1110 *Russian Chemical Bulletin, International Edition, Vol. 59, No. 6, pp. 1110—1115, June, 2010*

Quantum chemical calculations for the geometry and intramolecular rearrangements of a model nickel(II) *o*-semiquinone complex with a PCP pincer ligand*

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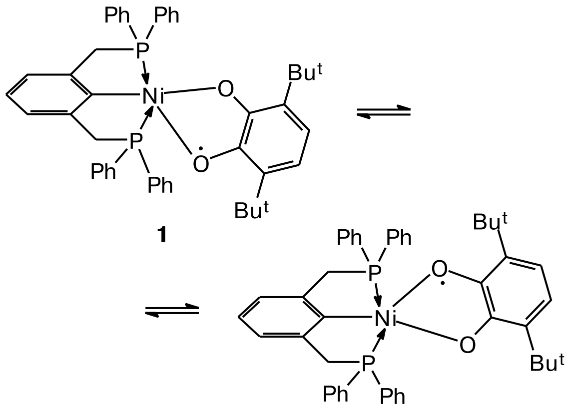
The structure and intramolecular rearrangements of the model five-coordinate nickel PCP-pincer complex with the *o*-semiquinone ligand were studied by the density functional theory method at the B3LYP/6-311++G(d,p) level. The isomerization associated with swing vibrations of the *o*-semiquinone ligand can occur virtually barrierless (0.7 kcal mol^{-1}). The dynamics of the coordination sphere determined by pendulum vibrations of the *o*-semiquinone ligand has the energy barriers of 4—5 kcal mol^{-1}, which is in good agreement with experimental data. A comparison of the results of calculations with the ESR spectroscopic data revealed the dependence of the types and the energy characteristics of intramolecular rearrangements on the nature of substituents at the phosphorus atom.

Key words: nickel(II) complex, *o*-semiquinone, intramolecular rearrangements, pincer ligand, quantum chemical calculations, density functional theory, B3LYP/6-311++G(d,p).

The ESR spectroscopy with the use of *o*-semiquinones as spin labels is an efficient tool for studying the composition, geometry, and chemical dynamics of dissolved coordination compounds[1] containing metal centers in the diamagnetic state. The ESR studies of solutions of pincer phosphine[2] and piperidine[3] complexes of Ni^{II} *o*-semiquinolates revealed the dynamics of the coordination sphere. Thus, pendulum vibrations of the bidentate *o*-semiquinone ligand (SQ) relative to the tridentate pincer moiety occur in five-coordinate phenyl nickel PCP-pincer complexes with *o*-semiquinone ligands (Ph$_2$PCP)Ni(SQ) **1** (Scheme 1).

Scheme 1



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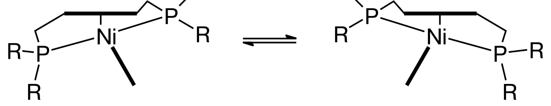
1′

It was found[4,5] that the replacement of phenyl groups at the phosphorus atoms by alkyl groups (compounds **2** and **3**) results in another type of dynamics associated with swing vibrations of these moieties (Scheme 2), a combination of both types of molecular motion being observed for compound **2**. In some cases, the thermodynamic and kinetic characteristics of these intramolecular rearrangements were investigated.[2,4]

Scheme 2



R = Pr^i (**2**), Cy (**3**)

To study the detailed mechanism and the energy characteristics of the intramolecular rearrangements in pincer

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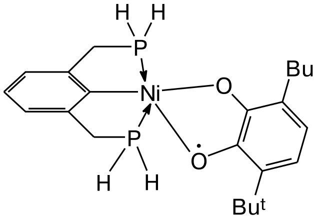
* Dedicated to Academician I. L. Eremenko on the occasion of his 60th birthday.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 6, pp. 1088—1093, June, 2010.

phosphine complexes of Ni^{II} *o*-semiquinolates and to investigate the characteristic features of the spin density distribution, we carried out quantum chemical calculations for model complex **4** containing hydrogens instead of phenyl or alkyl substituents at the phosphorus atoms. The use of model complex **4** allowed us to consider the intramolecular isomerization regardless of the nature of functional groups at the phosphorus atoms.



