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)

Published as part of the Crystal Growth & Design virtual special issue on Halogen Bonding in Crystal Engineering: Fundamentals and Applications

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Ⓢ *Supporting Information*

ABSTRACT: The behavior of a sterically crowded neutral pincer {2,6-bis[(di-*t*-butylphosphino)methyl]-phenyl}palladium (PCPPd) halides, PCPPdX (X = Cl, Br or I), as XB acceptors with strong halogen bond (XB) donors, iodine (I₂), 1,4-diiodotetrafluorobenzene (F4DIBz), and 1,4-diiodooctafluorobutane (F8DIBu) were studied in the solid state. The co-crystallization experiments afforded high-quality single crystals of XB complexes PCPPdCl−I₂ (**1a**), PCPPdBr−I₂ (**2a**), PCPPdI−I₂ (**3a**), PCPPdCl−F4DIBz (**1b**), PCPPdBr−F4DIBz (**2b**), and PCPPdBr−F8DIBu (**2c**). The 1:1 iodine complexes (**1a**, **2a**, and **3a**) all showed a strong halogen bonding interaction, the reduction of the sum of the van der Waals radii of halogen to iodine being 24.6 (**1a**), 23.9 (**2a**), and 19.4% (**3a**) with X···I−I angles of 177, 176, and 179°, respectively. While the pincer palladium chloride **1** and bromide **2** were

crystallographically isomorphous and showed similar XB behavior, the palladium iodide complex, **3**, exhibited markedly different properties, and unlike **1** and **2** it does not, under similar conditions, result in XB complexes with the weaker XB donors F4DIBz and F8DIBu. The results indicate that PCPPdI is not nucleophilic enough to have XB interactions with other donors than iodine. However, the weaker XB donors F4DIBz and F8DIBu form XB complexes with the chloride **1** and especially with the bromide **2**. The prevalence of the halogen bonding with **2** is probably not only electronic in origin, and it seems to offer the best balance between electron poorness and steric availability. The XB interactions with F4DIBz and F8DIBu are much weaker than with iodine, the reduction of the sum of the van der Waals radii of halogen to iodine being 13.5, 12.3, and 14.6% with C−I···X angles between 163 and 179° for **1b**, **2b**, and **2c**, respectively, and results in polymeric (···**1**···F4DIBz···**1**···F4DIBz···)$_n$, (···**2**···F4DIBz···**2**···F4DIBz···)$_n$, and (···**2**···F8DIBu···**2**···F8DIBu···)$_n$ one-dimensional zigzag chains in the solid state.
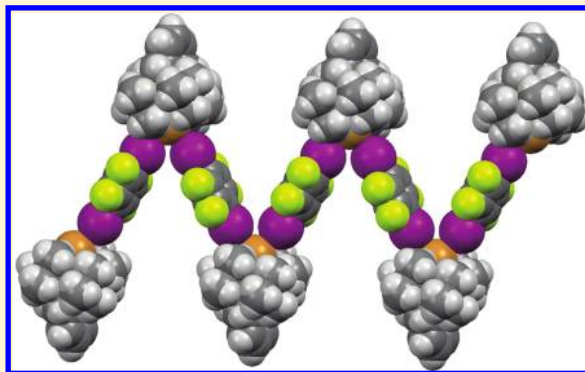
■ INTRODUCTION

Halogen atoms are common substituents in a highly diverse range of molecules and subject to noncovalent interactions in both solution and the solid state. Depending on their environment, they form two types of relatively strong highly directional intermolecular interactions: hydrogen bonds and halogen bonds. Intermolecular interactions based on hydrogen bonding (HB) and coordination bonds are by far the most frequently used tools in supramolecular chemistry and especially in crystal engineering.[1,2] During the past decade, another type of interaction known as halogen bonding (XB) has been intensively studied and can now be considered as a possible option in the

design and synthesis of new supramolecular systems with desired architectures and functions.[3] Halogen bonding, whose terminology emphasizes its similarity with hydrogen bonding, can be defined as any noncovalent interaction involving a halogen atom as an acceptor of electron density,[4] and the interaction with the electron donor is in most cases explained by the theory of σ-hole bonding;[5a−c] recently, alternative models of halogen bonding such as the lump-and-hole[5d] and the amphoteric halogen bonding[5e]

have also been proposed. The halogen bonding is highly directional and the interaction energies are usually comparable to hydrogen bonding. However, this general definition[4] of halogen bonding covers a vast family of such interactions and a very wide range of dissociation energies.[6]

