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Influence of substituents in the pyrazole pre-ligands on their reaction products with $(Phen)Pd(OAc)_2$

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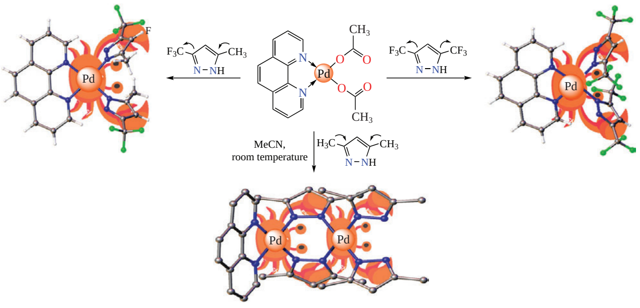
The unique palladium(II) complexes, namely, $(Phen)Pd((CF_3)_2pz)_2$, $(Phen)Pd(MeCF_3pz)_2$, and $[(Phen)Pd_2(\mu\text{-}dmpz)_2(dmpz)(Hdmpz)](OAc)_2H$, where $(CF_3)_2pzH$ is 3,5-bis(trifluoromethyl)pyrazole, $MeCF_3pzH$ is 3-methyl-5-trifluoromethylpyrazole, Hdmpz is 3,5-dimethylpyrazole, Phen is 1,10-phenanthroline, have been obtained by the reactions of $(Phen)Pd(OAc)_2$ with the corresponding free *NH*-pyrazoles. According to the X-ray data, in the mononuclear pyrazolate complexes the Pd^{II} atom has a square planar environment of nitrogen atoms of phenanthroline and two monodentate-bound pyrazolate anions. The binuclear pyrazolate-bridged complex is additionally stabilized by intramolecular hydrogen bonding of the terminal dmpz anion and Hdmpz.



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The chemistry of pyrazole and its analogues is one of the most relevant and promising areas of modern coordination chemistry. The pyrazole molecule contains two nitrogen atoms of different chemical nature. Due to the unshielded electron pair of its pyridine-type nitrogen atom, pyrazole can be coordinated by the metal centre while and the pyrrole-type NH fragment can be deprotonated to form the pyrazolate anion.[1–3] The reactions of pyrazoles with transition metal carboxylates can afford pyrazolate-bridge complexes of various dimensions.[4–10] The composition and structure of such products are determined primarily by the nature of the transition metal, the donor capacity of the anion of the initial complex, the reaction conditions (solvent polarity, temperature, *etc*.), as well as the nature of substituents in the pyrazole molecule.[11–14]

It was previously[15,16] found that the reactions of palladium phenanthroline triflate with 3,5-dimethylpyrazole and pyrazole at room temperature led to mononuclear complexes $[PdPhen(Hdmpz)_2]\cdot 2\,OTf$ and $[PdPhen(Hpz)_2]\cdot 2\,OTf$. At the same time, the introduction of electron-acceptor CF_3-substituents into pyrazole significantly enhances its acidity and facilitates the formation of the pyrazolate anion.[17–22] In fact,[23] the reaction of binuclear complex $[(Phen)_2Co_2(\mu\text{-}OH_2)(OAc)_4]$ with 3,5-bis(trifluoromethyl)pyrazole was accompanied by its deprotonation. The resulting metal pyrazolates can be considered as promising building blocks for obtaining homo- and heterometallic clusters with interesting physicochemical properties.

In this paper, we studied the effect of the 3,5-positioned substituents in the pyrazole core on the reaction outcome with $(Phen)Pd(OAc)_2$. The acidity of the selected $3,5\text{-}(CF_3)_2pzH$, $3\text{-}Me\text{-}5\text{-}CF_3pzH$ and Hdmpz, where $(CF_3)_2pzH$ is 3,5-bis(trifluoromethyl)pyrazole, $MeCF_3pzH$ is 3-methyl-5-trifluoromethylpyrazole, and Hdmpz is 3,5-dimethylpyrazole, is determined by the donor capacity of the substituents. Acceptor CF_3-groups enhance the acidic properties, and donor Me-groups weaken the acidity of pyrazole. As a result, the unique mononuclear complexes $(Phen)Pd((CF_3)_2pz)_2$ **1**, $(Phen)Pd(MeCF_3pz)_2$ **2**, and unusual binuclear complex $[(Phen)Pd_2(\mu\text{-}dmpz)_2(dmpz)(Hdmpz)](OAc)_2H$ **3** were obtained. The structure of the complexes was determined by X-ray analysis, the purity of the compounds obtained was confirmed by IR spectroscopy and elemental analysis.