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Calculation methods

Calculations were carried out by the density functional theory method at the B3LYP/6-311++G(d,p) level with the use of the Gaussian-03 program.[6] This method proved to be efficient for calculations of the energy characteristics of intramolecular rearrangements in nickel complexes.[7—9]

The stationary points on the potential energy surface were found by calculations of the force constants with full geometry optimization of the molecular structures. The structures corresponding to the energy minima on the potential energy surface were determined by the steepest descent method (the movement along the gradient from a saddle point to the adjacent stationary point, either saddle or minimum).[10]

The graphical representations of the molecular structures shown in Figs 1 and 2 were obtained with the ChemCraft program[11] using the atomic Cartesian coordinates obtained in the quantum chemical calculations.

Results and Discussion

As follows from the results of the calculations, the structure **A** with the symmetry C_s and the structure **B** with the symmetry C_1 correspond to the minima on the potential energy surface of complex **4**. The calculated bond lengths in the structures **A** and **B** (Fig. 1 and Table 1) are in good agreement with the X-ray diffraction data for the complexes with phenyl (**1**)[2] and isopropyl (**2**)[5] substituents, respectively. The exceptions are the distances between the nickel atoms and the oxygens in the axial position with respect to the PCP ligand. In our opinion, these differences are associated with the fact that model complex **4** does not contain bulky substituents at the phosphorus atoms, which could have a great effect on both the geometry of the isolated molecules and their crystal packing.

The small energy difference (0.3 kcal mol^{-1}) between the structures **A** and **B** (see Table 2) suggests that these structures are in the equilibrium. Actually, we located the transition structure **C**, in which one of the phosphorus atoms lies in the plane of the pincer ligand (see Fig. 1). The gradient descent from the transition structure **C** along the positive and negative directions of the transition vector leads to the structures **A** and **B**, respectively. Consequently, the structure **C** is responsible for the barrier to the intramolecular rearrangement characterized by swing vibrations of the *o*-semiquinone ligand (see Scheme 2). This barrier is as low as 0.7 kcal mol^{-1}, which is indicative of the dynamic equilibrium between two forms of complex **4** in solution. The calculated barrier is substantially lower than the experimental value (12.7 kcal mol^{-1}) for cyclohexyl PCP complexes.[4] Apparently, this is attributed to the absence of alkyl groups in model complex **4**.

With the aim of finding the transition state corresponding to the pendulum vibrations of the *o*-semiquinone ligand

Table 1. Selected bond lengths (*d*) in the structures **A**—**F** of complex **4**

Bond	*d*/Å					
	A^a	**B**^{b}	**C**	**D**	**E**	**F**
Ni—P(1)	2.215 (2.187)	2.216 (2.217)	2.220	2.183	2.185	2.188
Ni—P(2)	2.215 (2.167)	2.194 (2.198)	2.190	2.183	2.185	2.188
Ni—O(1)	1.942 (1.924)	1.938 (1.938)	1.944	2.168	2.111	2.159
Ni—O(2)	2.204 (2.060)	2.369 (2.218)	2.275	2.168	2.228	2.159
Ni—C(4)	1.951 (1.926)	1.948 (1.922)	1.948	1.954	1.954	1.951
P(1)—C(3)	1.847 (1.828)	1.848	1.846	1.848	1.844	1.846
P(2)—C(5)	1.847 (1.829)	1.848	1.852	1.848	1.844	1.846
O(1)—C(1)	1.294 (1.297)	1.292 (1.301)	1.293	1.276	1.276	1.276
O(2)—C(2)	1.274 (1.289)	1.269	1.271	1.276	1.275	1.276
C(1)—C(2)	1.477 (1.454)	1.484	1.480	1.485	1.485	1.485

[a] The experimental bond lengths for complex **1** are given in parentheses.

[b] The experimental bond lengths for complex **2** are given in parentheses.