The most robust and well-defined supramolecular complexes and networks derived from XB interactions are generally achieved by using XB donors where an iodine atom is covalently bound to a strongly electron withdrawing atom or molecular unit and a strong Lewis base is used as the XB acceptor.[7] The usefulness of these interactions in the design of supramolecular structures and solid state materials has been pioneered by the studies of co-crystals of perfluorocarbon (C_{PFC}) iodides and aliphatic (sp^3) or aromatic (sp^2) amines.[8] The self-assembly process of the molecular complexes is driven by a strong $C_{PFC}-I\cdots N$ interaction, where the contact distances are about 2.8 Å, corresponding to a remarkable (ca. 20%) reduction of the sum of the van der Waals (vdW) radii of nitrogen (1.55 Å) and iodine (1.98 Å) atoms.[8,9] The strong interaction between the highly polarized iodine and the nitrogen atom, manifested by the short and directional intermolecular contact, overrides the low attraction between the hydrocarbon and perfluorocarbon moieties and frequently yields stable crystalline products with high melting points. Typical packing in these co-crystals is governed by segregated molecular entities with columnar or layered packing[10] as a consequence of minimizing the less favorable vdW contacts.[11]

Regarding situations when halogens are XB acceptors, and thus acting as Lewis bases, the situation is somewhat more complex. The naked anions show decreasing XB acceptor efficiency in the series $I^- > Br^- > Cl^- > F^-$, consistent with their properties as nucleophiles. This is commonly rationalized as a charge transfer of nonbonding electrons of the halogenide anion to the σ^*-orbital of the X–D unit thereby explaining the typical elongation of the bond C–X for halocarbons or X–X for dihalogens.[12]

However, this trend is reversed when metal halides (M–X) act as XB acceptors. A few studies indicate that for a fixed XB donor halogen, the $R_{XX'}$ distance, after accounting for their different van der Waals radii, is shorter for lighter inorganic halogen M–X acceptors, and thus the interaction is stronger.[13] This hints that the electrostatic contribution is of larger importance than charge transfer since the lighter inorganic halides exhibit a higher negative electrostatic potential. It is, however, not known whether these trends are completely consistent for all transition metals M–X acceptors as only a limited number of such systems have been studied.[14]

Besides the obvious interest from a bonding point of view, the $M-X\cdots X-D$ interaction should be a strong and directional intermolecular interaction, thus providing a potentially useful way of combining inorganic and organic tectons for supramolecular recognition.

The few known crystal structures involving metal halides and X_2 can be divided into two main categories:

(1) Interaction between the halide ligand and the X_2 molecule in mononuclear metal complexes ($M-X\cdots X-X$ interaction)

(2) Dimeric or polymeric structures, in which two or more metal halide complexes are linked together by X_2 bridges ($M-X\cdots X-X\cdots X-M$ structures)

The known metal halide/X_2 systems involve metals such as Pt, Pd, Fe, Ir, Cu, Ni, Re, and Ru.[14e−n,15,16] Recently some of us

have reported new Ru-based XB systems, one with the known solar-cell N3 dye molecule.[17,18]

Palladium pincer complexes based on an aromatic backbone are highly versatile molecules showing high activity in a wide range of reactions from catalysis to bond activation.[19] In some of our work on carbon dioxide activation we have shown that the *trans* influence of the aryl group plays a large role in instilling reactivity in the X-group (Scheme 1).[20] Still, these

Scheme 1. The Different XB Donors (a−c) Co-Crystallized with the PCPPd Complexes 1−3
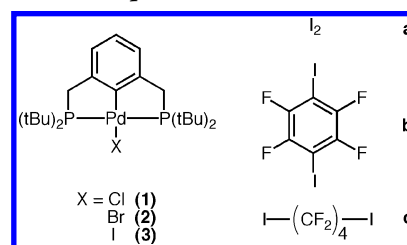
systems are typically highly thermally stable and we therefore thought it to be of interest to study their noncovalent interactions in solution and in the solid state. Previously, they have been shown to result in highly interesting channel structures based on weak hydrogen bonding.[21] Here we report on the formation of halogen bonded interactions using a sterically crowded pincer palladium model complex {2,6-bis[(di-*t*-butylphosphino)-methyl]-phenyl}palladiumhalide (PCPPdX) as XB acceptor and various electron poor iodine compounds as XB donors.

