Transformations of β-Hydroxo-Substituted η³-Allyl Pd Complexes in Neutral and Weakly Acidic Solutions

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Abstract—The oxidation of some β -hydroxo-substituted η^3 -allyl Pd complexes based on the simplest 1,3dienes is studied by the ¹H and ¹³C NMR methods in neutral and weakly acidic methods. The composition of the reaction products is determined by the nature of the oxidizing agent and the structure of allyl fragment. The method of selective oxidation of the β -carbon atom of the allyl ligand with the allyl–metal bond remaining unchanged is suggested.

The study of the structure and reactivity of the transition metal allyl complexes is an important direction in the coordination chemistry and controlled catalytic synthesis. The substituted η^3 -allyl Pd complexes play key role in the catalytic processes of oxidation of olefine and diene hydrocarbons to the oxygen-containing compounds and determine regio- and stereoselectivity of these processes. These reactions can be controlled mainly through the target action on the allyl intermediates. Today two methods are widely used by which this action can be realized in the catalytic synthesis: the introduction to the metal coordination sphere of a controlling ligand, which activates the allyl-metal bond and determines the direction of the complex decomposition and the selection of a reagent, which determines the nature of the products formed after the complex destruction. However, there is also one more method based on the selective action on the η^3 -allyl ligand without affecting its bond with Pd. This action can be realized through the reversible stabilization of the allyl-metal bond or by the choice of the respective reaction conditions.

The β -hydroxy-substituted η^3 -allyl complexes can be formed easily from the simplest 1,3-dienes in aqueous solutions of Pd(II) salts. Their structure is determined by the initial diene structure, since the nucleophilic attack at the primary cationic η^4 -dienepalladium intermediate is sufficiently regioselective (at its most substituted periphery) [1]. Nevertheless, in the case of 1,3-pentadiene, the position isomer (1-hydroxo-1,2,3 η^3 -pentenyl)palladium chloride (**II**) is formed in addition to the main isomer 4-hydroxo-1,2,3- η^3 -pentenylpalladium chloride (**I**). The ratio (%) of regio-isomers **I** and **II** is determined by the synthesis temperature: from 70 : 30 at 25°C to 60 : 40 at 0°C [2]



Note that complex **I** occurs in the reaction solution as equimolar mixture of two diastereomers (I-*R* and I-*S*).



We reported previously [3, 4] that the pH value is the main factor determining the course of transformation of complex I in aqueous solutions:

[†] Diseased.



In strongly acidic solutions (pH < 1), protodemetallation of the complex occurs that results in the formation of 1,3-pentadiene [5]. In alkaline solutions (pH > 7), the reductive destruction is observed with the formation of *trans*-3-pentene-2-one [6]. At pH 1–4, complex I reacts with hydrogen peroxide with a high selectivity and gives *trans*-pentene-1,4-diol (IV), whose further oxidation gives a mixture of ketodiol isomers, one of which is closed into a cycle of 2-methylfurane [7].

The reaction follows unusual route in a narrow interval of pH 5–7. Under these conditions, the hydroxyl group of the allyl ligand of complex I is oxidized to the carbonyl group without destruction of η^3 -allyl structure of the complex (allyl–metal bond).

The formation of carbonyl compounds after treatment of the Pd allyl complexes with typical oxidants was reported in [8, 9]. The data on the oxidation of the allyl complexes, in which the functional group of the allyl ligand can be oxidized without the destruction of the complex structure (i.e., with the allyl-metal bond remaining unchanged) are few in the literature and refer to substantially bulky allyl ligands [10, 11].

The possibility of such an oxidation for hydroxylcontaining complexes based on 1,3-pentadiene was reported in [2]. However, the data on stoichiometry and mechanisms of such reactions, as well as on the possibility of these reaction for the complexes obtained from another simplest 1,3-dienes are unavailable. Such reactions can be of interest for the researchers of organometallic compounds, since they allow one to modify the allyl ligand directly in the complex

The aim of this work was to establish the direction of transformations of complexes I and II and of some β -hydroxo-substituted complexes based on the simplest 1,3-dienes when treated with hydrogen peroxide and another oxidants in neutral and weakly acidic aqueous solutions and to choose the conditions for the selective formation of the corresponding carbonyl complexes.