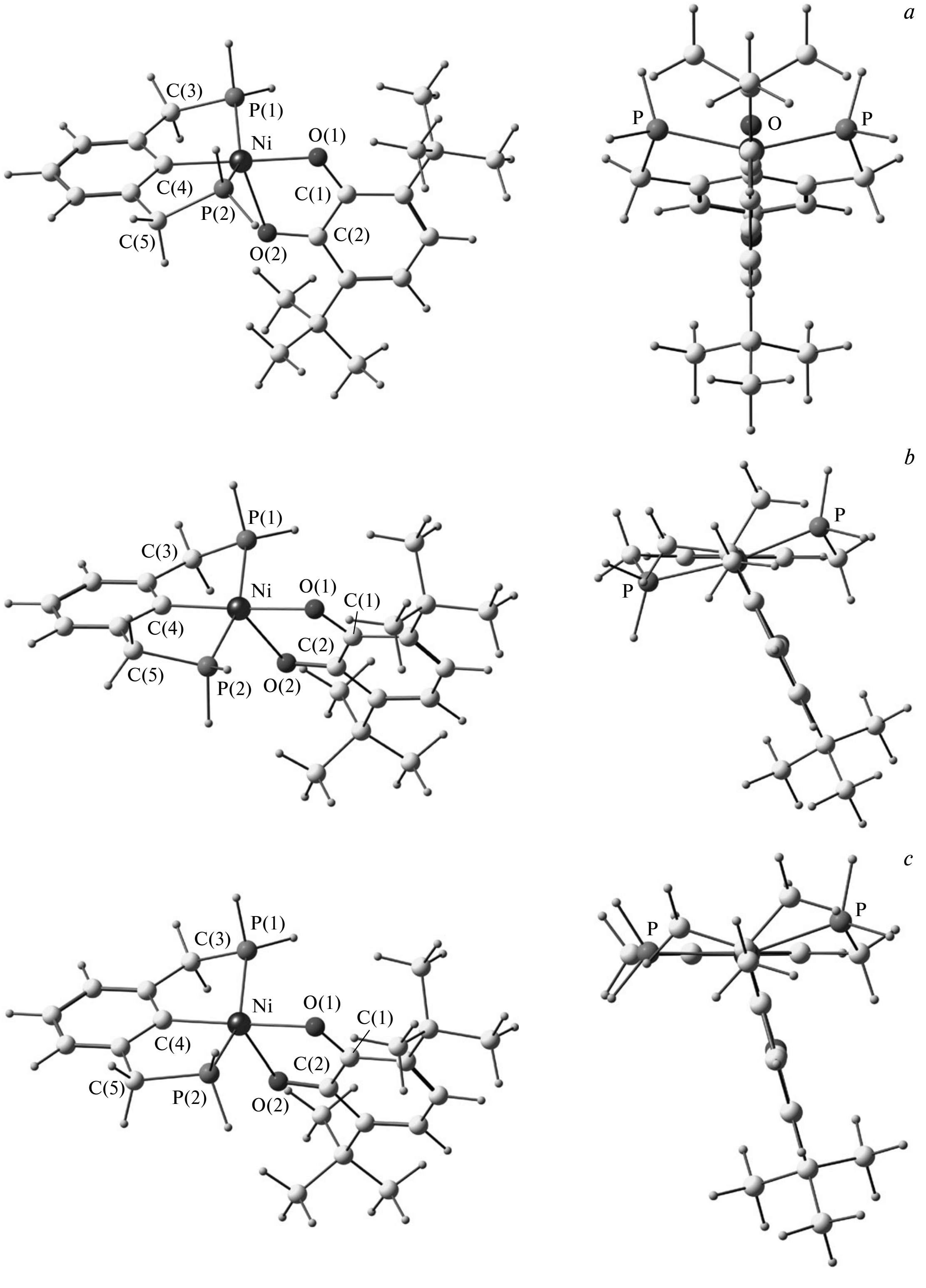

Fig. 1. Geometry of the structures **A** (*a*), **B** (*b*), and **C** (*c*) of model complex **4** (two projections) calculated at the B3LYP//6-311++G(d,p) level of theory.

(see Scheme 1), we considered the high-symmetry structure **D** (symmetry C_{2v}) with the planar pincer ligand (see Fig. 2, *a*). The calculations showed that this structure is 6.1 kcal mol^{-1} less stable than the structure **B**.