■ EXPERIMENTAL SECTION

General Procedures and Materials. All reactions were carried out under an atmosphere of nitrogen in a glovebox or using standard Schlenk or high-vacuum-line techniques. All nondeuterated solvents used for synthesis were vacuum-transferred from sodium/benzophenone ketyl directly to the reaction vessel except acetone which was used as received. Solvents for co-crystallization were used as received. All other commercially available reagents were purchased from Sigma Aldrich and used as received. Complex **1** was prepared according to the literature.[20b] ^1H, ^{13}C, and ^{31}P NMR spectra were recorded in benzene-d_6 on a Varian Unity INOVA 500 spectrometer operating at 499.77 MHz (^1H). Chemical shifts are given in ppm downfield from TMS using residual solvent peaks (^1H and ^{13}C NMR) or H_3PO_4 as reference.

Synthesis of PCPPdBr (2). 1,3-Bis(di-*t*-butylphosphinomethyl)-benzene (1.50 g, 3.80 mmol) was placed together with $PdBr_2$ (1.01 g, 3.80 mmol) in a thick-walled Strauss flask in a glovebox. THF (30 mL) was distilled into the flask and the mixture was allowed to stir at room temperature for 48 h. The resulting bright yellow solution was evaporated to dryness and the solids were recrystallized from hot hexane to give 2.05 g. ^1H NMR (C_6D_6) = 7.04 (m, 1H), 6.96 (m, 2H), 3.01 (vt, 4H, $^2J_{H-P}$ = 3.5 Hz), 1.34 (vt, 36H, $^3J_{H-P}$ = 6.5 Hz), ^{13}C NMR (C_6D_6) 151.4 (t, J = 12.5 Hz), 127.7 (m), 125.2 (s), 122.3 (t, J = 10.3 Hz), 35.4 (vt, J = 9.9 Hz), 29.7 (vt, J = 2.8 Hz), 26.6 (vt, J = 8.4 Hz); ^{31}P NMR (C_6D_6) = 73.18.

Synthesis of PCPPdI (3). To a 15 mL acetone solution of [2,6-Bis(di-*tert*-butylphosphinomethyl)phenyl]-(trifluoroacetato)palladium-(II) (490 mg, 0.80 mmol) sodium iodide was added (1.2 g, 8.0 mmol). The mixture was stirred at room temperature for 48 h. The solvent was evaporated and the product was extracted with toluene. After evaporation of solvent, a white solid (0.50 g, 94%) was obtained. ^1H NMR (C_6D_6) = 7.06 (m, 1H), 6.98 (d, 2H, $^3J_{H-H}$ = 7.5 Hz), 3.06 (vt, 4H, $^2J_{H-P}$ = 4 Hz), 1.35 (vt, 36H, $^3J_{H-P}$ = 6.5 Hz), ^{13}C NMR (C_6D_6) 151.1 (t, J = 10 Hz), 127.5 (m), 125.4 (s), 122.0 (t, J = 10 Hz), 36.3 (vt, J = 10 Hz), 35.8 (vt, J = 8 Hz), 29.9 (vt, J = 3 Hz); ^{31}P NMR (C_6D_6) = 74.55;

