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## **Sigma-hole and pi-hole interactions in chemistry of PdII carbene complexes**

The field of non-covalent interactions has grown explosively in the past decade due to their ability to control the structures and properties of the molecular and supramolecular systems from water association to protein folding. Most recent reports devoted to non-covalent interactions typically deal with two large groups of their donor participants, namely  $\sigma$ -hole donors (participating in hydrogen, halogen, chalcogen, pnictogen, tetrel, etc. bonding) and  $\pi$ -hole donors (capable of forming anion- $\pi$ , lone pair- $\pi$ , and  $\pi$ - $\pi$  contacts).

In this project focused on non-covalent interactions in transition metal complexes, we studied the isocyanide/diaminocarbene complexes of Pd<sup>II</sup> possessing potential donors/acceptors of non-covalent interactions. Depending on the structure of the isocyanide ligands and the carbene fragments these systems exhibit the rich diversity of structures displaying different types of  $\sigma$ -hole and  $\pi$ -hole non-covalent interactions, viz.  $\pi$ -hole- $\pi$  interactions, chalcogen bonding (CB), hydrogen bonding (HB). The results of this project could be considered from at least three perspectives:

(i) *Non-covalent interactions are able to control conformations of diaminocarbene complexes.* Previously unknown  $\pi$ -hole- $\pi$  interactions involving metal-bound isocyanides were verified in the studied isocyanide/diaminocarbene Pd<sup>II</sup> complexes. Moreover, these interactions in many instances determine the spatial conformation of diaminocarbene ligands, leading to stabilization of the preferential conformation.

(ii) *Introduction of donors of non-covalent interactions in carbene ligand could control the reactivity of diaminocarbene complexes* [1–3]. The introduction of thiazaheterocyclic fragment in structure of binuclear diaminocarbene Pd<sup>II</sup> complexes leads to emergence of intramolecular CBs in their structure, viz. S $\cdots$ Hal and S $\cdots$ N. The formation of such interactions drives the regioisomerization of these complexes and the equilibrium between them mainly depends on the energy difference between these two distinctive types of CB.

(iii) *Non-covalent interactions are able to cause the supramolecular association of diaminocarbene complexes in a solution* [4]. Our combined theoretical and experimental results demonstrate that the CBs, HBs, and metallophilic interactions collectively lead to the dimerization of diaminocarbene Pd<sup>II</sup> complexes not only in a solid state but even in a solution.

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