Bifurcated Halogen Bonding Involving Two Rhodium(I) Centers as an Integrated σ-Hole Acceptor

Anastasiya A. Eliseeva, Daniil M. Ivanov, Anton V. Rozhkov, Ivan V. Ananyev, Antonio Frontera,* and Vadim Yu. Kukushkin*

ABSTRACT: The complexes \([\text{RhX}(\text{COD})]_2\) (X = Cl, Br; COD = 1,5-cyclooctadiene) form cocrystals with σ-hole iodine donors. X-ray diffraction studies and extensive theoretical considerations indicate that the \(d_x^2\)-orbitals of two positively charged rhodium(I) centers provide sufficient nucleophilicity to form a three-center halogen bond (XB) with the σ-hole donors. The two metal centers function as an integrated XB acceptor, providing assembly via a metal-involving XB.

KEYWORDS: noncovalent interactions, metal-involving halogen bonding, rhodium cocrystals, bifurcate, assembly

INTRODUCTION

Halogen bonding (XB)\(^1,2\)—together with other types of noncovalent interactions (see a special issue of Chemical Reviews 2016, Issue 9, and also reviews\(^3\) )—has exponentially emerged as an important concept in supramolecular design and crystal engineering.\(^8\)–\(^10\) synthetic coordination chemistry,\(^11\) polymer science,\(^12\) XB-involving catalysis,\(^13\)–\(^16\) medicinal chemistry,\(^17,18\) and human physiology.\(^19\)

According to the IUPAC definition,\(^7\) XB is a net attractive interaction between an electronegative region (σ-hole; abbreviated as σh) associated with a halogen atom (XB donor) and a nucleophilic region on an XB-accepting center. Organic iodine(I)-based species, \(R^\text{EWG}-\text{I}\), featuring electron-donating groups (EWG) are the most often employed as σh donors, while commonly applied XB acceptors predominantly include electronegative heteroatoms bearing lone pair(s) and electron-donating carbon-based σ-h systems. Much less common is the application of positively charged \(d_x^2\)-orbital-donating metal centers as XB acceptors.

To date, metal-involving two-center XB have been recognized for \(\text{Ni}^{II}\), \(\text{Pd}^{II}\), \(\text{Pt}^{II}\), \(\text{Au}^{0}\), and \(\text{Au}^{+}\). In a few instances, a \(\text{M}^{II}\) center and the adjacent coordinated nonmetal atom function as an integrated XB acceptor to give three-center bifurcated \(\mu_2^\text{X} \cdot \cdot \cdot [\text{Pt}^{II}\text{Cl}^-] \) (X = Br, I)\(^25,26\) and \(\mu_2^\text{I} \cdot \cdot \cdot [\text{Pt}^{II}\text{Cl}^-] \)\(^28\) linkages.

If XB of iodine(I)-based σh donors with \(d^8\)-metals such as \(\text{Pd}^{II}\) and \(\text{Pt}^{II}\) are not unusual although still uncommon, similar contacts with rhodium(I) centers are nearly unique—the only one identified short contact between a \(\text{Rh}^{I}\) center and an iodine atom of \(\text{I}_2\)\(^32,33\) belongs to the category of coordinative,\(^34\) rather than conventional, XB.\(^1\)

We now report that simultaneous action of the \(d_x^2\)-orbitals of two positively charged rhodium(I) centers provides sufficient nucleophilicity to form three-center XB with the σh-donating iodine(I)-based organic species. This is the first example of three-center XB, where two metal centers function as an integrated XB acceptor, providing assembly via XB.