Table 1. Crystallographic Data for 1a, 1b, 2a, 2b, 2c, and 3a

complex	1a	1b	2a	2b	2c	3a
formula	$C_{24}H_{43}ClP_2PdI_2$	$C_{30}H_{43}ClP_2PdI_2F_4$	$C_{24}H_{43}BrP_2PdI_2$	$C_{30}H_{43}BrP_2PdI_2F_4$	$C_{28}H_{43}BrP_2PdI_2F_8$	$C_{24}H_{43}IP_2PdI_2$
F.W.	789.17	937.23	833.63	981.69	1033.67	880.62
space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$C2/c$	$C2/c$	$P2_1/c$
a [Å]	11.2074(2)	15.9789(4)	11.2641(3)	17.1567(6)	15.6991(5)	10.3069(4)
b [Å]	15.8342(4)	17.4537(5)	15.8359(5)	13.1863(6)	13.8991(6)	26.4128(9)
c [Å]	16.8635(3)	12.7454(3)	17.0352(5)	15.6856(7)	17.1536(7)	11.3538(4)
α [°]	90	90	90	90	90	90
β [°]	90.554(1)	91.485(2)	90.879(2)	93.978(2)	90.968(2)	102.766(2)
γ [°]	90	90	90	90	90	90
V [Å^3]	2992.5(1)	3553.4(2)	3038.3(2)	3540.1(3)	3742.4(3)	3014.5(2)
Z	4	4	4	4	4	4
D_{calc}	1.752	1.752	1.822	1.842	1.835	1.940
μ [mm^{-1}]	2.890	2.465	4.074	3.527	3.356	3.805
θ comp [%]	99.3	99.9	99.9	99.7	99.6	97.5
no. reflns	5245	6248	5347	3116	3291	5180
no. parameters	283	373	283	189	198	283
R_1 [$I > 2\sigma(I)$]	0.0257	0.0500	0.0505	0.0282	0.0367	0.0316
wR_2 [$I > 2\sigma(I)$]	0.0680	0.1202	0.0942	0.0622	0.0755	0.0914
GOF on F^2	1.057	1.071	1.094	1.032	1.073	1.052
ΔF max [e Å^{-3}]	0.637	1.218	0.963	0.517	0.529	0.816
ΔF min [e Å^{-3}]	−0.611	−1.102	−0.832	−0.578	−0.592	−1.144

Co-Crystallization of PCPPdCl–I₂ (1a). PCPPdCl (7.8 mg, 15.0 μmol) was dissolved in 5 mL of petroleum ether under gentle heating. Iodine (4.3 mg, 17.0 μmol) was dissolved in 3 mL petroleum ether in a separate vial where after the solution was added to the PCPPdCl solution. After 72 h, red-brown crystals had grown on the liquid−air interface.

Co-Crystallization of PCPPdCl–F4DIBz (1b). PCPPdCl (6.0 mg, 11.2 μmol) was dissolved in 5 mL of petroleum ether under gentle heating. 1,4-Diiodotetrafluorobenzene (9.0 mg, 22.4 μmol) was dissolved in 3 mL of petroleum ether in a separate vial whereafter the solution was added to the PCPPdCl solution. After four days, colorless crystals had formed on the bottom of the vial.

Co-Crystallization of PCPPdBr–I₂ (2a). A hexane solution (5 mL) of I₂ (8.9 mg, 0.035 mmol) was added dropwise to the PCPPdBr (20 mg, 0.035 mmol) solution in hexane (5 mL) and was left at room temperature for 24 h, after which the formation of high-quality crystals suitable for X-ray diffraction analysis was observed. The red-brown crystals formed were isolated by filtration and dried in air.

Co-Crystallization of PCPPdBr–F4DIBz (2b). PCPPdBr (20.0 mg, 34.5 μmol) was dissolved together with 1,4-diiodotetrafluorobenzene (6.9 mg, 17.2 μmol) in 5 mL of hexane giving colorless crystals.

Co-Crystallization of PCPPdBr–F8DIBu (2c). PCPPdBr (20.0 mg, 34.5 μmol) was dissolved together with 1,4-diiodoperfluorobutane (7.8 mg, 17.2 μmol) in 5 mL of hexane resulting in pink crystals.

Co-Crystallization of PCPPdI–I₂ (3a). PCPPdI (9.2 mg, 8.0 μmol) was dissolved together with iodine (1.9 mg, 7.3 μmol) in 2 mL of heptane. After 48 h, red-brown crystals had formed.