EXPERIMENTAL

The synthesis of hydroxo-containing η^3 -allyl Pd complexes was performed by reacting an aqueous solution of sodium tetrachloropalladate with the corresponding 1,3-diene at room temperature and vigorous stirring. The molar ratio of Na₂[PdCl₄] : 1,3-diene was 1 : 1.2. The reaction course was visually observed by the change of the color from red-brown (due to Na₂[PdCl₄]) to lemon yellow (typical of the η^3 -allyl complex). The diene excess was distilled off in vacuum. The solutions of the complexes were filtered off and

identified by the ¹H and ¹³C NMR methods. The spectral characteristics of the complexes coincide with the literature data [1]. The complexes remained stable for 5 days when stored at $\sim 0^{\circ}$ C.

The synthesis of the Pd allyl complexes containing the carbonyl group in the composition of the allyl fragment (further on "carbonyl complexes") was performed as follows. An excess of the acid formed after the synthesis of hydroxyl complexes in aqueous solutions was neutralized with sodium bicarbonate until termination of the gas liberation. The pH values of the reaction solutions were monitored using a pH-340 instrument. NaHCO₃ and Na₂[PdCl₄] taken in threefold excess were added to the solutions obtained. The reaction mixtures were stored for 1–3 days. The metallic palladium was filtered off, the reaction solution was extracted with CHCl₃ or CH₂Cl₂. The carbonyl-containing η^3 -alyl and nonconverted hydroxyl-containing complexes were separated in 1–2 h.

The η^3 -allyl complex based on 4-methyl-3-pentene-2-one (mesityl oxide) was prepared following the known procedure [12]. The complex was purified by recrystallization from THF heated to 50°C. The complex decomposed above the indicated temperature.

The ¹H and ¹³C NMR spectra were recorded on a Bruker DPX instrument (300.13 and 75.033 MHz, respectively). The identification of the products and the control of the reaction course were performed directly in the tube of NMR spectrometer. The reactions were carried out in the D₂O medium at 25°C. The organic products were analyzed by GC method (the column:9% IRTS-17 + 1%PEG 40 on polychrome; Chrom-4 (DIP) chromatograph).

The conditions of the oxidation of complexes I and II with hydrogen peroxide are as follows: $[\eta^3] = 0.1$ $(\eta^{3}\text{-complex}), [H_{2}O_{2}] = 0.4, [NaHCO_{3}] = 0.15, [NaCl] =$ 0.5 mol/l. Hydrochloric acid formed in the reaction solution in the synthesis of the initial hydroxyl-containing complexes was neutralized with NaHCO₃. The pH values were monitored before and in the course of a reaction. The oxidation of complexes I and II with Pd chloride was performed at $[\eta^3] = 0.1$, $[PdCl_4^{2-}] = 0.3$, $[NaHCO_3] = 0.3$, [NaCl] = 0.5 mol/l. In the case of MnO_2 , $[\eta^3] = 0.1$ mol/l, the quantity of MnO_2 in 100 ml of the reaction solution was 0.5 mol; the concentrations [NaHCO₃] and [NaCl] were 0.3 and 0.5 mol/l, respectively. Since MnO₂ complicates the NMR study of the reaction mixtures, the CDCl₃ extracts of the reaction solutions were analyzed.

The carbonyl-containing complexes were purified in pure form using liquid-adsorption column chromatagraphy (silica gel, glass column with l = 50 cm, d =1.5 cm) with acetone–chloroform, acetone–methylenechloride–chloroform, or acetone–methylenechloride–chloroform mixtures used as eluents. The fraction containing carbonyl complexes was stored at -18° C for 48–60 h until yellow crystals precipitated. The separated complexes were identified by the ¹H and ¹³C NMR method. The degree of separation was monitored by a thin-film chromatography on silica gel (Silufol uv 254) with the same organic mixtures used as eluents. The plates were developed in iodine chamber.