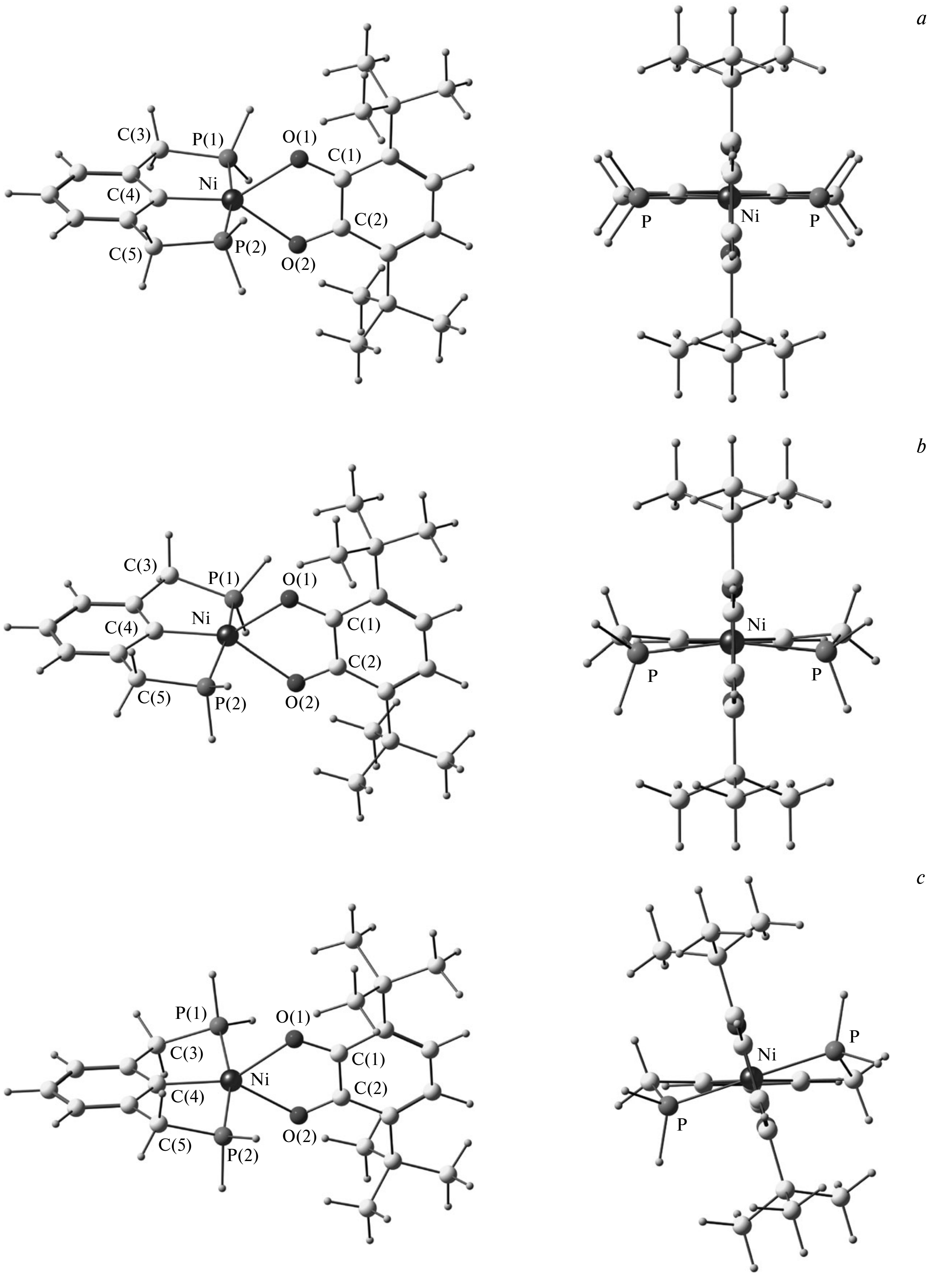

Fig. 2. Geometry of the structures **D** (*a*), **E** (*b*), and **F** (*c*) of model complex **4** (two projections) calculated at the B3LYP//6-311++G(d,p) level of theory.