RESULTS AND DISCUSSION

The \([\text{RhX}(\text{COD})]_2\) (X = Cl, Br; COD = 1,5-cyclooctadiene) complexes were cocrystallized with various iodine(I)-based σh donors, namely, 1,4-diodotetrafluorobenzene (\(\text{C}_6\text{F}_4\text{I}_2\)), 1,4-diiodobenzene (\(\text{C}_6\text{H}_4\text{I}_2\)), tetraiodoethylene (\(\text{C}_2\text{I}_4\)), and iodoform (\(\text{CHI}_3\)), to give the cocrystals\(^35\) \([\text{RhCl} \cdot \text{Cl} \cdot \text{I}(\text{COD})]_2\) (1), \([\text{RhCl} \cdot \text{Cl} \cdot \text{I}(\text{COD})]_2 \cdot 0.5(\text{C}_6\text{F}_4\text{I}_2)\) (2), \([\text{RhCl} \cdot \text{Cl} \cdot \text{I}(\text{COD})]_2 \cdot 0.5(\text{C}_2\text{I}_4)\) (3), \([\text{RhCl} \cdot \text{Cl} \cdot \text{I}(\text{COD})]_2 \cdot 1.5(\text{C}_2\text{I}_4)\) (4), and \([\text{RhCl} \cdot \text{Cl} \cdot \text{I}(\text{COD})]_2 \cdot 2(\text{CHI}_3)\) (5) studied by single-crystal X-ray diffraction (XRD; Section S1, Supporting Information).

In the structure of 1, two iodine centers from two \(\text{C}_6\text{F}_4\text{I}_2\) are linked to the \(\text{Rh}_2\text{Cl}_2\) core of the complex (Figure 1a), whereas in 2–5, \(\text{Rh}_2\text{X}_2\) (X = Cl, Br) entities interact with only one I of an appropriate σh donor (Figure 1b–e). In the case of 1, when the interaction with the iodine atoms occurs above and below the \(\text{Rh}_2\text{Cl}_2\) plane, the metal core is perfectly planar (r.m.s. deviation 0.000 Å). In 2–5, the \(\text{Rh}_2\text{X}_2\) functionality deviates from the planarity, with the Rh atoms tilted toward iodine centers of \(\text{REWG}-\text{I}\) species; the largest r.m.s. deviation of the core was found in 5 (0.302 Å for Br1).

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Figure 1. $\text{Ar}^\mu(\mu_4^4\text{-I}) \cdots [\text{Rh}_2\text{Cl}_2]$ and $\text{REWG}(\mu_2^2\text{-I}) \cdots [\text{Rh,Rh}]$ interactions in 1 (a), 2 (b), 3 (c), 4 (d), and 5 (e). Hereinafter the contacts shorter than $\Sigma R_{vdW}$ are given by dotted lines, and thermal ellipsoids are shown with the 50% probability.

Figure 2. 1D-chain (a) and the isolated clusters (b,c) formed by the $\text{Ar}^\mu(\mu_4^4\text{-I}) \cdots [\text{Rh}_2\text{Cl}_2]$ (1) and $\text{REWG}(\mu_2^2\text{-I}) \cdots [\text{Rh,Rh}]$ (2, 4) contacts.
Common to all structures is that I···Rh distances are significantly shorter than the sum of vdW radii ($\Sigma \rho_{vdW}$), considering the radius of I is 1.98 Å (the Bondi I radius), and the radius of Rh is 2.02 Å (the Batsanov Rh radius); the Rh radius is not given in the Bondi vdW radii list (Table S3).

The most intriguing feature of the crystal structure of 1 is the unique tetrafurcated $\text{Ar}^2(\mu_3-\text{I})$···[$\text{RhCl}_2^-$] short contacts, where one I center of $\text{R}^\text{EWG}$–I interacts with all four atoms of the Rh$_2$Cl$_2$ core—thus forming 1D-chain ⋯[$\text{RhCl}_2^-]$···[I($\text{Ar}^2$)]⋯[$\text{RhCl}_2^-]$ involving XB between iodine atoms of the perfluoroarene linkers and the Rh$_2$Cl$_2$ cores (Figure 2a). Notably, such XB-involving assembly through simultaneously two metal centers had not been conducted before this study.

