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Reverse Sandwich Structures from Interplay between Lone Pair $-\pi$ -Hole Atom-Directed C···d_z²[M] and Halogen Bond Interactions

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Supporting Information

ABSTRACT: 4-Bromo- and 4-iodo-5-nitrophthalonitriles (BNPN and INPN, respectively) were cocrystallized with the metal acetylacetonates $[M(acac)_2]$ (M = Pd (1), Pt (2)) to give the three adducts 1·2BNPN, 2·2BNPN, and 1·2INPN, exhibiting reverse arene sandwich solid-state structures. The inspection of the XRD data for the adducts revealed new types of (lone pair)[M]··· π -hole noncovalent interactions, namely atom-directed C···d_z²[M] noncovalent contacts. In addition, C–X···(O,O) (X = I, Br) bifurcated halogen bonds (XBs) along with some other types of short contacts were recognized. The XRD experiments were supported by Hirshfeld surface analysis and DFT calculations: i.e., topological analysis of the electron density distribution within the framework of the QTAIM method at the ω B97XD/DZP-DKH level of theory. Estimated energies of all studied noncovalent contacts vary from 0.6 to 3.8 kcal/mol.

1. INTRODUCTION

Although lone pair $-\pi$ (lp $-\pi$) and anion $-\pi$ interactions have been recognized only rather recently (for reviews see refs 1–5), for the past few years they have been efficiently utilized in mastering molecular materials,^{6–9} molecular recognition,¹⁰ drug design,^{11–14} catalytic process development,^{15–17} organic catalysis,^{18–21} and many other fields. Generally, (anion/lp) $-\pi$ interactions are defined as favorable noncovalent contacts between a negatively charged center or a lone pair of a neutral center and electron-deficient π systems.^{15,22,23} (Anion/lp) $-\pi$ interactions can be atom-directed,^{13,24} bond-directed (for instance, with a double bond in the electron-deficient arene ring^{25,26}), or cycle-directed: e.g., with arenes²⁷ and heterocycles²⁸ (Figure 1).



Figure 1. Types of $(anion/lp) - \pi$ interactions.

 $\begin{array}{c} & \text{Blurcated C-X-(0, 0) } B \\ \hline \\ & \downarrow \\$

Nonmetal centers bearing lone pairs, such as O, N, S, halogens, etc., typically act as acceptors for these interactions, whereas only a very few examples of lp(metal)… π -hole (π h) contacts^{29–31} have been documented. In our previous work,²⁹ we reported on the construction of *reverse sandwich structures* based upon square-planar platinum(II) and palladium(II) complexes and perfluoroarenes. Assembly of these species occurs via d_z²[M]… π h interactions, and the charge distribution at the metal center and at the arenes (Figure 2) is opposite to that of the classic sandwich complexes insofar as the positively



Figure 2. Reverse sandwich structure with schematic charge distribution.

Received: October 9, 2019 Revised: December 5, 2019 Published: December 19, 2019 charged metal center acts as a nucleophile.³² In the reported series of the reverse sandwiches,²⁹ the $d_z^{2}[M]\cdots\pi h$ interaction was directed strictly toward the centroid of the πh system (for acetylacetonate complexes; Figure 3a) or slightly deviated from the πh center (for the porphyrin Pt^{II}, the shift of the metal center projection from the ring center was 0.727(5) Å; Figure 3b).



Figure 3. Types of reverse arene sandwiches.

In a continuation of the previous work, we attempted the assembly of the $[M(acac)_2]$ (M = Pt (1), Pd (2)) complexes with 4-X-S-nitrophthalonitriles (X = Cl, Br, I; Figure 4), which



Figure 4. π -Hole donors studied in this work with atom numbering of C11 that is involved in $C \cdots d_z^2[M]$ interactions.

represent a new type of π h donor with an asymmetric electrostatic potential (ESP) profile. Here a π (hole) donor is a species featuring a region of positive electrostatic potential surface similarly to the σ (hole) donor defined by Politzer.³³ In recent years, the definition of π (hole) donor has become a commonly accepted term and it has been repeatedly used.^{34–36} In newly obtained sandwiches, in contrast to those observed previously, the lp(d_z²)- π h linkage is ideally oriented to the C11 of the phthalonitrile ring to give hitherto unreported atom-directed C···d_z²[M] interactions (Figure 3c). All of our results are consistently disclosed in sections that follow.

2. RESULTS AND DISCUSSION

2.1. σ/π -Hole Donors for This Study. As we were interested in expanding the list of simultaneous σ -hole (σ h) and π h donors (for our recent reports see refs 29, 30, 37, and 38), in this work we focused our attention on the three haloarenes depicted in Figure 4. In this series, 4-bromo-5-nitrophthalonitrile (BNPN) is the reagent with a broad

spectrum of applications. It is conventionally used in organic synthesis (including the design of novel monoamine oxidase A inhibitors^{39–42}) and in the development of phthalocyanine-based functional materials.^{43–48} Owing to the availability of strong electron-withdrawing groups (one nitro and two cyano groups) as well as a suitable leaving group (bromide anion), BNPN was recognized as a highly reactive substrate toward a diversity of S_NAr reactions. However, the ability of BNPN to serve as a strong σ h donors in the generation of halogen bonds (XBs) has never been studied. 4-Chloro-5-nitrophthalonitrile (CNPN) is also known, but its synthetic application, in comparison to BNPN, is limited to only two cases.^{49,50} 4-Iodo-5-nitrophthalonitrile (INPN) is an as yet unreported compound, and its synthesis and characterization are given in section 4.2.

2.2. X-ray Structure of INPN and σ/π -Hole Donor Properties of the Haloarenes. In our experiments, BNPN and CNPN upon crystallization from 1,2-dichloroethane and dimethyl sulfoxide, respectively, at room temperature gave crystals whose XRD structures exhibit NO₂/X disorder (Supporting Information). Previously the XRD structure of BNPN has been reported by Lin et al.,⁵¹ who did not observe the disorder, but the structure is still characterized by a high *R* value, thus making it unsuitable for an accurate inspection of noncovalent interactions.

In contrast, INPN forms a well-ordered structure, where we identified the C–I···N≡C XB⁵² (the distances are 3.006(6) Å for I1···N2 and 3.293(8) Å for I2···N5, which are less than the corresponding $\sum R_{vdW}$ (3.53 Å); Figure 5) along with lp(O)··· π h (the distances are 3.059(8) Å for O2···C11, 3.189(9) Å for O2··· C12, 3.086(9) Å for O4···C2, 3.128(8) Å for O4···C3, and 3.134(8) Å for O4···C4, which are less than the corresponding $\sum R_{vdW}$ (3.22 Å)) and lp(N)··· π h (the N6···C5 distance is 3.246(9) Å, which is less than the corresponding $\sum R_{vdW}$ (3.25 Å)) contacts (Figure 6).

It is noteworthy that relevant C–I···N≡C linkages were previously identified⁵³⁻⁶⁴ upon studies of linear supramolecular chains and some other more complex structures held by XB. Similar C···O lp(O)··· π h short contacts were observed in the structures of picryl iodide⁶⁵ and 2-nitroperfluorobiphenyl.⁶⁶ The related π h ability of *sym*-trichlorotrinitrobenzene toward self-association⁶⁷ and toward diacetone diperoxide⁶⁸ was also documented. In turn, lp(N)··· π h interactions involving cyano groups were identified in a substantial number of phthalonitriles, including hexa-⁶⁹ and tetracyanobenzenes,⁷⁰ and also tetrafluorophthalonitriles.⁷¹

To estimate the $\sigma h/\pi h$ donor abilities of CNPN, BNPN, and INPN, we calculated the molecular surface electrostatic potential $V_{\rm S}(\mathbf{r})$ (function that measures the electrostatic interaction between a unit point charge placed at \mathbf{r} and the system of interest) and analyzed ESP at the M06-2X/CEP-121G level of theory for the optimized equilibrium model structures of the three haloarenes (Figure 7). The estimated values of surface maxima located on the σ h of the halogen atoms ($V_{\rm S}(\mathbf{r})_{\max(\sigma\text{-hole})}$) and on the π h of the phenyl rings (above and below the plane) ($V_{\rm S}(\mathbf{r})_{\max(\pi\text{-hole})}$) in the optimized equilibrium model structures are given in Table 1. The values of $V_{\rm S}(\mathbf{r})_{\max(\sigma\text{-hole})}$ increase significantly in the order Cl < Br < I, whereas values of $V_{\rm S}(\mathbf{r})_{\max(\pi\text{-hole})}$ remain virtually unchanged.

2.3. General Description of the X-ray Structures of (1,2)·2BNPN and 1·2INPN. The complexes $[M(acac)_2]$ (M = Pd (1), Pt (2)) were corrystallized with BNPN or INPN in a 1:1 molar ratio upon evaporation of their CHCl₃-MeOH solutions



Figure 5. C-I···N=C XB in the crystal structure of INPN. Two crystallographically independent molecules of INPN are shown in each chain.



Figure 6. $lp(O) \cdots \pi h$ and $lp(N) \cdots \pi h$ interactions in the crystal structure of INPN. Two crystallographically independent types of INPN molecules as πh donors are shown.

to form the isostructural adducts (1,2)·2BNPN and 1·2INPN, respectively. All attempts to cocrystallize 2 with INPN and also 1 and 2 with CNPN were unsuccessful, and only crystals of the starting materials were obtained upon evaporation of the corresponding mixtures.

