which give the results of non-empirical calculations for $Pd(C_2H_4)_n$ and $Pd(CO)_4$, no data are given on the population of the *d* AO of the Pd atom.

The formation of a *d* vacancy when the palladium atom is introduced into a complex may take place both as a result of Pd → L transfer of electron density and as a result of the promotion of electrons from the 4*d* to the 5*s* and 5*p* AO of palladium. In all the systems given in Table 2 except $Pd(H_2)$, the effective charge of Pd is positive as a result of Pd → L charge transfer. In the case of $Pd(H_2)$, the coordination of molecular hydrogen is determined chiefly by the donor–acceptor interaction of the filled σ-orbital (bonding orbital) of H_2 with the 5*s* and 5*p* AO of the Pd atom,[41] and the calculation in a minimum basis set gives a negative charge on the Pd atom. The positive charge of Pd, obtained in Ref.56 using two-exponent basis functions for H, is due to the population of the diffuse components of the 1*s* AO of the H atom. The assignment of a corresponding proportion of electron density to hydrogen is not completely justified, since the diffuse components of the 1*s* AO of the H atom overlap considerably the diffuse orbitals of the Pd atom, and their overlap density cannot be separated unambiguously.

Table 2. Results of non-empirical calculations for various simple model complexes of Pd^0 and Pd^I.

Compound	Z_{Pd}, e	Q_s, e	Q_p, e	Q_d, e	E_d, kJ mole^{-1}	Refs.
Pd (H_2)*	−0.08	0.24	0.12	9.72	23	[56]
Pd (H_2)	0.07	0.11	0.09	9.73	27	[56]
Pd (CO)	0.06	0.28	0.22	9.56	192	[57]
Pd (CO)	0.01	0.19	0.08	9.72	75	[18]
Pd (C_2H_4)	0.10	—	—	—	50	[58]
Pd (C_2H_4)	0.19	—	—	—	272	[59]
PdH	0.11	0.44	0.08	9.37	108	[18]
PdH	0.32	0.35	0.11	9.22	135	[17]
PdH	0.15	0.58	0.09	9.18	193	[51]
PdC	0.20	0.10	0.11	9.59	130	[18]
PdC	0.28	0.09	0.11	9.52	121	[19]

Notes: E_d is the dissociation energy, Z_{Pd} the effective charge on the Pd atom, and Q_s, Q_p, and Q_d the total populations of the valence 4*d*, 5*s*, and 5*p* AO of the Pd atom.

*For $Pd(H_2)$ the first row gives the results of the calculation in a minimum basis set, and the second row the results for an expanded basis set.

On going along the series of compounds PdL from L = H_2 to CO and C_2H_4 [56,57,59] there is a considerable increase in the dative transfer of electron density to the ligand, corresponding (in the Dewar–Chatt–Duncanson model) to the π-component of the Pd–L interaction. This is related to the fact that the unoccupied π*-orbitals of CO and C_2H_4, taking part in the dative interaction, have much lower energies than the antibonding orbital of H_2. Comparison of the results of non-empirical calculations for $Pd(H_2)$ [56] and PdCO,[57] carried out with allowance for all the electrons, shows that the increase in the dative interaction on going from $Pd(H_2)$ to PdCO is also accompanied by an increase in the donor–acceptor component, that is a synergic effect is observed. This leads to an appreciable increase in the strength of the bond, which for L = CO or C_2H_4 shows clearly defined covalent character. The observed increase in the strength of the Pd–L bond corresponds to the decrease in the total population of the 4*d* AO and the increase in the populations of the 5*s* and 5*p* AO of the Pd atom.

Overall, however, the total population of the 5*s* and 5*p* AO of palladium in Pd^0 and Pd^I compounds is much lower than 1e, that is the corresponding value for typical Pd^{II} complexes. This is due primarily to the fact that the ligands in the Pd^0 and Pd^I compounds are capable of donor–acceptor

interaction with the 5*s* and 5*p* AO to a much smaller extent than in the case of the anionic ligands of Pd^{II} complexes. In the Pd^0 and Pd^I compounds, the increase in the covalent contribution to the Pd–L bonding, accompanying the change to the electron configurations d^9s^1 or d^9p^1, does not compensate the expenditure of energy in the electron promotion $4d \rightarrow 5s$ or $4d \rightarrow 5p$. As a result, for a coordinate bond in these compounds, the optimum electron configuration of Pd is one in which the 5s and 5p AO have a low population.

Calculated data on the strength of the Pd–L bond Pd^0 and Pd^I compounds are contradictory, as can be seen, for example, by comparing the values given in Table 2 for the Pd–L (L = CO, C_2H_4) coordination energies obtained in different studies. It is of interest to compare the energies of different Pd–L bonds for which non-empirical calculations have been carried out in comparable and sufficiently large basis sets and in the same pseudo-potential scheme for PdCO, PdH, and PdC.[18] The increase in the *d* vacancy (chiefly in the $4d_\sigma$ AO oriented in the bond direction) on going from the zero-valent palladium compound PdCO to the univalent palladium compound PdH decreases the Fermi repulsion interaction between the electron of the $4d_\sigma$ AO of the Pd atom and the σ-orbitals of the ligands. This electronic factor is responsible for the greater strength of the Pd–H bond, compared with the Pd–CO bond.

The Pd–C bond in palladium carbide is even stronger than the Pd–H bond, although the magnitude of the *d* vacancy is smaller in the first case.[18,19] This is explained by the specific features of the electronic structure of the C atom acting as ligand. In the case of PdC, the σ-orbital of the carbide atom is unoccupied, and the only repulsion interaction of the Fermi type is the interaction of the electrons of the filled levels $d_\pi - \phi_\pi(C)$, which is much weaker than the corresponding interaction of the σ-orbitals. The resulting Pd–C bond is a single σ-bond. This bond, although stronger than the Pd–CO and Pd–H bonds, according to Ref.19 should be weaker than M–C multiple bonds, where M represents metals of neighbouring groups of the periodic system.

The $Pd...C_2H_4$ bond energy has been estimated[58,59] by a non-empirical calculation in the valence approximation using different pseudo-potential schemes. The value E_d = 50 kJ mole^{-1} was obtained for the dissociation energy of the $Pd...C_2H_4$ bond;[58] this shows qualitative agreement with infrared and ultraviolet spectroscopic data for this compound isolated in an inert matrix, which indicate the formation of a weak $Pd...C_2H_4$ bond.[63]

The high value obtained in Ref.59 for E_d for $Pd...C_2H_4$ (see Table 2) is apparently due to the overestimation (in the pseudo-potential scheme used[59]) of the contribution of the dative interaction of the 4*d* AO of palladium with the antibonding σ*-orbital of ethylene. The data in Ref.58, where a different scheme was used to construct the pseudo-potential, and also the results of a calculation for PdC_2H_4 by the SCF-Xα-SW method,[64] in agreement with qualitative perturbation theory, indicate that there is practically no interaction of the 4*d* AO of palladium with the high-lying σ*-orbital of C_2H_4.

A comparative study of the electronic structure of Pd^0 and Pd^I compounds in a series of related compounds of metals of the platinum group has been carried out.[17,47,64–66,51] In all the M^0 compounds for which calculations were carried out, as in the M^{II} complexes examined above, the effective charge of M decreases (the covalent character of the M–L bonds increases) in the order Ni, Pd, Pt. This is due to the fact that, as noted above, the *d* AO of the heavy metals (palladium and platinum) form more covalent bonds with the ligand orbitals, compared with the 3*d* AO of nickel.

This conclusion is confirmed by an analysis of the dative component of the M–L interaction in the π-complexes $M(C_2H_4)$[64] and $M(O_2)(PH_3)_2$.[66] In the complexes of both types, the bonding interaction of the filled d_π orbitals of the M atoms with χ_π ligand orbitals of appropriate symmetry increases in the order Ni < Pd < Pt. This conclusion was reached in Ref.64 from an analysis of the correlation diagrams of the one-electron levels, obtained by the SCF-Xα-SW method, and in Ref.66 by comparing the contributions of the dative interaction to the covalent component E_{M-O_2}, obtained by the CNDO method. In the last case it was shown that, in spite of the decrease in the transfer of electron density and going from Ni to Pt, the energy contribution of the dative interaction increases because of the increase in the overlap of the d_π and χ_π orbitals and the corresponding increase in the contribution of the covalent bonding M–L.

The large contribution of the dative interaction is responsible for the greater strength of the coordinate bond in the $Pd(C_2H_4)$ system compared with the isoelectronic system $[Ag(C_2H_4)]^+$.[59] In the case of $Pd(C_2H_4)$, the main contribution to the bond is made by the dative interaction of the $4d_\pi$ AO of palladium with the π*-orbital of ethylene, whereas in the case of $[Ag(C_2H_4)]^+$ it is made by the donor–acceptor interaction of the 5*s* and 5*p* AO of silver with the σ-orbital of ethylene, and the bond energy in the first case is 2.3 times that in the second.

In all the compounds studied, the estimated strength of the Pd–L bonds is lower than that of the corresponding Pt–L bonds, but in the case of $M(O_2)(PH_3)_2$, and also the hydrides MH,[17] the $Pd...O_2$ and Pd...H bonds are less stable than the $Ni...O_2$ and Ni...H bonds. Experimental data obtained for complexes with molecular nitrogen (in matrices)[67] and phosphine complexes[68,69] of zero-valent metals of the platinum group show that in these complexes Pd^0 again forms the weakest bonds.