In contrast to 1, the crystal structure of 2 featured two [RhBr(COD)$_2$] per one C$_6$F$_4$I$_2$ entity; $\text{R}^\text{EWG}$–I links to the Rh$_2$Br$_2$ core of [RhBr(COD)$_2$] via two bifurcated $\text{R}^\text{EWG}(\mu_2-I)$···[Rh, Rh] short contacts (Figure 2b). This assembly results in a distortion of the Rh$_2$Br$_2$ entity, where the Rh atoms are tilted toward an I center of C$_6$F$_4$I$_2$. A similar 2:1 supramolecular cluster was found in 4 (Figure 2c). In the structures of 3 and 5, $\text{R}^\text{EWG}$–I and [$\text{RhCl}(\text{COD})]$$_2$ form 1:1 isolated clusters (Figure 1c,e), which are linked to each other via $\text{R}^\text{EWG}(\mu_2-I)$···[Rh, Rh] interactions. One of these contacts, namely C1S–I1S···Rh1 in 5, is the shortest one (3.4255(5) Å) among the other iodine–rhodium(I) contacts observed in this study. Other types of noncovalent interactions in the studied systems are represented by hydrogen bonds (HBs) and lone pair–$\pi$-hole (LP–$\pi$) interactions and are considered in Sections S1.3–1.4.

The variable-temperature XRD studies for 1 and 3 (five XRD experiments with heating from 100 to 300 K with 50 K per step), taken as examples, were performed to compare the response of the detected intermolecular contacts on temperature (Section S2). The $\text{R}^\text{EWG}(\mu_2-I)$···[Rh, Rh] contacts in both structures were found to be pronouncedly less flexible with respect to the temperature change than the HBs and LP–$\pi$ interactions. The largest lengthening of interatomic distances corresponding to the $\text{R}^\text{EWG}(\mu_2-I)$···[Rh, Rh] interactions is observed for C1S–I1S···Rh1 contact in 3; the I1S···Rh1 distance increases on 0.062 Å upon heating with 3.5952(6) Å at 100 K (Table S8).

Our search and processing of the Cambridge Structural Database (CSD) revealed only three relevant structures featuring I···[Rh]$^+$ short contacts (Section S3), whose geometric features are substantially different for all three structures and are consistent with coordinative XB,44,63–65 semicoordination38 bonding (Table S9). In structure NOCNOL (Figure S5b), we identified the previously overlooked C6–I1···Rh1 contact between two [Rh(acac)(CO)(P(C$_6$F$_5$I-2)Ph$_2$)$_2$] entities, with geometric characteristics specific to $\text{d}^\text{d}$-involving 4B,42,47 bonding ($\Sigma \rho_{vdW}$) less than 4.00 Å and angle distribution around the I atom ($\angle$C6–I1···Rh1) 169.02(8)$^\circ$) corresponding to XB according to the IUPAC criteria.46

We used the DFT study in combination to MEP, QTAIM, NCIplot, natural bond orbital (NBO), and ELF computational tools to shed light on the nature of the Rh–involving interactions. The molecular electrostatic potential (MEP) surfaces of the three XB donor molecules are represented in Figure S6. As expected, the iodofrom presents the least intense oh (+25.7 kcal/mol, Figure S6a) and for C$_6$F$_5$I$_2$ and C$_6$F$_5$I rh (+33.2 and +35.0 kcal/mol, respectively) are larger and more intense. The MEP surfaces of the [RhCl(COD)]$_2$ complex in both conformations (planar and nonplanar Rh$_2$Cl$_2$ core) are given in Figure 3. In the planar conformation, the minimum value of MEP is located at the Cl atoms (−23 kcal/mol), and it is slightly reduced at the Rh atoms (−19 kcal/mol). In the nonplanar conformation, the minimum value is found between the Cl atoms (−30 kcal/mol), and the value at the opposite site is reduced to −15 kcal/mol. Therefore, the MEP analysis reveals that the Ar$_2^2$(μ$_3$-I)···[RhCl$_2^-$] and $\text{R}^\text{EWG}(\mu_2-I)$···[Rh, Rh] interactions are electrostatically favorable, where the electron-rich Rh$_2$Cl$_2$ core interacts with the oh at the I atom, as is typical in XB.