In (1,2)·2BNPN and 1·2INPN, the M–O, C2–O1, and C2–C3 bond distances and the O–M–O angles are equal, within 3σ , to those in unassociated 1^{72} and 2^{73} as well as to those in the previously reported adducts (1,2)·2(1,4-FIB) (1,4-FIB = 1,4-diiodo-2,3,5,6-tetrafluorobenzene)^{31,74} and (1,2)·C₆F₆²⁹ (Table S2).

Despite the symmetry difference between the BNPN and INPN adducts (space group *P*1 for BNPN and *P*2₁/*n* for INPN), the structures display a similar motif when one $M(acac)_2$ unit is surrounded by eight haloarenes (Figure 8). With two exceptions, which will be considered later in section 2.7, all adducts display the same noncovalent interaction pattern, including C…M interactions and two bifurcated XBs along with some other less important contacts. Previously Rissanen and colleagues⁷⁵ reported a series of 1,4-FIB adducts with pincer (PCP)Pd^{II} chloride and bromide complexes, in which similar



Table 1. Results of the Hirshfeld Surface Analysis for 1 and 2 Fragments in the X-ray Structures of (1,2)·2BNPN and 1· 2INPN

X-ray structure	contributions of different intermolecular contacts to the molecular Hirshfeld surface ^a					
1·2BNPN	O-H 26.6%, H-H 22.7%, N-H 12.8%, C-H 10.6%, Br-O 5.3%, Br-H 5.0%, C-C 5.0%, O-C 4.6%, Pd-H 2.8%, O-N 1.5%, N-C 1.5%, Br-C 1.4%					
2·2BNPN	O-H 26.3%, H-H 22.2%, N-H 12.9%, C-H 10.7%, Br-O 5.3%, Br-H 5.3%, C-C 5.3%, O-C 4.9%, Pt-H 2.7%, O-N 1.7%, N-C 1.4%, Br-C 1.3%					
1·2INPN	O-H 21.6%, H-H 19.8%, N-H 17.1%, C-H 11.6%, I-O 6.5%, O-C 5.8%, I-H 5.6%, C-C 5.2%, Pd-H 2.3%, N-C 1.8%, O-N 1.5%					
^a The contributions of all other intermolecular contacts do not exceed						

"The contributions of all other intermolecular contacts do not exceed 1%.

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H C N O Br I Pd

Figure 8. Environments of 1 in 1·2BNPN (left) and 1·2INPN (right): views along the *a* axis (top) and *b* axis (bottom). Differently located substituted phthalonitriles are indicated by arrows.

molecular surroundings of the metal complexes were found for crystals of different symmetry group.

2.4. Hirshfeld Surface Analysis for the X-ray Structures. The analysis of molecular Hirshfeld surfaces of X-ray structures gives the possibility of an additional insight into the nature of intermolecular interactions in the crystal state. We carried out this analysis for 1 and 2 fragments in the X-ray structures of (1,2)·2BNPN and 1·2INPN to understand what kinds of intermolecular contacts give the largest contributions in crystal packing (Table 1). The results of the analysis reveal that in all cases crystal packing is determined primarily by intermolecular contacts involving hydrogen atoms: the contributions of O–H and H–H contacts are the greatest ($\geq 20\%$ for each of these two types of contacts), the contributions of N-H and C–H contacts are smaller, but also significant ($\geq 10\%$ for each of these two types of contacts), contributions of most contacts involving halogen atoms (viz. Br-O, Br-H, I-O, and I–H) as well as C–C contacts reach \geq 5% for each of these types of contacts, whereas contributions of Hal-C contacts are very small (do not exceed 2%), and contributions of other types of contacts (viz. O–C, M–H, O–N, and N–C) are in the range of 1 - 5%

Figure 9 depicts the Hirshfeld surfaces for (1,2)·2BNPN and 1·2INPN. For the visualization, we have used a mapping of the normalized contact distance (d_{norm}) . In these Hirshfeld surfaces, the regions of shortest intermolecular contacts (viz. C–X··· (O,O) bifurcated halogen bonds) are visualized by red circled areas.

Notably, the C···M interactions could also be alternatively considered as $d_{z^2}(Pd,Pt)\cdots\sigma^*(C-H)$ contacts. Conventionally the Hirshfeld analysis employs Bondi vdW radii, which are, as recognized in many reports, underestimated. Insofar as the C···



Figure 9. Hirshfeld surfaces for (1,2)·2BNPN and 1·2INPN (from left to right).

M interactions are slightly higher than the sum of Bondi vdW radii, the Hirshfeld analysis does not recognize these contacts, and in order to prove their existence from a theoretical viewpoint, we have carried out DFT calculations and QTAIM analysis (see section 2.8).

2.5. Atom-Directed $\mathbb{C} \cdot \cdot \cdot d_2^2 [\mathbb{M}^{II}]$ Interactions in the Shifted Reverse Sandwich Structures. All adducts exhibit the reverse arene sandwich structures (Figure 10). Although the $\mathbb{C} \cdot \cdot \mathbb{M}$ distances (3.498(2) and 3.434(3) Å for \mathbb{Pd}^{II} and 3.483(7) Å for \mathbb{Pt}^{II}) are larger than $\sum R_{vdW} (R_{vdW}(M) + R_{vdW}(C) = 3.33 Å$ for \mathbb{Pd} and 3.47 Å for \mathbb{Pt}), these weak interactions (0.9–1.3 kcal/mol) were confirmed by appropriate theoretical calculations (section 2.8). For comparison, we recently reported similar reverse arene sandwiches ($1 \cdot \mathbb{C}_6 \mathbb{F}_6$ and $2 \cdot \mathbb{C}_6 \mathbb{F}_6$), where $\mathbb{C} \cdot \cdot \mathbb{M}$ distances are even somewhat higher (3.5119(8) Å for $1 \cdot \mathbb{C}_6 \mathbb{F}_6$ and 3.557(2) Å for $2 \cdot \mathbb{C}_6 \mathbb{F}_6^{29}$), while values of the minimal $\mathbb{C} \cdot \cdots \mathbb{M}$ — O angles (α in Figure 11) are quite comparable with those of the current structures: viz. $68.72(7)^\circ$ ($1 \cdot 2 \mathbb{B} \mathbb{N} \mathbb{P} \mathbb{N}$), and 73.89(8)° ($1 \cdot 2 \mathbb{I} \mathbb{N} \mathbb{P} \mathbb{N}$) vs 67.70(3) and 68.11(4)° ($1 \cdot \mathbb{C}_6 \mathbb{F}_6$) and 68.20(8) and 68.51(8)° ($2 \cdot \mathbb{C}_6 \mathbb{F}_6$; see ref 29).

The comparison of the calculated ESP $(V_{\rm S}(\mathbf{r}))$ profiles for the three haloarene structures displayed above (section 2.2) and



Figure 10. C···M and C···Br noncovalent interactions in (1,2)·2BNPN and 1·2INPN.



Figure 11. Comparison of the interaction angles.

ESP ($V_{\rm S}(\mathbf{r})$) for M(acac)₂ given in our previous work²⁹ indicate that the C atoms of the arene ring exhibit substantially more positive ESP in comparison to those on the Pd^{II} and Pt^{II} centers. In the C···M contact, the aromatic C atom serves as an electrophilic π h donor, whereas the [M^{II}] center via its d_z² orbital acts as a nucleophile; the same situation has been previously observed²⁹ at the reverse sandwiches based upon symmetric perfluoroarenes. However, in this case one C···M contact, namely C11···M, is significantly shorter than the other C···M distances (Table 2). The DFT calculations conducted verified the availability of BCP solely for the C11···M interaction (section 2.8). On the basis of these data, the C11····M contact can be classified as an atom-directed lp interaction involving the d_z² orbital of the metal center. More detailed information on these interactions is collected in Table 4 (section 2.7).

The M···C interactions in the adducts could also be interpreted as agostic or anagostic⁷⁶ in view of the C–H covalent bond near the contact. However, we assume that the term "agostic interaction" is not sufficiently accurate because of the following. (i) The M···H distances (3.167, 3.207, and 3.167 Å in 1·2BNPN, 1·2INPN, and 2·2BNPN, correspondingly) are too far from the corresponding Bondi vdW sums (2.83 Å for Pd and 2.95 Å for Pt). (ii) The metals in 1 and 2 are nucleophiles





rather than electrophiles, as verified by the ESP calculations. This is also in line with their ability to form $lp(M)\cdots \pi h$ interactions with C_6F_6 , C_6F_5Cl , and perfluoropyridine.²⁹ (iii) There is electron deficiency of the C–H covalent bond caused by the collective action of four electron-withdrawing groups in BNPN and IPNP. The term "anagostic interaction" is more acceptable, taking into account the philicity (or, in other words, high affinity) of the interacting centers, but the M…C distances are still closer to Bondi vdW sums than the M…H distances. Moreover, our theoretical calculations (section 2.8) indicated the bond paths and the (3, -1) bond critical points between M and C atoms, rather than between M and H atoms.

Insofar as the energy of the C11 \cdots d_z²[M^{II}] contacts is small and it is less than that for C–X \cdots (O,O) bifurcated XB (Table S6), we assume that the described centroid to atom shift in the reverse sandwich structures is caused by an overlap of various intermolecular forces, which generally can be considered as the packing effects.

