Dedicated to Full Member of the Russian Academy of Sciences V.N. Charushin on his 60th anniversary

Palladium Complex of 6-(2-Hydroxy-5-methylphenyl)-3-(pyridin-2-yl)-1,2,4-triazin-5(2*H*)-one: Synthesis, Structure, and Catalytic Activity

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Abstract—Palladium(II) complex with 6-(2-hydroxy-5-methylphenyl)-3-(pyridin-2-yl)-1,2,4-triazin-5(2*H*)-one was synthesized for the first time. The ligand was prepared from 3-(pyridin-2-yl)-1,2,4-triazin-5(2*H*)-one and 4-methylphenol via nucleophilic substitution of hydrogen (S_N^H reaction). The complex was readily soluble in basic medium, and it effectively catalyzed Mizoroki–Heck reaction.

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Mizoroki–Heck reaction [1, 2], i.e., cross coupling of aryl halides with alkenes in the presence of palladium complexes (Scheme 1), has found wide application in modern organic synthesis [3].



The possibility for building up new C–C bond via simple experimental procedure makes this reaction a powerful tool for organic chemists. It should be emphasized that in the past year R.F. Heck was awarded the Nobel Prize for this reactions. Mizoroki–Heck reaction generally implies the use of palladium complexes with phosphine-containing ligands. Huang et al. [4] recently showed that palladium complexes with 2,2'-bipyridine ligands are very efficient catalysts in Mizoroki–Heck reaction [4]. Taking into account that these reactions require basic medium, anionic palladium complex is desirable or an acid residue should be present in one ring of the ligand. We synthesized a complex which met the above requirements.

The ligand, 6-(2-hydroxy-5-methylphenyl)-3-(pyridin-2-yl)-1,2,4-triazin-5(2*H*)-one (I, H_2L), was synthesized by us for the first time from 3-(pyridin-2-yl)-

1,2,4-triazin-5(2*H*)-one and *p*-methylphenol via S_N^H reaction [5] (Scheme 2). The reaction of H_2L with $PdCl_2$ in aqueous dimethylformamide gave the complex $Me_2NH_2^+[C_{15}H_{11}Cl_2N_4O_2Pd]^-$ (II). Its structure was studied by X-ray diffraction. The complex is mononuclear (see figure), the central metal ion has planar square configuration. The coordination entity is formed by two chlorine atoms and N,N-chelating moiety of the ligand. The latter is deprotonated at the N² atom, so that the complex is anionic. The counterion is outersphere dimethylammonium which is likely to be generated by partial hydrolysis of dimethylformamide during crystallization process. Contrary to the expectations, phenolic hydroxy group is not involved in coordination, as reported previously for copper(II) complexes [6]. The principal bond lengths and bond angles are given in table.

Additional analysis of the ligand structure in complex **II** showed that all three rings therein are planar, i.e. they are aromatic. The pyridine and triazine rings lie in one plane and are conjugated with each other. The substituted benzene ring deviates from that plane, the corresponding dihedral angle being 15.49°. The C–C bond lengths in the benzene and pyridine rings range from 1.353 to 1.413 Å; the N–C bonds in the triazine ring range from 1.366 to 1.376 Å.



Analysis of shortened O···O contacts showed that the crystalline structure of complex II is stabilized by both inter- and intramolecular hydrogen bonds. The phenolic hydroxy proton is infolved in bifurcate intramolecular hydrogen bond with the N^2 atom in the triazine ring $[O^2 - H^2 0.76(4), H^2 \cdots N^2 1.94(4), O^2 \cdots N^2$ 2.582(4) Å, $\angle O^2 H^2 N^2$ 141(3)°] and chlorine atom $[H^2 \cdots Cl^2 2.77(4), O^2 \cdots Cl^2 3.357(4) Å, \angle O^2 H^2 Cl^2$ 135(3)°]. The cation-anion interaction is characterized by intermolecular hydrogen bonding between the NH protons in dimethylammonium ion and carbonyl oxygen atom in the neighboring molecule: N^{1S} -H^{1SD} 0.900, $H^{1SD} \cdots O^1 [-x + 2, -y + 1, -z] 1.822(4)$, N^{1S}...O¹ [-x + 2, -y + 1, -z] 2.708(4) Å, $\angle N^{1S}H^{1SD}O^1$ [-x + 2, -y + 1, -z] 167.6(4)°; in addition, intermolecular hydrogen bond between the NH proton and Cl^2 is formed: N^{1S}-H^{1SE} 0.900, H^{1SE}...Cl² 2.394(4), N^{1S} ... Cl^2 3.229(4) Å.

