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# CRYSTAL STRUCTURE OF *cis*-[$PdCl_2(CNMes)_2$]

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The interaction between $PdCl_2(CH_3CN)_2$ and 2,4,6-$Me_3C_6H_2NC$ (MesNC) proceeds with the substitution of acetonitrile ligands and leads to the synthesis of a *cis*-[$PdCl_2(MesNC)_2$] complex. The structure of this compound is determined by single crystal X-ray diffraction (XRD). The complex has a slightly distorted square-planar structure of the metal center with two *cis*-positioned isocyanide ligands. In both CN isocyanide moieties the triple bonds have lengths similar to the lengths of the respective bonds in other isocyanide complexes. In the structure, the *cis*-[$PdCl_2(MesNC)_2$] complexes are bound by weak C–H···Cl hydrogen bonds and π-stacking interactions.

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In the recent decade, palladium complexes with acyclic diaminocarbene ligands are widely used as catalysts in the cross-coupling reactions [1, 2]. There are different methods of the synthesis of diaminocarbene complexes of palladium [1, 3, 4], while the most efficient and universal method is the coupling of isocyanide ligands in *bis*(isocyanide) complexes of palladium with NH-nucleophiles [1, 3, 5]. This, in its turn, determines the growth of the interest to the synthesis and study of the structure of *bis*(isocyanide) complexes of palladium(II) [6, 7].

Previously in the scientific literature, the syntheses of a series of complexes of palladium with isocyanide ligands were described, whose structure was determined on the basis of the studying of the data of IR and NRM spectroscopy. At the same time, now it is important to study not only the composition, but also the stereochemistry of these compounds, because the behaviors of *cis*- and *trans*-complexes differ relative to the reaction with N-nucleophiles. In this connection it is necessary to refine the spectral data on the structure of the above described *bis*(isocyanide) complexes of palladium(II) by the XRD method. So, in this article we report on the complete characterization (by spectroscopy and by the single crystal XRD method) of one of such derivatives (*cis*-[$PdCl_2(CNMes)_2$] complex).

The synthesis of the *cis*-[$PdCl_2(CNMes)_2$] complex was carried out by the substitution of nitrile ligands for isocyanide ones (Scheme 1) under the conditions proposed in the literature for other isocyanide complexes of the formula *cis*-[$PdCl_2(CNAr)_2$] [8-10].

**Experimental.** The $^1H$ and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker 400 MHz Avance spectrometer at room temperature. The chemical shifts (in ppm) were determined relative to the signal of internal standard tetramethylsilane (TMS), with the following signal shapes: *s* for a singlet, *d* for a doublet, *t* for a triplet, and *m* for a multiplet. The infrared spectra were recorded on a Shimadzu FTIR-8400S spectrophotometer (4000-400 $cm^{-1}$ samples pelleted with KBr). The mass-spectra were obtained on a Bruker micrOTOF spectrometer with electrospray ionization; the solvent was MeOH, MeCN or a MeOH/DMSO mixture, the region of $m/z$ = 50-3000. The values of $m/z$ are given for the signals of isotopologues with the

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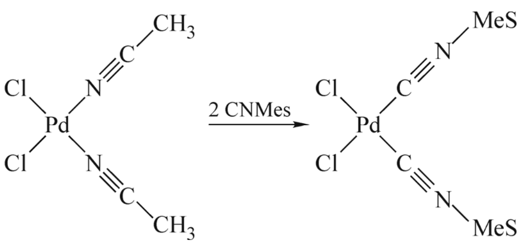

Scheme 1. Synthesis of *cis*-$[PdCl_2(CNMes)_2]$.

highest content. Organic and inorganic reagents and solvents were obtained from commercial sources and used without any further purification.