Thus analysis of the quantum-chemical data indicates that the electronic factor preventing the formation of strong bonds in Pd^0 compounds is the relatively small magnitude of the *d* vacancy, which is related to the fact that the energy of electron promotion $nd \rightarrow (n+1)s$ or $nd \rightarrow (n+1)p$ has the highest value among the elements of the platinum group. With increase in the oxidation number, the magnitude of the *d* vacancy increases, but in the case of the hydride PdH it is again lower than the corresponding values for NiH and PtH, and the population of the 5*s* AO of palladium is lower that that of the 4*s* AO of nickel and the 6*s* AO of platinum. The Fermi repulsion interaction of the electrons of the filled $4d_\sigma$ AO of palladium and the σ-orbitals of the ligands decreases the strength of the Pd–L bond.

Calculations for Pd^0 complexes with a coordination number $n > 1$ were carried out not only in Ref.66 but also in Refs.62, 59, and 70. An interesting characteristic feature of Pd^0 and Pt^0 complexes is that, in addition to 18-electron complexes ML_4, low-coordinate 16-electron trigonal planar complexes ML_3 are also known. Examples of these complexes are provided by the complexes of palladium with tertiary phosphine ligands $Pd(PR_3)_3$ and the mixed phosphine complexes $PdX(PR_3)_2$ (X = alkene, O_2).[71,72] 14-electron complexes $Pd(PR_3)_2$ have also been obtained.[16] Experimental data indicate that the strength of the coordinate bond in Pd^0 complexes and the reactivity of these complexes depend on the coordination number of palladium.[16,73] The aim of the theoretical study is to determine the electronic factors which, in addition to steric factors, determine the optimum coordination number for Pd^0 complexes.

Comparative calculations for PdL_n complexes with different coordination numbers n[59,70] show (in agreement with experimental data) that the strength of the Pd–L coordinate bond decreases with increase in n. Thus a non-empirical pseudo-potential calculation for the complexes $Pd(C_2H_4)_n$ with $n = 1$, 3, and 4[59] showed that the coordination energy E_c corresponding to one ethylene molecule decreases on going from $n = 1$ to $n = 3$ and $n = 4$ by factors of 1.2 and 1.4 respectively. The marked decrease in the calculated values of E_c on going from $n = 1$ to $n = 4$ explains the fact that the coordination number of palladium in the compounds $Pd(C_2H_4)_n$ synthesised in inert matrices does not exceed 3.[63]

The electronic factors responsible for the decrease in the strength of Pd–L coordinate bonds when L is an electron σ-donor were established[70] by CNDO calculations for the model phosphine complexes $Pd(PH_3)_n$ ($n = 1$–4) and the hypothetical complexes $Pd(H_2)(PH_3)_n$ ($n = 1$–3). In this case a criterion of coordinative unsaturation of the complexes is provided by the relative energy of the lowest unoccupied MO (LUMO), localised on the transition metal atoms.[74] For phosphine complexes of Pd^0, these orbitals consist chiefly of the 5*s* and 5*p* AO of the Pd atom. Analysis of the results of the calculations[70] showed that the $L_nPd...H_2$ coordination energy and the strength of the individual Pd–L bonds decrease considerably with decrease in the valence angle L–Pd–L, or, which is the same thing, with change in the formal hybridisation of the 5*s* and 5*p* AO of palladium. The energy of the LUMO of the complexes PdL_n increases with increase in n, that is, as expected, the coordinative unsaturation of the complexes decreases with increase in the number of phosphine ligands.

The electronic factor responsible for the relative stability of the coordinatively unsaturated complexes PdL_n is the fact that the transfer of electron density to the 5*p* AO of the Pd atom becomes energetically unfavourable with increase in n.

Thus in the unsaturated 16-electron complexes PdL_3 and even in the 14-electron complexes PdL_2, the population of the high-lying 5*p* AO of palladium involved in bonding may reach a value such that its increase on the coordination of new ligands is energetically unfavourable. The optimum coordination number of the complexes of the platinum group metals is therefore determined not only by steric factors but also by electronic factors, in particular the relative arrangement of the *s*, *p*, and *d* levels of the M atom. This conclusion makes it possible to explain the observed difference in the coordination numbers of complexes of Ni^0, Pd^0, and Pt^0 with the same phosphine ligands, and also the difference in the coordination numbers for complexes ML_n with ligands having similar steric characteristics but different electronic characteristics.[16,73]

Analysis of the results of these quantum-chemical calculations of the electronic structure of Pd^0 and Pd^I compounds leads to some general conclusions. For Pd^0 and Pd^I compounds, as in the case of Pd^{II} compounds, the magnitude of the vacancy in the valence *d* level correlates with the formal oxidation state of palladium. The population of the outer 5*s* and 5*p* AO generally increases with increase in the *d* vacancy. The relatively small magnitude of the *d* vacancy is the electronic factor decreasing the strength of the Pd–L bonds in the Pd^0 compounds. The strength of the M–L bonds in compounds of a metal in a low oxidation state generally increases in the order Ni < Pd < Pt, if the main contribution to the bond is made by the dative component of the M–L interaction. When the donor–acceptor component of the M–L interaction is decisive, the strength of the Pd–L bond may be the lowest among the platinum group metals. The electronic factor responsible for the possible existence of coordinatively unsaturated Pd^0 complexes PdL_n (where L is an electron σ-donor and $n = 2$ or 3) is the fact that, with increase in n, the filling of the high-lying 5*p* AO of palladium, involved in the formation of the Pd–L bonds, becomes energetically unfavourable.

3. The Electronic Structure of Palladium Clusters

In the present section, the results of the quantum-chemical study of atomic clusters Pd_n ($n = 2$–79)[51,75–85] and the few calculations for polynuclear complexes Pd_mL_n[34,86,87] are discussed. The experimental and theoretical study of clusters is an important independent field.[88] At the same time, quantum-chemical calculations for clusters, in particular palladium clusters, are also of interest for the theory of catalysis, particularly heterogeneous catalysts, in relation to the problem of studying the electronic structure and properties of catalytic systems. The cluster model makes it possible to obtain valuable information on the electronic nature of the Pd–Pd bond, and also on the dependence of the properties of the system on the number of Pd atoms.

A key cluster system is the simplest cluster Pd_2, for which experimental spectroscopic data are available.[89,90] The main aim of the quantum-chemical studies carried out in Refs.51 and 75 was the estimation of the strength of the bonds formed by two palladium atoms with filled *d* levels. The calculations for Pd_2 were carried out by the non-empirical SCF MO LCAO method[75] and also by the two-configuration SCF method,[51] in the valence approximation. A pseudo-potential non-empirical calculation has also been carried out for the cluster Pd_3.[75] A number of calculations for the clusters Pd_5, Pd_6, and Pd_{13}, and also a study of the adsorption of atomic oxygen and CO on Pd_5 clusters and of atomic hydrogen on Pd_6 clusters, have been carried out by the SCF-Xα-SW method.[76–78] The other cluster calculations[79–87] were carried out in the CNDO approximation, and also by the EHM.

The results of the calculations for Pd_2 carried out by different methods are contradictory. Thus the calculation by the two-configuration SCF method[51] gives the dissociation energy value $E_d = 72.3$ kJ mole^{-1}, in satisfactory agreement with the spectroscopic estimate of 63 ± 19 kJ mole^{-1}.[90] On the other hand, a non-empirical SCF MO LCAO calculation[75] in a minimum basis set with the addition of polarisation *d* functions gave a bond energy value close to zero. A calculation in a basis set selected according to the "counterbalance" scheme,[91] that is using a complete molecular basis set in the calculation for individual palladium atoms, gave a potential curve of the repulsion type. In Ref.75, a calculation for the cluster Pd_3 was carried out using the same basis set as for Pd_2, and, as in the case of Pd_2, it was concluded that no bond is formed. The standard choice of basis set and the use of the "counterbalance" scheme give the same value of E_d for Pd_3. The most stable Pd_3 structure examined was the linear structure.[75]

A possible reason for the lack of agreement in the results in Refs.51 and 75 may be that in Ref.75 the effects of Coulombic correlation, which are particularly important for transition metal clusters,[92] were not taken into account.

According to the results of non-empirical calculations[51,75] and CNDO and EHM calculations,[79–81] the bond between palladium atoms with a filled 4*d* level is due chiefly to the participation of the unoccupied 5*s* AO of the Pd atoms in the bonding interaction. According to Refs.75 and 79, palladium in Pd_2 has a valence electron configuration close to d^{10}. On the other hand, the electron configuration

calculated in Refs.51 and 81 is close to d^9s^1. This difference is undoubtedly due to the characteristic features of the calculation methods used.

A comparison[82] of the results of calculations for the clusters Pd_{13} and Pd_{19} by the standard EHM and the version self-consistent with respect to charges and configurations showed that the first method gives an insufficiently reliable picture of the electron density distribution. In the standard version, in particular, the total population of the 4*d* AO of palladium is lowered considerably, and this may be the reason for the electron configuration d^9s^1 obtained for Pd_2 in Ref.81. In the case of the non-empirical calculation,[51] the use of the atom pseudo-potential to take effective account of the interaction of the valence and core electrons gives an incorrect (compared with the experimental estimate[15]) difference in the energies of the configurations d^{10} and d^9s^1, and this may influence the calculated values of the population of the 5*s* AO. To obtain more reliable information on the electron configuration of Pd in Pd_2 it is apparently necessary to carry out a more rigorous non-empirical calculation with allowance for all the electrons, and also with allowance for the effects of Coulombic correlation.