2.6. C-X···(O,O) Bifurcated Halogen Bonds. In the crystal structures of (1,2)·2BNPN and 1·2INPN, we identified intermolecular bifurcated XBs between XNPN and the two O atoms of the acetylacetonate ligands (Figure 12 and Table 3). The Br…O1 and Br…O2 distances (3.263(3), 3.117(2) Å for 1. 2BNPN and 3.314(7), 3.164(6) Å for 2.2BNPN) are substantially less than the corresponding sum of Bondi vdW radii⁷⁷ ($\sum R_{vdW} = 3.37$ Å), and the C6–Br…O2 contact angle (164.76(9)° for 1.2BNPN and 164.2(3)° for 2.2BNPN) does not significantly deviate from 160°. Although the contact angle C6-Br...O1 (145.50(9)° for 1.2BNPN and 147.3(3)° for 2. 2BNPN) exhibits a higher deviation from 160°, the conducted DFT-QTAIM calculations still confirmed the availability of an XB between the Br atom of BNPN and the O atom of the acetylacetonate ligand (section 2.8). Currently only two examples of bifurcated XBs involving Br...O contacts have been reported: namely, in the $[Zn(acac)_2(H_2O)]$ ·1,4-FBB and $[Cu(acac)_2]$ ·1,4-FBB (1,4-FBB is 1,4-dibromo-2,3,5,6-tetrafluorobenzene) adducts⁷⁴ (see also Table S3). The zinc(II) adduct, similar to our BNPN adducts, exhibits different Br...O distances (3.117(2) and 3.169(2) Å), as well as diverse \angle (C-Br...O) (156.12(12) and 149.84(13)°), while in the Cu(acac)₂based adduct, both Br…O distances (3.360(2) Å) and \angle (C-Br...O) $(157.00(4)^{\circ})$ are equal.

In 1·21NPN, the I···O distances (3.200(2) and 3.212(2) Å) are equal, within 3σ , and are significantly shorter than the corresponding $\sum R_{vdW}$ (3.5 Å). In contrast to (1,2)·2BNPN, the values of the contact angles (154.96(4) and 155.79(9)°) are close to 160°. The I···O bifurcated XBs have previously been reported for a number of 1,4-FIB adducts including such metal

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Figure 12. Bifurcated C-X...(O,O) (X = Br, I) XB.

Table 3. Parameters of C-X···O (X = Br, I) XBs

interaction	param	1·2BNPN	2·2BNPN	1.2INPN
C6-X101	<i>d</i> (X1…O1), Å	3.263(3)	3.314(7)	3.200(2)
	$R_{\rm XO}^{a}$	0.97	0.98	0.91
	∠(C6–X1…O1), deg	145.50(9)	147.3(3)	154.96(4)
	calcd <i>E</i> _{int} (kcal/mol)	1.6	1.3	2.4-2.5
C6-X1O2	<i>d</i> (X1…O2), Å	3.117(2)	3.164(6)	3.212(2)
	$R_{\rm XO}^{a}$	0.92	0.94	0.92
	∠(C6–X1…O2), deg	164.76(9)	164.2(3)	155.79(9)
	calcd <i>E</i> _{int} (kcal/mol)	1.9	1.6-1.9	2.4-2.5

 ${}^{a}R_{\text{XO}}$ is a ratio of the interatomic distance to the sum of Bondi vdW radii. We defined E_{int} values for the studied contacts in accord with correlations proposed by Espinosa et al.⁸⁰ and Vener et al.⁸¹ on the basis of the results of DFT calculations and QTAIM analysis at the ω B97XD/DZP-DKH level of theory.

acetylacetonates as $[M(acac)_2]$ (M = Cu,^{31,74} Pd,^{31,74} Pt,³¹ V=O⁷⁴) and $[Zn(acac)_2(H_2O)]$;⁷⁴ this type of linkage was also detected in the (β -diketonate)Cu complex structure featuring an iodoethynyl moiety⁷⁸ and in the crystals of $[M(acac)_2(3-Ipy)_2]$

(M = Co, Ni; 3-Ipy is 3-iodopyridine).⁷⁹ In terms of geometrical parameters of the bifurcated XB, 1-2INPN is similar to the reported $[M(acac)_2] \cdot 2(1,4-FIB)$ (M = Pd, Pt) systems;



Figure 13. C...O₂N noncovalent interactions between BNPN molecules.



Figure 14. C…C noncovalent interactions in the (1,2)·2BNPN and 1·2INPN adducts.

however, 1·2INPN exhibits a shorter I···O separation. A detailed geometry comparison is given in Table S3.

2.7. Other Identified Noncovalent Interactions. We identified some additional short contacts that deserve attention. First, two C···O₂N interactions between two BNPN groups were detected in the BNPN adducts (Figure 13). The C···O distances are 3.168(3) Å for 1·2BNPN and 3.145(10) Å for 2·2BNPN, and these values are less than $\sum R_{vdW}$ (3.22 Å). Theoretically calculated energies accordingly to correlations proposed by Espinosa et al.⁸⁰ and Vener et al.,⁸¹ (ω B97XD/DZP-DKH level of theory) of these noncovalent interactions for the two adducts are comparable and are in the range from 0.9 to 1.1 kcal/mol. Interestingly, the \angle (H–C···O) values (74.3(5) and 75.55(15)°) are similar to the \angle (H–C···M) values (62.7(4) and 61.78(14)°) (β ; Figure 11).

Second, C...Br contacts between the Br atom of BNPN and the carbonyl C atom of one acetylacetonate ligand were found in both BNPN adducts. The C...Br distances (3.428(3) and 3.437(8) Å) are less than $\sum R_{vdW} (R_{vdW}(Br) + R_{vdW}(C) = 3.55 Å)$, whereas the angles (87.32(10) and 85.1(3)°) indicate the nucleophilic nature of the Br atoms in the C…Br lp $-\pi$ interactions; the calculated energy of these contacts is 1.3 kcal/mol. In contrast, for the INPN adduct such an interaction was not confirmed theoretically.

Third, C…C interactions between the C atom of one cyano group and the methylene C atom of the acetylacetonate ligands were observed in all three adducts (Figure 14). Although the C… C distances (3.397(4) and 3.408(8) Å) in the BNPN adducts are around $\sum R_{vdW}$ ($2R_{vdW}(C) = 3.4$ Å), these weak interactions (0.6–0.8 kcal/mol) were still supported by the obtained theoretical data (Table 4). In contrast, the C…C distance (3.319(5) Å) in the INPN adduct is less than the corresponding $\sum R_{vdW}$ (3.4 Å) and the theoretically calculated energy for this contact is slightly higher (0.9–1.1 kcal/mol). Similar non-covalent interactions.

interaction	param	1·2BNPN	2·2BNPN	1·2INPN
H11-C11M1-O2	d(C11…M1), Å	3.498(2)	3.483(7)	3.434(3)
	$R_{\rm CM}^{a}$	1.05	1.01	1.03
	∠(H11–C11…M1), deg	62.7(4)	61.78(14)	68.20(18)
	∠(C11…M1–O2), deg	68.72(7)	70.1(2)	73.89(8)
	calcd <i>E</i> _{int} (kcal/mol)	0.9-1.1	0.9-1.3	1.1-1.3
H8-C8-04	d(C8…O4), Å	3.168(3)	3.145(10)	
	$R_{\rm CO}^{a}$	0.98	0.98	
	∠(H8–C8…O4), deg	74.3(5)	75.55(15)	
	calcd <i>E</i> _{int} (kcal/mol)	0.9-1.1	0.9-1.1	
C2···Br1–C6	d(C2…Br1), Å	3.428(3)	3.437(8)	
	$R_{\rm CBr}^{a}$	0.97	0.97	
	∠(C2…Br1–C6), deg	87.32(10)	85.1(3)	
	calcd <i>E</i> _{int} (kcal/mol)	1.3	1.3	
C13…C3	d(C13…C3), Å	3.397(4)	3.408(8)	3.319(5)
	$R_{\rm CC}^{a}$	1.0	1.0	0.98
	calcd <i>E</i> _{int} (kcal/mol)	0.6-0.9	0.6-0.9	0.9-1.1

 ${}^{a}R_{CM}$, R_{CO} , R_{CB} , and R_{CC} are ratios of the interatomic distance to the sum of Bondi vdW radii. We defined E_{int} values for the studied contacts in accord with correlations proposed by Espinosa et al.⁸⁰ and Vener et al.,⁸¹ on the basis of the results of DFT calculations and QTAIM analysis at the ω B97XD/DZP-DKH level of theory.

We emphasize that all types of noncovalent interactions collectively affect the supramolecular assembly and the observed adducts could also be considered as those formed by $\pi - \pi$ stacking interactions, where the M(acac)₂ acts as the electron donor and a dicyanonitrobenzene is the π -acidic partner.