Table 2. Total energies (E_{tot}), total energies with zero-point vibrational energy corrections ($E_{\text{tot}} + ZPE$), relative total energies (ΔE), relative total energies with zero-point vibrational energy corrections ($\Delta E + ZPE$), and imaginary eigenvalues of the Hessian (λ) calculated at the B3LYP/6-311++G(d,p) level of theory

Structure	$-E_{\text{tot}}$	$-(E_{\text{tot}} + ZPE)$	ΔE	$\Delta E + ZPE$,	λ	s(Ni)*
	/au		/kcal mol^{-1}			
A (C_s)	3198.827470	3198.354491	0.3	0.2	0	0.02
B (C_1)	3198.827994	3198.354752	0.0	0.0	0	0.01
C (C_1)	3198.826925	3198.353989	0.7	0.5	1	0.02
D (C_{2v})	3198.818306	3198.346417	6.1	5.2	3	0.00
E (C_s)	3198.819202	3198.346810	5.5	5.0	1	0.00
F (C_2)	3198.821343	3198.348771	4.2	3.8	1	0.00

* s(Ni) are the spin densities on the Ni$^{\text{II}}$ atom.

An analysis of the force constant matrix showed that the structure **D** corresponds to the third-order stationary point, *i.e.*, it is characterized by the presence of three imaginary frequencies ($\lambda = 3$). The movement along the first transition vector of the structure **D** leads to two isomeric forms of the structure **A**, which differ in the position of the *o*-semiquinone moiety with respect to the plane of the pincer ligand, *i.e.*, the structure **D** does not correspond to a saddle point. The gradient descents along the second and third transition vectors of the structure **D** give the stationary points belonging to the structures **E** and **F**, which correspond to the true transition states. An analysis of the transition vector of the structure **E** (symmetry C_s) shows that it corresponds to the pendulum vibrations of the *o*-semiquinone ligand, resulting in two isomeric forms of the structure **A**. The barrier of this reaction is 5.5 kcal mol^{-1}.

The structure **F** (symmetry C_2) is characterized by a distortion of the pincer ligand, which is manifested in its twisting and the deviation of the phosphorus atoms from the plane of the ligand (see Fig. 2, *c*). The movement along the intrinsic reaction coordinate from the transition state **F** leads to isomeric forms of the structure **B** corresponding to minima on the potential energy surface. In the case of the pendulum vibrations of the *o*-semiquinone ligand, the barrier of the reaction is 4.2 kcal mol^{-1}.

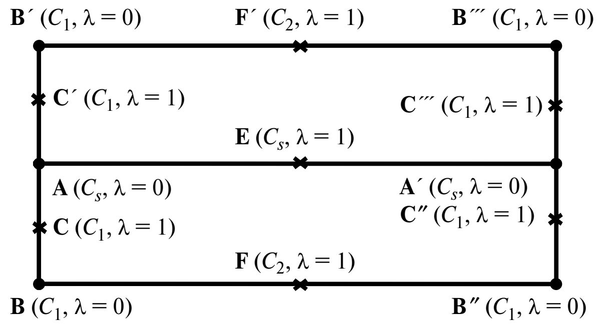

Fig. 3. Scheme of intramolecular rearrangements in complex **4**.

The results obtained for model complex **4** agree well with the ESR data (3.8—4.3 kcal mol^{-1}) for the complex with P(Ph)$_2$ groups[2] and suggest that the phenyl substituents, unlike the bulky *tert*-butyl and cyclohexyl substituents, do not cause steric hindrance to pendulum vibrations of the *o*-semiquinone ligand.

On the whole, the intramolecular rearrangements of the complexes under consideration can be represented by Fig. 3, which shows the presence of four forms of the structure **B**, whose isomerization is virtually barrierless and occurs through the path $\mathbf{B} \to \mathbf{C} \to \mathbf{A} \to \mathbf{C}' \to \mathbf{B}'$ corresponding to the swing vibrations of the *o*-semiquinone ligand or through the transition structures **F** and **F′** (pendulum vibrations). The isomerization of the structure **A** can also occur through two channels: through the transition state **E** or through the path $\mathbf{A} \to \mathbf{C} \to \mathbf{B} \to \mathbf{F} \to \mathbf{B}'' \to \mathbf{C}'' \to \mathbf{A}'$, which is energetically more favorable. Figure 4 shows the profiles of the reactions under consideration on the energy scale.

