ISSN 1070-3632, Russian Journal of General Chemistry, 2014, Vol. 84, No. 11, pp. 2138–2141. © Pleiades Publishing, Ltd., 2014.
Original Russian Text © M.A. Kinzhalov, A.M. Borozdinova, I.A. Boyarskaya, M.Yu. Skripkin, V.P. Boyarskii, 2014, published in Zhurnal Obshchei Khimii, 2014, Vol. 84, No. 11, pp. 1841–1844.

Reversible Chelating in Acyclic Diaminocarbene Palladium Complex Containing Hydrazide Fragment

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Received October 2, 2014

Abstract—Study of molar conductivity of several palladium(II) complexes has revealed that cationic acyclic diaminocarbene complexes of palladium(II) containing carbohydrazide fragment in the carbene ligand are capable of reversible cyclization to form a six-membered C,O-chelate. This process is favored by factors enhancing dissociation of the anionic ligand in the starting neutral compound. DFT simulation of cationic carbene complexes of palladium has confirmed possibility of such chelating.

Keywords: carbene complex of palladium, chelating, conductometry, quantum-chemical simulation, acyclic diaminocarbene

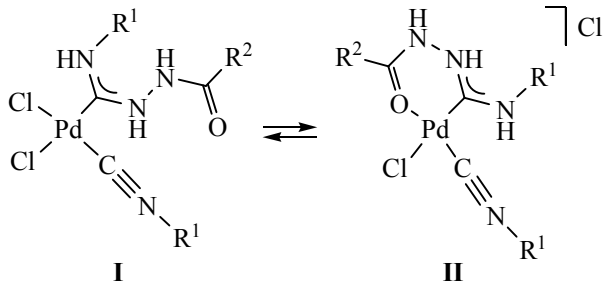
DOI: 10.1134/S1070363214110164

Complexes of palladium with acyclic (Pd-ADC) [1, 2] and heterocyclic (Pd-NHC) [3] diaminocarbene ligands have been recognized as the most efficient catalysts of various organic reactions. Of the former type of the complexes, those containing hydrazine fragment in the carbene ligand have revealed the highest activity [4–10]. In view of that, study of structural features of such coordination compounds is of special interest.

In particular, we have recently demonstrated [9] that type **I** complexes reveal high catalytic activity in the Suzuki reaction in aqueous medium. We have suggested that it is due to ability of such complexes to undergo intramolecular cyclization to form type **II** derivatives containing six-membered C,O-chelate ring (Scheme 1).

In order to verify this hypothesis, we took advantage of the approach combining experimental studies and theoretical simulation. In particular, degree of dissociation of the studied compounds was monitored using conductometric measurements. This method is known to provide information on the charges of ionic species and on degree of dissociation of weak electrolytes; in some cases, kinetics of the processes occurring in the solution, for example, of ligand exchange reactions, can be so studied [11, 12]. In this wotk we experimentally determined molar conductivity of solutions of compound **Ia** (a complex of type **I**) and of structurally similar carbene complex **III**. The complex **III** was somewhat different, primarily due to the absence of carbonyl group preventing formation of the C,O-chelate (Scheme 2).

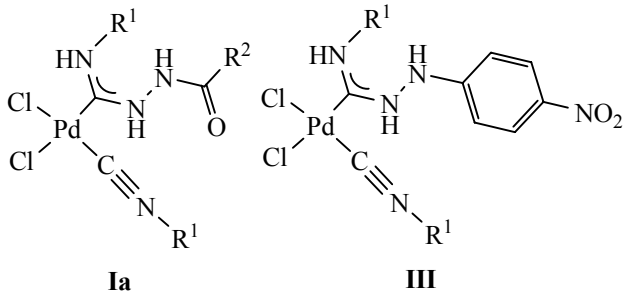
Scheme 1.



I **II**

R^1, R^2 = Alk, Ar.