2.8. Theoretical Study of Noncovalent Interactions in (1,2)·2BNPN and 1·2INPN. Inspection of the crystallographic data suggests the presence of various noncovalent interactions responsible for the formation of the supramolecular structure. With this in mind, in addition to the structural analysis, a detailed computational study is desirable. In order to confirm or disprove the hypothesis on the existence of these supramolecular contacts and quantify their energies from a theoretical viewpoint, we carried out DFT calculations and performed topological analysis of the electron density distribution within the framework of Bader's theory (QTAIM method)⁸⁴ for model supramolecular associates (Table S5 in the Supporting Information). This approach has already been successfully used by us in studies of various noncovalent interactions (see, for example, refs 29 and 85-89 and references therein). The results are summarized in Table S6, and the contour line diagrams of the Laplacian distribution $\nabla^2 \rho(\mathbf{r})$, bond paths, and selected zero-flux surfaces for different noncovalent interactions are shown in Figures 15 and 16. To visualize studied noncovalent interactions, a reduced density gradient (RDG) analysis⁹⁰ was carried out, and RDG isosurfaces are plotted in Figures 15 and 16

The QTAIM analysis performed for model supramolecular associates demonstrates the presence of appropriate bond critical points (3, -1) (BCPs) for all noncovalent interactions given in Table S6. The low magnitude of the electron density (0.005-0.011 au), positive values of the Laplacian (0.016-0.042 au), and close to zero positive energy density (0.001-0.002 au) in these BCPs are typical for noncovalent interactions. Unfortunately, one universal and generally accepted empirical correlation between the properties of electron density at BCPs and the strength of the noncovalent interactions is currently unavailable in the literature. However, the corresponding energy values can be normalized if some specific empirical correlations for determining the strength of these noncovalent interactions.

will be proposed in the future. We have defined energies for studied contacts according to the correlations proposed by Espinosa et al.⁸⁰ and Vener et al.⁸¹ and generally accepted for hydrogen bonds-one can state that strength of these supramolecular contacts vary from 0.6 to 2.5 kcal/mol. Note that Tsirelson et al.⁹¹ also proposed alternative correlations developed exclusively for noncovalent interactions involving bromine and iodine atoms, viz. $E_{int} = 0.58(-V(\mathbf{r}))$ or $E_{int} =$ $0.57G(\mathbf{r})$ and $E_{\text{int}} = 0.68(-V(\mathbf{r}))$ or $E_{\text{int}} = 0.67G(\mathbf{r})$, respectively, and in accord with these correlations, the strength of these supramolecular contacts can even reach 3.8 kcal/mol. The balance between the Lagrangian kinetic energy $G(\mathbf{r})$ and potential energy density $V(\mathbf{r})$ at the BCPs $(-G(\mathbf{r})/V(\mathbf{r}) > 1)$ for purely noncovalent interactions and $-G(\mathbf{r})/V(\mathbf{r}) < 1$ if some covalent component takes place)⁹² reveals that a covalent contribution is absent in all supramolecular contacts given in Table S6.

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3. CONCLUDING REMARKS

In this work, we demonstrated the ability of X-substituted phthalonitriles to form the *reverse sandwich structures* upon their cocrystallization with $[M(acac)_2]$ ($d^8M = Pt$, Pd) complexes. In these systems, the phthalonitriles act as π -hole donors components of the lp $-\pi$ h (lp is the d_{z^2} Pt^{II} or Pd^{II} orbital) interactions. The obtained data indicate the potential of arene cyanides as suitable and easily accessible simultaneous σ h/ π h donors for crystal engineering. Note that the vast majority of previously studied π h donors are based on perfluorinated arenes (see, for instance, refs 37 and 38).

In our recently reported series of the reverse sandwiches,²⁹ the $d_{z^2}[M]\cdots\pi$ -hole interaction was strictly directed toward the centroid of the π h system or slightly deviated from the π h center (Figure 3a,b). In the sandwiches obtained in this work, in contrast, the lp(d_{z^2})- π h linkage is oriented to C11 of the arene ring to provide the first example of atom-directed C… $d_{z^2}[M]$ interactions (Figure 3c). Such a centroid to atom shift is apparently due to the combined effect of all noncovalent interactions or, in other words, due to the packing effect. Although the performed theoretical calculations indicate that the $d_{z^2}[M]\cdots\pi$ -hole interaction energy is (1.5-2)-fold lower



Figure 15. Contour line diagrams of the Laplacian distribution $\nabla^2 \rho(\mathbf{r})$, bond paths, and selected zero-flux surfaces (left) and RDG isosurfaces (right) referring to the C···M (M = Pd, Pt) noncovalent interactions in the adducts. Bond critical points (3, -1) are shown in blue, nuclear critical points (3, -3) in pale brown, ring critical points (3, +1) in orange, and cage critical points (3, +3) in light green. Lengths are given in Å and RDG isosurface values in au.

than that for the bifurcated C–X···(O,O) XB, the adducts nevertheless form a reverse sandwich system as a result of the collective action of all intermolecular interactions. We hope that proper derivatization of electron-deficient arenes and their assembly with $d_{z^2}[M]$ centers can lead to discoveries of yet unknown bond-directed $d_{z^2}[M]$ contacts (Figure 3d) to achieve the remaining type of the reverse sandwich systems, and these works are underway in our group.

4. EXPERIMENTAL SECTION

4.1. Materials and Instrumentation. BPNP,⁵⁰ [Pd(acac)₂],⁹³ and [Pt(acac)₂]⁹⁴ were synthesized in accord with to the published procedures. Other reagents and solvents were obtained from commercial sources and used as received. Melting points were determined on an Electrothermal IA 9300 series Digital Melting Point Apparatus. The HRMS data were obtained on a Bruker micrOTOF spectrometer equipped with an electrospray ionization source; MeOH was used as a solvent, and AgNO₃ was used as an ionizing additive. The instrument was operated in positive ion mode



Figure 16. Contour line diagrams of the Laplacian distribution $\nabla^2 \rho(\mathbf{r})$, bond paths, and selected zero-flux surfaces (left) and RDG isosurfaces (right) referring to the C–X···(O,O) (X = Br, I) bifurcated XBs in the adducts. Bond critical points (3, -1) are shown in blue, nuclear critical points (3, -3) in pale brown, ring critical points (3, +1) in orange, and cage critical points (3, +3) in light green. Lengths are given in Å and RDG isosurface values in au.

using an m/z range of 50–3000. The capillary voltage of the ion source was set at -4500 V and the capillary voltage of the exit at 70–150 V. The nebulizer gas pressure was 0.4 bar and drying gas flow 4.0 L/min. The NMR spectra were recorded on a Bruker AVANCE III 400 spectrometer at ambient temperature in CDCl₃ or DMSO- d_6 (at 400 and 101 MHz for ¹H and ¹³C{¹H} NMR spectra, respectively). Chemical shifts are given in δ values (ppm) referenced to the residual signals of the undeuterated solvent: δ 7.29 (¹H) and 77.2 (¹³C) for CDCl₃ and δ 2.50 (¹H) and 39.52 (¹³C) for DMSO- d_6 .

4.2. Synthesis of 4-lodo-5-nitrophthalonitrile (INPN). KI (830 mg, 5 mmol) was added to a solution of BNPN (252 mg, 1 mmol) in MeCN (5 mL) The reaction mixture was stirred at 80 °C for 24 h, whereupon it was concentrated to dryness in vacuo at 40 °C followed by addition of a saturated solution of NaCl (7 mL). The product was extracted with DCM (three 10 mL portions), the extract was dried under anhydrous Na₂SO₄, and the solvent was removed in vacuo at 40 °C. Crude INPN was purified by column chromatography on silica gel using an ethyl acetate/hexane (1/8, v/v) mixture as an eluent: yellow powder, yield 212 mg (71%), mp 168–169 °C. IR (KBr, selected bands, cm⁻¹): ν (CN) 2238 (s). ¹H NMR (DMSO- d_6), δ : 8.98 (s, 1H), 8.76 (s, 1H). ¹³C NMR (CDCl₃), δ : 155.2, 146.9, 128.9, 119.4, 116.8, 113.2, 112.4, 92.8. HRMS-ESI: [M + Ag]⁺ m/z calcd for C₈H₂IN₃O₂ 405.8237, found 405.8230.

4.3. Synthesis of 4-Chloro-5-nitrophthalonitrile (CNPC). N,N,N-Trimethyl-1-phenylmethanaminium chloride (186 mg, 1 mmol) was added to a solution of BNPN (252 mg, 1 mmol) in MeCN (3 mL). The reaction mixture was stirred at 60 °C for 18 h,

whereupon it was concentrated to dryness in vacuo at 40 °C followed by addition of a saturated solution of NaCl (5 mL). The target product was extracted with CH₂Cl₂ (three 10 mL portions), the extract was dried under anhydrous Na₂SO₄, and then the solvent was removed in vacuo at 40 °C. Crude CNPN was purified by column chromatography on silica gel using an ethyl acetate/hexane (1/8, v/v) mixture as an eluent: colorless powder, yield 173 mg (83%), mp 156–157 °C. IR (KBr, selected bands, cm⁻¹): ν (CN) 2244 (s). ¹H NMR (CDCl₃) δ 8.31 (s, 1H), 8.08 (s, 1H). ¹³C NMR (CDCl₃) δ 149.9, 137.1, 133.2, 130.1, 119.9, 115.6, 112.9, 112.8. HRMS-ESI: [M + Ag]⁺ m/z calcd for C₈H₂ClN₃O₂ 313.8881, found 313.8918.

4.4. Synthesis of the Adducts. Single crystals were obtained by slow evaporation of a chloroform/methanol solution (1/1, v/v) of a mixture of 1 or 2 and BNPN (or INPN) taken in a 1/1 molar ratio in air at 10–15 °C. To prove the homogeneity of our samples, we measured space group and crystal lattice parameters of at least five crystals from three syntheses. Once we proved the identity of the structures, the best data set was chosen for the final structure solution.

4.5. X-ray Experiments and Refinement. X-ray diffraction studies of all adducts and BNPN were performed at 100 K on an Xcalibur Eos diffractometer using monochromated Mo K α (λ = 0.71073) radiation. The structures of all adducts and BNPN were solved by direct methods by means of the SHELX program⁹⁵ incorporated in the OLEX2 program package.⁹⁶ The carbon-bound H atoms were placed in calculated positions and were included in the refinement in the "riding" model approximation, with $U_{\rm iso}(H)$ set to $1.5U_{\rm eq}(C)$ and C–H to 0.98 Å for CH₃ groups, with $U_{\rm iso}(H)$ set to

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 $1.2U_{\rm eq}({\rm C})$ and C–H to 0.99 Å for CH₂ groups, and with $U_{\rm iso}({\rm H})$ set to $1.2U_{\rm eq}({\rm C})$ and C–H to 0.95 Å for CH groups. An empirical absorption correction was applied in the CrysAlisPro⁹⁷ program complex using spherical harmonics, implemented in the SCALE3 ABSPACK scaling algorithm. Supplementary crystallographic data for this paper have been deposited at Cambridge Crystallographic Data Centre (CCDC numbers 1957920–1957925) and can be obtained free of charge via www.ccdc.cam.ac.uk/data request/cif.

