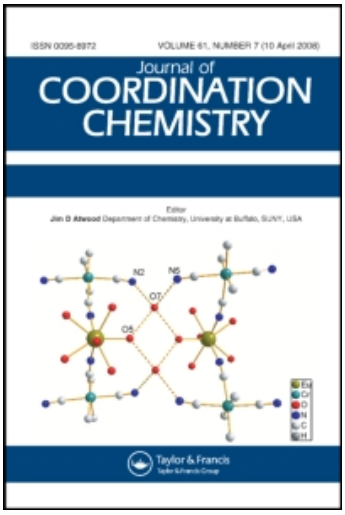

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Tautomerism, protonation regioselectivity of 2-pyrrolidone and its complexation with palladium(II): an insight from the viewpoint of quantum chemistry

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TAUTOMERISM, PROTONATION REGIOSELECTIVITY OF 2-PYRROLIDONE AND ITS COMPLEXATION WITH PALLADIUM(II): AN INSIGHT FROM THE VIEWPOINT OF QUANTUM CHEMISTRY

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It has been established (AM1, PM3, RHF/6-31G**, MP2/6-31G**//RHF/6-31G**) that in the gaseous phase and in aqueous solution, the most thermodynamically stable tautomer of 2-pyrrolidone is lactame. According to PM3 evaluations with an explicit accounting for aqueous medium, the state of tautomeric equilibrium serves as a prerequisite to participation of 2-pyrrolidone's lactime tautomer (pyrroline-2-ol) in complexation with palladium(II) in aqueous solution. 2-Pyrrolidone protonation in the gaseous phase and in aqueous medium has been shown to proceed *via* the oxygen atom, corresponding to expectations on mesomeric displacement of electron density in the amide fragment. The aqueous medium stabilizes 2-pyrrolidone's lactime tautomer to a greater extent than for lactame, and an *O*-protonated cyclic amide compared to an *N*-protonated one. The stereodirective character of palladium(II) complexation with chloride ion and pyrroline-2-ol has been explained. The initially formed tetragonal–pyramidal adduct with an axial organic ligand rearranges into a precursor of the *cis* product, an intermediate with an extra coordinated axial chlorine atom. The less thermodynamically stable *cis* isomer of $[PdCl_2(\text{pyrroline-2-ol})_2]$ appears because its precursor is a lower energy intermediate of associative nucleophilic substitution. At a supramolecular level, *cis* product is capable of being stabilized by means of intermolecular dipole–dipole association in a crystal.

Keywords: 2-Pyrrolidone; Tautomerism; Protonation; Palladium(II) complexes; Stereodirection of complexation; Quantum chemical consideration

INTRODUCTION

Palladium(II) complexes with organic ligands are promising as drugs [1]. The variety of palladium compound interactions with biological systems may eventually be reduced to coordination with functional groups of these systems [2]. When studying the reactions

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of palladium ion with bioligands, it is necessary to take into account the interaction between this ion and inorganic compounds present in the organism's fluids; inorganic ligands (H_2O, Cl^- and others) competing with biologically active substances for metal ion may diminish the latter's toxicity. On the other hand, the metal cation's binding with inorganic ligands can decrease the efficiency of drugs based on palladium compounds.

Acceptable drug preparations would more or less counterbalance these opposite tendencies in ligand complexes of palladium(II). Thus it should be advantageous to use chloride as an inorganic ligand, since it is present in biological fluids, e.g., blood plasma is a 0.86% (0.147 M) solution of sodium chloride, and gastric juice is a 0.1 M solution of hydrochloric acid [3].

2-Pyrrolidone (2-pyrrolidinone, pyrrolidine-2-one, 2-oxopyrrolidine, γ-butyrolactame) is a promising ligand for obtaining the biologically active complex compounds with platinum metal cations [4]. 2-Pyrrolidone is capable of exhibiting the lactame–lactime tautomerism [5,6].

In fairly acidic media, complexation with metal cations competes with protonation of 2-pyrrolidone capable of proceeding in principle *via* two centers, nitrogen and oxygen.