RESULTS AND DISCUSSION

The Effect of the Oxidant Nature on the Direction of Transformations of η^3 -Allyl Pd Complexes Based on 1,3-Pentadiene

According to the data in [6, 7], the oxidation of the hydroxyl group of complex I to the carbonyl group with hydrogen peroxide occurs in solution at pH 5–7. The main task at the first stage of a study was to establish the reaction stoichiometry.

The study of the products of reaction of complexes I and II with hydrogen peroxide (pH 5-7). While comparing the reaction paths of oxidation of complexes I and II with hydrogen peroxide under different conditions (pH 1-4 and 5-7), one should note that the reaction carried out at pH 5-7 has low selectivity. The process involves the induction period (4-20 min), which depends on the pH value. The optical density of the reaction solution changes slowly due to accumulation of the $PdCl_4^{2-}$ ions. Then, the metallic Pd is precipitated, which is accompanied by a vigorous decomposition of hydrogen peroxide. As follows from the ¹H NMR data, the only one reaction product formed in the induction period is diol IV. The spectral parameters of complexes I (I-R, I-S) and pentadiol IV agree well with the literature data [1, 2, 7].

The spectra of the reaction solutions recorded after the induction period contain, in addition to the signals of the starting isomeric complexes and diol **IV**, the signals of 1-acetyl- η^3 -allylpalladium chloride (**III**), whose spectral characteristics also coincide with the reported data [1, 7]. The color of the reaction solution gradually changed from dark brown to yellow, while its pH value decreased to 1–3. In 16 h, the content of **III** in the reaction mixture reached 40%.

It was shown that the excess of hydrogen peroxide, which was not used fully in the formation of **IV**, is decomposed by the metallic Pd being one of the reaction products. It was also discovered that on addition of PdCl₂ to the reaction solution, the induction period disappears. Taking into account the above data, we performed a series of experiments where the initial complexes were treated with $PdCl_2$ without the addition of hydrogen peroxide as an oxidant. The main product of the reaction carried out under these conditions was complex III. The results we obtained made it possible to suggest that the formation of complex **III** in the reactions of complexes **I** and **II** with hydrogen peroxide (pH 5–7) can be described by the following simultaneous and subsequent processes:



Complex III can form as a result of: 1) direct interaction of complex I with the $[PdCl_4]^{2-}$ ion, which accumulates in the reaction solution in the course of the induction period of diol IV formation; 2) interaction of $PdCl_4^{2-}$ with *trans*-3-pentene-2-one, formed due to the reductive destruction of complex I. Although the signals of this ketone were not recorded in the ¹H NMR spectra of the reaction solutions, the pH value (5–7) and the formation of metallic Pd do not allow one to exclude its formation as a result of the reductive destruction of complex I.

When a model reaction of *trans*-3-pentene-2-one with $PdCl_4^{2-}$ was performed under analogous conditions, the precipitation of the metallic Pd and the formation of acetylacetone were observed:

$$\xrightarrow{\text{O}} \xrightarrow{\text{PdCl}_2, \text{H}_2\text{O}} \xrightarrow{\text{O}} \xrightarrow{\text{O}} + \text{Pd}^0 + 2\text{HCl}.$$

The formation of the carbonyl complex III in this reaction was not established. On the other hand, the reaction of mesityl oxide with $PdCl_2$ performed even in an aqueous solution results in the corresponding carbonyl-containing allyl complex [12]:



One of the reasons for different reactivity of ketones can be the structure of their carbon framework. The steric and electronic effects of the methyl group at the second carbon atom of mesityl oxide hamper the double bond oxidation, and the process of complex formation becomes preferable. When *trans*-3-pentene-2-one is used as a substrate, the oxidation reaction prevails.

The yield of **III** in the reaction of the initial hydroxyl-containing complexes with PdCl₂ noticeably depends on the concentration of the Cl⁻ ions in the solution. Since an increase in the sodium chloride concentration increases the stability of the PdCl₄²⁻ ion, the content of **III** in the solution decreases (Fig. 1). At [NaCl] ≥ 2 mol/l, no carbonyl complex is formed.