X-ray diffraction studies of the INPN and CNPN crystals were performed using a Bruker Apex II CCD diffractometer equipped with a Cobra Oxford Cryosystem low-temperature device at 120 K (Mo K α radiation, graphite monochromator, ω scans). According to the Bruker CELL NOW (2008/4) indexing routine⁹⁸ (2144 nonunique reflections with $I > 2\sigma(I)$), the crystals of INPN are twins with two domains of similar figure of merit which are rotated against each other at 179.9°. Semiempirical absorption corrections with spherical harmonics modeling of diffracted beam absorption^{99,100} were made on the basis of the intensities of equivalent reflections with the help of the TWINABS routine¹⁰¹ for INPN diffraction data and the SADABS program¹⁰² for the CNPN diffraction data. These two structures were solved by the direct methods technique in the XS program.¹⁰³ The fullmatrix least-squares refinement of structural models was carried out in the SHELXL-2014/6 program⁹⁵ in the anisotropic approximation for probability density functions of non-hydrogen atoms. Positions of hydrogen atoms were calculated on the basis of geometric criteria; hydrogen atoms were refined within the riding model implemented in the SHELXL-2014/6 program and using the isotropic approximation for the probability density function. The CNPN structure was refined as positionally disordered with the superposition of the chlorine atom and NO2 group modeled with the help of restraints on interatomic distances and constraints on atomic displacement parameters (the population ratio was refined to 2/3). The approximate twinning factor for two components of the INPN crystal (0.326) was refined using the HKLF5/ BASF instructions in the SHELXL-2014/6 program.

4.6. Computational Details. Quantum chemical calculations have been carried out using the Gaussian-09¹⁰⁴ program package at the DFT level of theory. The single-point calculations based on the experimental X-ray geometries of (1,2)·2BNPN and 1·2INPN have been carried out using the dispersion-corrected hybrid functional ω B97XD, 105 and the Douglas-Kroll-Hess second-order scalar relativistic approach requested relativistic core Hamiltonian was used with the DZP-DKH basis sets¹⁰⁶⁻¹⁰⁹ for all atoms. The full geometry optimization of CNPN, BNPN, and INPN model structures has been carried out using the M06-2X functional,¹¹⁰ and the CEP-121G Stevens/Basch/Krauss ECP triple-split basis sets^{111–113} were used for all atoms. No symmetry restrictions have been applied during the geometry optimization procedure, and Hessian matrices were calculated analytically in all cases in order to prove the location of correct minima on the potential energy surfaces (no imaginary frequencies). The topological analysis of the electron density distribution with the help of the atoms in molecules (QTAIM) method developed by Bader⁸⁴ has been performed by using the Multiwfn program.¹¹⁴ The molecular surface electrostatic potentials have been calculated by using the Multiwfn program¹¹⁴ and plotted in the Chemcraft program (http://www.chemcraftprog.com). The Cartesian atomic coordinates for all model structures are presented in Tables S4 and S5 in the Supporting Information.

The Hirshfeld molecular surfaces were generated by the CrystalExplorer program.^{115,116} The normalized contact distances, d_{norm} ,¹¹⁷ based on Bondi van der Waals radii,⁷⁷ were mapped into the Hirshfeld surface. In the color scale, negative values of d_{norm} are visualized by the red color, indicating contacts shorter than the sum of van der Waals radii. The white color denotes intermolecular distances close to van der Waals contacts with d_{norm} equal to zero. In turn, contacts longer than the sum of van der Waals radii with positive d_{norm} values are colored blue.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.cgd.9b01334.

Detailed synthetic procedures for the preparation of INPN and CNPN, NMR and mass spectra of INPN and CNPN, crystal data and structure refinement details for CNPN, BNPN, and INPN, crystal data and structure refinement details for 1.2BNPN, 2.2BNPN, and 1.2INPN, parameters of the C-X...(O,O) halogen bonds with the bis-acetylacetonate complexes, additional results of DFT calculations, and Cartesian atomic coordinates of model supramolecular clusters (PDF)

Accession Codes

CCDC 1957920–1957925 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Kan, X.; Liu, H.; Pan, Q.; Li, Z.; Zhao, Y. Anion- π Interactions: From Concept to Application. *Chin. Chem. Lett.* **2018**, *29*, 261–266.

(2) Giese, M.; Albrecht, M.; Rissanen, K. Anion $-\pi$ Interactions with Fluoroarenes. *Chem. Rev.* **2015**, *115*, 8867–8895.

(3) Mahmudov, K. T.; Gurbanov, A. V.; Guseinov, F. I.; Guedes da Silva, M. F. C. Noncovalent Interactions in Metal Complex Catalysis. *Coord. Chem. Rev.* **2019**, 387, 32–46.

(4) Gamez, P.; Mooibroek, T. J.; Teat, S. J.; Reedijk, J. Anion Binding Involving π -Acidic Heteroaromatic Rings. *Acc. Chem. Res.* **2007**, *40*, 435–444.

(5) Schottel, B. L.; Chifotides, H. T.; Dunbar, K. R. Anion- π Interactions. *Chem. Soc. Rev.* **2008**, 37, 68–83.

(6) Giese, M.; Albrecht, M.; Rissanen, K. Experimental Investigation of Anion $-\pi$ Interactions – Applications and Biochemical Relevance. *Chem. Commun.* **2016**, *52*, 1778–1795.

(7) Hafezi, N.; Holcroft, J. M.; Hartlieb, K. J.; Dale, E. J.; Vermeulen, N. A.; Stern, C. L.; Sarjeant, A. A.; Stoddart, J. F. Modulating the Binding of Polycyclic Aromatic Hydrocarbons Inside a Hexacationic Cage by Anion- π Interactions. *Angew. Chem., Int. Ed.* **2014**, *54*, 456–461.

(8) Ballester, P. Experimental Quantification of Anion $-\pi$ Interactions in Solution Using Neutral Host–Guest Model Systems. *Acc. Chem. Res.* **2013**, *46*, 874–884.

(9) Yong, G.-P.; Zhang, Y.-M.; She, W.-L. Anion $-\pi$ Interactions in New Electron-Deficient π Systems: The Relevance to Solid Phosphorescent Colors. *CrystEngComm* **2012**, *14*, 3923.

(10) Chang, K.-C.; Sun, S.-S.; Odago, M. O.; Lees, A. J. Anion Recognition and Sensing by Transition-Metal Complexes with Polarized N–H Recognition Motifs. *Coord. Chem. Rev.* 2015, 284, 111–123.

(11) Lucas, X.; Bauzá, A.; Frontera, A.; Quiñonero, D. A Thorough Anion $-\pi$ Interaction Study in Biomolecules: On the Importance of Cooperativity Effects. *Chem. Sci.* **2016**, *7*, 1038–1050.

(12) Dawson, R. E.; Hennig, A.; Weimann, D. P.; Emery, D.; Ravikumar, V.; Montenegro, J.; Takeuchi, T.; Gabutti, S.; Mayor, M.; Mareda, J.; Schalley, C. A.; Matile, S. Experimental Evidence for the Functional Relevance of Anion $-\pi$ Interactions. *Nat. Chem.* **2010**, *2*, 533–538.

(13) Kozelka, J. Lone Pair $-\pi$ Interactions in Biological Systems: Occurrence, Function, and Physical Origin. *Eur. Biophys. J.* **2017**, 46, 729–737.

(14) Barbas, R.; Prohens, R.; Font-Bardia, M.; Bauzá, A.; Frontera, A. Hydrogen Bonding versus π -Interactions: Their Key Competition in Sildenafil Solvates. *CrystEngComm* **2018**, *20*, 4526–4530.

(15) Neel, A. J.; Hilton, M. J.; Sigman, M. S.; Toste, F. D. Exploiting Non-Covalent π Interactions for Catalyst Design. *Nature* 2017, 543, 637–646.

(16) Zhao, Y.; Domoto, Y.; Orentas, E.; Beuchat, C.; Emery, D.; Mareda, J.; Sakai, N.; Matile, S. Catalysis with Anion- π Interactions. *Angew. Chem., Int. Ed.* **2013**, *52*, 9940–9943.

(17) Berkessel, A.; Das, S.; Pekel, D.; Neudörfl, J.-M. Anion-Binding Catalysis by Electron-Deficient Pyridinium Cations. *Angew. Chem., Int. Ed.* **2014**, *53*, 11660–11664.

(18) Zhang, X.; Hao, X.; Liu, L.; Pham, A.-T.; López-Andarias, J.; Frontera, A.; Sakai, N.; Matile, S. Primary Anion $-\pi$ Catalysis and Autocatalysis. *J. Am. Chem. Soc.* **2018**, *140*, 17867–17871.

(19) Liu, L.; Cotelle, Y.; Bornhof, A.-B.; Besnard, C.; Sakai, N.; Matile, S. Anion- π Catalysis of Diels-Alder Reactions. *Angew. Chem., Int. Ed.* **2017**, *56*, 13066–13069.

