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The $\text{H}_2\text{C}(\text{X})\text{--X}\cdots\text{X}^-$ ($\text{X} = \text{Cl}, \text{Br}$) Halogen Bonding of Dihalomethanes

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Abstract

The dihalomethane–halide $\text{H}_2\text{C}(\text{X})\text{--X}\cdots\text{X}^-$ ($\text{X} = \text{Cl}, \text{Br}$) halogen bonding was detected in a series of the *cis*-[PdX(CNCy){C(NHCy)=NHC₆H₂Me₂NH₂}]X·CH₂X₂ ($\text{X} = \text{Cl}, \text{Br}$) associates by single-crystal XRD followed by DFT calculations. Although ESP calculations demonstrated that the σ -hole of dichloromethane is the smallest among all halomethane solvents (the maximum electrostatic potential is only 2.6 kcal/mol), the theoretical DFT calculations followed

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3 by Bader's QTAIM analysis (M06/DZP-DKH level of theory) confirmed the $\text{H}_2\text{C}(\text{X})\text{-X}\cdots\text{X}^-$
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6 halogen bond both in the solid state and gas phase optimized geometries. The estimated bonding
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8 energies in $\text{H}_2\text{C}(\text{X})\text{-X}\cdots\text{X}^-$ is in the 1.9–2.8 kcal/mol range.
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10 11 12 **Introduction**

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15 Orientation of solvent molecules around anions is intensively studied in crystal engineering,
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17 solution and colloid chemistry, and also in catalysis.¹⁻⁷ Among different anions, halides play
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19 especially important chemical and biological roles, in particular, in asymmetric catalysis,⁸⁻¹⁰
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21 design of artificial anion receptors, and in the ionic homeostasis of the living cells.¹¹⁻¹⁵ In most
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23 cases, solvation of halide anions proceeds through hydrogen bonding (HB) with solvent
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25 molecules.
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30 Halomethanes—apart from positive H centers responsible for HBs—featuring an
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32 alternative type of partial positive charge centers, viz. the σ -holes¹⁶ of covalently bound chlorine,
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34 bromine, or iodine atoms, which may be responsible for non-covalent contacts. The calculations
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36 conducted by us in this work (**Table 1, Figure 1**) and previously by some other groups¹⁷⁻¹⁹ (for
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38 more details see Supporting information, **Table SI1**) clearly indicate that the values of
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40 electrostatic potential on the σ -holes, and correspondingly the ability of forming XBs,
41
42 substantially depend on amount and type of halogen atoms in the halomethanes. These XBs were
43
44 widely studied for *effective* halomethane XB donors (CBr_4 ,¹⁹⁻²¹ CHI_3 ,^{22,23} CFBr_3 ,¹⁹ CCl_3Br ,²⁴ and
45
46 CHBr_3 ;^{19,20} for full description of the $\text{C-X}\cdots\text{X}^-$ XBs, the $\text{X}\cdots\text{X}^-$ distances and the $\angle(\text{C-X}\cdots\text{X}^-)$
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48 angles see Supporting information, **Table SI2**), whereas the relatively *inactive* (**Table 1, Figure**
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50 **1**) XB donors such as CCl_4 and CHCl_3 quite rarely form XBs.²⁵⁻²⁶
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3 **Table 1.** Maximum electrostatic potentials ($V_S(\mathbf{r})_{\max}$, kcal/mol) on the halogen atoms calculated
4 (see Experimental) on the 0.001 a.u. molecular surfaces for CH_3X , CH_2X_2 , CHX_3 , and CX_4 ($\text{X} =$
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parentheses).

X	Cl	Br	I
CH_3X	-7.7	4.8 (15%)	15.1 (48%)
CH_2X_2	2.6 (8%)	13.7 (43%)	23.1 (73%)
CHX_3	10.4 (33%)	19.9 (63%)	28.1 (89%)
CX_4	16.0 (51%)	24.1 (77%)	31.5 (100%)