Oxidation of regio-isomers I and II. One of the most interesting aspects of the reaction under consideration is different reactivity of regio-isomers I and II. The analysis of the ¹H NMR spectra recorded in a dynamic mode during the induction period shows that diol IV is formed directly from position isomer II. Shown in Fig. 2a is a fragment of the spectrum of a starting reaction solution (containing three complexes I-*R*, I-*S*, and II), which exhibits the signals from protons of the methyl groups of the complexes (three doublets with close upfield intensities ($\delta \approx 1.4$ ppm) and the signals from the allyl protons (H¹) in a region of ~5.5 ppm. One should note that in an aqueous solution, the signals from the allyl protons in enantiomer complexes I-*R* and I-*S* are indistinguishable.

The same fragments of the spectrum recorded 20 min after the addition of H_2O_2 to the reaction solution are shown in Fig. 2b. The comparative analysis of the spectra in Fig. 2a and Fig. 2b indicates that in the upfield region, the signal from the methyl group protons of complex II almost disappears, while the doublet signal of the CH₃ group of diol IV appears instead. In the downfield region, the intensity of the signal from the allyl protons of complex II significantly decreases, and a multiplet signal from the protons at the double bond of complex IV appears. The intensity of the signals of enantiomers of I remains almost unchanged. The ratio of I : II in the reaction solution before the reaction was 1 : 0.75, while after the induction period is was 1 : 0.18. The ¹H NMR kinetic data revealed that the content of diol **IV** and complex **I** in the reaction solution does not almost change after termination of the induction period (Fig. 3).

The results obtained convincingly prove that diol **IV** is formed from the position isomer **II** during the induction period, i.e., the initial complexes have different reactivity under the indicated conditions.

It was shown [7] that during oxidation with hydrogen peroxide in an acid medium, diol **IV** is formed from two regio-isomers that are spent at almost equal rate:



This fact seems unusual and is explained by the author by symmetric structure of σ -allylpalladium intermediates obtained from complexes I and II at the stage of oxopallaladization of a double bond.

The observed difference in the reactivity of complexes I and II in a neutral medium is likely to be due to their interaction with different oxidants. Taking into account that the oxidation potential of hydrogen peroxide decreases substantially when going from an acid medium to a neutral medium [13] and that the primary alcohols (complex II) are oxidized more readily than the secondary alcohols (complex I), one can suggest that under the reaction conditions, H_2O_2 oxidizes only regio-isomer II to diol IV, while complex I is oxidized with PdCl₂ to the carbonyl complex III.

The above data indicate that the oxidation of the hydroxyl group of complex I to the carbonyl group takes place without H_2O_2 participation. Complex III is formed as a result of interaction of complex I with PdCl₂. Therefore, it was necessary to study in detail the reactions of complexes I and II with Pd chloride.

The study of the product of reactions of complexes I and II with PdCl₂ and MnO₂ (pH 5–7). The analysis of the ¹H NMR spectra of reactions of complexes I and II with PdCl₂ in solutions showed that with a threefold excess of NaHCO₃ used to neutralize acids formed in the reaction, the carbonyl complex III is obtained at a high selectivity with conversion of I and II equal to 88%. In addition to complex **III**, the spectrum of reaction solution also exhibits the signals due to the aldehyde complex **V**:



Its quantity is about 5%, which is insufficient for reliable identification. In order to accumulate the aldehyde complex in the reaction solution, we used a mixture of hydroxo-substituted complexes synthesized from 1,3-pentadiene at 0°C as the initial complexes. In the indicated conditions, the content of regio-isomer **II** reaches 40%. The analysis of the spectra of reaction solutions for contact time $\tau = 36$ h showed that the content of the aldehyde complexes **I** and **II** was close to 90%. The low content of complexe **V** is explained by isomerization of complex **II** under the action of NaHCO₃, which was used to maintain pH value of the reaction solution at a level of 5–7.

Vol. 31 No. 10 2005



Fig. 1. The curve of the complex **III** yield vs. the Cl⁻ concentration in the reaction mixture ($\tau = 24$ h).

Thus, it was established that the position isomer II shows selectivity with respect to the oxidants used, because its reaction with H_2O_2 and $PdCl_2$ results in different products (pentadiol IV and aldehyde complex V, respectively).