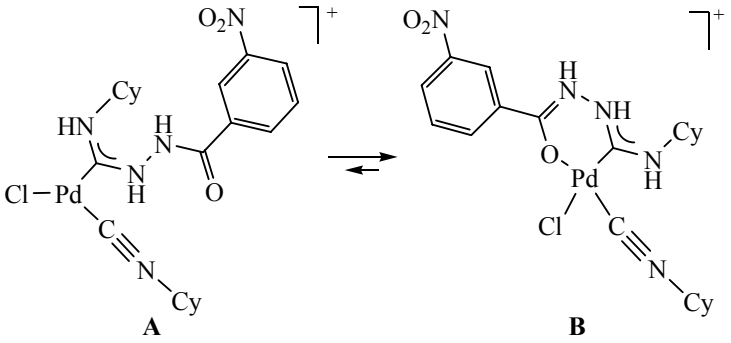
Scheme 2.



Ia **III**

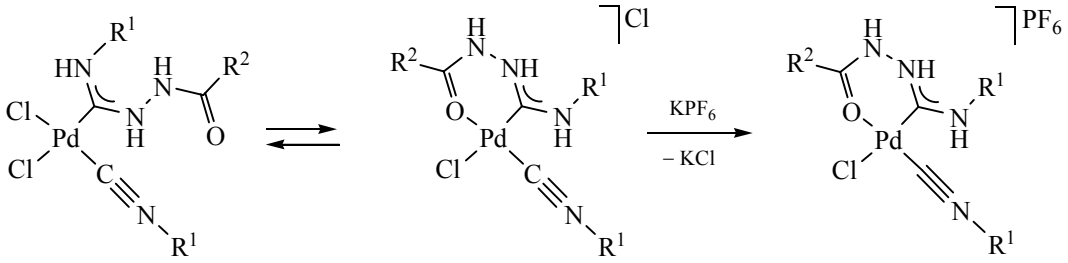
R^1 = Cy; R^2 = 3-$NO_2C_6H_4$.

Scheme 3.



A **B**

Scheme 4.



Ia **IIa** **IV**

R^1 = Cy; R^2 = 3-$NO_2C_6H_4$.

Complexes **Ia** and **III** were prepared using the published procedures ([9] and [8], respectively). The measurement was performed in methanol at 21.0±1.0°C. Molar conductivities were of 56.2±1.7 (**Ia**) and 32.2±0.5 (**III**) Ω^{-1} cm^{-1} mol^{-1}, somewhat lower than typical molar conductivity of the 1 : 1 electrolytes (80–100 Ω^{-1} cm^{-1} mol^{-1}); that could point at incomplete dissociation of the complexes. The higher degree of dissociation of complex **Ia** reflected in its higher molar conductivity could be due to possibility of stabilization of the complex cation (formed in the course of dissociation) via chelating (Scheme 3).

The enhanced stability of the chelate form of complex cation **B** as compared to that of the open form **A** was confirmed by quantum-chemical simulation. The simulation performed in the 6-31 basis set via the DFT/B3LYP method [13] revealed that energy of cyclic cation **B** in chloroform solution was 21 kJ/mol lower than that of the corresponding non-chelated ion **A**. The solvation was accounted for using the PCM method. With methanol used as solvent instead of chloroform, the difference was down to 12 kJ/mol due to better solvation of the open form with a protic polar solvent; however, the cyclic form **B** remained more stable.

We further tried to prepare a stable complex containing cation **B** in the ionic form. To do so, we introduced the starting complex **Ia** into the reaction with potassium hexafluorophosphate in acetonitrile at ambient temperature (Scheme 4).

The prepared complex **IV** was stable in air. It was isolated in pure form and characterized by elemental analysis (C, H, and N), mass spectrometry (ESI^+-MS), IR, ^1H, and $^{13}C–\{^1H\}$ spectroscopy.

