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Unusual condensation of acetone giving η^3-allyl ligand in the $[Pd(\eta^3\text{-}C_6H_9O)(\mu\text{-}Cl)]_2$ complex

Inessa A. Efimenko,*[a] Alexey S. Kubasov,[a] Nina A. Ivanova,[a] Olga S. Erofeeva[a] and Ludmila I. Demina[b]

[a] *N. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, 119991 Moscow, Russian Federation. E-mail: ines@igic.ras.ru*

[b] *A. N. Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, 119991 Moscow, Russian Federation*

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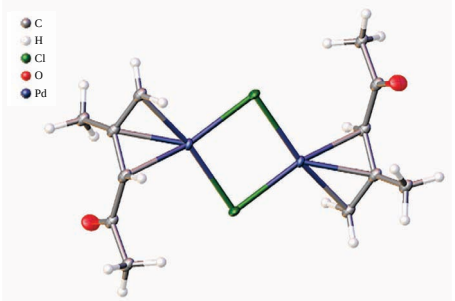
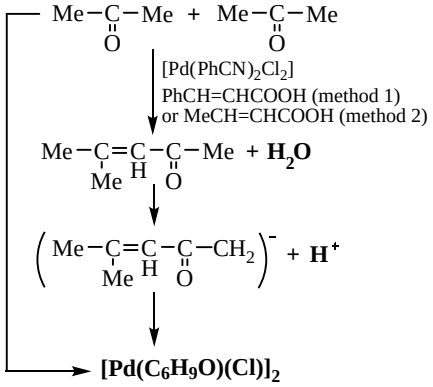
A one-step reaction was discovered giving the η^3-allyl complex $[Pd(\eta^3\text{-}C_6H_9O)(\mu\text{-}Cl)]_2$. The formation of the substituted η^3-allyl ligand in the complex occurs as a result of the condensation of acetone at room temperature in a solution containing $[Pd(PhCN)_2Cl_2]$ and organic acids. The structure of the resulting Pd^{II} complex was determined by single crystal X-ray diffraction analysis.



Keywords: acetone condensation, η^3-allyl ligand, one-step reaction, η^3-allyl Pd^{II} complex.

To date, numerous different chloro-bridged η^3-allyl complexes of Pd^{II} have been synthesized and their structures have been studied. These complexes play an important role in the catalysis and control of catalytic syntheses of various organic compounds[1,2] and are key intermediates in the syntheses of polyfunctional compounds.[3–8] Of particular interest are compounds containing functional groups in the allyl ligand. The presence of such groups significantly expands the synthetic capabilities of η^3-allyl complexes,[9–11] including η^3-allyl complexes of Pd^{II} with N-heterocyclic carbenes, which exhibit high antitumor activity.[12] The first η^3-allylpalladium complex, $[Pd(\eta^3\text{-}C_3H_5)(\mu\text{-}Cl)]_2$, was obtained by reacting palladium chloride with unsaturated allyl alcohol or allyl chloride due to the transformation of double bonds in the allylic compounds in the presence of palladium into an η^3-allyl ligand coordinated by palladium.[13–15] To date, numerous palladium complexes with substituted η^3-allyl ligands have been synthesized by direct conversion of various unsaturated organic compounds to the allyl ligand.[16] However, this now popular method, based on the use of pre-synthesized unsaturated compounds, can be considered as a two-step synthesis of η^3-allylpalladium complexes. The condensation reaction of acetone molecules in the presence of an acid to form unsaturated mesityl oxide was first discovered in 1838 and became the basis for a method for the synthesis of unsaturated compounds using aldol-crotonic condensation.[17]

The complex $[Pd(\eta^3\text{-}C_6H_9O)(\mu\text{-}Cl)]_2$ **1** is formed in one step in an acetone solution containing $[Pd(PhCN)_2Cl_2]$ and cinnamic acid Ph–CH=CH–COOH (method 1) or crotonic acid Me–CH=CH–COOH (method 2).[†] A comparison of the spectral characteristics of the compounds obtained by both methods indicates that, regardless of the nature of the acids used in the reaction, these compounds are identical and their composition is expressed by the formula $[Pd(\eta^3\text{-}C_6H_9O)(\mu\text{-}Cl)]_2$. The data obtained indicate the discovery of a hitherto unknown one-step reaction for the direct synthesis of the η^3-allyl ligand in complex **1** upon the condensation of two acetone molecules. The sequence of reactions for the formation of this complex is presented in Scheme 1.



Scheme 1 Intra-cascade reactions of one-step formation of complex $[Pd(\eta^3\text{-}C_6H_9O)(\mu\text{-}Cl)]_2$.