The catalytic efficiency of the newly synthesized complex was studied in reactions of phenyl halides with butyl acrylate (Scheme 3). The products were identified by GC–MS and ¹H NMR. The reactions of butyl acrylate with iodo- and bromobenzenes quantitatively afforded butyl cinnamate. However, no coupling product was detected in the reaction of butyl



acrylate with chlorobenzene. Using the reaction with iodobenzene as model we found that the amount of the catalyst can be reduced to 0.01 mol % without loss in the yield. Further reduction of its amount to 0.001 mol % was accompanied by decrease of the yield to 90% according to the GC–MS data.

Butyl acrylate reacted with substituted iodobenzenes (*o*-iodotoluene, 1-iodo-3,4-dimethoxybenzene, and *p*-iodonitrobenzene) in the presence of 0.1 mol % of the catalyst to give the corresponding substituted butylcinnamates in quantitative yield.

We also tried 2-vinylpyridine as activated alkene. The reaction of iodobenzene with 2-vinylpyridine gave (E)-2-styrylpyridine in 80% yield (GC–MS;



Structure of the molecule of dimethylammonium [6-(2-hy-droxy-5-methylphenyl)-5-oxo-3-(pyridin-2-yl)-5*H*-1,2,4-tri-azin-4-ido]dichloropalladate(II) (**II**) according to the X-ray diffraction data.

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	Bond	d, Å	Bond angle	φ, deg
	Pd^1-Cl^1	2.2934(9)	$N^4Pd^1N^1$	80.25(10)
	Pd^1-Cl^2	2.2940(9)	$Cl^1Pd^1N^1$	175.44(8)
	Pd^1-N^1	1.990(2)	$Cl^1Pd^1N^4$	95.31(8)
	Pd^1-N^4	2.024(3)	$Cl^2Pd^1N^1$	94.48(8)

Principal bond lengths and bond angles in molecule II

Scheme 4). However, in the reaction with *p*-iodonitrobenzene the yield of 2-(4-nitrostyryl)pyridine was as poor as 8% (GC–MS).



EXPERIMENTAL

The ¹H NMR spectra were recorded on a Bruker BioSpin Avance DRX-400 spectrometer at 400 MHz using CDCl₃ as solvent and tetramethylsilane as internal reference. Quantitative analysis of the products was performed by GLC (internal normalization technique) on a Shimadzu GC 2010 chromatograph equipped with a flame-ionization detector and a ZB-5 capillary column, 30 m×0.25 mm, film thickness 0.25 μ m (polymethylsiloxane containing 5% of phenyl groups); carrier gas nitrogen, split ratio 1:30, flow rate 1.0 ml× min⁻¹; oven temperature programming from 40°C (3 min) to 290°C at a rate of 10 deg/min; injector temperature 280°C, detector temperature 320°C.

The products were identified by gas chromatography-mass spectrometry using an Agilent GC 7890A-MS 5975C system (quadrupole detector); electron impact, 70 eV; HP-5MS capillary column, 30 m× 0.25 mm, film thickness 0.25 µm; carrier gas helium, split ratio 1:50, flow rate 1.0 ml/min; oven temperature programming from 40°C (3 min) to 290°C at a rate of 10 deg/min (20 min at the final temperature); injector temperature 250°C, ion source temperature 230°C, quadrupole temperature 150°C, interface temperature 280°C.