Treatment of palladium(II) chloride with 2-pyrrolidone [7] in water-contaminated acetone gave $[Pd(C_4H_7NO)_4Cl_2]$, whose structure was determined by X-ray structural analysis [8]. The substance obtained included an electroneutral complex—dichlorobis-(pyrroline-2-ol)palladium—with two 2-pyrrolidone molecules bound to it by intermolecular hydrogen bonds OH$\cdots$O [8]. The fundamental peculiarities of the complexation are the lactime (pyrroline-2-ol) structure of the organic ligand, coordination at nitrogen and *cis* geometry [8]. Usually, complexation reactions lead to *trans* isomeric products [9,10]. However, *cis* isomers are more interesting as potential antitumor preparations. Therefore, the stereoselectivity of complexation is important.

The present work examines quantum chemical investigations into tautomerism and regioselectivity of 2-pyrrolidone protonation in the gaseous phase and aqueous solution, as well as the stereochemistry of palladium(II) complexation with chloride and pyrroline-2-ol.

Computational Methods

Gaseous-phase quantum chemical computations were performed by means of the AM1 [11] and PM3 [12] methods using software from the *MOPAC* package [13,14] with complete geometry optimization (Broyden–Fletcher–Goldfarb–Shanno function minimizer [15] involving Thiel's fast minimization algorithm [16]. Molecule graphical images and the preliminary optimization were realized by the molecular mechanics method (the MMX procedure) [17]) with *PCMODEL* software [17]. In quantum chemical computations, the condition of the gradient norm not exceeding 0.02 kcal/(mol Å) was preset.

In calculating the rotational contributions to thermodynamic functions the symmetry number was taken as unity.

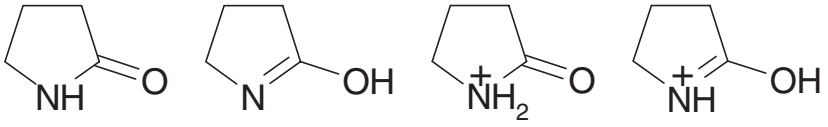
For computing clusters with 107 water molecules included, the PM3 method was used, within the *HyperChem* package [*HyperChem*^{TM}, Hypercube, Inc., 1115 NW 4th Street, Gainesville, Florida 32601, USA]. Complete geometry optimization was carried out by means of the Polak–Ribiere conjugate gradient algorithm [15]. A minimal distance of 1.7 Å was assumed between the solute and water molecules.

Ab initio computations within the framework of the 6-31G** [13] basis were performed using the *HyperChem* software package with complete geometry optimization. Electronic correlation was allowed for by means of Möller–Plesset second-order theory [13] for the optimized conformations of molecular systems.

RESULTS AND DISCUSSION

Tautomerism and Protonation Regioselectivity for 2-Pyrrolidone

Using the semiempirical AM1 and PM3 methods, along with *ab initio* (RHF/6-31G** and MP2/6-31G**//RHF/6-31G**) methods, we have explored the electronic structure of 2-pyrrolidone (**I**), its lactime tautomer (**II**), as well as conjugate acids of **I** formed on **I** protonation at nitrogen (**III**) and oxygen (**IV**) atoms.



I **II** **III** **IV**

In the gaseous phase, the lactame oxo tautomer is the most thermodynamically stable (Tables I and II). Our standard heat of formation of lactame agrees with the results of calorimetric study of 2-pyrrolidone, according to which $\Delta H_{f(exper)} = -47.175$ kcal/mol [18].

The IR spectrum of 2-pyrrolidone vapor [19] involves the bands assigned as indicated in Table III. O–H and C=C bond vibration frequencies are absent in the spectrum. Therefore, 2-pyrrolidone as a vapor exists in the lactame form.