The results of QTAIM analysis and DFT calculations are gathered in Figure 4 (for 1–2) and Figure S7 (3–5). The distribution of bond critical points (CPs) and bond paths in the dimer of 1 reveals that the I atom is connected to the four atoms of the Rh$_2$Cl$_2$ core by means of four CPs. The value of $\rho(r)$ at the bond CP (connecting the I to the closest Cl atom) is the largest one. In 2–5, the I atom is interconnected to both Rh atoms of the core by two bond CPs and bond paths. Remarkably, in these complexes, it is not connected to the bridging Cl/Br ligands because of the different geometry of the Rh$_2$X$_2$ core compared with 1. The values of $\rho(r)$ at the bond CPs that characterize the I···Rh interaction correlate with the experimental distances (Table S3), that is, the $\rho(r)$ values at the CPs increase as the I···Rh distance decrease. In Figures 4 and S7, we also included the interaction energies that are moderately strong, ranging from −8.05 kcal/mol to −9.89 kcal/mol, in agreement with the MEP analysis commented above (Figures 3 and S6). The QTAIM analysis reveals that there are additional interactions that also stabilize the assembly apart from the $\text{R}^\text{EWG}(\mu_2-I)$···[Rh, Rh] interaction, which are C–H···F and/or C–H···I contacts. To measure the contribution of the $\text{R}^\text{EWG}(\mu_2-I)$···[Rh, Rh] interaction, some theoretical models (Figures 4c,d and S7d–f) were
concluded that the REWG(whole systems to those of the mutated systems, it can be
strong H-bonding. By comparing the interaction energies of the
interaction ranges from
shape and extension of the green (meaning weak attractive)

Figure 4. (a,b) AIM distribution of bond, ring, and cage critical points
(green, yellow, and blue spheres, respectively) and bond paths for
compounds 1 and 2. (c,d) Theoretical models used to evaluate the
REWG(μ2-I)···[Rh,Rh] interactions.

used where the COD was simplified (replaced by two ethene units)
and, consequently, the C−H···F/I are not formed. The
interaction energies of the mutated complexes are given at the
bottom of figures and reveal that the REWG(μ2-I)···[Rh,Rh]
interaction ranges from −6.4 to −7.56 kcal/mol, thus similar to
strong H-bonding. By comparing the interaction energies of the
whole systems to those of the mutated systems, it can be
concluded that the REWG(μ2-I)···[Rh,Rh] XB interaction clearly
dominates the formation of the assemblies.

The noncovalent interaction plot (NCIplot) has been also
computed because it is convenient to identify which regions in a
supramolecular complex interact (Figures 5 and S8). In 1−5, the
shape and extension of the green (meaning weak attractive)

iso-surfaces clearly demonstrate that indeed the interaction of the
C−I bond is with the whole [Rh2Cl2] core with some
participation of the C−H bonds of the COD ligand. Therefore,
the energetic MEP and NCIplot results indicate that the
interaction between the XB donor molecules and the [RhX−
(COD)]2 can be defined as an XB, where the whole Rh2X2 core
interacts as an unconventional electron donor.