Thus even for the simplest palladium cluster, the data on the nature of the Pd–Pd bond are still unreliable. With allowance for this, the analysis of the results of calculations for more complex clusters can be carried out primarily on the basis of qualitative conclusions about the regular features of the change in the electron characteristics in a series of related systems. Calculations for clusters larger than Pd_2 have been carried out by the EHM,[82–85] and Pd_{13} has also been studied by the SCF-Xα-SW method.[76]

In Ref.76 it was found that an appreciable charge accumulates on the central Pd atom in Pd_{13}. The orbitals localised on the outer atoms are mainly the HOMO, many of which are non-bonding. In turn, a low-lying bonding MO with an appreciable contribution from the 5*s* AO of palladium is localised chiefly on the central Pd atom. These results show qualitative agreement with the results of a calculation for the cluster Pd_{19}, self-consistent with respect to charges and configurations, carried out by the EHM.[83]

The adsorption of atomic hydrogen on Pd clusters was studied in Refs.77, 79, and 85, and the adsorption of atomic oxygen and CO on Pd_5 was studied in Ref.78 (the calculations for the reaction of H_2 with Pd_2 and Pd_9 clusters, carried out in Ref.85, will be discussed in section IV). For all the clusters, an appreciable contribution to the Pd–L bond is made by the 5*s* and 5*p* AO of palladium. Thus in the octahedral cluster Pd_6H, according to the results of a calculation by the SCF-Xα-SW method,[77] the contribution of the 5*s* and 5*p* AO of palladium to the MO corresponding to the Pd–H bond is 76% of the contribution of the *d* AO.

In Ref.78, the same method was used to carry out a calculation for two structures of $Pd_5(O)$ modelling two possible versions of the coordination of O on a metallic palladium surface. In the first structure, the O atom is coordinated to the central Pd atom of a Pd_5 cluster (all the Pd atoms lie in the same plane). In the second structure, four Pd atoms lie in same plane, and the O atom and the fifth Pd atom lie on the principal axis of Pd_4, on different sides of this plane. The calculated spectra and the experimental infrared spectra for the adsorption of atomic oxygen on metallic palladium were compared. It was concluded that the single-point adsorption of O corresponds to the experimentally observed form of adsorption with a weak O–M bond, and that the many-point adsorption corresponds to the form of adsorption with a relatively strong O–M bond.

The electronic structure of dinuclear palladium complexes has been studied.[34,86,87] In Ref.87, calculations were carried out for the linear systems formed by the Pd^0 phosphine complexes $Pd_2(PH_3)_2$ and $Pd_2(PPhH_2)_2$, and also for a number of structures $Pd_2(PPhH_2)_2$, modelling the intramolecular coordination Pd...P in the dinuclear complexes $Pd_2(PPh_3)_2$.[93,94] The results of the population analysis indicate that a weak Pd–Pd bond is formed. This bond, in agreement with the results obtained for the dinuclear clusters Pd_2, can be described as a σ-bond produced mainly by the interaction of the $4d_{z^2}$ AO of one Pd atom and the 5*s* AO of the other Pd atom.

As noted in Ref.87, the formation of a Pd–Pd multiple bond might have been expected for the linear structures. Thus in terms of the concept of isolobality developed by Hoffmann,[95] if the difference in the filling of the orbitals are ignored, the fragment PdL, which has boundary sp_z, p_x, and p_y orbitals, can be compared with a CH group. As shown by the analysis in Ref.87, however, Pd–Pd multiple bonds involving *spd* hybrid orbitals are not formed, since electron promotion for the 4*d* to the high-lying 5*p* AO is energetically unfavourable.

The unoccupied 5*p* AO of palladium in Pd_2L_2 can take part in additional interactions. Thus the bonding donor–acceptor interaction of the 5*p* AO of a Pd atom with a phenylphosphine ligand of a neighbouring Pd atom (more accurately with the filled π-orbital of the aromatic ring) leads to additional stabilisation of the complex Pd_2L_2 and is possibly the reason for the observed stability of the coordinatively unsaturated complexes $Pd_2(PPh_3)_2$.[87]

In dinuclear and polynuclear Pd^{II} compounds, the distance between the palladium atoms is usually appreciably greater than the sum of their covalent radii. The electronic structure of the complex of palladium with dithioacetic acid $Pd_2(CH_3CSS)_4$, which has a short Pd–Pd bond and in which all four dithioacetate ligands occupy bridging positions, has been studied.[86] It is of interest to compare the results obtained with the results of a calculation[34] for the complex $Pd_2Cl_6^{2-}$ with two bridging ligands, where it is known that there is no direct Pd–Pd interaction. According to Refs.34 and 86, the absolute magnitude of the effective charge of the bridging ligands Cl and CH_3CSS ($Z_{Cl} = -0.41e$, $Z_{CH_3CSS} = -0.50e$) is smaller than that of the corresponding values $Z_{Cl} = -0.60e$ and $Z_{CH_3CSS} = -0.53e$ for the terminal Cl atoms in $Pd_2Cl_6^{2-}$ and the ligands CH_3CSS in the mononuclear complex $Pd(CH_3CSS)_2$. The Pd–Pd bond in $Pd_2(CH_3CSS)_4$ is a weak σ-bond. In Ref.34 it was noted that it is important to take account of configuration interaction in the calculation of the electronic spectra of $Pd_2Cl_6^{2-}$. Allowance for this factor leads to a marked displacement of the bands in the calculated spectra of $Pd_2Cl_6^{2-}$ to longer wavelengths compared with $PdCl_4^{2-}$, and to better agreement with the experimental data.[96–98]

IV. THE QUANTUM-CHEMICAL STUDY OF REACTIONS INVOLVING PALLADIUM COMPOUNDS

The results of the quantum-chemical study of the key elementary stages of processes catalysed by palladium complexes, or reactions responsible for the production of the catalyst, will be examined. The quantum-chemical mechanisms of the most important reactions of palladium compounds, namely the reaction of Pd^{II} and Pd^0 complexes with molecular hydrogen, the hydroxopalladation of alkenes, and various other reactions, have been studied.[55,56,79,85,99–105] The first non-empirical calculations in this field were carried

out in studies of the reaction of molecular hydrogen[56] and methane[99] with a palladium atom, and also the calculation for the model reaction of the insertion of CO into the Pd–H bond in the $[HPdCO]^+$ system.[100] The other calculations were carried out by the CNDO method using the parametrisation schemes proposed in Refs.36 and 37, and also by the EHM.

1. The Study of the Reaction of Molecular Hydrogen with Palladium Compounds

An important preparatory stage in catalytic processes involving the reactions of molecular hydrogen is the coordination of H_2 to a transition metal atom. In all published quantum-chemical studies of the activation of H_2 by the reaction with palladium compounds,[55,56,79,85,101,102] the initial systems examined contained H_2 coordinated in the molecular form to a Pd atom or (in polynuclear systems) at a Pd–Pd bond.

The calculations show that molecular hydrogen can be coordinated as an isolated ligand. The results of a complete non-empirical calculation for the simplest system $Pd(H_2)$,[56] partly discussed above are of particular interest. According to Ref.56, the Pd...H_2 interaction gives a complex containing bound (albeit weakly) molecular hydrogen. Thus the calculation in the largest of the basis sets used in Ref.56 for a fixed H–H bond length (R(H–H) = 0.074 nm) gives for the optimum T-shaped structure with R(Pd–H) = 0.2 nm a bond energy of E_d = 27 kJ mole^{-1}. As noted above, the coordination of H_2 involves chiefly a donor–acceptor interaction with the outer 5*s* and 5*p* AO of the Pd atom. The results of Ref.56 led to the general suggestion that transition metals can form stable complexes with molecular hydrogen as an isolated ligand. The theory of this type of coordinate bond was developed in Ref.106. A recent report[107] of the direct structural identification of tungsten and molybdenum complexes with molecular hydrogen confirmed this suggestion.

The activation of molecular hydrogen in a catalytic process involving transition metals leads finally to the rupture of the H–H bond. Both homolytic and heterolytic rupture of the H–H bond can be expected, depending on the nature of the transition metal, its oxidation state, and the nature of the coordinated ligands. The role of the electronic factors determining the mechanism of the activation of H_2 in its reaction with palladium compounds has been studied.[55,79,85,101,102] In Ref.101, a CNDO calculation was carried out for the heterolytic rupture of the H–H bond by a dissociative replacement mechanism in the reaction of H_2 with Pd^{II} complexes. In the other works cited, the homolytic rupture of the H–H bond in the reaction of H_2 with Pd^0 compounds was modelled.

The heterolytic rupture of the H–H bond is regarded as the initial stage in the selective catalytic hydrogenation of unsaturated compounds.[93,108–110] The starting materials in this reaction are mixed Pd^{II} complexes PdX_2L, where L is phosphine ligand. An interesting feature of this reaction is that the complexes PdX_2L_2 with oxygen-containing ligands X show a much higher activity towards H_2 than the corresponding complexes with halide ligands. From an analysis of experimental data, a four-centre mechanism was proposed for this reaction,[109,110] according to which the central atom captures a hydride ion, while the coordinated anionic ligand facilitates the capture by accepting the proton liberated:

$$PdX_2L_2 + H_2 \rightarrow (H)XPdL_2 + HX$$

The process is controlled by the interaction of the orbitals which are involved to the greatest extent in the bonds which are being formed or being broken in the dissociative replacement. These orbitals are the 1*s* AO of the H atoms, the localised hybrid orbitals of the Pd and X atoms, taking part in the Pd–X bonds, and the orbital of the unshared pair of the ligand X. In the state in which the H_2 molecule occupies a vacant coordination position in the original complex, the highest occupied MO are the MO of the unshared pair of X and the MO which corresponds to the antibonding combination of the bonding orbitals of the H–H and Pd–X bonds. The lowest unoccupied MO is the bonding combination of the antibonding orbitals of the H–H and Pd–X bonds. In the final state, the highest occupied MO will be the orbital of the unshared pair of X, formed as a result of the rupture of the Pd–X bond, and the MO which corresponds to the antibonding combination of the bonding orbitals of the Pd–H and H–X bond. The lowest unoccupied MO will be the bonding combination of the antibonding orbitals of the Pd–H and H–X bonds.