IR spectrum of chelate **IV** revealed slight shifting of absorption bands of stretching vibrations of C≡N (from 2235 to 2230 cm^{-1}) and of diaminocarbene fragment (from 1582 to 1580 cm^{-1}) as compared with the spectrum of initial complex **Ia**. ^{13}C NMR spectrum of compound **IV** showed significant broadening and upfield shift (by 10 ppm) of the signal of carbene carbon atom; furthermore, the signal of carbohydrazide carbon was shifted to higher frequency by about 5 ppm, and that of the isocyanide carbon was shifted to lower frequency by 5 ppm (all the spectral changes are

described as compared to the spectrum of the starting complex **Ia**).

Hence, the spectral data pointed at noticeable redistribution of the electron density in the molecule upon formation of complex **IV**. The results suggested that the complex existed in ionic form, containing palladium cation in the six-membered metallocycle.

Noteworthily, such chelate compounds can be formed from aminohydrazidocarbene complexes under the action of weak base present in the reaction medium in the course of palladium-catalyzed cross-coupling reactions in aqueous medium: the process is accompanied by exchange of the chloride ligand with the hydroxyl one, location in the outer sphere being more typical of the latter ligand [14].

In general, the results presented here show that diaminocarbene complexes of palladium(II) containing the $CONHNH_2$ hydrazide fragment are more ionic than those containing hydrazine fragment. The enhanced dissociation of complexes **I** in polar solvents as compared with complexes **III** is due to the cation stabilization via formation of the six-membered C,O-chelate cycle.

Preparation of complex IV. A solution of 0.10 mmol of KPF_6 in 2 mL of CH_3CN was slowly added upon stirring to a solution of 0.10 mmol of compound **Ia** in 3 mL of CH3CN. The reaction mixture was stirred at room temperature during 1 h and then evaporated under reduced pressure at $T < 45$°C. The solid residue was extracted with CH_2Cl_2 (2 × 5 mL), the formed pale-yellow solution was evaporated, washed with Et_2O (3 × 1 mL), and dried in air at room temperature. Yield 51 mg (75 %). IR spectrum (KBr), ν, cm^{-1}: 3239 m (N–H), 2934–2856 m (C–H), 2230 s (C≡N), 1697 s (C–O), 1582 s ($C_{carbene}$–N), 1534 s (NO_2), 1351 s (NO_2), 1097 m (O–C, C=N), 718 m [δ(C–H_{arom})]. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.43–2.22 m (20H, CH_2), 4.0–4.2 m (1H, CHNC), 4.2–4.4 m (1H, CHNH), 7.46 br.s (1H, $C_{carbene}$–NH–Cy), 7.66 d.d (1H, C^5H_{arom}, $^3J_{HH}$ 7.6, 7.6 Hz), 8.28–8.38 m (2H, C^4H_{arom}, C^6H_{arom}), 8.70 s (1H, C^2H_{arom}), 9.44 br.s (1H, NH), 9.84 br.s (1H, NH). ^{13}C–{^{1}H} NMR spectrum ($CDCl_3$), δ_C, ppm: 22.9 (CH_2), 24.5 (CH_2), 24.7 (CH_2), 24.9 (CH_2), 31.6 (CH_2), 32.9 (2C, CH_2), 56.5 (CH), 60.8 (CH), 113.7 (C≡NCy), 123.5 (CH_{arom}), 127.1 (CH_{arom}), 130.2 (CH_{arom}), 132.0 (C_{arom}), 133.9 (CH_{arom}), 148.0 (C_{arom}), 164.4 (CO), 170.2 ($C_{carbene}$). Mass spectrum (ESI^+, 70 eV, MeOH): *m*/*z* 504.1261 $[M - Cl - PF_6 - H]^+$ (calc. 504.1243).

ACKNOWLEDGMENTS

The research was performed using equipment of the Resource Centers of St. Petersburg State University: "Research Resources Center for Magnetic Resonance" and "Center for chemical analysis and materials research."

This work was financially supported by Russian Foundation for basic research (project no. 14-43-00017).

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