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Mixed-ligand azomethine–benzimidazole palladium complex

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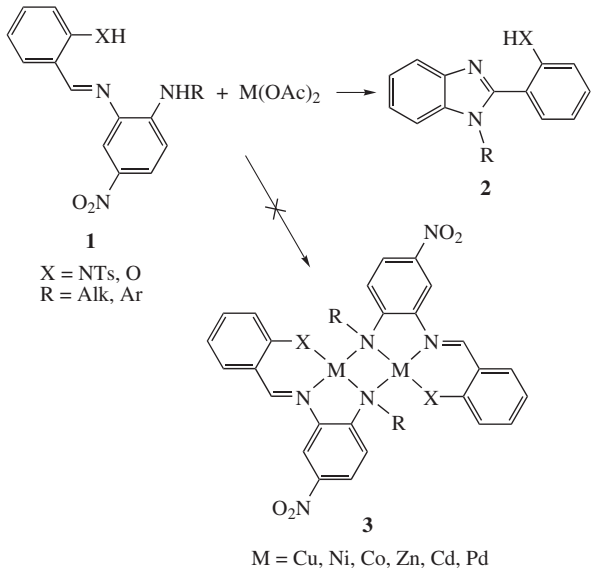
An unusual palladium complex simultaneously containing azomethine and benzimidazole ligands was isolated after template reaction of *o*-tosylaminobenzaldehyde, 2-butylamino-5-nitroaniline and palladium diacetate and its structure was determined by X-ray diffraction analysis.

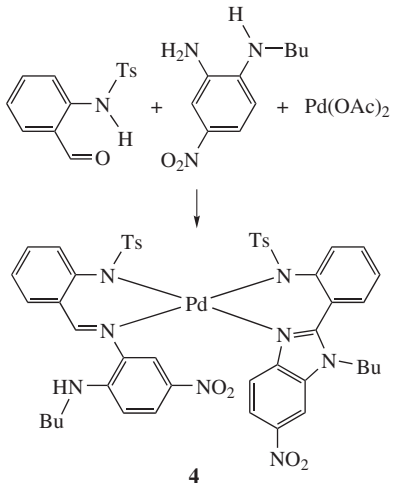
Recently,[1] we have found that the direct or template interaction of the imines of 2-alkyl(aryl)amino-5-nitroaniline **1** with metal acetates in the presence of air leads to benzimidazole derivatives **2** instead of expected binuclear complexes **3** (Scheme 1). Chelates **3** have been subsequently obtained by similar coupling in an argon atmosphere.[2,3]



Scheme 1

The elemental analysis of a compound obtained in the template interaction of 2-tosylaminobenzaldehyde and 2-*n*-butylamino-5-nitroaniline with palladium diacetate (Scheme 2) in air exhibited the presence of a metal atom, which means the formation of a complex.† We performed the X-ray diffraction (XRD) investigation of the crystal structure of this compound.

† Complex **4**: A solution of 0.22 g (1 mmol) of palladium acetate in 10 ml of acetone was added to a solution of 0.275 g (1 mmol) of *o*-tosylaminobenzaldehyde[4] and 0.02 g (1 mmol) of 2-butylamino-5-nitroaniline[2] in 20 ml of methanol. The resulting mixture was heated in a water bath for 1 h. The precipitate formed after cooling was filtered off, washed with 5 ml of methanol and dried *in vacuo*. Dark-brown crystals were obtained by slow crystallization from $CHCl_3$–MeOH mixture (1:2); mp 235–236 °C. Yield 0.25 g (50%). Found (%): C, 55.85; H, 4.47; N, 10.94; S, 6.15; Pd, 10.12. Calc. for $C_{48}H_{47}N_8O_8S_2Pd$ (%): C, 55.73; H, 4.58; N, 10.83; S, 6.20; Pd, 10.29.