X-ray Crystallography. Suitable crystals of 1a, 1b, 2a, 2b, 2c, and 3a for single crystal X-ray diffraction analysis were selected and the data collections were performed using a Bruker Kappa Apex II diffractometer with graphite-monochromatized Mo K$_\alpha$ (λ = 0.71073 Å) radiation at 123.0(1) K. Collect software[22] was used for the data data collection and DENZO-SMN[23] for the processing. The structures were solved by direct methods with SIR97[24] and refined by full-matrix least-squares methods with SHELXL97,[25] which is implemented in WinGX program package.[26] All C−H hydrogen positions were calculated in the idealized positions by using a riding atom model after the anisotropic refinement of all non-hydrogen atoms of the structure. Detailed crystallographic data for all structures are summarized in Table 1.

■ RESULTS AND DISCUSSION

The behavior of the PCPPdX complexes as halogen bond acceptors was studied by mixing equal amounts of the pincer complex with strong halogen bond donors, namely, iodine (I₂, a), 1,4-diiodotetrafluorobenzene (F4DIBz, b), and 1,4-diiodooctafluorobutane (F8DIBu, c) (Scheme 1). These experiments afforded high-quality single crystals for 1a, 1b, 2a, 2b, 2c, and 3a (Table 1). Of these strong XB donors iodine forms the strongest halogen bonds known while the F4DIBz and F8DIBu show noticeable shorter but still strong XB interaction with nucleophilic atoms (XB acceptors), such as N, O and S,[3−8] but no previous halogen bonded complexes of the Pd-pincer or any of this type of neutral organometallic complex with high *trans* influence ligands have been reported.[27] In order for the XB interaction to occur, the XB acceptor atom has to be nucleophilic enough; that is, they have to have an excess of electrons, viz. either as an anion or free electron pair[3] for the interaction with the σ-hole of the XB donor).[5]

All pincer palladium halides turned out to be nucleophilic enough to form a strong XB complex with iodine. Table 2 lists the XB interaction distances and angles, and Figure 1 depicts the ball-and-stick as well as CPK plots of the iodine complexes 1a, 2a, and 3a.

The strength of the XB interaction is generally estimated by the "shortness" of the XB(acc.)···XB(donor) distance, that is, the reduction of the sum of the van der Waals radii (rsvdW) and the Y−XB(acc.)···XB(donor) angles (close to 180° for strong XB) of the interacting atoms. The vdW radii for Cl, Br, and I atoms are 1.75, 1.85, and 1.98 Å, respectively, and the corresponding sum of the vdW radii are Cl + Cl = 3.50; Cl + Br = 3.60; Cl + I = 3.73; Br + Br = 3.70; Br + I = 3.83; and I + I = 3.96 Å.

A reduction of 25% from the sum of vdW radii is considered a strong XB interaction, viz. a halogen bond and is encountered with either iodine (reduction up to 30%) and iodo- or diiodoperfluoroalkane/benzene (reduction up to 25%) complexes of amines.[3] Recently, some of us have reported[28] very short

Table 2. The XB and Other Relevant Interaction Distances (Å) and Angles (°) for 1a, 1b, 2a, 2b, 2c, and 3a

	1a	1b	2a	2b	2c	3a
Pd1−C1/Å	2.020(4)	2.016(7)	2.022(8)	2.031(5)	2.020(6)	2.036(6)
Pd1−P1/Å	2.316(1)	2.308(2)	2.325(2)	2.325(1)	2.312(1)	2.319(2)
Pd1−P2/Å	2.311(1)	2.308(2)	2.318(2)	2.325(1)	2.312(1)	2.322(2)
Pd1−X1/Å	2.446(1)	2.414(2)	2.553(1)	2.540(1)	2.553(1)	2.722(1)
X1···I/Å	2.812(1)	3.228(2)	2.913(1)	3.357(1)	3.269(1)	3.193(1)
		3.229(2)		3.357(1)	3.269(1)	
I1−I2/I2−I3/Å	2.748(1)		2.763(1)			2.774(1)
Pd1−X1−X2/°	124.26(4)	143.34(7)	122.37(3)	139.54(1)	129.23(1)	111.27(2)
		131.05(7)		139.54(1)	129.23(1)	
I−X−I/°		85.17(4)		80.91(1)	101.55(2)	
X3−X2−X1/°	177.06(2)	174.9(2)	75.84(3)	170.0(1)	179.4(2)	179.10(2)
		163.1(2)		170.0(1)	179.4(2)	
rsvdW/%	24.6	13.5	23.9	12.3	14.6	19.4
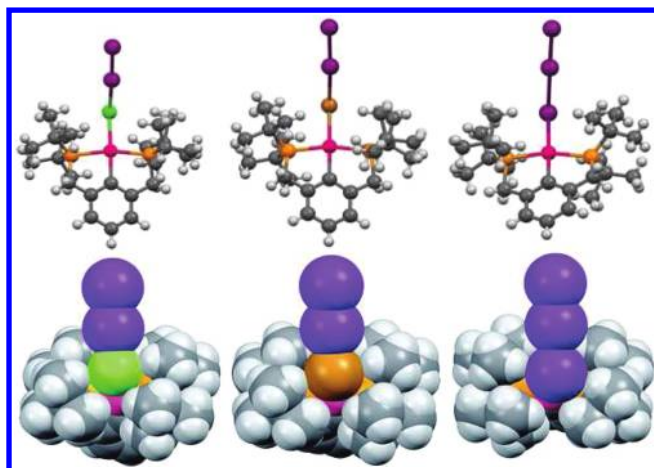
Figure 1. The ball-and-stick (top) and CPK plots (below) for **1a** (left), **2a**, and **3a** (right).