TABLE I Computed standard physical quantities of tautomers and protonated forms of 2-pyrrolidone

Tautomer	ΔH_f (kcal/mol)		S (cal/mol K)		ΔG_f (kcal/mol)		μ (D)		
	AMI	*PM3*	*AMI*	*PM3*	*AMI*	*PM3*	*AMI*	*PM3*	*RHF/6-31G***
Molecule									
I	−44.42	−50.16	74.93	75.02	−18.45	−24.21	3.83	3.52	4.29
II	−31.15	−39.86	72.74	73.73	−4.52	−13.52	1.45	1.57	1.33
Cation									
III	121.16	119.79	75.38	76.28	151.66	150.02	–	–	–
IV	115.87	113.48	73.88	74.89	139.09	146.51	–	–	–

TABLE II Energy differences of molecular systems from *ab initio* computations

Energy difference	ΔE (kcal/mol)	
	*RHF/6-31G***	*MP2/6-31G**//RHF/6-31G***
E (**II**) − E (**I**)	14.23	13.94
E (**IV**) − E (**III**)	−17.52	−10.85

TABLE III Principal bands in the IR spectrum of 2-pyrrolidone gas

Frequency (cm^{-1})	*Relative transmission*	*Assignment*
3474	0.777	Stretching vibration of free N–H group
2986	0.681	Asymmetric stretches of C–H bonds in CH_2 groups
2882	0.671	Symmetric stretches of C–H bonds in CH_2 groups
1757	0.037	Amide I (C=O stretch)
1422	0.718	Shear vibrations in CH_2 groups
1257 and 1236 (doublet)	0.521	Amide III
1075	0.859	Carbon skeleton vibrations

TABLE IV Quantum chemical PM3 computations for supermolecules involving molecular systems **I**–**IV** and 107 water molecules

Cluster	*HyperChem cubic cell side* (Å)	*Water molecule quantities per unit volume for cubic cell* ($Å^{-3}$)	*Gradient norm* (kcal/mol Å)
Computation routine characteristics			
I + 107 H_2O	15.020	0.0316	0.627
II + 107 H_2O	15.020	0.0316	0.653
III + 107 H_2O	15.020	0.0316	0.606
IV + 107 H_2O	15.020	0.0316	0.628
107 H_2O	14.949	0.0320	0.639
Molecular system		$\Delta\Delta H_f$ (kcal/mol)[a]	
A	B		
I	**II**	−4.51	
IV	**III**	−54.6	

[a] $\Delta\Delta H_f = \Delta H_f$ (A · 107 H_2O) − ΔH_f (B · 107 H_2O).

The experimental values of the dipole moment of 2-pyrrolidone (in cyclohexane, benzene, carbon tetrachloride and 1,4-dioxane) fall within the range 3.1–3.96 D [20,21], indicative of γ-butyrolactame occurrence in the oxo form **I**. Thus in the gaseous phase, and in cyclohexane, benzene, carbon tetrachloride and 1,4-dioxane, 2-pyrrolidone exists as the lactame oxo tautomer.

Judging by the dipole moments of isolated molecules of tautomers, nonspecific solvation in polar solvents such as water should facilitate displacement of the tautomeric equilibrium toward the oxo form. The actual situation is somewhat different. Using the PM3 method, we have computed clusters including the molecular systems **I**–**IV** and 107 water molecules (Table IV), 729 water molecules within a 28-Å-sided cubic cell correspond to the liquid water density [22]. The results presented in Table IV show that in our computations, analogously to the literature [23–27], the density of water molecules in a cell approaches this value for liquid, even if partial occupation of the cell volume by species **I**–**IV** is disregarded.

PM3 consideration with an explicit accounting for medium in the supramolecular approximation has exhibited (Table IV) that the oxo form remains preferable in aqueous solution. However, the difference in standard heats and free energies for tautomer formation decreases significantly, as compared to the gaseous phase, from specific solvate–solvent interactions. The role of solvent–solvent interactions is evident even from the data of the PM3 quantum chemical method, which underestimates the energies of hydrogen bonds important for specific hydration.