The intermediate cyclic state of the system can be examined by analogy with a five-orbital system of the polyene type,[111] if it is assumed that the ends of the chain are the orbitals of the anionic ligand X, not interacting with one another. The correlation diagram for this process differs from the familiar diagram[112] for the symmetry-forbidden redistribution of the bonds in the four-centre four-electron system

$$X{-}X' + Y{-}Y' \rightarrow XY + X'Y'$$

only in the presence of the unshared pair of the anionic ligand X. This difference, however, may lead to significant differences in the energies of these two processes. The non-bonding orbital of the unshared electron pair of the ligand X correlates with the practically non-bonding HOMO of the intermediate state, so that the dissociative replacement, generally speaking, is not symmetry-forbidden.

The initial stage of this process was modelled in Ref.101. The calculation was carried out after selecting structures describing the coordination of H_2 in the unoccupied coordination position of square complexes $PdX_2(PH_3)_2$, where X = Cl, OH, $OCOCH_3$, and also structures in which the coordinated H_2 molecule was displaced towards the anionic acido-ligand.

The calculations show that one of the electronic factors responsible for the heterolysis of H_2 is the donor–acceptor interaction of the filled σ-orbital of H_2 (the bonding combination of the 1*s* AO of hydrogen) with the unoccupied 5*sp* hybrid orbital. The rehybridisation of this orbital when H_2 is displaced towards the acido-ligand X ensures a bonding Pd...H_2 interaction when H_2 approaches X in all the structures examined. This bonding interaction facilitates the heterolysis. The donor–acceptor transfer of electron density $\sigma(H_2) \rightarrow 5sp$(Pd) to the H atoms produces a positive charge, which is responsible for the direct reaction of the coordinated H_2 molecule with the anionic acido-ligand X. This interaction leads finally to the heterolytic rupture of the H–H bond.

The rupture of the H–H bond corresponds to the filling of the σ^*-orbital of H_2 (antibonding combination of the 1*s* AO of hydrogen). In the case of dissociative replacement by a four-centre mechanism being considered, the metal-complex system does not have a high symmetry, and the filling of $\sigma^*(H_2)$ involves the mixing of the LUMO of the original structure, which contains a contribution from $\sigma^*(H_2)$, with the orbital of the unshared pair of the ligand X and the occupied MO containing a contribution from the bonding σ-orbital of H_2. The resulting HOMO of the

transition state has a node at the H atom closest to the anionic ligand, and describes the polarisation of the coordinated H_2 molecule.

The electronic factors stabilising the HOMO of the intermediate state should also stabilise the intermediate state as a whole, that is it should lower the activation barrier of the reaction. In the case being considered, where the HOMO has an electron density deficit at the H atom closest to X, this electronic factor is the Coulombic attraction $H^{\delta+}...X^{\delta-}$. The calculation in Ref.101 indicates that there is appreciable direct interaction between the coordinated H_2 molecule and the oxygen-containing anionic ligands OH and $OCOCH_3$, to which the main contribution is made by the Coulombic attraction $H^{\delta+}...OR^{\delta-}$.

Analysis of the two-centre components E_{HX} and the relative energies of the structures modelling the displacement of H_2 towards X shows[101] that the heterolytic rupture of the H–H bond should be easier for complexes with oxygen-containing ligands than for chloride complexes. This is because the ligand OR has a greater affinity for the H atom carrying the positive charge. Greater basic strength in X should also facilitate the stabilisation of the final state, making the formation of HX energetically more favourable. The results of the calculations in Ref.101 make it possible to explain the available experimental data and confirm the four-centre mechanism, proposed[109,110] on the basis of these data, for the heterolytic rupture of the H–H bond in the reaction with Pd^{II} complexes.

In the reaction of molecular hydrogen with Pd^0 compounds, the activation of H_2 takes place by a different mechanism, namely the oxidative addition of H_2 with the homolytic rupture of the H–H bond:

$$M_n + H_2 \rightarrow \begin{matrix} H \\ \diagdown \\ \diagup \\ H \end{matrix} M_n$$

For example, the dissociative chemisorption of H_2 on metallic palladium takes place by the oxidative addition mechanism.[113] This mechanism was studied by quantum-chemical methods in Refs.79, 85, and 102. In Ref.102, the complete non-empirical SCF MO LCAO method in a minimum basis set was used to carry out a calculation for the dissociation of H_2 in the coordination sphere of a Pd atom. In Ref.79, the CNDO method was used to study the reaction of H_2 with a Pd_2 cluster, and in Ref.85 a calculation was carried out for the Pd_9H system by the EHM. In addition, in Ref.55, the CNDO method and the parametrisation scheme used in Ref.79 were used to carry out a comparative calculation for the reaction of H_2 with mononuclear phosphine complexes of Pd^0 and Pt^0 of the type ML_2, and also with a dinuclear complex Pd_2L_2.

In Ref.102, the dissociation of H_2 in the $Pd(H_2)$ system was modelled by increasing the H–Pd–H angle (α) for a fixed bond length R(Pd–H) = 0.17 nm, since the optimum Pd–H bond length was found to be close to 0.17 nm both for the original complex with molecular hydrogen (α = 25°) and for the final linear dihydride structure.

With increase in the angle α, the population of the 5*s* and 5*p* AO of the Pd atom increases sharply, and in the case of angular structures with $\alpha \cong 90–148°$ the valence electron configuration of the Pd atom becomes close to d^9s^1. With further increase in α, the symmetry of the Pd orbitals involved in the H–Pd–H interaction changes. This leads to inversion of the populations of the boundary orbitals; the highest occupied MO is then the orbital corresponding to the interaction of the $5p_z$ AO of the Pd atom with the σ^*-orbital of H_2, and the valence electron configuration of Pd becomes close to d^9p^1.[102]

It was found that the formation of the dihydride is energetically unfavourable. This is due to the fact that the covalent bonding of the 1*s* AO of hydrogen with the hybrid *sp* (for $\alpha < 148°$) and *pd* (for $\alpha > 148°$) orbitals of Pd does not compensate the expenditure of energy in the electron promotion from the 4*d* AO to the high-lying 5*s* and 5*p* AO of the Pd atom. As a result, the molecular complex (α = 25°) is most stable. The angular structure undergoes an activationless transformation into the molecular complex The linear structure has a higher energy than the angular structure, but there is an energy barrier between them, associated with the rearrangement of the electron configuration $d^9s^1–d^9p^1$. It follows from the results in Ref.102 that for a metal such as palladium, the dissociation of hydrogen on a single centre is impossible, since it involves the promotion of an appreciable electronic charge to the high-lying 5*s* and 5*p* AO of palladium.

In Ref.79, where a CNDO calculation was carried out for the Pd_2H_2 system, it was again concluded that the dissociation of H_2 to give terminal hydride bonds Pd–H is energetically unfavourable. The molecular complex in which the H_2 molecule, coordinated in a bridging position, is arranged symmetrically and perpendicular to the Pd–Pd axis, is most stable. The structures Pd–Pd–H_2 with single-point coordination of H_2 are less stable, but all the structures with H_2 in the molecular form are more stable than the linear and rectangular dihydride structures.[79]

The conclusion[56,79,101] regarding the relative stability of the molecular coordination of H_2 in its single-point and two-point interaction with Pd atoms agrees qualitatively with the results of an experimental study of the chemisorption of H_2 on the surface of palladium black.[113] In this study[113] pulse volatilisation under super-high vacuum conditions ($\sim 5 \times 10^{-9}$ mmHg) detected four different states of chemisorbed H_2 on the palladium surface. The study of the physical characteristics of these states indicated that the state which is formed at a temperature below 100 K and which is desorbed at 250 K with an activation energy of 54–58 kJ $mole^{-1}$ probably corresponds to the molecular state of chemisorbed hydrogen. According to Ref.113, this molecular state may play the role of intermediate in the absorption of molecular hydrogen by metallic palladium.

The EHM has been used[85] to study the dissociative chemisorption of H_2 in the model cluster system Pd_9–H_2. In this case the dissociation of H_2 is energetically favourable.

The picture of the dissociative interaction of H_2 with one and with two Pd atoms obtained in Refs.79 and 102 shows complete agreement with the results of the comparative calculation[55] by the CNDO method for the interaction of H_2 with mononuclear phosphine complexes of Pd^0 and Pt^0 of the type $M(PH_3)_n$ and the dinuclear complex $Pd_2(PH_3)_2$. The latter models the complex $Pd_2(PPh_3)_2$ formed by the reduction of the compound $[(Ph_3P)Pd(OAc)_2]$ by molecular hydrogen.[93,94] $Pd_2(PPh_3)_2$ reacts with H_2 and palladium (II) complexes to form the polynuclear complexes $[(PhP)_2Pd_5]_n$ responsible for the catalysis.