The synthesis of complexes **1–3** was carried out by the reactions of $(Phen)Pd(OAc)_2$ with 2 equiv. of the corresponding free *NH*-pyrazoles in acetonitrile at room temperature (Scheme 1).[†] As a result, in the cases of fluorinated substituents in the pyrazole molecule, complete exchange of acetate anions for pyrazolate anions occurs with the formation of mononuclear complexes **1** and **2**.

According to X-ray data (Figure 1),[‡] in a mononuclear complex **1** palladium(II) atom is located in a square planar

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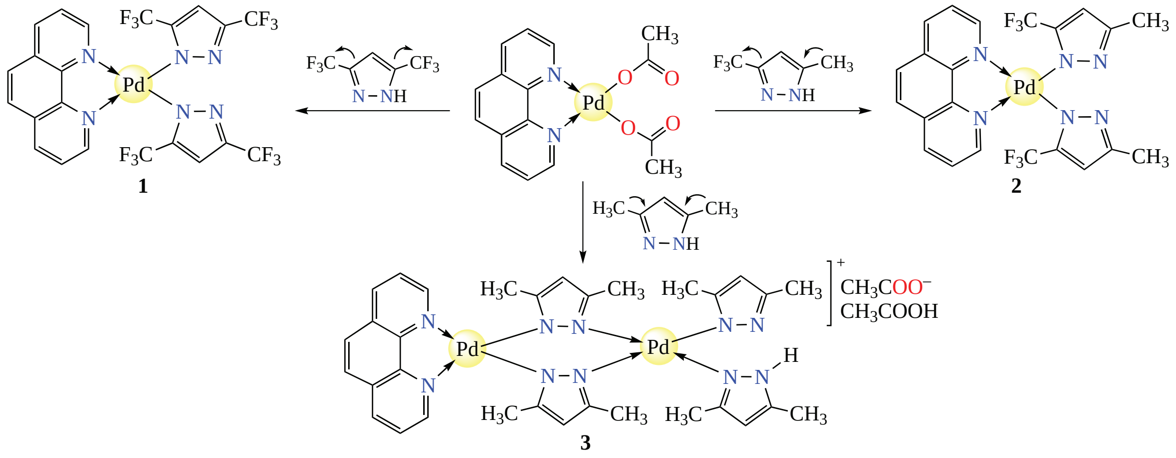
[†] *Complexes* **1**–**3**. Pyrazole derivative (0.5 mmol) $[3,5\text{-}(CF_3)_2pzH$ (0.1 g), $3\text{-}Me\text{-}5\text{-}CF_3pzH$ (0.075 g) or Hdmpz (0.048 g)] was added to a solution of $(Phen)Pd(OAc)_2$ (0.1 g, 0.25 mmol) in acetonitrile (20 ml). The formed solution was stirred at room temperature for 1 h and then kept for a day at 5 °C. The obtained yellow crystals were separated from the mother liquor by decantation and dried in air. The yield of **1** was 0.11 g (62%), the yield of **2** was 0.1 g (70%), the yield of **3** was 0.08 g (35%).

Commercial reagents and solvents were used for the synthesis. Complex $(Phen)Pd(OAc)_2$ was obtained as reported.[24]

[‡] *Crystal data for* **1**. $C_{22}H_{10}F_{12}N_6Pd$, $M = 692.76$, monoclinic, $P2_1/n$, $a = 9.2257(12)$, $b = 15.6123(19)$ and $c = 16.004(2)$ Å, $V = 2304.1(5)$ Å^3,



Scheme 1 *Reagents and conditions*: (Phen)Pd(OAc)$_2$/pyrazole molar ratio is 1 : 2, MeCN, room temperature, 1 h, then 5 °C, 1 day.