The state of the 2-pyrrolidone tautomeric equilibrium in the presence of water could be a prerequisite for participation of just the lactime tautomer of 2-pyrrolidone in complex formation with palladium(II) [8].

We have established that 2-pyrrolidone protonation in gaseous phase proceeds *via* oxygen, consistent with mesomeric displacement of electron density in the amide fragment.

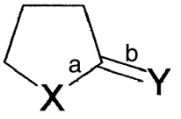
The importance of the mesomeric effect follows from comparison of the corresponding bond orders in Molecule **I**, and in the model systems pyrrolidine (**V**) and cyclopentanone (**VI**) (Table V).

The mesomeric shift of electron density toward oxygen is confirmed by an increase in negative Mulliken charge on this atom in Molecule **I**, as compared to **VI** (Table VI).

Protonation of 2-pyrrolidone at oxygen is more favored for aqueous solution than for the gaseous phase (Table IV). Thus, hydronium ion should not compete with metal ion for nitrogen of the organic ligand on complexation in acidic medium. Obviously, the reversible binding of oxygen by Lewis acid (vaguely resembling protonation at oxygen), when 2-pyrrolidone interacts with Pd(II) in acetone [7], blocks the *O*-center and promotes complexation by nitrogen. The role of electrophile weakly bound to oxygen could be performed also by a proton occurring in the process of palladium(II) hydrolysis caused by water contaminating a solvent.

It has previously been suggested [28–30] on the basis of quantum chemical computations of hydration enthalpies $\Delta H_{aq} = \Delta H_f(A \cdot nH_2O) - \Delta H_f(A) - \Delta H_f(nH_2O)$ that phenothiazine protonation favors hydration. Positive ΔH_{aq} values change sign as a result of protonation, apparently due to change in hydrophilic hydration from negative into positive on accepting a proton. Similar change in the hydrophilic hydration type takes place in moving from the 2,6-diphenyl-4-(4-dimethylaminostyryl)pyrilium

TABLE V Some bond orders in Molecules **I**, **V** and **VI**



Molecule	*X*	*Y*	*Bond order*			
			AM1		*PM3*	
			a	*b*	*a*	*b*
I	NH	O	1.086	1.765	1.057	1.824
V	NH	H_2	0.990	–	0.992	–
VI	CH_2	O	0.931	1.918	0.935	1.922

TABLE VI Charge on oxygen atom in Molecules **I** and **VI**

Molecule	*Charge*		
	AM1	*PM3*	*RHF/6-31G****
I	−0.355	−0.350	−0.607
VI	−0.290	−0.315	−0.532

TABLE VII Hydration enthalpies for the molecular systems **I–IV**

Molecular system	ΔH_{aq} (kcal/mol)
I	−9.57
II	−15.37
III	−4.91
IV	−53.2

cation with positive charge delocalized over the heterocycle, to the sulfur-containing analog with greater positive charge localized on the sulfur atom to a considerable extent [31,32].

We have found that as one passes from 2-pyrrolidone **I**, and its hydroxy tautomer **II**, to the protonated forms **III**, **IV**, the hydration enthalpies (A = **I**, **II**, **III**, **IV**; $n = 107$) move toward negative quantities (Table VII). Therefore, as in the case of phenothiazines, the protonation of 2-pyrrolidone assists the hydration. Hydrophilic hydration occurs mainly by electrostatic interaction, which increases as the molecular system gains in charge.

The hydration enthalpy of lactime tautomer **II** is more negative than the corresponding value for oxo form **I**. The same situation is observed for the hydration enthalpy of *O*-protonated 2-pyrrolidone with respect to the hydration enthalpy of the *N*-protonated one (Table VII).

Aqueous medium stabilizes the hydroxy form **II** of cyclic amide to a greater extent than lactame tautomer **I**. That is why, as mentioned above, the presence of water in acetone for [$PdCl_2$(pyrroline-2-ol)$_2$] synthesis could assist the complexation of palladium(II) with the tautomeric form **II**. For cation **IV**, additional stabilization in aqueous solution compared to the molecular system **III** is peculiar.