[†] *Synthesis of $[Pd(\eta^3\text{-}C_6H_9O)(\mu\text{-}Cl)]_2$* **1**. *Method 1*. The complex was obtained by stirring a solution of $[Pd(PhCN)_2Cl_2]$ (0.384 g, 1 mmol) in acetone (30 ml) with a solution of cinnamic acid (0.294 g, 2 mmol) in acetone (5 ml) for 10 h. The resulting cherry-colored solution was left to crystallize at 6 °C. The crystalline precipitate that formed after 4 months was filtered off, washed with acetone (2 × 7 ml) and dried *in vacuo* to constant weight. From the crystalline deposit thus obtained, a single crystal was selected for X-ray diffraction analysis. Yield 44.5%. Found (%): C, 30.96; H, 3.93. Calc. for $C_{12}H_{18}Cl_2O_2Pd_2$ (%): C, 30.11; H, 3.79.

Method 2. Complex **1** was prepared by stirring a solution of $[Pd(PhCN)_2Cl_2]$ (0.384 g, 1 mmol) in acetone (30 ml) with a solution of crotonic acid (0.172 g, 2 mmol) in acetone (5 ml) for 10 h. The subsequent procedure was similar to that in Method 1. Found (%): C, 30.99; H, 3.90. Calc. for $C_{12}H_{18}Cl_2O_2Pd_2$ (%): C, 30.11; H, 3.79.

This scheme of the one-step formation of complex **1** in acetone in the presence of $[Pd(PhCN)_2Cl_2]$ and organic acids at room temperature shows possible intermediate stages: the formation of mesityl oxide and its conversion to the η^3-allyl ligand coordinated to palladium. It should be noted that complex **1** is insoluble in any of the wide range of solvents used.

To study the structure of complex **1**, single-crystal X-ray diffraction‡ and IR spectroscopy§ methods were used. Main crystallographic data, experimental parameters and structure refinement characteristics of structure **1** were obtained by known methods.[18–21]

The molecular configuration of complex **1** (Figures 1 and 2) shows that the Pd atoms in the dimeric palladium complex $[Pd(\eta^3\text{-}C_6H_9O)(\mu\text{-}Cl)]_2$ coordinate η^3-allyl ligands turned in different directions. The distance between Pd atoms of neighboring molecules in the crystal structure of complex **1** is 3.951(2) Å. The results of the crystallographic study of complex **1** were analyzed by comparison with the crystallographic data[22] of the complex $[Pd(\eta^3\text{-}C_3H_5)(\mu\text{-}Cl)]_2$ **2** to determine the effect of the substituent in the η^3-allyl ligand. In addition, the structural data of complex **2a,** obtained after cooling complex **2** to −140 °C, were considered.[23] Complexes **1**, **2** and **2a** are dimeric structures whose centers are planar rhombuses (see Figure 2) formed by Pd and Cl atoms. The Pd···Pd and Cl···Cl distances in complexes **1**, **2** and **2a** are nearly the same: 3.451(2), 3.460 ± 0.007 and 3.475 ± 0.002 Å and 3.366(4), 3.328 ± 0.015 and 3.362 ± 0.0035 Å, respectively. The Pd–Cl–Pd angle also does not differ significantly in complexes **1**, **2** and **2a** and is 91.42(14)°, 92.2 ± 0.3° and 92.1 ± 0.2°, respectively, while the Cl–Pd–Cl angle takes the values 88.58(14)°, 87.8 ± 0.3° and 88.3 ± 0.2°, respectively.

The η^3-allyl system is planar, with the center of symmetry on the Pd–C(4) line. The planes of the allyl ligands in dimers **1**, **2** and **2a** deviate from the Pd_2Cl_2 plane. The dihedral angles between the plane of the η^3-allyl ligand and the Pd_2Cl_2 plane are 110.8°, 108.2° and 111.5° in complexes **1**, **2**[22] and **2a**,[23] respectively. In reference compound **2**, the dihedral angle changes both upon cooling to −140 °C and upon the introduction of substituents into the η^3-allyl ligand, leading to complex **1**. It was found that in the structure of complex **2a**, determined at −140 °C, the central C(4) atom of the allyl ligand lies 0.52 Å below the Pd_2Cl_2 plane, while the C(5) and C(3) atoms are 0.101 and 0.53 Å above this plane, respectively.[23] At the same time, a very slight rotation of the allyl moiety around an axis perpendicular to the Pd_2Cl_2 plane was detected. At low temperature, the angle C(5)–C(4)–C(3) in complex **2a** is 119.8 ± 0.91°, which is significantly less than the same angle in complex **2**, which is 128.6 ± 3.3°. The value of the angle C(5)–C(4)–C(3) in complex **1**, equal to 113.1(15)°, was also smaller, which indicates that the value of this angle in complexes **1** and **2** is influenced by additional factors, namely, cooling or the introduction of a substituent at one of the terminal atoms, changing the state of the entire η^3-allyl system. Analysis of the angles with the vertex at the C(4) atom inside the η^3-allyl ligand showed that in complex **1** the Pd–C(4)–C(5) and Pd–C(4)–C(3) angles are the same and equal to 70.6(9)° and 69.9(9)°, respectively, while in complex **2** similar angles are slightly smaller and amount to 66.4 ± 1.9° and 64.9 ± 1.9°, respectively, which demonstrates that the substituent at the C(3) atom affects the internal crystallographic characteristics of the η^3-allyl complex. The angles at the central Pd atom do not change. The angles C(4)–Pd–C(5) and C(4)–Pd–C(3) in complex **1** are characterized by the same values of 38.4(6)° and 38.6(6)°, respectively. The C(5)–C(4) and C(3)–C(4) distances in the