**Synthesis of *cis*-$[PdCl_2(CNMes)_2]$ complex.** 1.12 g (7.7 mmol) of solid CNMes were added to the suspension of 1.0 g (3.85 mmol) of $PdCl_2(CH_3CN)_2$ in 50 ml of $CHCl_3$. The reaction mixture was boiled at stirring for 3 h and then cooled till room temperature, and the solvent was evaporated. The produced colorless substance was washed with $Et_2O$ (in 3 portions of 20 ml each) and dried in the air. The yield was 1.7 g (94 %). The analytical sample for XRD was prepared by gaseous diffusion of $Et_2O$ into the solution of the complex in $CH_2Cl_2$ at 20 °C. The copper–copper(II) sulfate reference anode (70 V, MeOH)was used: calculated for $C_{20}H_{22}Cl_2N_2PdNa^+$: 489.0087, found: $m/z$ 489.0072 $[M+Na]^+$. The IR spectrum (KBr, some selected bands, $cm^{-1}$): ν(C–H) 2950, 2920 (m), ν(N≡C) 2214 (s). The $^1H$ NMR spectrum ($CDCl_3$, δ, ppm): 2.34 (s, 6H, $CH_3$), 2.44 (s, 12H, $CH_3$), 6.97 (s, 4H, $CH_{arom}$). The $^{13}C\{^1H\}$ NMR spectrum ($CDCl_3$, δ, ppm): 18.5 (4C, $CH_3$), 21.4 (2C, $CH_3$), 122.4 (2C, CN), 127.5 (2C, C *ipso*), 129.1 (4C, CH *meta*), 136.0 (4C, C *ortho*), 141.8 (2C, C *para*).

**Single crystal X-ray diffraction analysis.** For the X-ray diffraction analysis, the crystal was fixed by a micromount and placed on an Agilent Technologies Excalibur Eos diffractometer equipped with a plane X-ray CCD detector. The measurements were carried out at temperature of 100 K using monochromatic Mo$K_\alpha$ radiation. The unit cell parameters were refined by the least-square method on the 2θ values of 35860 reflections in the range of 5.348-54.996°. The structure was solved by the direct method and refined to $R_1 = 0.0286$ ($wR_2 = 0.0595$) for 7585 independent reflections with $|F_0| \geq 4\sigma_F$ using the SHELX software package [11] embedded in the OLEX2 complex [12]. The absorption correction was introduced empirically in the program CrysAlisPro program [13] by means of spheric harmonics, implemented in the SCALE3 ABSPACK scaling algorithm. The hydrogen atoms were included in the refinement with the fixed positional and temperature parameters. The CCDC no. 1413220 contains additional crystallographic data for this work and can be obtained free of charge from the Inorganic Crystal Structure Database via the web-site: www.ccdc.cam.ac.uk/data_request/cif. The crystallographic data are as follows: $2(C_{20}H_{22}Cl_2N_2Pd)$ $M = 935.39$, monoclinic crystal symmetry, $P2_1/n$ space group, $a = 13.4639(3)$ Å, $b = 22.0592(5)$ Å, $c = 13.7830(4)$ Å, $\alpha = 90°$, $\beta = 101.265(3)°$, $\gamma = 90°$, $V = 4014.73(17)$ Å$^3$, $Z = 8$ (4 pairs), $D_{calc} = 1.464$ g/cm$^3$, $\mu = 1.195$ mm$^{-1}$, crystal size (mm) 0.25×0.15×0.12, the total number of reflections 35860, independent reflections with $I > 2\sigma(I)$ 9214 ($R_{int} = 0.0408$), $R_1(|F_0| \geq 4\sigma_F)/R_1$ (all data) = 0.0286/0.0412, $wR_2(|F_0| \geq 4\sigma_F)/wR_2$ (all data) = = 0.0595/0.0649, $S = 1.054$, $\rho_{min}$, $\rho_{max}$, e/Å$^3$ = –0.60, 0.62.

**Results and discussion.** The stretching bands ν(C≡N) are observed at 2214 $cm^{-1}$ in the IR spectrum of the complex. The increase in the frequency of vibration absorption ν(CN) at the transformation of the isocyanide from the free state (ν(CN) in MesNC 2114 $cm^{-1}$ [14]) to the coordination state indicates the increase in the electrophilic character of the isocyanide carbon atom and, thus, indirectly proving an increase in the reactivity to nucleophiles [15-17]. In the $^{13}C$ NMR spectrum, the coordination of isocyanide to the palladium atom is accompanied with a sharp change in the chemical shift of the end carbon atom to the lower frequency region ($\delta_C$ in MesNC is 166.9 ppm [14], $\delta_C$ in *cis*-$[PdCl_2(CNMes)_2]$ is 122.4 ppm), which is characteristic for other isocyanide complexes [7, 18].