Complexation of Palladium(II) with Chloride Ion and Pyrroline-2-ol

In accordance with the HSAB principle [33–35], nitrogen is an intermediate base as a ligating center, while oxygen is a hard-basic donor [36]. Palladium(II) cation is a soft acid [36]. For complex formation a soft-intermediate interaction resulting in a Pd–N bond is preferable to Pd–O bond formation. Experimental data show: in water-containing acetone, Pd(II) ion coordinates pyrroline-2-ol (II) by the nitrogen atom, but not acetone or water *via* the oxygen center [7,8]. So we have taken into account only structures with Pd–N (not Pd–O) bonds, and treated the corresponding mechanistic paths.

Using the PM3 method, we have computed the electron structure of molecules of *cis* (**VII**) and *trans* (**VIII**) isomers of dichloro-bis-(pyrroline-2-ol)palladium, as well as trichloro(pyrroline-2-ol)palladium (**IX**) – an anionic complex preceding the systems **I** and **II** (Figs. 1–3).

Molecules **VII** and **VIII** have C_2 point group symmetry. For substance **VII** this geometry is supported by X-ray structural analysis [8].

Table VIII provides the computed standard heats of formation and dipole moments of Molecules **VII** and **VIII**. On interaction between palladium(II) chloride and 2-pyrrolidone, of two feasible isomeric mixed ligand complexes, the less stable **VII** forms.

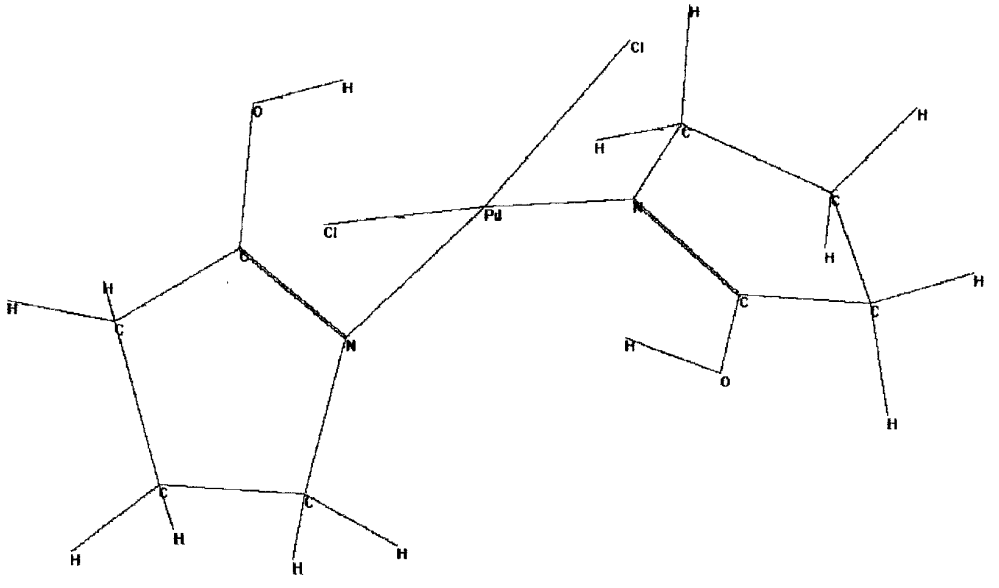


FIGURE 1 Graphical image of *cis*-dichloro-bis-(pyrroline-2-ol)palladium (**VII**).