Table 2 gives the calculated values of the spin density on the Ni$^{\text{II}}$ atoms for the structures **A**—**F** of complex **4**; for all the stationary points found in the calculations, the spin density is close to zero; in the transition states **E** and **F**, the spin density is equal to zero. The spin densities on the atoms with the largest populations in the structures **A** and **B** corresponding to the minima on the potential energy surface are given in Table 3 (see the atomic numbering scheme in Fig. 1). As can be seen from Table 3, the spin densities are located mainly on the oxygen atoms of the *o*-semiquinone ligand.

Table 3. Spin densities (s) for the structures **A** and **B** of complex **4** calculated at the B3LYP/6-311++G(d,p) level of theory

Structure	s					
	P(1)	P(2)	O(1)	O(2)	C(1)	C(2)
A (C_s)	0.004	0.004	0.210	0.280	0.174	0.102
B (C_1)	0.003	0.002	0.209	0.276	0.180	0.095

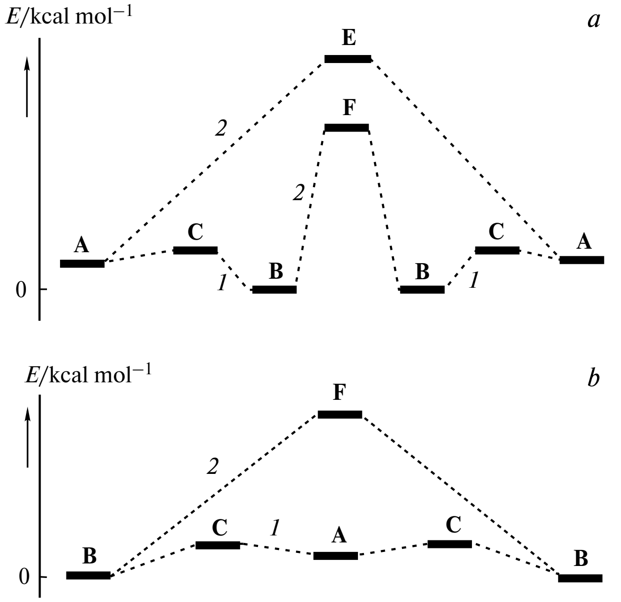

Fig. 4. Energy profiles for the isomerization of the structures **A** (*a*) and **B** (*b*) of complex **4** along the paths corresponding to the swing (*1*) and pendulum (*2*) vibrations.

It should be noted that the ratio of the spin densities on the P(1) and P(2) atoms in the structure **B** of complex **4** is in good agreement with the corresponding experimental hyperfine coupling constants (25.3 E and 15.7 E).[5] This result supports the above conclusions.

Therefore, in the present study the structure and the intramolecular rearrangements of the model five-coordinate nickel(II) PCP-pincer complex with the *o*-semiquinone ligand **4** were investigated by the density functional theory method at the B3LYP/6-311++G(d,p) level. Two minima corresponding to the structures **A** and **B** were found on the potential energy surface. The isomerization of the structure **B** associated with the swing vibrations of the *o*-semiquinone ligand can occur virtually barrierless (0.7 kcal mol^{-1}). The dynamics of the coordination sphere is determined by the pendulum vibrations of the *o*-semiquinone ligand and occurs through the transition states **E** and **F** with the barriers of 5.5 and 4.2 kcal mol^{-1}, respectively. This agrees well with the experimental values. A comparison of the results of the calculations for model complex **4** and the ESR data for the real structure leads to the conclusion that the types and the energy characteristics of intramolecular rearrangements strongly depend on the nature of the substituents at the phosphorus atom. The calculated ratio of the spin densities on the phosphorus atoms and the absence of the spin density on the nickel atom are in good agreement with the ESR data. On the whole, the calculation scheme adequately describes the experimental data.

This study was financially supported by the Russian Foundation for Basic Research (Project No. 09-03-12109 ofi-m) and the Ministry of Education and Science of the Russian Federation (Project RNP 2.2.1.1/2348).

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Received December 21, 2009;
in revised form February 15, 2010