The X-ray diffraction data for complex II were acquired at 295(2) K from a $0.27 \times 0.09 \times 0.01$ -mm

fragment of a single crystal on an Xcalibur 3 automatic diffractometer (CCD detector, MoK_{α} irradiation, graphite monochromator). Absorption by the crystal was taken into account analytically according to the multifaceted crystal model [7]. Monoclinic crystal system, space group $P2_1/n$; unit cell parameters: a =12.9723(14), b = 7.3095(8), c = 20.859(3) Å; $\beta =$ $98.991(9)^{\circ}$; V = 1953.6(4) Å³; $C_{17}H_{19}Cl_2N_5O_2Pd$; Z =4; $d_{\text{calc}} = 1.709 \text{ g/cm}^3$. Total of 12528 reflection intensities were measured in the ranges $-17 \le h \le 16, -9 \le$ $k \le 9, -15 \le l \le 27$; 4668 reflections were independent. The structure was solved by the direct method and was refined by the full-matrix least-squares procedure in anisotropic approximation for non-hydrogen atoms using SHELX-97 software package [8]. The final refinement parameters were: S = 1.008, $R_1 = 0.0344$, $wR_2 = 0.0558$ [for reflections with $I > 2\sigma(I)$] and $R_1 =$ 0.0859, $wR_2 = 0.0598$ (for all reflections). The maximal and minimal residual electron density peaks were 0.632 and $-0.382 \ \bar{e}/\text{Å}^3$.

6-(2-Hydroxy-5-methylphenyl)-3-(pyridin-2-yl)-1,2,3-triazin-5(2H)-one (I). Air was passed over a period of 15 h through a mixture of 0.3 g (1.73 mmol) of 3-(pyridin-2-yl)-1,2,4-triazin-5(2H)-one, 12 ml of trifluoroacetic acid, and 0.187 g (1.73 mmol) of 4-methylphenol. The mixture was evaporated, the residue was treated with 5 ml of water, and the precipitate was filtered off, washed with water $(3 \times 5 \text{ ml})$, and dried under reduced pressure. Yield 0.158 g (33%), mp 247–249°C (from MeCN). ¹H NMR spectrum (DMSO-*d*₆), δ, ppm: 2.07 s (3H, CH₃), 6.81 m (1H, Harom), 7.14 m (1H, Harom), 7.39 s (1H, Harom), 7.74 m (1H, pyridine), 8.13 m (1H, pyridine), 8.36 d (1H, pyridine), 8.84 d (1H, pyridine). Found, %: C 64.44; H 4.54; N 19.76. C₁₅H₁₂N₄O₂. Calculated, %: C 64.29; H 4.29; N 20.00.

Dimethylammonium [6-(2-hydroxy-5-methylphenyl)-5-oxo-3-(pyridin-2-yl)-5*H*-1,2,4-triazin-4ido]dichloropalladate(II) (II). A solution of 0.0105 g (0.06 mmol) of palladium(II) chloride in 2 ml of water was added to a solution of 0.0166 g (0.06 mmol) of ligand I in 5 ml of DMF. The product separated from the resulting solution upon slow evaporation at 70°C. Found, %: C 43.22; H 4.03; Cl 15.04, N 14.83; Pd 22.45. $C_{17}H_{19}Cl_2N_5O_2Pd$. Calculated, %: C 43.37; H 4.15; N 14.64; Cl 14.86; Pd 22.06.

Reaction of iodobenzene with butyl acrylate. Palladium complex (II), 0.001 mmol, was dissolved in 3.0 ml of DMF, 0.2040 g (1 mmol) of iodobenzene, 0.1923 g (1.5 mmol) of butyl acrylate, and 0.3707 g (2 mmol) of tributylamine were added, and the mixture was heated for 16 h at 140°C in a sealed ampule. The ampule was opened, the mixture was evaporated under reduced pressure (10 mm) at 40°C, the residue was treated with 6 ml of toluene, and the toluene extract was washed with 3 ml of 0.5 M aqueous sodium hydroxide and water (2×6 ml) and dried over sodium sulfate.

Reactions of other halobenzenes with alkenes were carried out in a similar way.

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