Comparative calculations for mononuclear complexes of Pd^0 and Pt^0 and also dinuclear Pd^0 complexes, are of interest, since these complexes show different reactivities towards H_2. Thus mononuclear phosphine complexes PdL_n, where L is a phosphine ligand, do not react with molecular hydrogen,[71,73] the dinuclear complex $Pd_2(PPh_3)_2$ adds on H_2 easily and reversibly,[93,94] and the Pt^0 complexes PtL_2 undergo dissociative addition of hydrogen under mild conditions to give dihydride complexes of Pt^{II}.[73]

The change from mononuclear Pd complexes to the dinuclear complex corresponds to an increase in both the stability of the molecular complexes $L_nPd_m(H_2)$ with respect to

dissociation to L_nPd_m and H_2 and the relative stability of the dihydride structure HPd_mL_nH compared with the corresponding molecular complex $L_nPd_m(H_2)$. The explanation is that the formation of multicentre bonds Pd...H_2...Pd in the molecular complex and of multicentre hydride bonds Pd–H–Pd with the same strength as the corresponding bonds in the mononuclear complexes requires a smaller total transfer of electronic charge from the 4*d* to the 5*s* and 5*p* AO of palladium. In all the hydride structures, the population of the 5*s* and 5*p* AO is much greater than in the corresponding complexes with the H_2 molecule, and the hydride H atoms carry a negative charge.[55]

The dissociative addition of H_2 to the dinuclear complex Pd_2L_2 is energetically unfavourable, although to a smaller extent than the dissociative addition of H_2 to the mononuclear complexes PdL_n. The highest stability corresponds to the dinuclear structure in which the hydrogen molecule is arranged symmetrically and at right angles to the Pd–Pd bond. In the case of dinuclear structures in which H_2 is coordinated to one palladium atom, the $H_2...Pd_m$ coordination energy is lower and almost the same as for the mononuclear complexes. For reaction with two Pd atoms, the coordination energy of H_2 increases additively, and this is responsible for the additive character of the outer slightly filled 5*s* and 5*p* AO of the Pd atom with the σ-orbital of H_2.[55]

The platinum complexes have a greater ability to undergo the dissociative addition of H_2, compared with the palladium complexes.[55] This difference is due to the fact that the transitions $d \rightarrow s$ and $d \rightarrow p$ take place more readily in the case of platinum.

The above results[55] make it possible to explain experimental data on the difference in the reactivities of mononuclear and dinuclear Pd^0 complexes, and also Pt^0 complexes, with respect to molecular hydrogen. A comparison of calculated and experimental data[55] indicated that the compound formed by the reaction of $Pd_2(PPh_3)_2$ with H_2 is apparently the first example of a complex with H_2 in the molecular form. As noted above, similar complexes were recently identified for tungsten and molybdenum.[107]

These calculation results show the role of the outer *s* and *p* orbitals of the transition metal in oxidative addition. In the case of Pd^0 compounds, the oxidative addition of H_2 to one or two palladium atoms is energetically unfavourable because the formation of "normal" covalent bonds Pd–H involves considerable expenditure of energy to give the Pd atom a valence electron configuration close to d^9s^1. It may be assumed that with increase in the number of palladium atoms reacting directly with H_2, the strength of the $Pd_m...H_2$ bond will increase (both for structures with molecular H_2 and for dihydride structures), just as it increases, according to calculations,[55] on going from mononuclear to dinuclear systems.

Thus the dissociative chemisorption of molecular hydrogen on a metal is due to the multicentre interactions of the H atoms of the dissociating molecule with several metal atoms on the surface. According to Refs.55 and 114, a possible mechanism for the dissociative chemisorption of H_2 in its reaction with polynuclear palladium systems involves the initial adsorption of the H_2 molecule on a Pd atom or a Pd–Pd bond, after which the H atoms move apart into neighbouring interstices. The stabilisation of the resulting hydride structures takes place as a result of the increase in the number of metal atoms with which the hydrogen atoms interact.

The principal results of quantum-chemical studies of the reaction of molecular hydrogen with Pd^0 and Pd^{II} compounds can be summarised. The initial stage of the reaction of molecular hydrogen with Pd^{II} and Pd^0 compounds is the formation of a bound molecular complex in which H_2, acting as an isolated ligand, occupies a vacant position in the coordination sphere of Pd. The electronic factors facilitating the heterolytic rupture of the H–H bond in the reaction of H_2 with Pd^{II} complexes are the high basic strength of the anionic ligands and the involvement of the outer 5*s* and 5*p* AO of the Pd atom. The fact that the oxidative addition of H_2 to one Pd atom in Pd^0 compounds is unfavourable is related to the appreciable expenditure of energy required to give the Pd atom the configuration d^9s^1 necessary for the formation of covalent Pd–H bonds. The greater ability of phosphine complexes of Pt^0 to undergo the dissociative addition of H_2, compared with phosphine complexes of Pd^0, is due to the greater ease of $d \rightarrow s$ and $d \rightarrow p$ promotion in the case of platinum. The dissociative chemisorption of molecular hydrogen on metallic palladium is due to the multicentre interaction of the H atoms of the dissociating molecule with several metal atoms on the surface.

2. The Study of Hydroxopalladation

The practical importance of hydroxopalladation as an effective industrial method for obtaining carbonyl compounds from alkenes[7] is responsible for the interest in the mechanism of nucleophilic addition to the double bond, catalysed by palladium(II) complexes. It has been established experimentally,[7,9,10] that under the conditions of the reaction, the mononuclear π-complexes $PdCl_2(OH)(C_2H_4)^-$ and $PdCl_2(H_2O)(C_2H_4)$, and also the dinuclear derivatives $Pd_2Cl_5(OH)(C_2H_4)^{2-}$ and $Pd_2Cl_5(H_2O)(C_2H_4)^-$, are formed.

It is considered[115] that the hydroxo-complexes can be converted into σ-bonded organopalladium compounds by the inner-sphere *cis*-migration of the coordinated hydroxo-group to the coordinated alkene molecule. In solutions with high concentrations of H_3O^+ ions and (or) Cl^- ions, however, when the formation of hydroxo-complexes is hindered, according to Ref.116 *trans*-attack by the non-coordinated nucleophile on the coordinated alkene molecule takes place, that is the reaction involves an outer-sphere mechanism.

CNDO[36,104] and EHM[103] calculations have been carried out for nucleophilic *trans*-attack in model palladium π-complexes. *cis*-Attack in alkene complexes of Pd^{II} and nucleophilic addition in hydroxomercuration have also been studied.[36]

A mechanism has been proposed[115] for the stabilisation of the intermediate state in *cis*-attack by a coordinated hydroxo-group on a coordinated alkene. According to this mechanism,[115] the approaching ligands form a "quasi-π-allyl" orbital system. The electron density on the C atom closest to the nucleophile decreases, and that on the neighbouring C atom of the double bond increases. The stabilisation of the transition state in this case may be due to the donor–acceptor transfer of electron density from a non-bonding orbital of the quasi-allyl fragment to orbitals of the central atom.[117] In the case of square planar Pd^{II} complexes, this acceptor orbital is the partly filled $4d_{x^2-y^2}$ AO of palladium. As noted in Ref.115, the presence of the partly filled *d* orbital in Pd^{II} may facilitate nucleophilic *cis*-attack for the palladium systems, compared with the corresponding process for Hg^{II} complexes with the electron configuration d^{10}.

The results of a comparative calculation[36] for nucleophilic *cis*-attack on the alkene in the systems $[PdL_2(C_nH_{2n})(OH)]^-$ and $HgX(C_nH_{2n})(OH)$, where X = F, Cl, or Br, and $C_nH_{2n} = C_2H_4$, C_3H_6, or C_4H_8, confirm the proposed[115] "quasi-π-allyl" stabilisation mechanism. In accordance with the "quasi-allyl" model, it was found[36] that the alkene is appreciably polarised by the nucleophilic group. Thus for

$PdCl_2(C_2H_4)(OH)^-$, the effective charge of the C atom closest to OH^- is +0.12e, whereas the charge on the farther removed C atom is −0.32e. The contributions of the 4*d* AO of the Pd atom to the Pd–C and Pd–O bonding interactions are much greater than the corresponding contributions of the 5*d* AO of the Hg atom in the systems $Hg(C_nH_{2n})(OH)$.

A calculation[36] for intermediate structures $PdCl_2(OH)(C_3H_6)^-$ corresponding to nucleophilic attack at different atoms of propene showed that nucleophilic attack at the less extensively hydrogenated position of the alkene is facilitated by the polarisation of the alkene molecule as a result of the hyperconjugation of the methyl group. This explains why Markovnikov's rule is obeyed in this reaction.

To determine the role of the central atom in nucleophilic *trans*-attack on a coordinated alkene, a comparative calculation was carried out[103] for the addition of the hydride ion to ethylene in the model systems $H^-...C_2H_4$ and $H^-...(C_2H_4)PdCl_3^-$. The reactivity of coordinated ethylene towards the addition of H^- depends markedly on the nature of the coordination of ethylene to palladium.

The reaction of H^- with the symmetrical π-complex $(\eta^2\text{-}C_2H_4)PdCl_3^-$ is less favourable than the reaction with free ethylene. The deactivation of coordinated ethylene is due to the increase (compared with free ethylene) in the energy of the lowest unoccupied π*-MO, which makes the main contribution to the interaction of the symmetrically coordinated ethylene with H^-.

The displacement of ethylene with a change from the symmetrical coordination of the η_2-type to coordination of the η_1-type causes H^- attack to be facilitated, compared with free ethylene. This is due to the increase in the strength of the bond formed by Pd with the nearest C atom, and the corresponding localisation of the LUMO on the farther removed C atom, which is attacked by the nucleophile. There is a particularly large change in the contribution of the π-orbital of C_2H_4 to the bonding; in the original structure, the interaction of this orbital with the 1s AO of the H atom is a repulsion, whereas in the structure with unsymmetrical coordination of ethylene the π-orbital makes a significant contribution to the $H^-...C_2H_4$ bonding interaction.