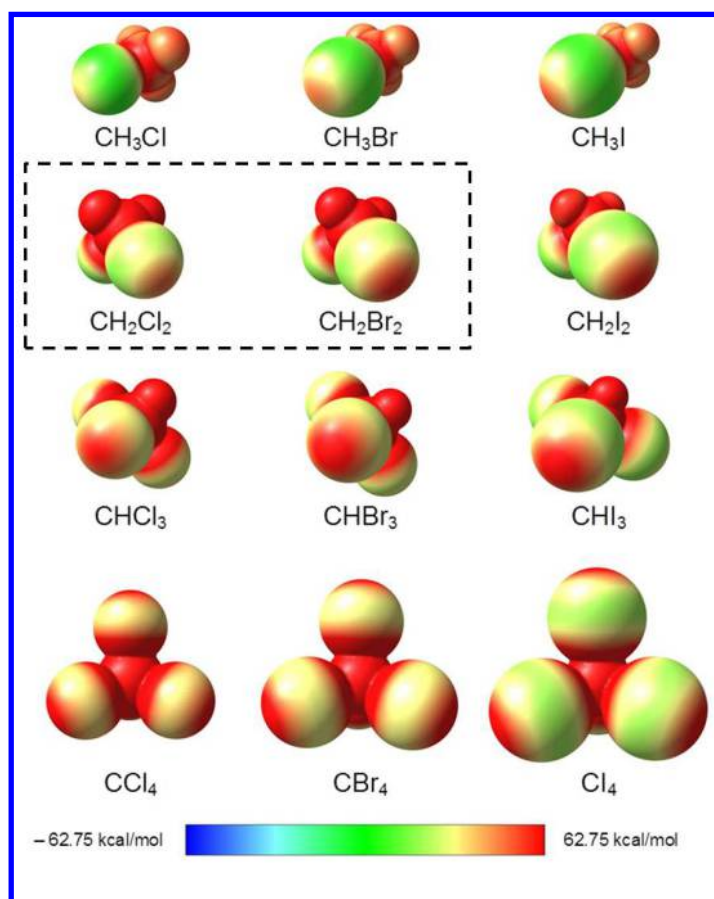


Figure 1. ESP distribution in the $\text{CH}_n\text{X}_{4-n}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}; n = 1-3$) halomethane molecules.

Until now only a few publications were devoted to XBs in condensed phases involving CH_2Cl_2 , as the weakest σ -hole donor among halomethane solvents, and also with its bromine congener, CH_2Br_2 . Thus, the possibility of CH_2Cl_2 to behave as XB donor was acknowledged by statistical analyses of CCDC structures conducted by Allen *et al.*²⁷ and Mooibroek *et al.*²⁸ In the former report,²⁷ a possibility for the formation of various $\text{H}_2\text{C}(\text{Cl})-\text{Cl}\cdots\text{X}-\text{C}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) short contacts was indicated, but the angle parameters were not specified and therefore the ability of CH_2Cl_2 behave as XB donor was not fully confirmed. The latter article²⁸ gives certain statistical evidences favoring $\text{H}_2\text{C}(\text{Cl})-\text{Cl}\cdots\text{D}$ ($\text{D} = \text{F}, \text{Cl}, \text{Br}, \text{I}, \text{N}, \text{O}, \text{S}$) contacts, which can be treated as dichloromethane-involved XBs.