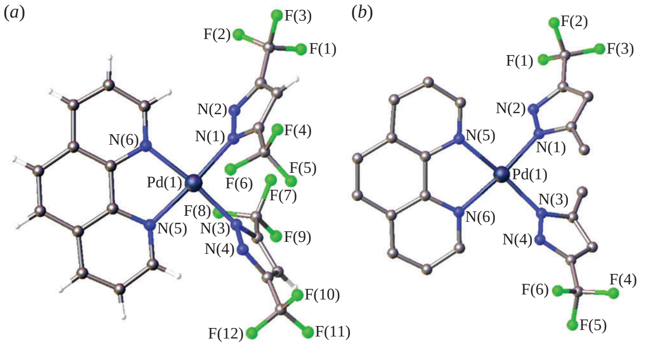


Figure 1 General view of complexes (*a*) **1** and (*b*) **2**.

environment of four nitrogen atoms, two of which belong to a coordinated phenanthroline molecule [Pd(1)–N(5) 2.028(3) Å, Pd(1)–N(6) 2.035(3) Å], and two N-atoms of two pyrazolate anions [Pd(1)–N(3) 2.006(3) Å, Pd(1)–N(1) 2.012(3) Å]. Complex **2** has a similar structure, there is only a slight shortening of the palladium bond with the nitrogen atoms of the pyrazolate anion [Pd(1)–N(3) 1.994(19) Å, Pd(1)–N(1) 1.986(2) Å].

The crystal packing of complexes **1** and **2** is stabilized due to π···π interactions between Phen molecules with the formation of supramolecular chains (Figure 2). The distance and angle between the planes for **1** are 3.662 Å and 0.00°, for **2** they are 3.635 Å and 0.00°, respectively.

The structure of these complexes is confirmed by IR spectroscopy. Strong bands of CF$_3$-groups are present in the spectra, namely, at 1257, 1220, 1138 cm^{-1} in **1**, 1264, 1220, 1132 cm^{-1} in **2**. Bands at 3140, 1522 and 714 cm^{-1} in **1** and 1125, 1544 and 724 cm^{-1} in **2** correspond to fluctuations of Phen aromatic rings. In complex **2**, fluctuations of the CH$_3$ substituent at the pyrazole occur [1436 cm^{-1}, see Online Supplementary Materials, Figure S1(*a*),(*b*)].

Such mononuclear complexes can be considered as potential metal-containing ligands, since they have terminal pyrazolate anions containing free electron pairs and can be further coordinated by the chelate type. Mononuclear complexes with monodentate-bound pyrazolate anions are unique compounds. Previously,[28,29] only isolated examples of mononuclear zinc and cerium pyrazolates were documented.

When reacting (Phen)Pd(OAc)$_2$ with more basic Hdmpz, an incomplete exchange of acetate anions for pyrazolate anions occurs resulting in a binuclear complex [(Phen)Pd$_2$(μ-dmpz)$_2$(dmpz)(Hdmpz)](OAc)$_2$H **3** (with a yield of 35%, see Scheme 1). In complex **3** (Figure 3),† two palladium(II) atoms are connected by the pyrazolate bridges and

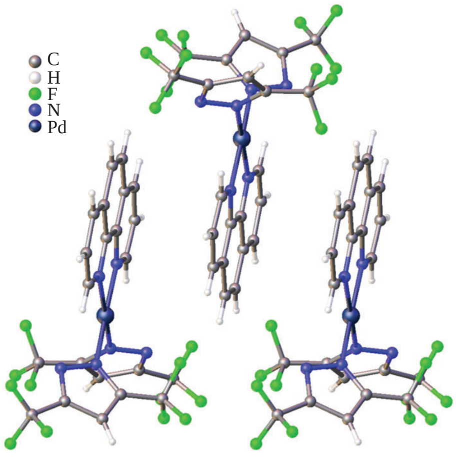


Figure 2 Fragment of the crystal packing of complex **1**.

$Z = 4$. Total of 16748 reflections were collected, from which 5288 were independent. The final refinement parameters were $R_1 = 0.0823$, $wR_2 = 0.0627$ for the reflections with $I > 2\sigma(I)$. GOOF 1.131. Maximum and minimum of residual electronic density were 1.07 and –0.83 e Å^{-3}.

Crystal data for **2**. $C_{22}H_{16}F_6N_6Pd$, $M = 585.2$, monoclinic, $C2/c$, $a = 31.339(2)$, $b = 31.339(2)$ and $c = 25.5616(18)$ Å, $V = 4281.8(5)$ Å^3, $Z = 4$. Total of 24085 reflections were collected, from which 6245 were independent. The final refinement parameters were $R_1 = 0.0360$, $wR_2 = 0.0704$ for the reflections with $I > 2\sigma(I)$. GOOF 1.013. Maximum and minimum of residual electronic density were 1.00 and –0.60 e Å^{-3}.