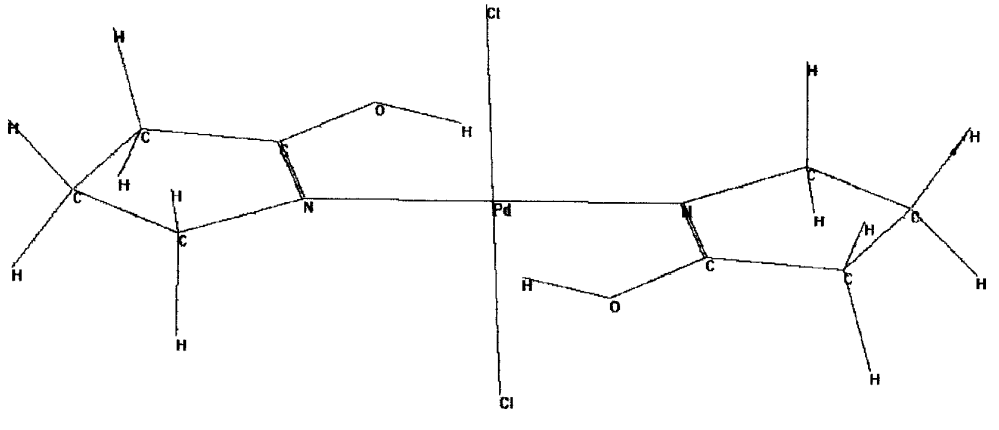


FIGURE 2 Graphical image of *trans*-dichloro-bis-(pyrroline-2-ol)palladium (**VIII**).

In Complex **IX** the greatest negative charge (−0.493) occurs on the chlorine atom *trans* to the organic ligand. The least negative charges (−0.438; −0.437) are localized on *cis* chloro ligands. If ligand substitution proceeded by a dissociative (S_N1) mechanism [9,10], elimination of chloride ion from the *trans* position with respect to the organic ligand, followed by the formation of **VIII**, would be expected. However, ligand substitution in palladium(II) complexes occurs by an associative mechanism (S_N2) involving the appearance of trigonal–bipyramidal or tetragonal–pyramidal intermediates [9,10].

For elucidating the possible kinetic aspects of complex formation in the system palladium(II)–2-pyrrolidone–chloride, we have used the PM3 method to simulate theoretically feasible intermediates (**X**–**XII**) with pentacoordinated palladium, from

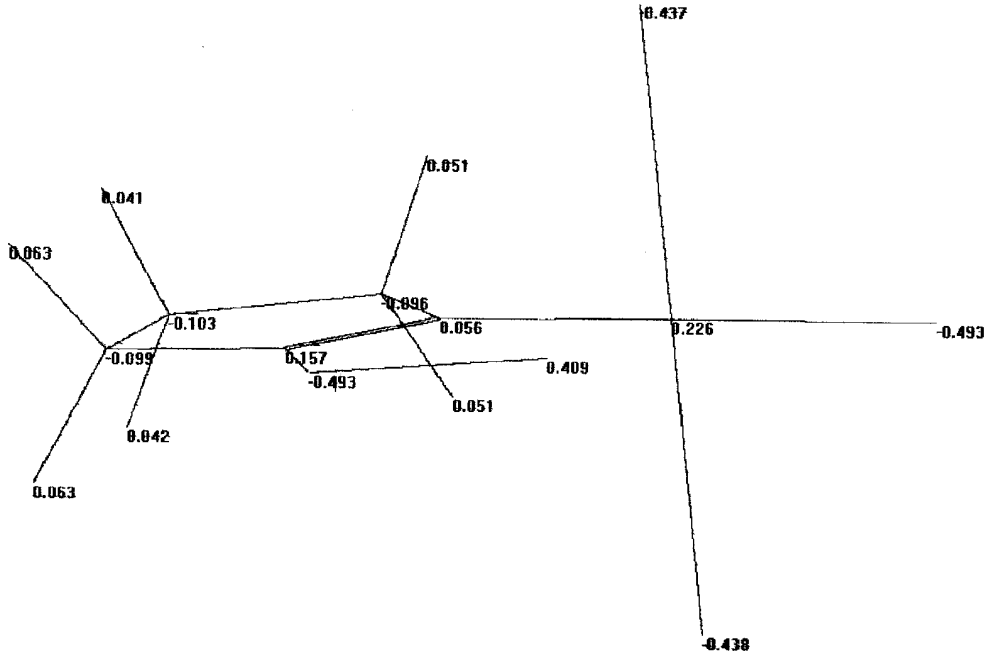


FIGURE 3 Graphical image and Mulliken charges on atoms of the trichloro(pyrroline-2-ol)palladium anion (**IX**).

