Mendeleev 2021

XII International Conference on Chemistry for Young Scientists

BOOK OF ABSTRACTS

BIFURCATED HALOGEN BONDING INVOLVING TWO RHODIUM(I) CENTERS AS AN INTEGRATED XB ACCEPTOR

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Halogen bonding (XB) — together with other types of noncovalent interactions — has exponentially emerged as an important concept in supramolecular design and crystal engineering, synthetic coordination chemistry, polymer science, XB-involving catalysis, medicinal chemistry, and human physiology. To date, metal-involving two-center XBs have been recognized for Ni^{II}, Pd^{II}, Pt^{II}, Au^{0}, and Au^{I}. In a few instances, a M^{II} center and the adjacent coordinated non-metal atom function as an integrated XB acceptor to give three-center bifurcated μ_2-X···[Pt^{II},Cl] (X = Br, I) and μ_2-I···[Pt^{II},C] linkages. In this work, we found that simultaneous action of the d_z^2-orbitals of two positively charged rhodium(I) centers provide sufficient nucleophilicity to form three-center XBs with σ-hole (σh) donating iodine(I)-based organic species [1].

The $[RhX(COD)]_2$ (X = Cl, Br; COD = 1,5-cyclooctadiene) complexes were co-crystallized with various iodine(I)-based XB donors to give corresponding co-crystals **1**–**5** studied by single-crystal X-ray diffraction (XRD; Fig. 1). Upon analysis of noncovalent forces in the XRD structures of the obtained adducts, we recognized hitherto unknown $Ar^F(\mu_4\text{-I})\cdots[Rh_2Cl_2]$ and $R^{EWG}(\mu_2\text{-I})\cdots$[Rh,Rh] XBs involving iodine centers of σh donors and $[Rh_2X_2]$ metal cores of the rhodium(I) complexes (Fig. 1). We examined the geometric and energetic features of the detected contacts using the combined experimental and theoretical approaches. The noncovalent XB nature of the observed interactions was confirmed theoretically by the DFT calculations via several computational tools (QTAIM, DFT energies, NCI and EDD plots, MEP surfaces, ELF analysis).

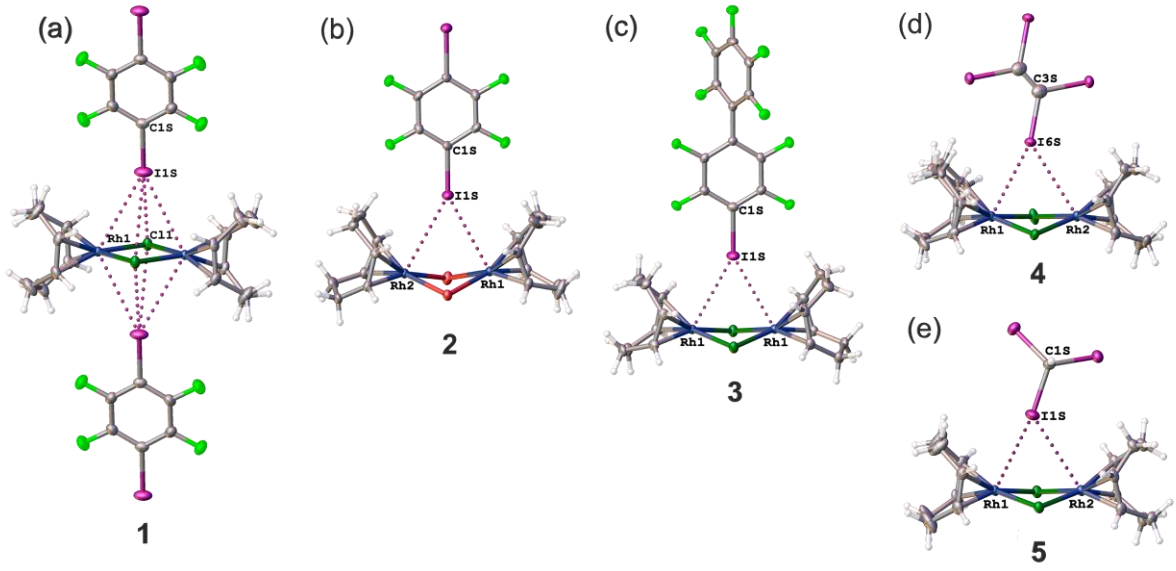

Figure 1. The $Ar^F(\mu_4\text{-I})\cdots[Rh_2Cl_2]$ and $R^{EWG}(\mu_2\text{-I})\cdots$[Rh,Rh] interactions in **1** (a), **2** (b), **3** (c), **4** (d), and **5** (e). The XBs are given by dotted lines and thermal ellipsoids are shown with the 50% probability.

In this work, we found the first example of the three-center XB that involves simultaneously two metal centers functioning as integrated XB acceptor toward iodine(I)-based σh donors. Moreover, we performed the assembly through two- or more metal-involving XBs exploring the potential of $\cdots[Rh_2Cl_2]\cdots I(Ar^F)I\cdots[Rh_2Cl_2]\cdots$ or tetrafurcated $Ar^F(\mu_4\text{-I})\cdots[Rh_2Cl_2]$ interactions.

References

[1] Eliseeva A.A., Ivanov D.M., Rozhkov A.V., Ananyev I.V., Frontera A., Kukushkin V.Yu. *JACS Au* **2021**, *1,* 356.

Acknowledgements. This work was supported by the Council for Grants of the President of Russian Federation (project MK-1614.2021.1.3).