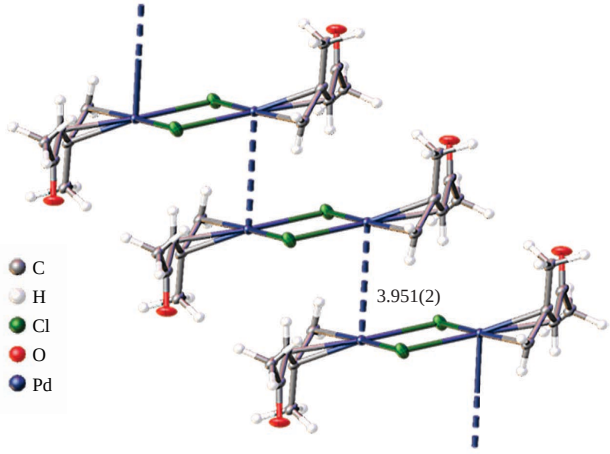


Figure 1 Molecular packing diagram illustrating intermolecular Pd···Pd interactions in the crystal structure of complex **1**.

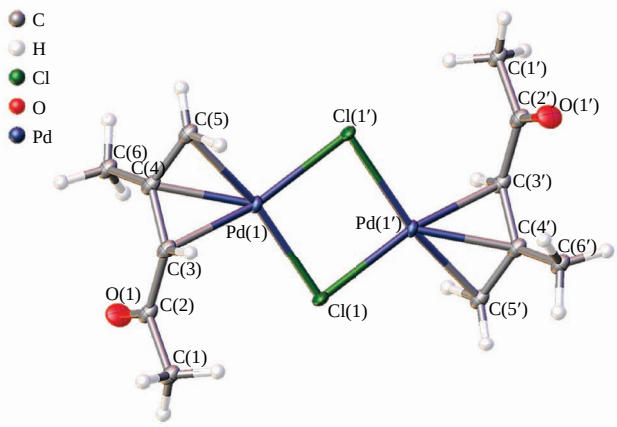


Figure 2 Molecular structure of complex **1**. Thermal ellipsoids are drawn at 50% probability level. Selected bond distances (Å) and angles (°): Pd(1)···Pd(1′) 3.451(2), Cl(1)···Cl(1′) 3.366(4), Pd(1)–Cl(1) 2.419(4), Pd(1)–Cl(1′) 2.401(4), Pd(1)–C(3) 2.117(17), Pd(1)–C(4) 2.146(17), Pd(1)–C(5) 2.132(16), C(4)–C(3) 1.41(2), C(5)–C(4) 1.41(2), O(1)–C(2) 1.22(2), C(2)–C(3) 1.53(2), C(4)–C(6) 1.50(2), Cl(1)–Pd(1)–Cl(1′) 88.58(14), Pd(1)–Cl(1)–Pd(1′) 91.42(14), Cl(1)–Pd(1)–C(5) 169.0(5), Cl(1)–Pd(1)–C(4) 134.2(5), Cl(1)–Pd(1)–C(3) 102.5(5), Cl(1′)–Pd(1)–C(3) 168.8(5), Pd(1)–C(4)–C(5) 70.6(9), Pd(1)–C(4)–C(3) 69.9(9), C(5)–Pd(1)–C(3) 67.1(10), C(5)–C(4)–C(3) 113.1(15), C(4)–Pd(1)–C(5) 38.4(6), C(4)–Pd(1)–C(3) 38.6(6), C(5)–C(4)–Pd(1) 70.3(9), C(3)–C(4)–Pd(1) 69.6(9).