Further insight into the nature of the I⋯Rh interactions can be

gained from the 3D electron deformation density (EDD) plot
(Figure 6) as it provides information on charge concentration

CC) and charge depletion (CD) regions in the molecule. In
the case of 1, the 3D EDD plot clearly depicts the charge depletion
region of I facing an extended charge concentration region on
both Rh-atoms and one Cl atom of the planar Rh2Cl2 core. In 2,
the 3D EDD plot is slightly different, showing that the CC region
is located at the Rh-atoms, without any participation of the
bromine atoms. Moreover, the CD region of I is significantly
polarized toward both Rh atoms. This EDD analysis supports
the halogen bonding nature of the REWG(μ2-I)···[Rh,Rh]
contacts and evidence that in both complexes the interaction
is attractive in nature, in agreement with the NCIplot and
energetic analyses. Finally, the EDD plots also reveal higher
charge displacement for the H atoms of COD pointing to the
perfluoroarene molecule in the adduct of compound 2
compared with 1, in line with the QTAIM distribution of CPs
and NCIplot shown in Figures 4−S.

In an effort to investigate the existence of LP → σ*(C−I)
interactions in compounds 1 and 2, we have performed a NBO
analysis focusing on the second-order perturbation analysis,
since it is convenient to evaluate donor−acceptor interactions.
The results are summarized in Table S10, where we gather all
orbital donor−acceptor interactions involving the antibonding
C−I bond and their concomitant stabilization energy, E(C). In
both complexes, we found two contributions, one from the filled
d2(Rh) orbital to the empty σ*(C−I) and a second
contribution from one free LP of the halogen atom to the
σ*(C−I). In case of 1, the latter contribution [LP(Cl) → 
σ*(C−I)] is more relevant than the former d2(Rh) → σ*(C−
I). In contrast, in compound 2, the LP(Br) → σ*(C−I)
is negligible, and the most important contribution is the
d2(Rh) → σ*(C−I), which is slightly larger than that of compound 1, in
line with the distortion of the Rh2Br2 core in 2, where the Rh
atoms are tilted toward an I center of C6F4I2.

Figure 5. NCI surfaces of the dimers of 1 (a) and 2 (b). The gradient
cutoff is ρ = 0.04, the isosurface is s = 0.35 au, and the color scale
is −0.04 < sign(z)ρ < 0.04 au. NCI surfaces for the dimers of 3−5 are
given in Figure S8.

Figure 6. Theoretical (M06−2x/def2-TZVP) 3D electron deformation
density (EDD) plots in 1 (a) and 2 (b). CC and CD values are
represented by blue and red colors. Δρ(r) isosurfaces are drawn at
0.005 au.
To further verify whether the observed I–Rh contacts are XBs, we performed Electron Localization Function (ELF) analysis for 1–5. A combination of the ELF and QTAIM methods is represented in Figures 7 and S9; ELF projections for the ArF(μ-1)···[Rh2Cl2] and RSWG(μ-1)···[Rh2Cl2] contacts were plotted along with CPs and bond paths. The inspection of the ELF data proves the XB nature of the ArF(μ-1)···[Rh2Cl2] and RSWG(μ-1)···[Rh2Cl2] interactions involving iodine centers of Rh donors and [Rh2X3] metal cores of the rhodium(I) complexes. The noncovalent XB nature of the detected contacts was confirmed theoretically by the DFT calculations using several computational tools (QTAIM, DFT energies, NCI and EDD plots, MEP surfaces, ELF analysis).

To summarize, we found the three-center XB that involves simultaneously two metal centers functioning as integrated o-h acceptor toward iodine(I)-based o donors. Moreover, we performed the assembly through two- or more metal-involving XBs exploring the potential of …[RhCl2]−I(ArF)···[RhCl2] or tetrafurcated ArF(μ-1)···[Rh2Cl2] interactions.