TABLE VIII Heats of formation (ΔH_f) and dipole moments (μ) of molecules **VII** and **VIII**

Compound	ΔH_f (kcal/mol)	μ (D)
VII	−198.96	11.8
VIII	−206.71	0.016

which three anionic adducts in the form of tetragonal pyramids have been deduced (Figs. 4–6). X-ray data confirm the tetragonal–pyramidal structure of a number of palladium(II) and platinum (II) [37] complexes.

Comparison of the standard heats of formation of the anionic intermediates **X**–**XII** (Table IX) shows that the initially formed adduct **X** with an axial organic ligand (vertex of a pyramid) should tend to regroup into Complex **XI** with axial chloride, preceding the *cis* product **VII**. The formation of another adduct, **XII**, with an axial chloro ligand, which is a precursor to the *trans* product **VIII**, is thermodynamically unfavorable. Consequently, between two possible complexes of composition $[PdCl_2L_2]$, where L = 2-pyrrolidone in the lactime form, *cis* isomer **VII** is kinetically preferred. The dipole moment of *cis* isomer **VII** is much greater than that of the *trans* form **VIII** (Table VIII), and at the supramolecular level the *cis* product can be stabilized by intermolecular dipole–dipole association in a crystal.

The less thermodynamically stable *cis* isomer of $[PdCl_2(pyrroline\text{-}2\text{-}ol)_2]$ appears because its structural precursor is energetically the most preferable tetragonal–pyramidal

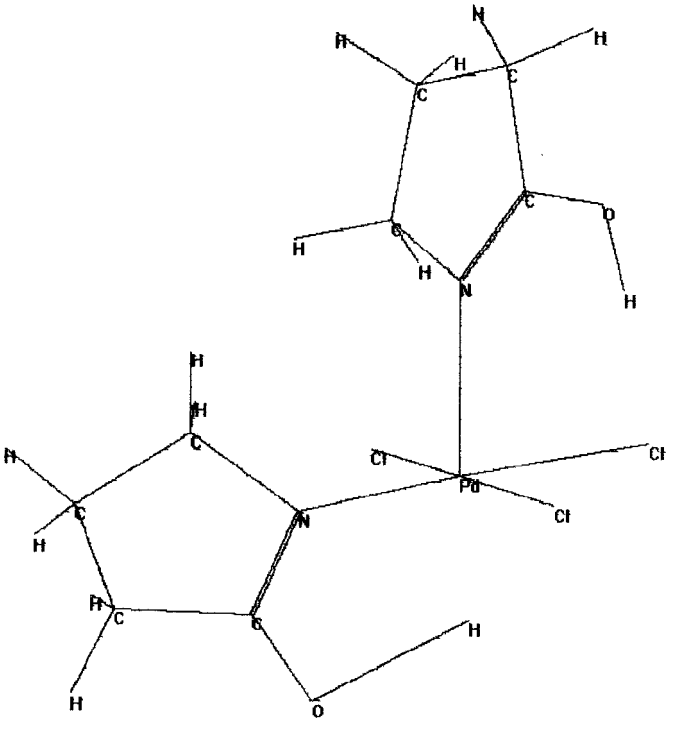


FIGURE 4 Graphical image of anionic intermediate (**X**).