In order to prove the structure of the complex in the solid phase, we used the XRD method which made it possible to determine the *cis*-configuration of isocyanide ligands.

The $C_{20}H_{22}Cl_2N_2Pd$ organometallic complexes constitute the base of the crystal structure of the *cis*-$[PdCl_2(CNMes)_2]$ compound (Fig. 1). The crystallographic independent part of the structure consists of two such complexes (the atomic

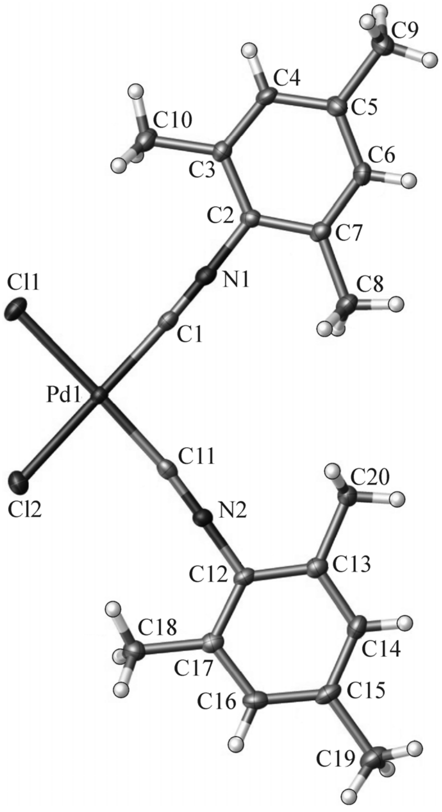

**Fig. 1.** Structure of the product with atomic numbering.

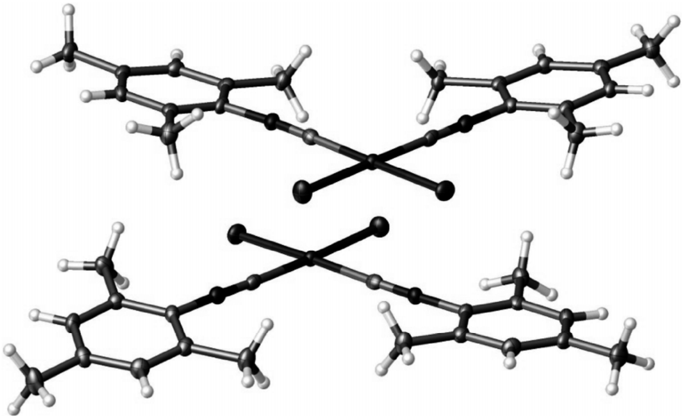

**Fig. 2**. Arrangement of molecules in the cell.

numbering is uniform for the complexes using the letter "A" for the second complex). The XRD data show that the complex has a slightly distorted square-planar structure of the metal center with the angles between the planes (in which the $C_{10}H_{11}N$ and $PdCl_2$ *radicals* are located) in the range of 5.43(4)-6.13(4)° and 8.18(4)-9.66(4)° for the two $C_{10}H_{11}N$ *radicals* respectively. The ligands consist of two *cis* configurated isocyanide fragments (the Pd–C bond lengths are in the range of 1.934(3)-1.945(3) Å) and two chlorine atoms (the Pd–Cl bond lengths in the range of 2.3016(6)–2.3091(6) Å). The C–N–C–Pd fragments are nearly linear (the values of the Pd–C–N and C–N–C angles are in the range of 174.0(2)-179.5(2)°). In both CN isocyanide fragments, the triple bonds have the lengths (1.141(3)-1.150(3) Å) similar to the lengths of the like bonds in other isocyanide complexes of palladium (1.142(9) Å and 1.127(9) Å in *cis*-$[PdCl_2(CNCy)_2]$ [19]; 1.145(8) Å and 1.157(9) Å in *cis*-$[PdCl_2(CNXyl)_2]$ [20]). In the structure, the *cis*-$[PdCl_2(MesNC)_2]$ complexes are bound by weak C–H···Cl hydrogen bonds and π-stacking interactions (Fig. 2).

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