Although Pd chloride is a standard reagent of oxidation of the hydroxyl groups to the carbonyl groups, it seems unreasonable to use it in the case, when the Pd allyl complex serves as "substrate". Therefore, we performed a series of experiments to find an oxidant that can selectively oxidize the hydroxyl-containing complexes I and II to the corresponding carbonyl complexes under mild conditions.

The hydroxyl groups in the allyl alcohold are usually oxidized by Mn dioxide. The ¹H NMR data indicate that the reactions of complexes I and II with MnO_2 lead to the formation of the carbonyl complex III.



Fig. 2. Fragments of the ¹H NMR spectra (D_2O , 25°C): (a) the initial complexes **I**-*S*, **I**-*R*, and **II**; (b) the reaction solution in 20 min after introduction of hydrogen peroxide.

However, the reaction solution spectra also contain signals from the product of a reductive destruction of complex I, i.e., *trans*-3-pentene-2-one, whose concentration in the reaction mixture reaches 20%. In this case, Mn dioxide acts not only as an oxidant, but also as nucleophilic agent, which causes the destruction of the initial complexes and thus reduces the reaction selectivity with respect to the carbonyl complexes.

Thus, one can conclude that the composition of the products of oxidation of hydroxyl-containing complexes based on 1,3-pentadiene in neutral solutions is determined by the nature of the oxidant used. The formation of the carbonyl complex **III** is the most selective, when the initial complexes react with Pd chloride.

The Effect of Alkyl Substituents in the Allyl Ligand on the Direction of Transformations of η^3 -Allyl Pd Complexes Based on the Simplest 1,3-Dienes

Taking into account the data obtained for the complexes based on 1,3-pentadiene, we studied the reactions of some hydroxyl-containing complexes based on the simplest 1,3-dienes (1,3-butadiene (VI), isoprene (VII), 2-methyl-1,3-pentadiene (VIII)) with different reagents (H_2O_2 , MnO_2 , $PdCl_2$) in aqueous solutions at pH 5–7. Our task was to select an oxidant that can give the corresponding carbonyl-containing complexes with a high selectivity and conversion and to establish the influence of the allyl fragment structure on the reactivity of the initial hydroxyl-containing complexes.

In the case of MnO_2 , complexes **VI** and **VII** were found to undergo the reductive destruction with the formation of unsaturated aldehydes. The signals of the respective aldehyde complexes in the reaction solutions were not recorded.

The reaction of complex VIII with MnO_2 proceeds at very low rate. Complex VIII is stable to oxidation and though the signals of the carbonyl complex based on VIII were recorded in the reaction solution, its content did not exceed 2% at the reaction time equal to 72 h.

The above facts indicate that the reaction of the hydroxyl-containing complexes, which differ in the structure of allyl fragment, with MnO_2 can be written as follows:



RUSSIAN JOURNAL OF COORDINATION CHEMISTRY

Content of $I\!\!-\!\!IV$ in the reaction mixture, %



Fig. 3. The plot of the composition of the reaction mixture (**I**, $\mathbf{II} + \mathbf{H}_2\mathbf{O}_2$) vs. reaction time: (1) **I**, (2) **II**, (3) **III**, and (4) **IV**.

The carbonyl complexes are formed in the reaction with hydrogen peroxide as a result of simultaneous and subsequent reactions only in the case of complexes **I** and **VIII**. The ¹H NMR spectra of the reaction solutions show that the interaction of complexes **VI** and **VII** with hydrogen peroxide in neutral aqueous solutions results in their destruction and formation of unsaturated aldehydes and diols. Thus, for complexes based on isoprene (**VII**), the reductive destruction proceeds with a high selectivity and yields methylcrotonaldehyde. The spectrum of reaction solution of complex **VI** contains the signals due to crotonaldehyde and *trans*-2-butene-1,4-diol (Table 1).

The study of the oxidation of complexes **VI–VIII** with Pd chloride showed that the corresponding carbonyl-containing complexes (1-acetyl- η^3 -bute-nyl)palladium chloride (**IX**), (1-acetyl-2-methyl- η^3 -butenyl)palladium chloride (**XI**), (1-acetyl-2-methyl- η^3 -pentenyl)palladium chloride (**XI**) are formed with a high selectivity and conversion of the initial complexes equal to 85% independent of the structure of the allyl fragment.