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2
3 Rodríguez and Bertrán²⁹ conducted NMR correlation analysis for CH₂X₂ (X = Cl, Br, I)
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5 in solvents of different basicity. The observed differences in ¹H chemical shifts indicated that
6
7 behavior of CH₂Cl₂ and CH₂Br₂ in these solutions is almost the same and the contribution of
8
9 XBs to the solvation process is expected to be identical. Insofar as it was assumed²⁹ that CH₂Cl₂
10
11 forms only HB, it collaterally means that CH₂Br₂ does not form XBs in solutions. Jin *et al.*¹⁷
12
13 recently carried out EPR correlation study of the solvation of 2,2,6,6-tetramethyl-1-piperidin-1-
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15 yloxy free radical (TEMPO) by various solvents—including CH₂Cl₂ and CH₂Br₂—and found
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17 that the solvation is different in halogenated and in halogen-free solvents because of the C–
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19 X•••O–N XB. Subsequent theoretical calculations demonstrated comparable energies of HB and
20
21 XB in the observed solvent–TEMPO weak interactions.
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28 In the solid state, dibromomethane forms the H₂C(Br)–Br•••Br–C,^{30,31} H₂C(Br)–Br•••O,³²
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30 and H₂C(Br)–Br•••N³³ types of XB. Concurrently, XBs involving CH₂Cl₂ as the weakest XB
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32 donor among halomethane solvents, were described only in three works. The H₂C(Cl)–Cl•••Cl–C
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34 XBs were found in the crystalline CH₂Cl₂³⁴ and the unusual H₂C(Cl)–Cl•••N≡[Os] halogen
35
36 bonds were discussed in a review.³⁵ Eventually, some of us recently reported that CH₂X₂ (X =
37
38 Cl, Br) form the H₂C(X)–X•••Cl–[Pt] (X = Cl, Br) XBs with chloride ligands in platinum(II)
39
40 PANT complexes.³⁶ In the context of this work, one should stress that XBs of CH₂Cl₂ or CH₂Br₂
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42 with *any of the halide anions* are yet unreported.
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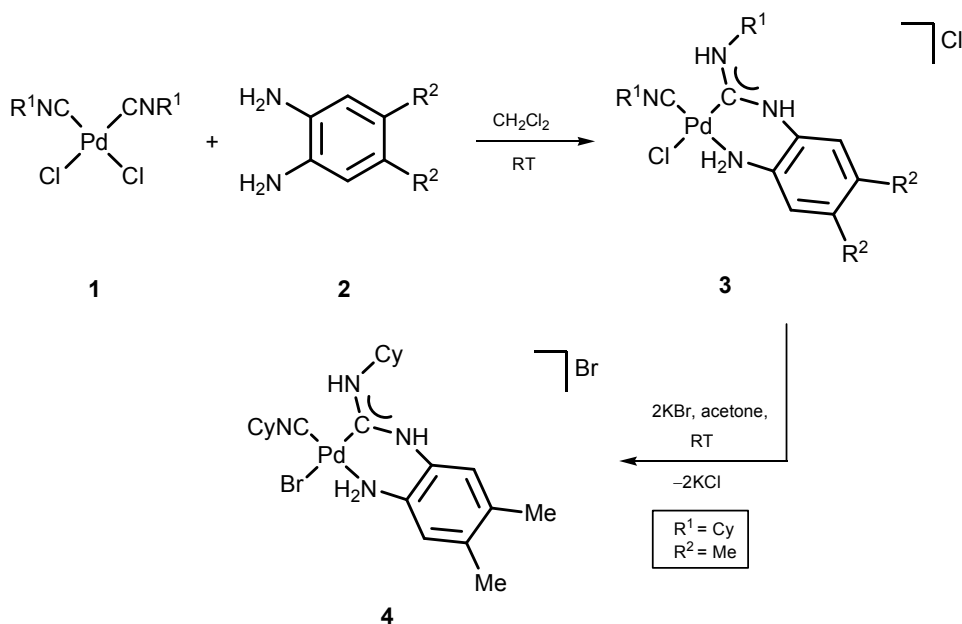
48 Previously we demonstrated that cationic 1,3,5-triazapentadienato nickel(II) and
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50 platinum(II) complexes can be used as scaffolds for a numerous solvent–chloride clusters held
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52 by simultaneous HBs^{26,37–40} and XBs.²⁶ We now expand a range of metal-based platforms, which
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54 can be applied for recognition of novel types of XB, by using acyclic diaminocarbene
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3 palladium(II) complexes (**Scheme 1**) known as catalysts for various organic transformations.⁴¹⁻⁴⁷

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5 We found that these palladium species can be co-crystallized with very weak XB donors such as
6 dichloromethane and dibromomethane giving solvates featuring $\text{H}_2\text{C}(\text{X})-\text{X}\cdots\text{X}^-$ (X = Cl, Br)
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8 XBs and our findings are the first recognition of XB between uncomplexed halides and
9 dihalomethanes.
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14 15 16 **Results and Discussion**