(20) Macchione, M.; Goujon, A.; Strakova, K.; Humeniuk, H. V.; Licari, G.; Tajkhorshid, E.; Sakai, N.; Matile, S. A Chalcogen-Bonding Cascade Switch for Planarizable Push-Pull Probes. *Angew. Chem., Int. Ed.* **2019**, *58*, 15752–15756.

(21) Lee, L. M.; Tsemperouli, M.; Poblador-Bahamonde, A. I.; Benz, S.; Sakai, N.; Sugihara, K.; Matile, S. Anion Transport with Pnictogen Bonds in Direct Comparison with Chalcogen and Halogen Bonds. *J. Am. Chem. Soc.* **2019**, *141*, 810–814.

(22) Mooibroek, T. J.; Gamez, P.; Reedijk, J. Lone Pair $-\pi$ Interactions: A New Supramolecular Bond? *CrystEngComm* **2008**, *10*, 1501.

(23) Bauzá, A.; Mooibroek, T. J.; Frontera, A. The Bright Future of Unconventional σ/π -Hole Interactions. *ChemPhysChem* **2015**, *16*, 2496–2517.

(24) Fanfrlík, J.; Švec, P.; Růžičková, Z.; Hnyk, D.; Růžička, A.; Hobza, P. The Interplay between Various σ - and π -Hole Interactions of Trigonal Boron and Trigonal Pyramidal Arsenic Triiodides. *Crystals* **2017**, *7*, 225.

(25) Wang, H.; Wang, W.; Jin, W. J. σ -Hole Bond vs π -Hole Bond: A Comparison Based on Halogen Bond. *Chem. Rev.* **2016**, *116*, 5072–5104.

(26) Rosokha, S. V.; Kochi, J. K. Fresh Look at Electron-Transfer Mechanisms via the Donor/Acceptor Bindings in the Critical Encounter Complex. *Acc. Chem. Res.* **2008**, *41*, 641–653.

(27) Singh, S. K.; Das, A. The $n \rightarrow \pi^*$ Interaction: A Rapidly Emerging Non-Covalent Interaction. *Phys. Chem. Chem. Phys.* **2015**, *17*, 9596–9612.

(28) Calabrese, C.; Gou, Q.; Maris, A.; Caminati, W.; Melandri, S. Probing the Lone Pair $\cdots \pi$ -Hole Interaction in Perfluorinated Heteroaromatic Rings: The Rotational Spectrum of Pentafluoropyridine-Water. J. Phys. Chem. Lett. 2016, 7, 1513-1517.

(29) Rozhkov, A. V.; Krykova, M. A.; Ivanov, D. M.; Novikov, A. S.; Sinelshchikova, A. A.; Volostnykh, M. V.; Konovalov, M. A.; Grigoriev, M. S.; Gorbunova, Y. G.; Kukushkin, V. Y. Reverse Arene Sandwich Structures Based upon π -Hole…[M^{II}] ($d^8M = Pt$, Pd) Interactions, Where Positively Charged Metal Centers Play the Role of a Nucleophile. *Angew. Chem., Int. Ed.* **2019**, *58*, 4164–4168.

(30) Katkova, S. A.; Mikherdov, A. S.; Kinzhalov, M. A.; Novikov, A. S.; Zolotarev, A. A.; Boyarskiy, V. P.; Kukushkin, V. Y. (Isocyano Group π -Hole)…[D-M^{II}] Interactions of (Isocyanide)[M^{II}] Complexes, in Which Positively Charged Metal Centers (d⁸-M = Pt, Pd) Act as Nucleophiles. *Chem. - Eur. J.* **2019**, *25*, 8590–8598.

(31) Rozhkov, A. V.; Novikov, A. S.; Ivanov, D. M.; Bolotin, D. S.; Bokach, N. A.; Kukushkin, V. Y. Structure-Directing Weak Interactions with 1,4-Diiodotetrafluorobenzene Convert One-Dimensional Arrays of $[M^{II}(acac)_2]$ Species into Three-Dimensional Networks. *Cryst. Growth Des.* **2018**, *18*, 3626–3636.

(32) Muetterties, E. L.; Bleeke, J. R.; Wucherer, E. J.; Albright, T. Structural, Stereochemical, and Electronic Features of Arene-Metal Complexes. *Chem. Rev.* **1982**, *82*, 499–525.

(33) Clark, T.; Hennemann, M.; Murray, J. S.; Politzer, P. Halogen Bonding: The σ -Hole. J. Mol. Model. **2007**, 13, 291–296.

(34) Galmés, B.; Franconetti, A.; Frontera, A. Nitropyridine-1-Oxides as Excellent π -Hole Donors: Interplay between σ -Hole (Halogen, Hydrogen, Triel, and Coordination Bonds) and π -Hole Interactions. *Int. J. Mol. Sci.* **2019**, *20*, 3440.

(35) Prohens, R.; de Sande, D.; Font-Bardia, M.; Franconetti, A.; González, J. F.; Frontera, A. Gallic Acid Dimer As a Double π -Hole Donor: Evidence from X-Ray, Theoretical Calculations, and Generalization from the Cambridge Structural Database. *Cryst. Growth Des.* **2019**, *19*, 3989–3997.

(36) Bauzá, A.; Sharko, A. V.; Senchyk, G. A.; Rusanov, E. B.; Frontera, A.; Domasevitch, K. V. π -Hole Interactions at Work: Crystal Engineering with Nitro-Derivatives. *CrystEngComm* **2017**, *19*, 1933–1937.

(37) Eliseeva, A. A.; Ivanov, D. M.; Novikov, A. S.; Kukushkin, V. Y. Recognition of the π -Hole Donor Ability of Iodopentafluorobenzene-a Conventional σ -Hole Donor for Crystal Engineering Involving Halogen Bonding. *CrystEngComm* **2019**, *21*, 616–628.

(38) Novikov, A. S.; Ivanov, D. M.; Bikbaeva, Z. M.; Bokach, N. A.; Kukushkin, V. Y. Noncovalent Interactions Involving Iodofluorobenzenes: The Interplay of Halogen Bonding and Weak $Lp(O) \cdots \pi$ -Hole Arene Interactions. *Cryst. Growth Des.* **2018**, *18*, 7641–7654.

(39) Chirkova, Z. V.; Kabanova, M. V.; Filimonov, S. I.; Abramov, I. G.; Petzer, A.; Engelbrecht, I.; Petzer, J. P.; Yu Suponitsky, K.; Veselovsky, A. V. An Investigation of the Monoamine Oxidase Inhibition Properties of Pyrrolo[3,4-f]Indole-5,7-Dione and Indole-5,6-Dicarbonitrile Derivatives. *Drug Dev. Res.* **2018**, *79*, 81–93.

(40) Chirkova, Z. V.; Kabanova, M. V.; Filimonov, S. I.; Abramov, I. G.; Petzer, A.; Petzer, J. P.; Suponitsky, K. Y. An Evaluation of Synthetic Indole Derivatives as Inhibitors of Monoamine Oxidase. *Bioorg. Med. Chem. Lett.* **2016**, *26*, 2214–2219.

(41) Chirkova, Z. V.; Kabanova, M. V.; Filimonov, S. I.; Abramov, I. G.; Petzer, A.; Petzer, J. P.; Firgang, S. I.; Suponitsky, K. Y. Inhibition of Monoamine Oxidase by Indole-5,6-Dicarbonitrile Derivatives. *Bioorg. Med. Chem. Lett.* **2015**, *25*, 1206–1211.

(42) Filimonov, S. I.; Chirkova, Z. V.; Abramov, I. G.; Firgang, S. I.; Stashina, G. A.; Strelenko, Y. A.; Khakimov, D. V.; Pivina, T. S.; Samet, A. V.; Suponitsky, K. Y. Base-Induced Transformations of Ortho-Nitrobenzylketones: Intramolecular Displacement of Nitro Group versus Nitro-Nitrite Rearrangement. *Tetrahedron* **2012**, *68*, 5991– 5997.

(43) Znoiko, S. A.; Petlina, A. I.; Shaposhnikov, G. P.; Smirnov, N. N. Synthesis of Magnesium Octa-4,5-Phenoxyphthalocyanine and Sulfoand Alkylsulfamoyl Derivatives on Its Basis. *Russ. J. Gen. Chem.* **2018**, 88, 1148–1153.

(44) Abramova, M. B.; Shaposhnikov, G. P.; Znoiko, S. A.; Abramov, I. G.; Maizlish, V. E.; Mikhailova, A. I. Nucleophilic Substitution of 4-

Crystal Growth & Design

Bromo-5-Nitrophthalodinitrile: XVII. Synthesis and Properties of Bifunctionally Substituted Metal Phthalocyanines with Aryloxy and Nitro Groups. *Russ. J. Gen. Chem.* **2018**, *88*, 1425–1429.

(45) Morozova, A. P.; Znoiko, S. A.; Vashurin, A. S.; Zav'yalov, A. V.; Maizlish, V. E.; Shaposhnikov, G. P. Synthesis and Properties of Cobalt(II) Tetrakis-[4,5-Di(4'-Carboxy)Phenylene(Oxy/Sulfanyl/ Amino)]Phthalocyanines. *Russ. J. Gen. Chem.* **2018**, *88*, 2020–2027.

(46) Vashurin, A.; Maizlish, V.; Kuzmin, I.; Znoyko, S.; Morozova, A.; Razumov, M.; Koifman, O. Symmetrical and Difunctional Substituted Cobalt Phthalocyanines with Benzoic Acids Fragments: Synthesis and Catalytic Activity. *J. Porphyrins Phthalocyanines* **2017**, *21*, 37–47.