The reaction of the hydroxyl complex **VII** with $PdCl_2$ yields the aldehyde complex **X**. The ¹H and ¹³C NMR data, in particular, the downfield shift of the H³ proton signal and the values of the chemical shifts in the ¹³C spectrum confirm that complex **X** occurs in the solution as *anti*-configuration.

The prevalence in the reaction mixture of *anti*-isomer is unusual for η^3 -allyl Pd complexes with nonbulky substituents, which can be explained by either the steric factor (the repulsion of the methyl and carbonyl

2005

No 10

Vol. 31

Compound	δ, ppm	Multiplicity	J, Hz
$\begin{array}{c} H^1 & O \\ CH_3 & H^4 \\ H^3 \end{array}$	$H^1 = 6.85$	Multiplet	$^{1-4}J = 15.5, \ ^{1}J_{\rm CH_3} = 6.8$
	$H^3 = 6.15$	Multiplet	${}^{3-4}J = 7.9, {}^{3}J_{\rm CH_3} = 1.5, {}^{1-3}J = 15.5$
	$H^4 = 9.45$	Doublet	$^{3-4}J = 7.9$
	$CH_3 = 2.01$	Multiplet	${}^{1}J_{\rm CH_3} = 6.8, \; {}^{3}J_{\rm CH_3} = 1.5$
H ¹ OH CH ₂ CH ₂	$H^1 = H^3 = 5.85$	Triplet*	
	CH ₂ = 4.28	Doublet	
H^{3} OH H^{3}			
CH ₃ O	$H^3 = 4.88$	Doublet	$^{3-4}J = 8.7$
CH_3 H^4 H^4	$H^4 = 8.82$	Multiplet	$^{4-3}J = 8.7, \ ^{3}J_{\rm CH_3} = 1.23$
	CH ₃ = 2.23	Doublet	${}^{3}J_{\rm CH_{3}} = 1.14$
	CH ₃ = 1.49	Doublet	${}^{3}J_{\rm CH_{3}} = 1.09$

Table 1. The parameters of the ¹H NMR spectra of the products of reactions of complexes **VI** and **VII** with MnO_2 (the CDCl₃ extracts) and H_2O_2 (D₂O)

* Multiplet signals in the proton spectrum of *trans*-butene-1,4-diol are poorly resolved and therefore, the spin-spin coupling constants were not determined for this compound.

groups) or electronic factor (coupling of unshared electron pairs of the O atom with unoccupied d orbitals of the Pd atom). As follows from IR spectra of complex **X**, the frequency of the stretching vibrations of the C=O bond almost coincides with the corresponding frequency in the spectrum of 2-methyl-butene-2-al. Thus, the steric factor becomes the key factor.

Complex **VIII** is oxidized with Pd chloride very slowly. The signals from complex **XI** appear in the reaction solution only after 36 h. The carbonyl complex **XI** was identified as *anti*-isomer, although when synthesized from mesityl oxide, it occurred as a mixture of *syn-* and *anti-*isomers (3 : 2), which was confirmed by the spectral method. Obviously, the formation of only one *anti-*isomer in the reaction of complex **VII** oxidation with Pd chloride can be explained by the reduced stability of *syn-*isomer due to the steric interaction of the methyl and acetyl groups, as in the case of complex **X**. It cannot be excluded also that *syn-*isomer cannot be detected in the spectrum because of the low reaction rate.

With account of the above factors, the transformations of the simplest 1,3-diene hydrocarbons in the reaction with Pd chloride in neutral aqueous solutions can be represented by the following scheme:



 $R^1 = H, CH_3; R^4 = H, CH_3.$

At pH 5–7, the corresponding carbonyl-substituted complexes (**III**, **IX–XI**) are formed almost quantitatively. They were detected and characterized by the ¹H and ¹³C NMR method in the reaction solutions and were isolated as yellow crystals. The spectral characteristics of the complexes are presented in Table 2.