### CONCLUSIONS

We examined the geometric and energetic features of the I⋯[Rh3] interactions using the combined experimental and theoretical approaches to arrive at a comprehensive understanding of these forces involved where positively charged rhodium(I) centers are functioning as Lewis bases. We demonstrated that the [RhX(COD)]2 (X = Cl, Br) complexes can be cocrystallized with RSWG−Is forming cocrystals 1–5. Upon analysis of noncovalent forces in the XRD structures of 1–5, in addition to rather conventional intermolecular contacts, we recognized hitherto unknown ArF(μ-1)···[Rh2Cl2] and RSWG(μ-1)···[Rh2Cl2] interactions involving iodine centers of Cl donors and [Rh2X3] metal cores of the rhodium(I) complexes. The noncovalent XB nature of the detected contacts was confirmed theoretically by the DFT calculations using several computational tools (QTAIM, DFT energies, NCI and EDD plots, MEP surfaces, ELF analysis).

To summarize, we found the three-center XB that involves simultaneously two metal centers functioning as integrated o-h acceptor toward iodine(I)-based o donors. Moreover, we performed the assembly through two- or more metal-involving XBs exploring the potential of …[RhCl2]−I(ArF)···[RhCl2] or tetrafurcated ArF(μ-1)···[Rh2Cl2] interactions.

### EXPERIMENTAL SECTION

**Starting Materials and Cocry crystallization**

RhCl3·3H2O, RhBr3·3H2O, 1,5-cyclooctadiene, Na2CO3, 1,4-C6F4I2, C12F9I42 and [RhX(COD)]2 (X = Cl, Br)43 were synthesized via previously published procedures. Single crystals of 1–3 and 5 were obtained by slow evaporation of a dichloromethane solution (4 mL) of a mixture of the corresponding [RhX(COD)]2 (14 mmol) and REWG (7 mg, 14 mmol); the reaction mixture was taken in 1:1 molar ratio at RT. Single crystals of 4 were prepared from a dichloromethane–nitromethane solution (1:1, v/v, 4 mL) of a mixture of [RhCl(COD)]2 (7 mg, 14 mmol) and C12I4 (7 mg, 14 mmol); the reaction mixture was stirred under ultrasonic treatment for complete homogenization, and then left to stand at RT for slow evaporation. Yellow crystals of 1–5 suitable for XRD were released after 3–4 d.

**X-ray Structure Determinations**

Suitable single crystals of 1–5 were studied on a Bruker Apex II Duo CCD diffractometer (Mo Kα (λ = 0.71073), graphite monochromator, ω-scans). The crystals of 2, 4, and 5 were kept at 120 K during data collection. The intensity data were integrated by the SAINT program44 and were corrected for absorption and decay using SADABS.45 All structures were solved by direct methods using SHELXS44 and were refined against F2 using SHELXL-2018.46 All non-hydrogen atoms were refined with individual anisotropic displacement parameters. The hydrogen atoms in all structures were placed in ideal calculated positions and refined as riding atoms with relative isotropic displacement parameters.

Variable-temperature single-crystal XRD studies of 1 and 3 were performed using Bruker APEX II DIO diffractometer equipped with Oxford Cryosystems Cobra low-temperature device and CCD detector. Diffraction data sets were collected (Mo Kα radiation, graphite monochromator, ω-scans) at five temperatures (100, 150, 200, 250, 300 K) for the same crystal sample once mounted on a glass needle using two-part adhesive. No structural phase transitions have been detected for crystals 1 and 3 in the studied temperature range. The main crystallography data and refinement details are listed in Tables S1, S6–S7. CCDC numbers 2054735–2054747 contain all supporting structural and refinement data.
Computational Details