Scheme 2

XRD analysys‡ revealed that the coordination environment of the central atom in compound **4** is formed by four nitrogen atoms of two different chelate ligands, imine and benzimidazole (Figure 1). The complex forms a crystal solvate with chloroform in a 1:0.125 ratio.

The Pd–N bond lengths vary in a narrow range of 2.015(3)–2.032(3) Å with the shortest distance for Pd–N_{bzm}. The conformation of six-membered metallocycles Pd(1)N(3)C(9)C(8)N(1)

‡ *X-Ray diffraction analysis*. Crystals of **4** ($C_{48}H_{48}N_8O_8S_2Pd{\cdot}0.13CHCl_3$) are orthorhombic, space group *Pbca*, at 120(2) K: a = 15.752(2), b = = 19.293(3) and c = 32.622(6) Å, V = 9914(3) Å^3, Z = 8, M = 1050.39, d_{calc} = 1.408 g cm^{-3}, μ(MoKα) = 0.539 cm^{-1}, F(000) = 4332.3. Intensities of 56751 reflections were measured with a Smart 1000 CCD diffractometer [λ(MoKα) = 0.71073 Å, 2.20 < θ < 27.00°], and 11896 independent reflections (R_{int} = 0.0576) were used in the further refinement. The structure was solved by direct method and refined by the full-matrix least-squares technique against F^2 in the anisotropic–isotropic approximation. The hydrogen atom positions were calculated. The refinement converged to wR_2 = 0.1090 and GOF = 1.093 for all independent reflections [R_1 = 0.0496 was calculated against F for 6374 observed reflections with $I > 2\sigma(I)$]. All calculations were performed using SHELXL ver. 5.1.

CCDC 691816 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2008.

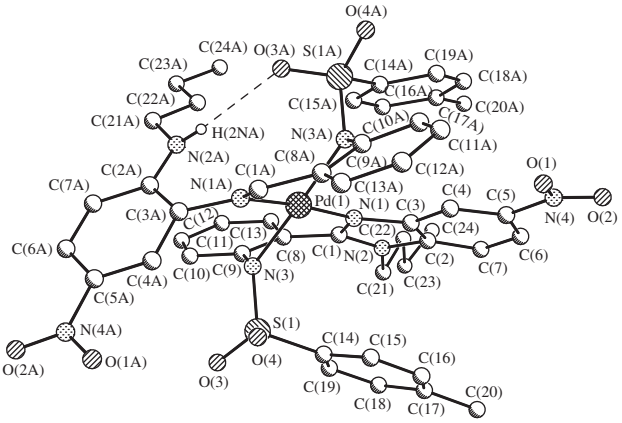


Figure 1 Structure of the complex **4**.

and Pd(1)N(3A)C(9A)C(8A)N(1A) is sofa, atoms Pd(1) and N(1)/N(1A) deviate from the average plane of other atoms by 1.46, 0.63 and 1.22, 0.28 Å, respectively.

The conformation of complex **4** is stabilised by the intramolecular H-bond N(2A)–H(2NA)···O(3A) [(2NA)H···O(3A) 2.36 Å, N(2A)–H(2NA)O(3A) 139°, N(2A)···O(3A) 3.048(2) Å] between two ligands of the same complex molecule (Figure 1). At the same time, the mutual disposition of nitrobenzimidazole and *p*-tolyl rings allows us to suppose the presence of π-stacking interaction between the above cycles (Figure 2).

The imidazole and phenyl rings are almost coplanar (the dihedral angle is equal to 10.6°) and there are shortened contacts between C(1)···C(19) and N(1)···C(14) atoms with the lengths of 3.323(3) and 3.371(3) Å, respectively (Figure 3). These parameters are close to the values for 1-ethyl-2-(2-tosylaminophenyl)-5-nitrobenzimidazole [C···C 3.426(1) and N···C 3.216(1) Å].[1] To proof the presence of stacking interaction in compound **4**, we performed the quantum chemical calculation of the molecule of **4**[§] with the topological analysis of the $\rho(r)$ function obtained.