Thus, Pd chloride is the sole reagent that can be used in order to carry out the selective oxidation of the hydroxyl groups in the β -position of the allyl ligand for a series of η^3 -allyl Pd complexes without the destruction of the complex structure (allyl-metal bond), independent of the allyl fragment structure. The above data

Table 2. The parameters of the ¹H and ¹³C NMR spectra of the carbonyl-containing η^3 -allyl complexes III, V, IX–XI*



Complex	¹ H NMR; δ , ppm	Multiplicity	J, Hz	¹³ C NMR; δ, ppm
syn-IX	$R^1 = 5.95 (1H)$	Multiplet	$^{1-5}J = 6.0, ^{1-2}J = 12.5, ^{1-3}J = 10.8$	$C^1 = 113.80$
$(\mathbf{R}^{T} = \mathbf{R}^{T} = \mathbf{R}^{4} = \mathbf{H})$	$R^4 = 9.61 (1H)$	Doublet	$^{4-3}J = 5.3$	$C^2 = 67.28$
	$H^5 = 4.34 (1H)$	Doublet	$^{5-8}J = 6.0$	$C^3 = 71.80$
	$H^2 = 3.43 (1H)$	Doublet	$^{5-9}J = 12.5$	$C^4 = 200.32$
	$H^3 = 3.83 (1H)$	Multiplet	$^{1-3}J = 10.8, ^{4-3}J = 5.3$	
anti-X	$R^1 = 2.43 (3H)$	Singlet		$C^1 = 128.82$
$(R^{1} = CH_{3}, R^{3} = R^{4} = H)$	$R^4 = 8.65 (1H)$	Doublet	$^{4-3}J = 7.7$	$R^1 = 22.89$
	$H^5 = 4.42 (1H)$	Singlet		$C^2 = 63.61$
	$H^2 = 2.60 (1H)$	Singlet		$C^3 = 76.88$
	$H^3 = 5.18 (1H)$	Doublet	$^{4-3}J = 7.7$	$C^4 = 188.83$
syn-V	$R^1 = 6.12 (1H)$	Multiplet	$^{1-5}J = 6.3, ^{1-2}J = 11.9, ^{1-3}J = 10.8$	
$(R^3 = CH_3, R^1 = R^4 = H)$	$R^4 = 9.55 (1H)$	Doublet	$^{4-3}J = 7.3$	**
	$R^5 = 1.62 (3H)$	Doublet	$^{1-5}J = 6.3$	
	$H^2 = 3.85 (1H)$	Doublet	$^{1-2}J = 11.9$	
	$H^3 = 5.58 (1H)$	Multiplet	$^{1-3}J = 10.8, ^{4-3}J = 7.2$	
syn-III	$R^1 = 6.31 (1H)$	Multiplet (d.d.d)	$^{1-5}J = 7.2, ^{1-2}J = 12.5, ^{1-3}J = 10.8$	$C^1 = 110.65$
$(R^{T} = R^{3} = H, R^{4} = CH_{3})$	$R^4 = 2.49 (3H)$	Singlet		$C^2 = 65.84$
	$H^5 = 4.49 (1H)$	Doublet	$^{1-5}J = 7.2$	$C^3 = 71.52$
	$H^2 = 3.63 (1H)$	Doublet	$^{1-2}J = 12.5$	$C^4 = 208.24$
	$H^3 = 4.05 (1H)$	Doublet	$^{1-3}J = 10.8$	$R^4 = 29.14$
anti-XI	$R^1 = 2.26 (3H)$	Singlet		$C^1 = 124.96$
$(R^{1} = R^{2} = CH_{3}, R^{3} = H)$	$R^4 = 2.46 (3H)$	Singlet		$C^2 = 67.84$
	$H^5 = 3.93 (1H)$	Singlet		$C^3 = 73.24$
	$H^2 = 3.00 (1H)$	Singlet		$R^1 = 23.10$
	$H^3 = 3.72 (1H)$	Singlet		$C^4 = 202.78$
				$R^4 = 30.96$

*a—The numbering of the protons and substituents in the 1 H NMR spectra; b—the numbering of carbon atoms and substituents in the 13 NMR spectra.

**The ${}^{13}C$ spectral parameters of complex V were not determined because of its low concentration in the reaction solutions.

were obtained for the first time in the chemistry of η^3 -allyl Pd complexes.

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