Figure 2. Packing of **1a** (left), **2a** (middle), and **3a** (right).

XB(acc.)···XB(donor) distances with amines and haloamides as alternative XB donors (rsvdW reduction up to 29%).

A quick glance at the I$_2$-complexes **1a**, **2a**, and **3a** reveals a close similarity (see Figure 1), and the XB distances and angles indicate a very strong interaction (rsvdW of 24.6, 23.9, and 19.4% and I−I···X angles of 177, 176, and 179° for **1a**, **2a**, and **3a**, respectively). The order of the halogen bond strength, based on the rsvdW, is reversed, I < Br < Cl, compared to the general trend observed for XB interactions, namely, Cl < Br < I. Instead, it follows the order that is usually observed when metal halides are used as XB acceptors. Thus, the XB interaction seems to be mainly electrostatic despite the fact that the metal center is highly electron rich. Note that even though the complexes **1a**, **2a**, and **3a** could be considered formally to contain an Cl−I−I⁻, Br−I−I⁻, or I−I−I⁻ moiety, this formulation is not correct, since the interaction between the PCPPdX and iodine molecule is noncovalent and it easily dissociates to PCPPdX and I$_2$.

A more detailed inspection reveals that **1a** and **2a** are isomorphous (Table 1) with very similar bond distances and angles (Table 2), while the structure of **3a** is markedly different, both crystallographically, as seen by the unit cell parameters, and in the molecular structure as the Pd1−X1−I angle, which is 123−124° in **1a** and **2a**, is only 111° in **3a**. This 12° narrower angle between Pd−I and the I$_2$ molecule in **3a** affects the packing (Figure 2, right) slightly and gives a shorter intermolecular Pd−I···I−I···π interaction to the benzene ring of the adjacent
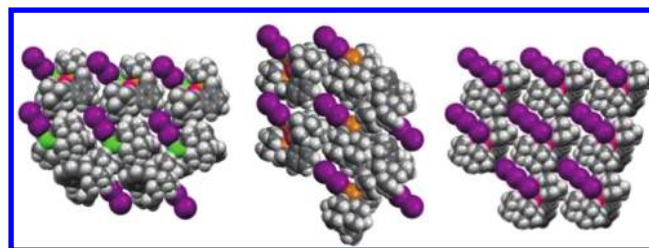
pincer complex, the Pd−I···I···C(arom.) contact distance being 3.450(7) Å, which is slightly shorter than the svdW of iodine and carbon atoms. This interaction does not exist in the structures of **1a** or **2a**.

Unlike nitrogen Lewis bases, a one electron pair XB acceptor, the Pd pincer complexes can in principle act as a triple XB acceptor, thus potentially giving Pd-X···(XB(donor))$_2$ or Pd-X···(XB(donor))$_3$ complexes.[3] For example, in (2,6-bis-(dimethylaminomethyl)phenyl-C,N,N′)-iodo-palladium(II) bis(di-iodine)[29] the anionic iodide forms intermolecular bonds to three I$_2$ molecules (Pd−I···I: 3.27−3.29 Å). Clearly, the bulky *tert*-butyl groups prevents this in **1a**, **2a**, and **3a** and only a single interaction is observed.