Crystal data for **3**. $C_{36}H_{44}N_{10}O_4Pd_2$, $M = 893.61$, triclinic, $P\bar{1}$, $a = 10.4370(2)$, $b = 13.6164(3)$ and $c = 14.1746(3)$ Å, $V = 1812.89(7)$ Å^3, $Z = 2$. Total of 29696 reflections were collected, from which 8337 were independent. The final refinement parameters were $R_1 = 0.0290$, $wR_2 = 0.0684$ for the reflections with $I > 2\sigma(I)$. GOOF 1.063. Maximum and minimum of residual electronic density were 1.12 and –0.84 e Å^{-3}.

X-ray diffraction study of complexes **1**–**3** was carried out at 296 K on a Bruker Apex II CCD diffractometer. A semiempirical adsorption correction was applied using the SADABS program.[25] The structures were solved using the Shelxtl program[26] and refined in a full-matrix OLS using the Olex2 program[27] in an anisotropic approximation for non-hydrogen atoms. The hydrogen atoms of NH and OH groups are located from the difference Fourier syntheses, and the remaining hydrogen atoms were placed in calculated positions. All of them are refined in the isotropic approximation using a riding model with $U_{\text{iso}}(\text{H}) = 1.5\,U_{\text{eq}}(\text{C,O})$ for hydrogen atoms of methyl groups and water molecule, and $U_{\text{iso}}(\text{H}) = 1.2\,U_{\text{eq}}(\text{C,N})$ for other atoms. Crystal data and structure refinement parameters for **1**–**3** are given in Table S1, the main bond lengths and angles are shown in Table S2 (see Online Supplementary Materials).

CCDC 2296188–2296190 contain 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.

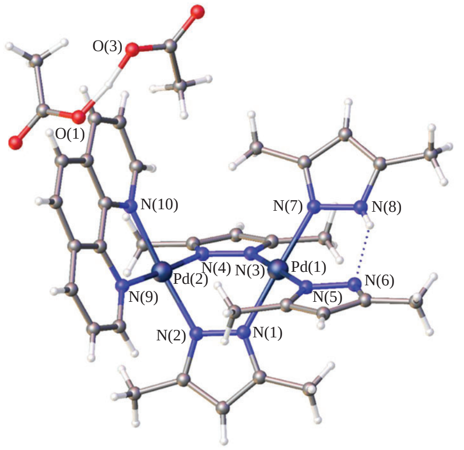


Figure 3 Crystal structure of complex **3**.

are located at a distance of 3.287 Å, which is shorter than in other palladium pyrazolate bridge complexes.[28,29] One palladium atom is located in a flat-square environment of two Phen nitrogen atoms [(Pd(2)–N(10) 2.047(2) Å, Pd(2)–N(9) 2.038(2) Å] and two dmpz nitrogen atoms [Pd(2)–N(4) 1.995(2) Å, Pd(2)–N(2) 1.991(2 Å]. The second Pd^{II} atom is surrounded by four nitrogen atoms of pyrazole molecules, namely, two bridging [(Pd(1)–N(3) 2.026(2) Å, Pd(1)–N(1) 2.007(2) Å] and two terminal [Pd(1)–N(7) 2.032(2) Å, Pd(1)–N(5) 2.007(2) Å]. One of terminal pyrazoles is deprotonated while the second pyrazole is neutral resulting in the formation of the $[(Phen)Pd_2(\mu\text{-dmpz})_2(dmpz)(Hdmpz)]^+$ cation. In the outer sphere of this complex there is an anti-ion pair $[(AcO)_2H]^-$. The terminal molecules of pyrazole are bound by the hydrogen interaction with N···NH distance of 2.652(3) Å (see Figure 3). The presence of protonated pyrazole is confirmed by IR spectra (3415 cm^{-1}). The OH group of acetic acid bound by a hydrogen bond with the acetate anion gives a strong band at 2920 cm^{-1}. The strong bands at 1426 and 1415 cm^{-1} correspond to fluctuations in the carbonyl group of the acetate anion [see Figure S1(*c*)]. The same binding of terminal anionic dmpz and neutral (Hdmpz) was observed previously[30,31] in complex $[Pd_2(\mu\text{-dmpz})_2(dmpz)_2(Hdmpz)_2]$.

To summarize, the nature of substituents on pyrazole core affects the products of the reaction with $(Phen)Pd(OAc)_2$. In the cases of acceptor CF_3-substituents, monodentate-bound pyrazolate anions are formed while in the cases of donor CH_3-substituents an incomplete ion exchange of acetate anions for pyrazolates occurs, which gives a binuclear pyrazolate-bridging complex containing an external [AcO–H–OAc] pair.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2024.01.016.

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