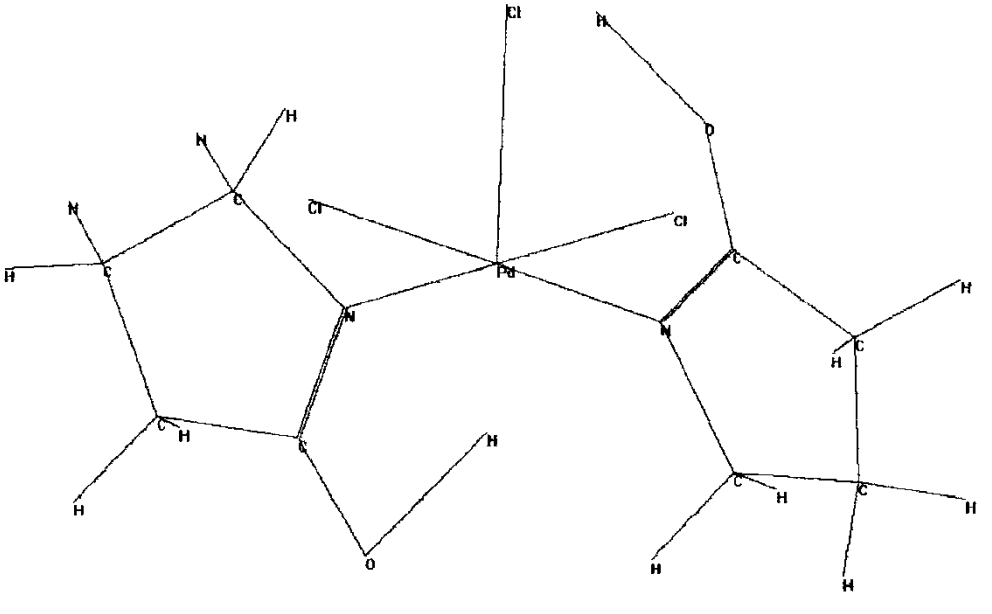


FIGURE 5 Graphical image of anionic intermediate (**XI**).

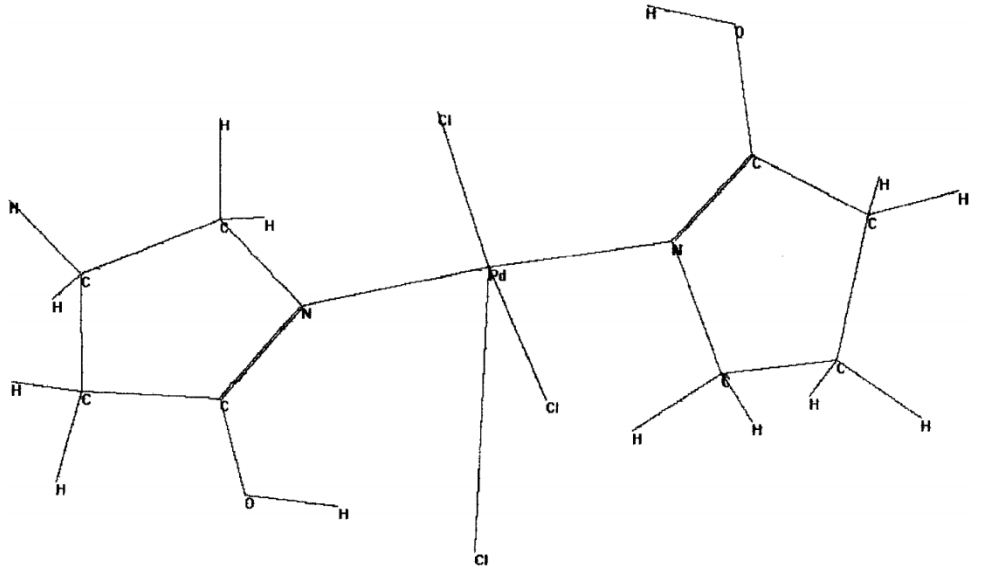


FIGURE 6 Graphical image of anionic intermediate **XII**.

TABLE IX Heats of formation (ΔH_f) of anions **X**–**XII**

Anion	ΔH_f (kcal/mol)
X	−317.24
XI	−333.03
XII	−277.61

intermediate with an axial chloro ligand. The reaction $[PdCl_3L]^- + L \rightarrow [PdCl_2L_2] + Cl^-$ (L = pyrroline-2-ol) is kinetically controlled and proceeds by the lower activation energy.

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