We reasoned that if linear diiodo-perfluoroalkanes or -benzenes were used as XB donors there would be a better possibility for multiple interactions and for this experiment we chose to use 1,4-diiodotetrafluorobenzene (F4DIBz, **b**) and 1,4-diiodoocta-fluorobutane (F8DIBu, **c**) which both offer a linear XB donor with nearly equal intramolecular I···I distances, being 7.0 Å in **b** and 7.6 Å in **c**. As the XB donor is now in itself bis-functional with two strongly polarized iodine atoms, it has the possibility to interact with two different pincer complexes. Thus, it should be possible to get multiple interactions both on the acceptor and donor side. Of the six possible combinations, we were only able to get stable crystals of three. Complexes **1b**, **2b**, and **2c** exhibit double halogen bonding as shown in Figure 3. The absence of any complexes with **3** seems to point in the same direction as previously discussed, namely, that the halogen bonds formed by the Pd complexes are mainly electrostatic in character and hence the Pd−I moiety is a too weak XB acceptor. The prevalence of the Pd−Br in halogen bonding (forms crystals with all studied XB donors) is probably not only electronic in origin, and we propose that the Pd−Br systems strikes the best balance between electron poorness and steric availability; the longer Pd−Br bond opens up the possibility for
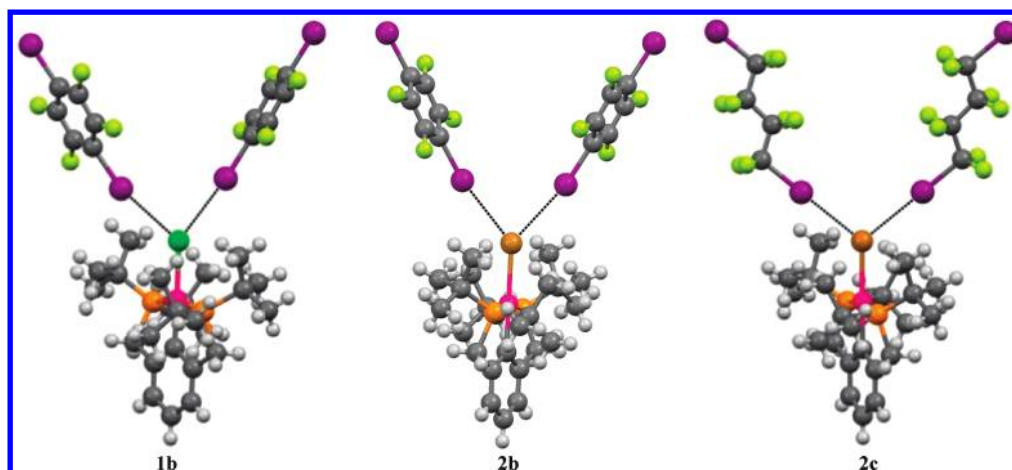
Figure 3. The ball-and-stick presentation of the double halogen bonding of 4FDIBz and 8FDIBu to **1** (left) and **2**.
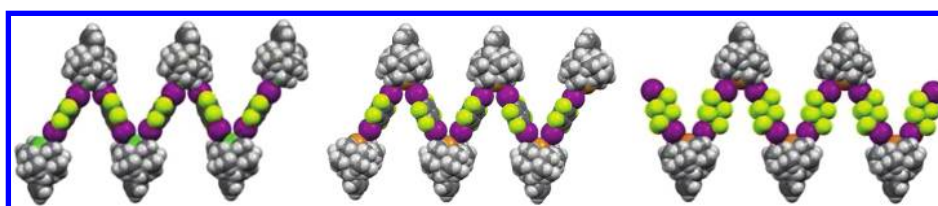