Thus it is the possibility of unsymmetrical coordination of the alkene to the central Pd atom in the intermediate state of the nucleophilic *trans*-addition that is responsible for the activation of the alkene in this reaction. The approach of the HO^- ion to the ethylene molecule might have led to the production of the carbanion $CH_2CH_2OH^-$. The formation of this species, however, is energetically so unfavourable that ethylene (unlike acetylene, whose antibonding orbitals are slightly lower than those of ethylene) not only does not react with the hydrated OH^- ion but also does not even react with fused NaOH. The function of the palladium atom in the scheme examined[103] evidently reduces to the stabilisation of the unstable carbanion produced. A comparative calculation for the systems $H^-...(C_2H_4)ML_n$, where ML_n = $PdCl_3^-$, $PtCl_3^-$, $(C_5H_5)_2WH^+$, $Fe(CO)_5^{2+}$, $Fe(CO)_4$, $(C_5H_5)Fe(CO)_2^+$, and $Ni(PH_3)_2$, showed that palladium and platinum have the greatest ability to activate alkenes towards nucleophilic addition.

Calculations[36] for the nucleophilic *trans*-attack by the hydroxide anion in model complexes of Pd^{II} and Hg^{II} indicate that the reactivity of the fragment ML_n towards *trans*-attack by OH^- increases with increase in its acceptor power, which can be estimated from the extent of the transfer of electronic charge from X in the complexes $X[ML_n]^q$. Calculations for the complex $PdX_3(C_2H_4)^-$ and the hypothetical π-complexes $[Hg(C_2H_4)]^{2+}$ and $[HgX(C_2H_4)]^+$, where X = F, Cl, Br, showed[36] that the electron density on the C atom decreases on going from free ethylene to ethylene coordinated to Pd^{II}, and decreases further on going to ethylene coordinated to Hg^{II}. The strength of the C...O bond formed in the nucleophilic addition of OH^- increases in the same order. The quantum-chemical data obtained agree with the difference in the kinetics of the corresponding reactions; hydroxomercuration is very rapid,[118] hydroxopalladation is slow,[119] and OH^- does not add on to free ethylene in the absence of a catalyst.

An increase in the reactivity of complexes $X[ML_n]^q$ with respect to *trans*-attack by the OH^- anion with increase in the acceptor power of the fragment $X[ML_n]^q$ was also observed for π-allyl complexes.[104] Thus the replacement of the anionic ligand Cl^- (a strong electron σ-donor) by the neutral ligands PH_3 and CO (weaker σ-donors, which also have π-acceptor properties) leads to an increase in the energy of the addition of OH^- and to an increase in the two-centre component of the total energy E_{OC} in the order: $PdCl_2(\pi\text{-}C_3H_5)^- \ll PdCl(PH_3)(\pi\text{-}C_3H_5) < PdCl(CO)(\pi\text{-}C_3H_5) < Pd(PH_3)_2(\pi\text{-}C_3H_5)^+$. The quantum-chemical data obtained agree with the experimentally observed[120] increase in the rate of nucleophilic addition to $[PdCl(\pi\text{-}C_3H_5)]_2$ when triphenylphosphine is added to the reaction mixture.

The EHM has been used[105] to study the stage following the nucleophilic addition in the catalytic oxidation of ethylene to acetaldehyde, that is the decomposition of the β-hydroxyethyl σ-complex (β-palladiumethanol) formed in the preceding stage; this decomposition is accompanied by the intramolecular 1,2-transfer of hydrogen. The authors cited,[105] however, in fact carried out the calculation not for β-palladiumethanol but for the system $M(CH_2\text{–}CH_2\text{=}O)$ with a quinquevalent carbon atom, and this lowers the value of the results of this study.

The above quantum-chemical studies of the separate stages of hydroxopalladation lead to some general conclusions. The electronic factor stabilising the transition state of nucleophilic *cis*-addition to alkenes is the donor–acceptor interaction of the non-bonding orbital of the "quasi-π-allyl" system with the slightly filled orbitals of palladium. In the case of nucleophilic *trans*-attack, the activation of the alkene towards the addition of the nucleophilic group is due to the possible unsymmetrical coordination $L_nM...C_nH_{2n}$. The reactivity of the coordinated alkene increases with increase in the acceptor properties of ML_n.

3. Non-Empirical Calculations for the Model System $PdCH_4$ and the Insertion of CO into a Pd–H Bond

The results of non-empirical calculations by the SCF MO LCAO method in a minimum basis set will be examined for two model reactions: the reaction of methane with a palladium atom[99] and the insertion of CO at the Pd–H bond in the systems $[HPdCO]^+$ and H_2PdCO.[100] In Ref.99 the authors continued for the model system $Pd...CH_4$ the study of the activation of saturated compounds by reaction with a palladium atom, begun in Ref.56 with a calculation for the simplest system $Pd(H_2)$ (see above). The problem of the interaction of saturated hydrocarbons with transition metal atoms or ions is of considerable importance for the theoretical analysis of associative and dissociative chemisorption, and also for an understanding of the key reactions in catalysis by metal complexes, namely oxidative addition and reductive elimination.[121]

For the calculation,[99] three symmetrical structures were selected, in which methane is oriented with one, two, or three H atoms directed towards the Pd atom. As in the case of the $Pd...H_2$ interaction examined above, the results

of the calculation for Pd...CH_4 show that the outer 5*s* and 5*p* AO play an important role in the interaction of the Pd atom with saturated compounds. It is the participation of these orbitals in the bonding that enables the Pd atom with its filled *d* level to act as an electron acceptor in the reaction with methane. The absolute magnitude of the calculated values of the Pd...CH_4 bond energy decreases with increase in the number of H atoms directed towards the Pd atom, but the values are nevertheless close to one another. The equilibrium Pd–H distance also increases in this order.

The energy of the bond formed by molecular hydrogen with the Pd atom, calculated in the same basis set, is almost double the energy of the bond formed by methane.[56] At first sight this result appears strange, since judging from the energy of the LUMO and the experimental ionisation potentials, methane should be a better electron donor than hydrogen. In this case, however, the reaction is determined by the geometric factor, that is not by the difference in the energies of the levels but by the degree of overlap of the filled orbitals of CH_4 with the filled 4*d* and vacant 5*s* and 5*p* AO of the Pd atom.

In the structure in which only one H atom of methane can be in direct contact with the Pd atom, the overlap conditions are responsible for the weaker donor–acceptor interaction compared with H_2. In the structures in which the CH_4 molecule is oriented with two or with three H atoms directed towards the Pd atom, however, the principal role in the interaction with Pd is played by the C atom. The latter has a much larger covalent radius than the hydrogen atom, so that there is a greater Fermi repulsion interaction between the valence electron levels of Pd and CH_4. As a result, the complex of palladium with molecular hydrogen is more stable than the complex with methane.

The results[99] show that methane (and apparently alkanes in general), like hydrogen, can take part in a bonding interaction with the Pd atom in which the most important role is played by the overlap of the localised orbitals of the ligand with the diffuse outer orbitals of the transition metal.

The insertion of CO at a Pd_{surf}–H bond

$$Pd_{surf}-H + CO \rightleftarrows Pd_{surf}-CHO$$

which has been studied[100] by a non-empirical calculation for simple molecular models, is one of the stages (possibly the limiting stage) in the heterogeneous catalytic reduction of CO by hydrogen. The catalyst in this reaction is palladium deposited on an oxide support.[2] In an earlier paper[57] on the calculation of the electronic structure of the model system Pd(CO) the authors cited[100] suggested that the ability to insert CO into the M–H bond to give a formyl complex should increase with increase in the acceptor power of the transition metal. This suggestion is confirmed by experimental data which show that the active species in the reduction of CO are ionic forms of Pd stabilised by the carrier. It has also been found that the rate of the reduction of CO by hydrogen on palladium catalysts increases with increase in the electron–acceptor properties of the carrier.[2]

The dependence of the direction and the energy barrier of the migration on the magnitude of the effective charge on the Pd atom has been studied[100] by comparative calculations for the model systems $[HPdCO]^+$ and H_2PdCO. The first models the limiting case of a strongly electron-accepting environment; the second, which differs from the first in the addition of the hydride ion, which is a strong σ-donor, models the coordinative saturation of Pd in an electron-donor environment. For each system, the calculations were carried out for three structures: the original carbonyl hydride structure, an intermediate structure with a bridging Pd–H–C bond, and the final formyl structure. It was found that the addition of the hydride ion leads to a complete qualitative change in the nature of the potential curve for the migration of H to the CO group. The $[HPdCO]^+$ system can be regarded as structurally non-rigid, since there is no energy barrier to migration, and the formyl structure is even slightly more stable than the carbonyl hydride structure. On the other hand, in the case of the H_2PdCO system, the formyl structure is energetically unfavourable, and the barrier for the reverse reaction of elimination is ~15 kcal $mole^{-1}$. The fact that the migration of H to CO is energetically unfavourable in the last case is due to the extensive population of the 5*s* and 5*p* AO of palladium, preserved throughout the reaction.

From these results it was concluded[100] that, in agreement with experimental data, the increase in the positive charge on the Pd atom accompanying an increase in its acceptor power favours the relative stabilisation of the formyl structure. Correspondingly, an increase in the acceptor properties of the carrier may facilitate the formyl mechanism of the reduction of CO by hydrogen on palladium catalysts.

Thus the energy effect of the above model reactions and the electron density distribution accompanying them depend to a significant extent on the participation of the outer 5*s* and 5*p* AO of the Pd atom in the bonding interaction.

---o0o---

The above review of the results of quantum-chemical studies shows that the electronic structure and reactivity of palladium compounds are determined to a large extent by the characteristic features of the electronic structure of the Pd atom. These characteristic features, as noted above, are the complete filling of the 4*d* level in the ground state of the atom and the presence of diffuse outer 5*s* and 5*p* AO.

Further progress in the understanding of the mechanism of the reactions of palladium compounds will probably be associated to a large extent with the accumulation and analysis of experimental and theoretical data on the electronic character and relative strength of Pd–L bonds in series of complexes of different transition metals. In particular, the study of the electron density distribution in palladium systems in order to determine the preferred direction of attack on these complexes by different reagents is of considerable interest.