(47) Filippova, A.; Vashurin, A.; Znoyko, S.; Kuzmin, I.; Razumov, M.; Chernova, A.; Shaposhnikov, G.; Koifman, O. Novel Co(II) Phthalocyanines of Extended Periphery and Their Water-Soluble Derivatives. Synthesis, Spectral Properties and Catalytic Activity. J. Mol. Struct. 2017, 1149, 17–26.

(48) Negrimovsky, V.; Komissarov, A.; Perepukhov, A.; Suponitsky, K.; Perevalov, V.; Lukyanets, E. Phthalocyanines with Phosphonate Moiety via C-Nucleophilic Substitution in Phthalonitriles. *J. Porphyrins Phthalocyanines* **2013**, *17*, 587–595.

(49) Shishkina, V.; Maizlish, V. E.; Shaposhnikov, G. P.; Smirnov, R. P. Synthesis and Properties of Metal Tetrahalotetranitrophthalocyanines. *Russ. J. Gen. Chem.* **1998**, *68*, 813–817.

(50) Shishkina, O. V.; Maizlish, V. E.; Shaposhnikov, G. P.; Lyubimtsev, A. V.; Smirnov, R. P.; Baran'ski, A. Halonitrophthalimides and Phthalodinitriles Derived from Them. *Russ. J. Gen. Chem.* **1997**, *67*, 789–792.

(51) Lin, M.-J.; Wang, J.-D.; Chen, N.-S.; Huang, J.-L. A Convenient Synthesis of a Substituted Phthalocyanine Compound. *J. Coord. Chem.* **2006**, *59*, 607–611.

(52) Desiraju, G. R.; Ho, P. S.; Kloo, L.; Legon, A. C.; Marquardt, R.; Metrangolo, P.; Politzer, P.; Resnati, G.; Rissanen, K. Definition of the Halogen Bond (IUPAC Recommendations 2013). *Pure Appl. Chem.* **2013**, *85*, 1711–1713.

(53) Bond, A. D.; Griffiths, J.; Rawson, J. M.; Hulliger, J. Inducing Structural Polarity Using Fluorinated Organics: X-Ray Crystal Structures of p-XC₆F₄CN (X = Cl, Br, I). *Chem. Commun.* **2001**, *1*, 2488–2489.

(54) Desiraju, G. R.; Harlow, R. L. Cyano-Halogen Interactions and Their Role in the Crystal Structures of the 4-Halobenzonitriles. *J. Am. Chem. Soc.* **1989**, *111*, 6757–6764.

(55) Mariaca, R.; Labat, G.; Behrnd, N.-R.; Bonin, M.; Helbling, F.; Eggli, P.; Couderc, G.; Neels, A.; Stoeckli-Evans, H.; Hulliger, J. Preparation of Donor–Acceptor Substituted Fluorostilbenes and Crystal Chemistry of Fluorinated (*E*)-4-(4-Halogeno-Styryl)-Benzonitriles. *J. Fluorine Chem.* **2009**, *130*, 175–196.

(56) Dey, A.; Desiraju, G. R. Correlation between Molecular Dipole Moment and Centrosymmetry in Some Crystalline Diphenyl Ethers. *Chem. Commun.* **2005**, 2486–2488.

(57) Ojala, C. R.; Ojala, W. H.; Britton, D. 4-(4-Chlorobenzylidenehydrazonomethyl)Benzonitrile and the Bromo and Iodo Analogs. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **2008**, *64*, o37–o40.

(58) Ateş, Ö. D.; Zorlu, Y.; Kanmazalp, S. D.; Chumakov, Y.; Gürek, A. G.; Ayhan, M. M. Halogen Bonding Driven Crystal Engineering of Iodophthalonitrile Derivatives. *CrystEngComm* **2018**, *20*, 3858–3867.

(59) Dumele, O.; Wu, D.; Trapp, N.; Goroff, N.; Diederich, F. Halogen Bonding of (Iodoethynyl)Benzene Derivatives in Solution. *Org. Lett.* **2014**, *16*, 4722–4725.

(60) Borgen, B.; Hassel, O.; Römming, C.; Block-Bolten, A.; Toguri, J. M.; Flood, H. Mutual Arrangement of Iodo-Cyano-Acetylene Molecules in the Solid. *Acta Chem. Scand.* **1962**, *16*, 2469–2470.

(61) Britton, D.; Gleason, W. B. Structure of 4-Cyano-4'-Iodobiphenyl at 297 and 183 K. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1991**, 47, 2127–2131.

(62) Ojala, C. R.; Ojala, W. H.; Gleason, W. B.; Britton, D. Crystal Structures of *p*-Iodo-*N*-(*p*-Cyanobenzylidene)aniline and *p*-Cyano-*N*-(*p*-Iodobenzylidene)aniline. *J. Chem. Crystallogr.* **1999**, 29, 27–32.

(63) Britton, D. 2-Fluoro-6-Iodobenzonitrile. *Acta Crystallogr., Sect. E: Struct. Rep. Online* **2001**, *57*, 0702–0704. (64) Frausto, F.; Smith, Z. C.; Haas, T. E.; Thomas, S. W. Two-Dimensional Bricklayer Arrangements of Tolans Using Halogen Bonding Interactions. *Chem. Commun.* **2015**, *51*, 8825–8828.

(65) Huse, G.; Powell, H. M. 266. The Crystal Structure of Picryl Iodide. J. Chem. Soc. 1940, 254, 1398.

(66) Hamor, M. J.; Hamor, T. A. Structures of Polyfluoroaromatic Compounds. IV. Crystal Structure of 2-Nitrononafluorobiphenyl. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1978**, 34, 2994– 2997.

(67) Gerard, F.; Hardy, A.; Becuwe, A. Structure of 1,3,5-Trichloro-2,4,6-Trinitrobenzene. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1993**, *49*, 1215–1218.

(68) Landenberger, K. B.; Bolton, O.; Matzger, A. J. Energetic-Energetic Cocrystals of Diacetone Diperoxide (DADP): Dramatic and Divergent Sensitivity Modifications via Cocrystallization. *J. Am. Chem. Soc.* **2015**, *137*, 5074–5079.

(69) Drück, I.; Kutoglu, A. Benzenehexacarbonitrile at 120 K, C12N6. Acta Crystallogr., Sect. C: Cryst. Struct. Commun. **1983**, 39, 638–640.

(70) Prout, C. K.; Tickle, I. J. Molecular Complexes. Part XIV. Crystal and Molecular Structure of the π^* -Electron-Acceptor Molecule 1,2,4,5-Tetracyanobenzene. *J. Chem. Soc., Perkin Trans.* 2 **1973**, 520–523.

(71) Hibbs, D. E.; Overgaard, J.; Platts, J. A.; Waller, M. P.; Hursthouse, M. B. Experimental and Theoretical Charge Density Studies of Tetrafluorophthalonitrile and Tetrafluoroisophthalonitrile. *J. Phys. Chem. B* **2004**, *108*, 3663–3672.

(72) Hamid, M.; Zeller, M.; Hunter, A. D.; Mazhar, M.; Tahir, A. A. Redetermination of Bis(2,4-Pentanedionato)Palladium(II). *Acta Crystallogr., Sect. E: Struct. Rep. Online* **2005**, *61*, m2181–m2183.

(73) Ha, K. Crystal Structure of Bis(Pentane-2,4-Dionato-K2O,O') Platinum(II), Pt(C5H7O2)2. Z. Kristallogr. - New Cryst. Struct. 2011, 226, 329–330.

(74) Stilinović, V.; Grgurić, T.; Piteša, T.; Nemec, V.; Cinčić, D. Bifurcated and Monocentric Halogen Bonds in Cocrystals of Metal(II) Acetylacetonates with *p*-Dihalotetrafluorobenzenes. *Cryst. Growth Des.* **2019**, *19*, 1245–1256.

(75) Johnson, M. T.; Džolić, Z.; Cetina, M.; Wendt, O. F.; Öhrström, L.; Rissanen, K. Neutral Organometallic Halogen Bond Acceptors: Halogen Bonding in Complexes of PCPPdX (X = Cl, Br, I) with Iodine (I₂), 1,4-Diiodotetrafluorobenzene (F4DIBz), and 1,4-Diiodooctafluorobutane (F8DIBu). *Cryst. Growth Des.* **2012**, *12*, 362–368.

(76) Brookhart, M.; Green, M. L. H.; Parkin, G. Agostic Interactions in Transition Metal Compounds. *Proc. Natl. Acad. Sci. U. S. A.* 2007, *104*, 6908–6914.

(77) Bondi, A. Van Der Waals Volumes and Radii. *J. Phys. Chem.* **1964**, 68, 441–451.

(78) Gamekkanda, J.; Desper, J.; Đaković, M.; Aakeröy, C.; Sinha, A. The Role of Halogen Bonding in Controlling Assembly and Organization of Cu(II)-Acac Based Coordination Complexes. *Crystals* **2017**, *7*, 226.

(79) Borovina, M.; Kodrin, I.; Đaković, M. Testing the Limits of Halogen Bonding in Coordination Chemistry. *CrystEngComm* **2018**, 20, 539–549.

(80) Espinosa, E.; Molins, E.; Lecomte, C. Hydrogen Bond Strengths Revealed by Topological Analyses of Experimentally Observed Electron Densities. *Chem. Phys. Lett.* **1998**, *285*, 170–173.

(81) Vener, M. V.; Egorova, A. N.; Churakov, A. V.; Tsirelson, V. G. Intermolecular Hydrogen Bond Energies in Crystals Evaluated Using Electron Density Properties: DFT Computations with Periodic Boundary Conditions. J. Comput. Chem. **2012**, 33, 2303–2309.