‡ *Crystal data for* $[Pd(\eta^3\text{-}C_6H_9O)(\mu\text{-}Cl)]_2$ **1**. $C_{12}H_{18}Cl_2O_2Pd_2$, M = = 477.96, monoclinic, space group $C2/c$, a = 23.467(5), b = 4.6160(9) and c = 14.616(3) Å, β = 110.952(9)°, V = 1478.7(5) Å^3, Z = 4, d_{calc} = = 2.147 g cm^{-3}, μ(MoKα) = 4 mm^{-1}, F(000) = 928, λ(MoKα) = 0.71073 Å, 2θ angle range of 2.984–56.114°. Total of 3881 reflections were collected (1713 independent reflections, R_{int} = 0.0612) and used in the refinement, which converged to wR_2 = 0.2575, GOOF =1.129 for all independent reflections (R_1 = 0.0935). Final indexes: R_1 = 0.1221, wR_2 = 0.2735, residual electron density: 2.91/−2.46 e/Å^{-3}. Experimental data were acquired on a Bruker SMART APEX2 automated diffractometer (MoKα radiation, graphite monochromator, ω–ϕ scanning). Data were indexed and integrated using the SAINT program. An absorption correction based on equivalent reflectance measurements (SADABS) was applied. The structures were solved by the direct method followed by Fourier difference synthesis calculations. All non-hydrogen atoms were refined in the anisotropic approximation. All hydrogen atoms of the CH and CH_2 groups were refined using the riding model with thermal parameters U_{iso} = 1.2 U_{equiv} (U_{iso}) of the corresponding non-hydrogen atom (1.5U_{iso} for Me groups). All calculations were performed using the SHELXTL program. The structure was solved and refined using the OLEX2 software complex.

CCDC 2340671 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

§ IR spectra were recorded by the ATR method using the Pike attachment. FTIR spectra were measured on a JASCO FT/IR-6600 spectrometer equipped with an ATR PRO ONE Technologies attachment with a PKS-D1F diamond crystal using the ATR method in the range of 4000–250 cm^{-1}.

η^3-allyl moiety of complex **1** are the same and both are equal to 1.41(2) Å, while their corresponding values in complex **2** are close: 1.37 ± 0.040 and 1.35 ± 0.045 Å. At the same time, the Pd–C(4) distance in complex **1** is 2.146(17) Å, which is significantly greater than the similar distance in complex **2**, equal to 2.02 ± 0.037 Å. There are no similar data for complex **2a**.[23] The C–C distances in the substituents in the η^3-allyl ligand of complex **1** have the usual values.

The IR spectrum of complex **1** was analyzed by comparison with the spectrum of the simple η^3-allyl complex **2**, studied previously.[24] The IR spectrum of complex **1** shows bands of asymmetric [ν_{as}(CCC)] and symmetric [ν_s(CCC)] stretching vibrations at 1411 and 1032 cm^{-1}, respectively. The position of the bands confirms the presence of a coordinated allyl group in the resulting complex. In the IR spectrum of complex **2**,[22] bands of asymmetric stretching vibrations ν_{as}(CCC) were detected at 1458 cm^{-1} and symmetric ones ν_s(CCC) at 1021 cm^{-1}. The band of bending vibrations of the C–C–C group δ(CCC) appears at 552 cm^{-1} in the spectrum of complex **1** and at 511 cm^{-1} in the spectrum of complex **2**. The δ(CCC) band in the spectrum of complex **1** is located in a higher frequency region relative to the corresponding band in the spectrum of complex **2** that may indicate the formation of a stronger bond between Pd and the η^3-allyl ligand, which is confirmed by the position of the ν(Pd–C) bands at 417 cm^{-1} in the spectrum of complex **1** compared to the corresponding frequency of 401 cm^{-1} in the spectrum of complex **2**. Bands, corresponding to the stretching vibrations ν(Cl–Pd–Cl) of the Pd–Cl bridging bonds, were recorded at 345 and 328 cm^{-1} in the spectrum of complex **1**, and at 364 cm^{-1} with a shoulder in the spectrum of complex **2**. This suggests that the strengthening of the allylic bond leads to a weakening of the Pd–Cl bridging bonds in complex **1**.

Thus, in this work, a one-step reaction was discovered for the conversion of two acetone molecules into a substituted η^3-allyl ligand coordinated to palladium in the $[Pd(\eta^3\text{-}C_6H_9O)(\mu\text{-}Cl)]_2$ complex. The reaction occurs under mild conditions, namely, at room temperature. Based on X-ray diffraction analysis and IR spectroscopy data, it was shown that the presence of a substituent at the C(3) atom of the η^3-allyl fragment leads to structural changes in this fragment, accompanied by strengthening of the bond of the η^3-allylic ligand with palladium and weakening of the Cl–Pd–Cl bridging bonds. The complex obtained in this work can be considered as a precursor for heterogeneous catalysts in organic reactions.

This work was performed within the framework of the State assignment of IGIC RAS and IPCE RAS in the field of fundamental scientific research. X-ray diffraction studies were carried out using the equipment of the Center for collective use at IGIC RAS. IR spectra were obtained using the equipment of the Center for the collective use of physical research methods at IPCE RAS.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2024.09.040.

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