REFERENCES

1. G.C.Bond, Catalysis by Metals, Acad.Press, New York, 1962.
2. M.A.Vannice, Catal.Rev., 1976, 14, 153.
3. M.L.Poutsma, L.F.Elek, P.A.Ibarbia, A.P.Risch, and J.A.Rabo, J.Catal., 1978, 52, 157.

4. J.Smidt, W.Hafner, and R.Jira, Angew.Chem., 1959, 71, 176.
5. I.I.Moiseev, M.N.Vargaftik, and Ya.K.Syrkin, Dokl.Akad.Nauk SSSR, 1960, **130**, 820.
6. I.I.Moiseev, M.N.Vargaftik, and Ya.K.Syrkin, Dokl.Akad.Nauk SSSR, 1960, **133**, 377.
7. I.I.Moiseev, "π-Kompleksy v Zhidkofaznom Okisleniya Olefinov" (π-Complexes in the Liquid-Phase Oxidation of Alkenes), Izd.Nauka, Moscow, 1970, p.240.
8. I.I.Moiseev and M.N.Vargaftik, Dokl.Akad.Nauk SSSR, 1966, **166**, 370.
9. I.I.Moiseev, M.N.Vargaftik, and Ya.K.Syrkin, Dokl.Akad.Nauk SSSR, 1963, **153**, 140.
10. P.M.Henry, J.Amer.Chem.Soc., 1964, **86**, 3246.
11. P.M.Maitlis, "The Organic Chemistry of Palladium", Acad.Press, New York-London, 1971, Vol.1, p.319; Vol.2, p.216.
12. E.V.Leonova, V.Kh.Syundyukova, F.S.Denisov, A.A.Koridze, V.F.Khandkarova, and A.Z.Rubezhov, "Metody Elementoorganicheskoi Khimii. Kobal't, Nikel', Platinovye Metally" (Methods of Organometallic Chemistry. Cobalt, Nickel, and the Platinum Metals), Izd.Nauka, Moscow, 1978.
13. F.R.Hartley, "The Chemistry of Platinum and Palladium", Applied Sci.Publ., Bristol, 1973.
14. R.S.Nyholm, Proc.Chem.Soc., 1961, 273.
15. C.W.Bauschlicher, Chem.Phys.Letters, 1982, **91**, 4.
16. S.Otsuka, T.Yoshida, M.Matsumoto, and K.Nakatsu, J.Amer.Chem.Soc., 1976, **98**, 5850.
17. P.S.Bagus and C.Bjoerkman, Phys.Rev., 1981, **23A**, 461.
18. G.Pacchioni, J.Koutecky, and P.Fantucci, Chem. Phys.Letters., 1982, **92**, 486.
19. I.Shim and K.A.Gingerich, J.Chem.Phys., 1982, **76**, 3833.
20. S.S.Batsanov, "Elektrootritsatel'nost' Elementov i Khimicheskaya Svyaz'" (The Electronegativity of Elements and the Chemical Bond), Izd.Sibir.Otd. Akad.Nauk SSSR, Novosibirsk, 1962, p.30.
21. G.M.Zhidomirov, A.A.Bagatur'yants, and I.A.Abronin, "Prikladnaya Kvantovaya Khimiya" (Applied Quantum Chemistry), Izd.Khimiya, Moscow, 1979.
22. A.Serafini, J.C.Barthelat, and P.Durand, Mol. Phys., 1978, **36**, 1341.
23. J.A.Pople, D.P.Santry, and G.A.Segal, J.Chem. Phys., 1966, **44**, 136.
24. M.J.S.Dewar and G.Klopman, J.Amer.Chem.Soc., 1967, **89**, 3089.
25. R.Hoffmann, J.Chem.Phys., 1963, **39**, 1397.
26. N.M.Klimenko, "Itogi Nauki i Tekhniki. Seriya: Stroenie Molekul i Khimicheskaya Svyaz'" (Progress in Science and Technology. Series: The Structure of Molecules and the Chemical Bond), Izd.VINITI, Moscow, 1978.
27. J.C.Slater, "Self-Consistent Field Methods for Molecules and Solids" (Translated into Russian), Izd.Mir, Moscow, 1978.
28. M.E.Ruiz, J.P.Daudey, and O.A.Novaro, Mol. Phys., 1982, **46**, 853.
29. M.Benard, J.Demuynck, M-M.Rohmer, and A.Veillard, Colloq.int.CNRS, 1977, 17.
30. R.P.Messmer, L.V.Interrante, and K.H.Johnson, J.Amer.Chem.Soc., 1974, **96**, 3847.
31. P.I.Vadash, A.A.Voityuk, and L.I.Mazalov, Zhur.Strukt.Khim., 1980, **21**, 34.
32. E.Tondello, L.Di Sipio, G.De Michelis, and L.Oleari, Inorg.Chim.Acta, 1971, **5**, 305.
33. S.Sakaki and H.Kato, Bull.Chem.Soc.Japan, 1973, **46**, 2227.
34. V.I.Baranovskii, M.K.Davydova, N.S.Panina, and A.I.Panin, Koord.Khim., 1976, **2**, 409.
35. C.K.Joergensen, "Absorption Spectra and Chemical Bonding in Complexes", Pergamon Press, Oxford-London-New York-Paris, 1962, p.287.
36. S.Sakaki, H.Kato, H.Kanai, and K.Tarama, Bull. Chem.Soc.Japan, 1974, **47**, 377.
37. O.V.Gritsenko, V.A.Korsunov, A.A.Bagatur'yants, I.I.Moiseev, I.V.Kalechits, and V.B.Kazanskii, Kinetika i Kataliz, 1979, **20**, 1146.
38. V.I.Nefedov, Ya.V.Salyn, I.I.Moiseev, A.P.Sadovskii, A.S.Berenblyum, A.G.Knizhnik, and S.L.Mund, Inorg.Chim.Acta, 1979, **35**, L346.
39. V.I.Nefedov, "Itogi Nauki i Tekhniki. Seriya: Stroenie Molekul i Khimicheskaya Svyaz'" (Progress in Science and Technology. Series: The Structure of Molecules and the Chemical Bond), Izd.VINITI, Moscow, 1973, p.147.
40. V.I.Nefedov, A.P.Sadovskii, L.N.Mazalov, A.V.Belyaev, and E.S.Gluskin, Zhur.Strukt. Khim., 1971, **12**, 681.
41. P.J.Hendra and P.J.D.Park, Spectrochim.Acta, 1967, **23A**, 1635.
42. V.I.Baranovskii, Koord.Khim., 1976, **2**, 599.
43. A.A.Voityuk, P.I.Vadash, and L.N.Mazalov, Zhur.Strukt.Khim., 1980, **21**, 28.
44. A.A.Bagatur'yants, Zhur.Fiz.Khim., 1983, **57**, 1100 [Russ.J.Phys.Chem., 1983(5)].
45. M.L.Schneider and H.M.M.Shearer, J.Chem.Soc., Dalton Trans., 1973, 354.
46. P.J.Hay, J.Amer.Chem.Soc., 1981, **103**, 1390.
47. S.M.Vinogradova and Yu.G.Borod'ko, Zhur.Fiz. Khim., 1973, **47**, 789 [Russ.J.Phys.Chem., 1973(4)].
48. Z.P.Bruvers and I.V.Zuika, Koord.Khim., 1980, **6**, 577.
49. Yu.A.Bankovskii, "Khimiya Vnutrikompleksnykh Soedinenii Merkaptokhinolina i Ego Proizvodnykh" (The Chemistry of Inner-Complex Compounds of Quinolinethiol and Its Derivatives), Izd.Zinatne, Riga, 1978, p.369.
50. J.N.Murrell, S.F.A.Kettle, and J.M.Tedder, "Valence Theory" (Translated into Russian), Izd. Mir, Moscow, 1968, p.105.
51. H.Basch, D.Cohen, and S.Topiol, Isr.J.Chem., 1980, **19**, 233.
52. S.V.Pestrikov, L.M.Sverzh, and I.I.Moiseev, Kinetika i Kataliz, 1969, **10**, 74.
53. I.I.Moiseev, in "Soviet Scientific Reviews. Section B. Chemistry Rev." (Edited by M.E.Vol'pin), OPA, Amsterdam, 1982, Vol.4, p.139.
54. O.N.Temkin and G.L.Bruk, Uspekhi Khim., 1983, **52**, 206 [Russ.Chem.Rev., 1983(2)].
55. O.V.Gritsenko, A.A.Bagatur'yants, I.I.Moiseev, and I.V.Kalechits, Kinetika i Kataliz, 1981, **22**, 1431.
56. A.A.Bagatur'yants, N.A.Anikin, G.M.Zhidomirov, and V.B.Kazanskii, Zhur.Fiz.Khim., 1981, **55**, 2035 [Russ.J.Phys.Chem., 1981(8)].
57. N.A.Anikin, A.A.Bagatur'yants, G.M.Zhidomirov, and V.B.Kazanskii, Zhur.Fiz.Khim., 1981, **55**, 2030 [Russ.J.Phys.Chem., 1981(8)].
58. J.Garcia-Prieto and O.A.Novaro, Mol.Phys., 1980, **1**, 205.
59. J.N.Murrell and C.E.Scollary, J.Chem.Soc., Dalton Trans., 1977, 1034.