(82) Mikherdov, A. S.; Kinzhalov, M. A.; Novikov, A. S.; Boyarskiy, V. P.; Boyarskaya, I. A.; Avdontceva, M. S.; Kukushkin, V. Y. Ligation-Enhanced π -Hole··· π Interactions Involving Isocyanides: Effect of π -Hole··· π Noncovalent Bonding on Conformational Stabilization of Acyclic Diaminocarbene Ligands. *Inorg. Chem.* **2018**, *57*, 6722–6733. (83) Ivanov, D. M.; Kirina, Y. V.; Novikov, A. S.; Starova, G. L.; Kukushkin, V. Y. Efficient π -Stacking with Benzene Provides 2D Assembly of Trans-[PtCl2(p-CF3C6H4CN)2]. *J. Mol. Struct.* **2016**, *1104*, 19–23.

Crystal Growth & Design

(84) Bader, R. F. W. A Quantum Theory of Molecular Structure and Its Applications. *Chem. Rev.* **1991**, *91*, 893–928.

(85) Kinzhalov, M. A.; Kashina, M. V.; Mikherdov, A. S.; Mozheeva, E. A.; Novikov, A. S.; Smirnov, A. S.; Ivanov, D. M.; Kryukova, M. A.; Ivanov, A. Y.; Smirnov, S. N.; Kukushkin, V. Yu.; Luzyanin, K. V. Dramatically Enhanced Solubility of Halide-Containing Organometallic Species in Diiodomethane: The Role of Solvent…Complex Halogen Bonding. *Angew. Chem., Int. Ed.* **2018**, 57, 12785–12789.

(86) Baykov, S. V.; Dabranskaya, U.; Ivanov, D. M.; Novikov, A. S.; Boyarskiy, V. P. Pt/Pd and I/Br Isostructural Exchange Provides Formation of C–I···Pd, C–Br···Pt, and C–Br···Pd Metal-Involving Halogen Bonding. *Cryst. Growth Des.* **2018**, *18*, 5973–5980.

(87) Ivanov, D. M.; Novikov, A. S.; Ananyev, I. V.; Kirina, Y. V.; Kukushkin, V. Y. Halogen Bonding between Metal Centers and Halocarbons. *Chem. Commun.* **2016**, *52*, 5565–5568.

(88) Adonin, S. A.; Bondarenko, M. A.; Abramov, P. A.; Novikov, A. S.; Plyusnin, P. E.; Sokolov, M. N.; Fedin, V. P. Bromo- and Polybromoantimonates(V): Structural and Theoretical Studies of Hybrid Halogen-Rich Halometalate Frameworks. *Chem. - Eur. J.* **2018**, *24*, 10165–10170.

(89) Adonin, S. A.; Udalova, L. I.; Abramov, P. A.; Novikov, A. S.; Yushina, I. V.; Korolkov, I. V.; Semitut, E. Y.; Derzhavskaya, T. A.; Stevenson, K. J.; Troshin, P. A.; Sokolov, M. N.; Fedin, V. P. A Novel Family of Polyiodo-Bromoantimonate(III) Complexes: Cation-Driven Self-Assembly of Photoconductive Metal-Polyhalide Frameworks. *Chem. - Eur. J.* **2018**, *24*, 14707–14711.

(90) Johnson, E. R.; Keinan, S.; Mori-Sanchez, P.; Contreras-Garcia, J.; Cohen, A. J.; Yang, W. Revealing Noncovalent Interactions. *J. Am. Chem. Soc.* **2010**, *132*, 6498–6506.

(91) Bartashevich, E. V.; Tsirelson, V. G. Interplay between Non-Covalent Interactions in Complexes and Crystals with Halogen Bonds. *Russ. Chem. Rev.* **2014**, *83*, 1181–1203.

(92) Espinosa, E.; Alkorta, I.; Elguero, J.; Molins, E. From Weak to Strong Interactions: A Comprehensive Analysis of the Topological and Energetic Properties of the Electron Density Distribution Involving X–H···F–Y Systems. J. Chem. Phys. **2002**, 117, 5529–5542.

(93) Cui, Y.; Wang, L.; Kwong, F.; Tse, M.; Chan, A. A Highly Efficient Chiral-Bridged Diphosphine Ligand Modified Cationic Palladium(II) Catalyst System for Asymmetric Alternating Copolymerization of Propene and Carbon Monoxide. *Synlett* **2009**, 2009, 2696–2700.

(94) Werner, A. Ueber Acetylacetonverbindungen Des Platins. Ber. Dtsch. Chem. Ges. **1901**, 34, 2584–2593.

(95) Sheldrick, G. M. Crystal Structure Refinement with SHELXL. Acta Crystallogr., Sect. C: Struct. Chem. 2015, 71, 3–8.

(96) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. OLEX2 : A Complete Structure Solution, Refinement and Analysis Program. J. Appl. Crystallogr. **2009**, *42*, 339–341.

(97) CrysAlisPro, Version 1.171.136.120; Agilent Technologies Ltd.: release 127-106-2012.

(98) Sheldrick, G. M. CELL_NOW, Version 2008/4; Georg-August-Universität Göttingen: Göttingen, Germany, 2008.

(99) Blessing, R. H. An Empirical Correction for Absorption Anisotropy. Acta Crystallogr., Sect. A: Found. Crystallogr. **1995**, 51, 33–38.

(100) Blessing, R. H. Outlier Treatment in Data Merging. J. Appl. Crystallogr. 1997, 30, 421-426.

(101) Sheldrick, G. M. *TWINABS, Version 2012/1;* Georg-August-Universität Göttingen: Göttingen, Germany, 2012.

(102) Krause, L.; Herbst-Irmer, R.; Sheldrick, G. M.; Stalke, D. Comparison of Silver and Molybdenum Microfocus X-Ray Sources for Single-Crystal Structure Determination. *J. Appl. Crystallogr.* **2015**, *48*, 3–10.

(103) Sheldrick, G. M. XS, Version 2013/1; Georg-August-Universität Göttingen: Göttingen, Germany, 2013.

(104) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Keith, T.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; J, C.; Fox, D. J. *Gaussian 09, Revision C.01*; Gaussian, Inc.: Wallingford, CT, 2010.

(105) Chai, J.-D.; Head-Gordon, M. Long-Range Corrected Hybrid Density Functionals with Damped Atom–Atom Dispersion Corrections. *Phys. Chem. Chem. Phys.* **2008**, *10*, 6615.

(106) Barros, C. L.; de Oliveira, P. J. P.; Jorge, F. E.; Canal Neto, A.; Campos, M. Gaussian Basis Set of Double Zeta Quality for Atoms Rb through Xe: Application in Non-Relativistic and Relativistic Calculations of Atomic and Molecular Properties. *Mol. Phys.* **2010**, *108*, 1965–1972.

(107) Canal Neto, A.; Jorge, F. E. All-Electron Double Zeta Basis Sets for the Most Fifth-Row Atoms: Application in DFT Spectroscopic Constant Calculations. *Chem. Phys. Lett.* **2013**, *582*, 158–162.

(108) de Berrêdo, R. C.; Jorge, F. E. All-Electron Double Zeta Basis Sets for Platinum: Estimating Scalar Relativistic Effects on Platinum(II) Anticancer Drugs. *J. Mol. Struct.: THEOCHEM* **2010**, *961*, 107–112.

(109) Jorge, F. E.; Canal Neto, A.; Camiletti, G. G.; Machado, S. F. Contracted Gaussian Basis Sets for Douglas–Kroll–Hess Calculations: Estimating Scalar Relativistic Effects of Some Atomic and Molecular Properties. *J. Chem. Phys.* **2009**, *130*, 064108.

(110) Zhao, Y.; Truhlar, D. G. The M06 Suite of Density Functionals for Main Group Thermochemistry, Thermochemical Kinetics, Noncovalent Interactions, Excited States, and Transition Elements: Two New Functionals and Systematic Testing of Four M06-Class Functionals and 12 Other Function. *Theor. Chem. Acc.* **2008**, *120*, 215–241.

(111) Stevens, W. J.; Basch, H.; Krauss, M. Compact Effective Potentials and Efficient Shared-exponent Basis Sets for the First- and Second-row Atoms. *J. Chem. Phys.* **1984**, *81*, 6026–6033.

(112) Stevens, W. J.; Krauss, M.; Basch, H.; Jasien, P. G. Relativistic Compact Effective Potentials and Efficient, Shared-Exponent Basis Sets for the Third-, Fourth-, and Fifth-Row Atoms. *Can. J. Chem.* **1992**, *70*, 612–630.

(113) Cundari, T. R.; Stevens, W. J. Effective Core Potential Methods for the Lanthanides. *J. Chem. Phys.* **1993**, *98*, 5555–5565.

(114) Lu, T.; Chen, F. Multiwfn: A Multifunctional Wavefunction Analyzer. J. Comput. Chem. 2012, 33, 580-592.

(115) Spackman, M. A.; Jayatilaka, D. Hirshfeld Surface Analysis. CrystEngComm 2009, 11, 19-32.

(116) Wolff, D. J.; McKinnon, J. J.; Turner, M. J.; Jayatilaka, D.; Spackman, M. A. *CrystalExplorer (Version 3.1)*; University of Western Australia: 2012.

(117) McKinnon, J. J.; Jayatilaka, D.; Spackman, M. A. Towards Quantitative Analysis of Intermolecular Interactions with Hirshfeld Surfaces. *Chem. Commun.* **2007**, *37*, 3814.