The energetic features of the complexes included in this study were calculated at the M06-2X/def2-TZVP$^{59}$ level of theory using the crystallographic coordinates. For the calculations, the GAUSSIAN-16 program has been used.$^{47}$ The basis set superposition error for the calculation of interaction energies has been corrected using the counterpoise method.$^{60}$ The MEP surfaces have been computed at the same level of theory and represented using the 0.001 au isosurface. The NCI plot index$^{58}$ computational tool has been used to characterize noncovalent interactions using the M06-2X/def2-TZVP level wave function. They correspond to both favorable and unfavorable interactions, as differentiated by the sign of the second density Hessian eigenvalue and defined by the isosurface color. The color scheme is a red-yellow-green-blue scale with red for $\rho_{\text{rep}}$ (repulsive) and blue for $\rho_{\text{at}}$ (attractive). Yellow and green isosurfaces correspond to weakly repulsive and attractive interactions, respectively. The QTAIM analysis$^{50}$ has been performed using the AIMAll program at the same level of theory.$^{31}$ The EDD plots were computed using the M06-2X/def2-TZVP$^{29}$ wave function by means of the MULTIWFN v. 3.7 program$^{52}$ by considering the halogen donor and metal complex as fragments. The EDD grid data generated with the MULTIWFN v. 3.7 program was saved as a cube file and visualized using Gaussview program.$^{53}$ The NBO 3.1 has been used to evaluate donor–acceptor interactions$^{54}$ as implemented in GAUSSIAN-16. The ELF analysis$^{55–58}$ has been performed in MULTIWFN 3.7.$^{32}$

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacsau.1c00012.

XRD studies (Sections S1–S2), processing of the CSD (Section S3), and theoretical calculations (Section S4) (PDF)

Accession Codes

Supporting crystallographic data have been deposited at Cambridge Crystallographic Data Centre (CCDC 2054735–2054747) and can be obtained free of charge via www.ccdc.cam.ac.uk/data_request.cif.

AUTHOR INFORMATION

Corresponding Authors

Antonio Frontera  – Department of Chemistry, Universitat de les Illes Balears, 07122 Palma de Mallorca (Balears), Spain; orcid.org/0000-0001-7840-2139; Email: toni.frontera@uib.es

Vadim Yu. Kukushkin  – Institute of Chemistry, Saint Petersburg State University, 199034 Saint Petersburg, Russian Federation; Laboratory of Crystal Engineering of Functional Materials, South Ural State University, 454080 Chelyabinsk, Russian Federation; orcid.org/0000-0002-2253-085X; Email: v.kukushkin@spbu.ru

Authors

Anastasiya A. Eliseeva  – Institute of Chemistry, Saint Petersburg State University, 199034 Saint Petersburg, Russian Federation; orcid.org/0000-0003-2982-3804

Daniil M. Ivanov  – Institute of Chemistry, Saint Petersburg State University, 199034 Saint Petersburg, Russian Federation; orcid.org/0000-0002-8658-7281

Anton V. Rozhkov  – Institute of Chemistry, Saint Petersburg State University, 199034 Saint Petersburg, Russian Federation; orcid.org/0000-0002-8658-7281

Ivan V. Ananyev  – A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 119991 Moscow, Russian Federation; orcid.org/0000-0001-6867-7534

Complete contact information is available at: https://pubs.acs.org/doi/10.1021/jacsau.1c00012

Author Contributions

A.A.E.–conceptualization, investigation, writing; D.M.I.–conceptualization; A.V.R.–investigation; I.V.A.–investigation; A.F.–computational study, writing; V.Y.K.–conceptualization, writing, project administration.

Notes

The authors declare no competing financial interest.

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ABBREVIATIONS

XB, halogen bond(ing); σh, σ-hole; COD, 1,5-cyclooctadiene; R$^{\text{Iang}}$–I, organic iodine(I)-based species featuring electron-withdrawing group; XRD, X-ray diffraction; $2\Sigma_{\text{vdW}}$, sum of vdW radii; HB, hydrogen bond; LP–π, lone pair–π-hole interaction; CSD, Cambridge Structural Database; MEP, molecular electrostatic potential; CP, bond critical point; NCIPlot, noncovalent interaction plot; EDD, electron deformation density; CC, charge concentration; CD, charge depletion; NBO, natural bond orbital; ELF, electron localization function; ED, electron density; ESP, electrostatic potential; CCDC, Cambridge Crystallographic Data Centre.

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