60. J.Demuynck, Chem.Phys.Letters, 1977, **45**, 74.
61. R.Osman, C.S.Ewig, and J.R.Van Wazer, Chem. Phys.Letters, 1976, **39**, 27.
62. R.Osman, C.S.Ewig, and J.R.Van Wazer, Chem. Phys.Letters, 1978, **54**, 392.
63. G.A.Ozin and W.J.Power, Inorg.Chem., 1977, **16**, 212.
64. R.P.Messmer and K.H.Johnson, U.S.Dep.Commer. Nat.Bur.Stand.Spec.Publ., 1976(455), 67.
65. D.A.Brown and A.Owens, Inorg.Chim.Acta, 1971, **5**, 675.
66. S.Sakaki, K.Hori, and A.Ohyoshi, Inorg.Chem., 1978, 17, 3183.
67. W.E.Klotzbuecher and G.A.Ozin, J.Amer.Chem.Soc., 1975, **97**, 2672.
68. T.Kruck, Angew.Chem., Int.Ed., 1967, **6**, 53.
69. R.D.Johnston, F.Basolo, and R.G.Pearson, Inorg. Chem., 1971, **10**, 247.
70. O.V.Gritsenko, A.A.Bagatur'yants, I.I.Moiseev, V.B.Kazanskii, and I.V.Kalechits, Kinetika i Kataliz, 1981, **22**, 354.
71. T.Yoshida and S.Otsuka, J.Amer.Chem.Soc., 1977, **99**, 2134.
72. R.Ugo, G.La Monica, F.Cariati, S.Cenini, and F.Conti, Inorg.Chim.Acta, 1970, **4**, 390.
73. T.Yoshida, T.Yamagata, T.H.Tulip, J.A.Ibers, and S.Otsuka, J.Amer.Chem.Soc., 1978, **100**, 2063.
74. J.W.Lauher, J.Amer.Chem.Soc., 1978, **100**, 5305.
75. J.Garcia-Prieto and O.A.Novaro, Int.J.Quantum. Chem., 1980, **18**, 595.
76. R.P.Messmer, S.K.Knudson, K.H.Johnson, J.B.Diamond, and C.Y.Yang, Phys.Rev., 1976, **13B**, 1396.
77. R.P.Messmer, D.R.Salahub, K.H.Johnson, and C.Y.Yang, Chem.Phys.Letters, 1977, **51**, 84.
78. B.-H.Chen, D.C.Foyt, and J.M.White, Surface Sci., 1977, **69**, 218.
79. M.B.Kuz'minskii, A.A.Bagatur'yants, G.M.Zhidomirov, and V.B.Kazanskii, Kinetika i Kataliz, 1981, **22**, 151.
80. R.C.Baetzold, Photogr.Sci.Eng., 1973, **17**, 78.
81. R.C.Baetzold, J.Catal., 1973, **29**, 129.
82. R.C.Baetzold, J.Phys.Chem., 1978, **82**, 738.
83. R.C.Baetzold and R.E.Mack, J.Chem.Phys., 1975, **62**, 1513.
84. R.C.Baetzold, M.G.Mason, and J.F.Hamilton, J.Chem.Phys., 1980, **71**, 366.
85. R.C.Baetzold, Surface Sci., 1975, **51**, 1.
86. G.Ciullo and O.Piovesana, Inorg.Chem., 1980, **19**, 2871.
87. O.V.Gritsenko, Summary of Candidate's Thesis, Kurnakov Institute of General and Inorganic Chemistry, Academy of Sciences of the USSR, Moscow, 1982.
88. M.B.Kuz'minskii and A.A.Bagatur'yants, "Itogi Nauki i Tekhniki. Ser.Kinetika i Kataliz" (Progress in Science and Technology. Series: Kinetics and Catalysis), Vol.8, Izd.VINITI, Moscow, 1980, p.99.
89. S.S.Lin, B.S.Strauss, and A.Kant, J.Chem.Phys., 1969, **51**, 78.
90. V.N.Kondrat'ev (Editor), "Energii Razryva Khimicheskikh Svyazei. Potentsialy Ionizatsii i Srodstvo k Elektronu" (The Energies of Rupture of Chemical Bonds. Ionisation Potentials and Electron Affinity), Izd.Nauka, Moscow, 1974.
91. S.F.Boys and F.Bernardi, Mol.Phys., 1970, **19**, 553.
92. T.H.Dunning, B.H.Botch, and J.F.Harrison, J.Chem.Phys., 1980, **72**, 3419.
93. A.S.Berenblyum, A.G.Knizhnik, S.L.Mund, and I.I.Moiseev, Izv.Akad.Nauk SSSR, Ser.Khim., 1979(8), 1687.
94. A.S.Berenblyum, A.G.Knizhnik, S.L.Mund, and I.I.Moiseev, J.Organomet.Chem., 1982, **234**, 219.
95. M.Elian, M.M.L.Chen, R.Hoffman, and D.M.P.Mingos, Inorg.Chem., 1976, **15**, 1148.
96. O.A.Lobaneva, M.A.Kononova, and M.K.Davydova, Dokl.Akad.Nauk SSSR, 1970, **194**, 133.
97. O.A.Lobaneva, M.A.Kononova, and M.K.Davydova, Vestnik Leningrad.Gos.Univ., 1971(22), 149.
98. O.A.Lobaneva, M.A.Kononova, N.T.Kunaeva, and M.K.Davydova, Zhur.Neorg.Khim., 1972, **17**, 3011 [Russ.J.Inorg.Chem., 1972(11)].
99. N.A.Anikin, A.A.Bagatur'yants, G.M.Zhidomirov, and V.B.Kazanskii, Zhur.Fiz.Khim., 1982, **56**, 3003 [Russ.J.Phys.Chem., 1982(12)].
100. N.A.Anikin, A.A.Bagatur'yants, G.M.Zhidomirov, and V.B.Kazanskii, Zhur.Fiz.Khim., 1983, **57**, 653 [Russ.J.Phys.Chem., 1983(3)].
101. O.V.Gritsenko, A.A.Bagatur'yants, I.I.Moiseev, V.B.Kazanskii, and I.V.Kalechits, Kinetika i Kataliz, 1980, **21**, 632.
102. A.A.Bagatur'yants, N.A.Anikin, G.M.Zhidomirov, and V.B.Kazanskii, Zhur.Fiz.Khim., 1982, **56**, 3017 [Russ.J.Phys.Chem., 1982(12)].
103. O.Eisenstein and R.Hoffmann, J.Amer.Chem.Soc., 1981, **103**, 4308.
104. S.Sakaki, M.Nishikawa, and A.Ohyoshi, J.Amer. Chem.Soc., 1980, **102**, 4062.
105. S.Shinoda and Y.Saito, J.Mol.Catal., 1977, **2**, 369.
106. A.A.Bagatur'yants, O.V.Gritsenko, and G.M.Zhidomirov, Zhur.Fiz.Khim., 1980, **54**, 2993 [Russ.J.Phys.Chem., 1980(12)].
107. G.J.Kubas, R.R.Ryan, B.I.Swanson, P.J.Vergamini, and H.Wasserman, J.Amer.Chem.Soc., 1984, **106**, 451.
108. A.S.Berenblyum, L.I.Lakhman, I.I.Moiseev, and E.D.Radchenko, Izv.Akad.Nauk SSSR, Ser.Khim., 1976, 2417.
109. A.S.Berenblyum, L.I.Lakhman, I.I.Moiseev, and E.D.Radchenko, Koord.Khim., 1976, **2**, 841.
110. A.S.Berenblyum, A.G.Knizhnik, S.L.Mund, and I.I.Moiseev, Izv.Akad.Nauk SSSR, Ser.Khim., 1978, 2711.
111. M.V.Bagilevskii, "Metod Molekulyarnykh Orbit i Reaktsionnaya Sposobnost' Organicheskikh Molekul" (The Molecular Orbital Method and the Reactivity of Organic Molecules), Izd.Khimiya, Moscow, 1969, p.304.
112. R.G.Pearson, "Symmetry Rules in Chemical Reactions" (Translated into Russian), Izd.Mir, Moscow, 1969, p.592.
113. G.Alefeld and J.Voelkl (Editors), "Hydrogen in Metals. Vol.2. Application-Oriented Properties" (Translated into Russian), Izd.Mir, Moscow, 1981, p.107.
114. O.V.Gritsenko, A.A.Bagatur'yants, I.I.Moiseev, V.B.Kazanskii, and I.V.Kalechits, "Tezisy Dokladov VII Vsesoyuznogo Soveshchaniya po Fizicheskim i Matematicheskim Metodam v Koordinatsionnoi Khimii" (Summaries of Papers Presented at the Seventh All-Union Conference on Physical and Mathematical Methods in Coordination Chemistry), Izd.Shtiintsa, Kishinev, 1980, p.148.

115. I.I.Moiseev, American Chemical Society. Preprints of Division of Petroleum Chemistry, 1969, **14**(2), B49.
116. J.E.Bäckvall, B.Akermark, and S.O.Ljunggren, J.Amer.Chem.Soc., 1979, **101**, 2411.
117. A.A.Bagatur'yants, O.V.Gritsenko, and I.I.Moiseev, Koord.Khim., 1978, **4**, 1779.
118. J.Halpern and H.B.Tinker, J.Amer.Chem.Soc., 1967, **89**, 6427.
119. P.M.Henry, J.Amer.Chem.Soc., 1972, **94**, 4437.
120. B.M.Trost, L.Weber, P.E.Strege, T.J.Fullerton, and T.J.Dietsche, J.Amer.Chem.Soc., 1978, **100**, 3416.
121. A.E.Shilov and A.A.Shteinman, Kinetika i Kataliz, 1977, **18**, 1129.

Zelinskii Institute of
Organic Chemistry,
Academy of Sciences
of the USSR, Moscow

Kurnakov Institute of
General and Inorganic
Chemistry,
Academy of Sciences
of the USSR, Moscow