In addition, the DFT calculation of isolated molecule of complex **4** totally represented the experimental data of the mutual disposition of interacting aromatic rings, but the distance between them increased by 0.1–0.2 Å as against the XRD data. As in the case of the earlier investigated ligand, in complex **4**, it appears to be the result of the influence of the medium polarity. At the same time, we cannot exclude that the weakening of stacking interaction in the isolated molecule is the consequence of an incorrect description of dispersive interactions in the DFT theory.

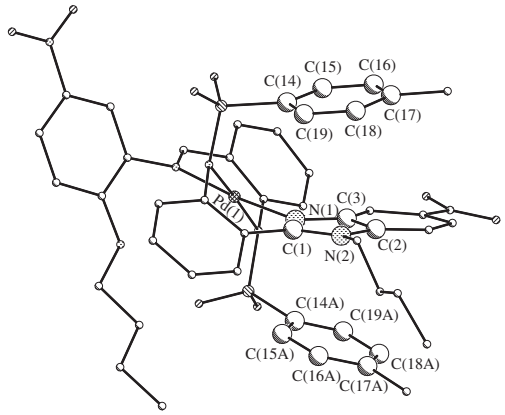


Figure 2 Projection of the molecule of **4** illustrating possible intramolecular stacking interaction. Cyclic fragments that can be probably involved in stacking interaction are depicted by larger balls.

§ DFT calculations of **4** were performed with the Priroda program package at the PBE/TZ2P level of theory.[5] Topological analysis of the $\rho(r)$ function was performed using the MORPHY 98 program,[6] basing on the wave functions obtained from the B3LYP calculations.

The critical point search revealed that bond critical points (3, –1) (BCP) are located not only in the case of all expected bonds but also for intramolecular N–H···O hydrogen bond and for two C···C contacts that can be considered as stacking interaction. These interactions correspond to a closed-shell type of interatomic interactions (the values of laplacian and electron energy density are both positive). The corresponding values of $\rho(r)$ in BCP are 0.14 and 0.04–0.05 eÅ^{-3} for N–H···O bond and stacking interactions.

Taking into account that within the topological analysis of $\rho(r)$ it is possible to estimate the energy of weak interactions using the Lecomte correlation scheme,[7] we found that the energy of intramolecular H-bond is 5.2 kcal mol^{-1}, and that of stacking interaction is 1.0 kcal mol^{-1} (Figure 3). Note that this value is close to the experimental energy of intramolecular stacking interaction in the crystal of 1-ethyl-2-(2-tosylaminophenyl)-5-nitrobenzimidazole (1.2 kcal mol^{-1}) though in this case the strength of stacking interaction is limited with the presence of competitive intramolecular H-bond that fixes the molecular conformation and constrains the mutual orientation of aromatic rings, while in the case of compound **4** the H-bonded cycle is 'replaced' by metallocycle, that is more flexible.

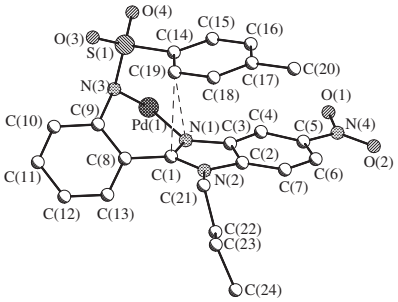


Figure 3 Fragment of molecule of **4** illustrating the formation of stacking in benzimidazole ligand. Azomethine ligand is ommited for clarity.

We can conclude that such stacking interactions are the common feature for 1-alkyl(aryl)-2-(tosylaminophenyl)-5-nitrobenzimidazoles that are persist both for N–H···N bonded cycles and metallocycle. The formation of stacking interaction together with intramolecular H-bond stabilizes the unusual hybrid complex, which contains *in situ* benzimidazole and azomethine ligands.

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