Figure 4. CPK presentation of the polymeric halogen bonding in **1b** (left), **2b** (middle), and **2c** (right) leading to 1-D zigzag strands.
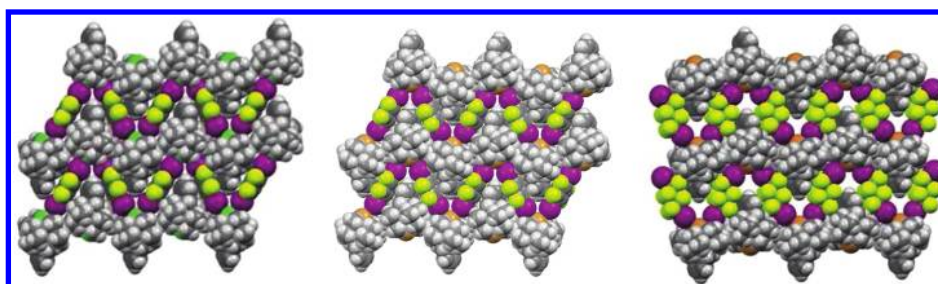

Figure 5. A CPK packing plots of **1b** (left), **2b** (middle), and **2c** (right).

a double halogen bond also in the case of the slightly more crowded halogen bond donor, 8FDIBu. Despite the much weaker polarization of the iodine in 4FDIBz and 8FDIBu, the XB interactions are still strong, but significantly longer than for the corresponding iodine complexes. The rsvdW's are now 13.5, 12.3, and 14.6% for **1b**, **2b**, and **2c**, respectively, with C–I···X angles between 163 and 179°.

The angle Pd–X···I is 143° and 131° for **1b** and 140° (×2) and 130° (×2) for **2b** and **2c**, respectively. This kind of M–X···(I)2 double halogen bonding motif is totally unprecedented and has not been reported earlier.[27] Only bromoiodomethane[30] shows a vaguely similar but much weaker motif. In **1b**, **2b**, and **2c** the Pd–X···(I)$_2$ moiety is trigonally planar.

The "bite-angle", I–X–I (X = Cl, Br or I), varies more than any other structural parameter, being 85.17° for the **1b** and 80.91° for **2b**, but opens up to 101.54° for **2c**. This is probably due to the larger steric demand of the bulkier 8FDIBu as compared to 4FDIBz and not due to any bonding resemblance to the T-shaped XY$_3$ interhalogen compounds.

This unique binding mode of the Pd-pincer complexes and the bis-functional nature of the 4FDIBz and 8FDIBu leads to polymeric one-dimensional (1-D) zigzag strands (Figure 4).

These 1-D strands then stack tightly in the other two dimensions creating a 3-D layer structure without any voids in the

case of **1b** and **2b** (Figure 5). The 0.6 Å longer 8FDIBu does not allow a similar tight packing of the 1-D strands and very small voids, so small that no solvent molecule could fit into it (Figure 5, right), are created into the lattice of **2c**.

■ CONCLUSIONS

We have performed the first systematic study of a triad of PCPPdX (X = Cl, Br, I) halogen bonding complexes with typical XB donors. The complete set was obtained for I$_2$ giving linear Pd–X···I units showing a clear trend toward a strong electrostatic component in the halogen bond, despite the electron-rich metal center resulting in XB strength Cl > Br > I. The XB behavior of PCPPdI clearly differs from the corresponding chloride and bromide with XB donors weaker than iodine, and the PCPPdI does not form any isolable halogen bonded complexes with 1,4-diiodotetrafluorobenzene (F4DIBz) and 1,4-diiodooctafluorobutane (F8DIBu) as the corresponding chloride and bromide does. Thus, the weaker electronic XB acceptor capacity of PCPPdI coupled with the bulky ligands severely hinders or prevents the possible double XB interaction observed for the PCPPdCl and PCPPdBr. The linear bis-functional XB donors F4DIBz and F8DIBu form 1-D zigzag chains with PCPPdCl and PCPPdBr due to the sufficiently strong XB

interaction between the donor and acceptor moieties, while the steric bulkiness of the *t*-butyl groups in the PCP-core prevents the possible triple interaction observed in some iodo-palladium complexes. Also it is clear that the PCPPdBr strikes the best balance for such interactions, being sufficiently sterically accessible and still electron poor enough to facilitate the halogen bond with all the studied XB donors.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic information files (CIF) for **1a**, **1b**, **2a**, **2b**, **2c**, and **3a**. This information is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENTS

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