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19 Recently we reported^{48,49} the reaction between
20 *cis*-[PdCl₂(CNR¹)₂] (**1**) and benzene-1,2-diamines (**2**) that leads to the
21 *cis*-[PdCl(CNR¹){C(NHR¹)=NHC₆H₂(R²)₂NH₂}]Cl (R¹ = Cy (cyclohexyl), 2-Cl-6-MeC₆H₃, 2,6-
22 Me₂C₆H₃; R² = H, Me, Cl, **3a-d**) complexes bearing Cl⁻ as the counterion (**Scheme 1**).
23
24 Complexes **3b**, **3c**, and **3d** (**Table 1**) were characterized by single-crystal X-ray diffraction
25 (XRD) as dichloromethane solvates **3b**•CH₂Cl₂, **3c**•1½CH₂Cl₂, and **3d**•CH₂Cl₂•H₂O (**Figure 2**,
26 left).^{48,50} In these three structures, only N–H⋯Cl⁻, O–H⋯Cl⁻ (in **3d**•CH₂Cl₂•H₂O), and C–
27 H⋯Cl⁻ hydrogen bonds were observed and no halogen bonds were detected.
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Scheme 1. Syntheses of **3** and **4**.

Table 2. Numbering of complexes and their halomethane associates.

Complex	R ¹	R ²	CH ₂ X ₂	Associate	X-ray
3a	Cy	Me	CH ₂ Cl ₂	3a •CH ₂ Cl ₂	This work
3a	Cy	Me	CH ₂ Br ₂	3a •CH ₂ Br ₂	This work
3b	2-Cl-6-MeC ₆ H ₃	Me	CH ₂ Cl ₂	3b •CH ₂ Cl ₂	Ref ⁴⁸
3c	2-Cl-6-MeC ₆ H ₃	Cl	CH ₂ Cl ₂	3c •1½CH ₂ Cl ₂	Ref ⁴⁸
3d	2,6-Me ₂ C ₆ H ₃	Me	CH ₂ Cl ₂	3d •CH ₂ Cl ₂ •H ₂ O	Ref ⁵⁰
4	Cy	Me	CH ₂ Cl ₂	4 •CH ₂ Cl ₂	This work
4	Cy	Me	CH ₂ Br ₂	4 •CH ₂ Br ₂	This work

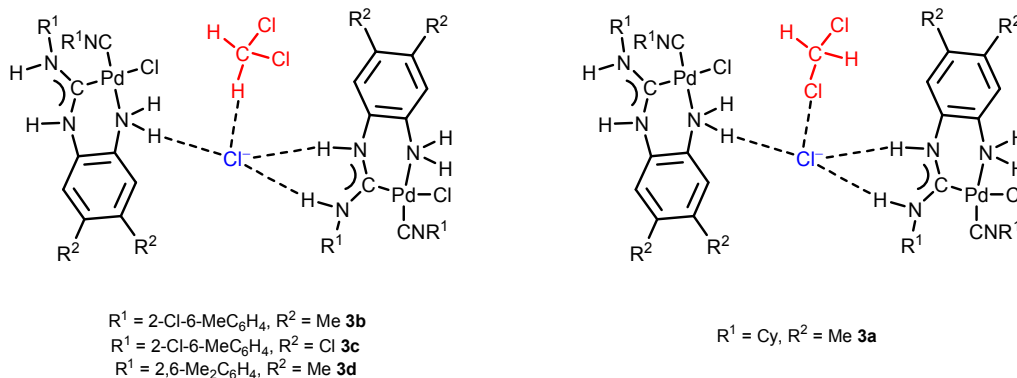


Figure 2. The environment of Cl^- in previously reported solvates **3b**• CH_2Cl_2 , **3c**• $1\frac{1}{2}\text{CH}_2\text{Cl}_2$, and **3d**• CH_2Cl_2 • H_2O (left) and in **3a**• CH_2Cl_2 studied in this work (right).

We now found that **3a** is crystallized with dichloromethane giving **3a**• CH_2Cl_2 , where the $\text{H}_2\text{C}(\text{Cl})\text{-Cl}\cdots\text{Cl}^-$ short contacts (**Figure 2**, right) were identified. These contacts can be interpreted as XBs accordingly to the IUPAC “distance” and “angle” criteria.⁵¹ Indeed, the distances $d(\text{Cl}\cdots\text{Cl}) = 3.276(3)$ and $3.236(3)$ Å are sufficiently less than the sum of the Rowland’s vdW^{52} radii ($2R_{\text{vdW}}(\text{Cl}) = 3.52$ Å) and the angles $\angle(\text{C-Cl}\cdots\text{Cl}) = 166.3(3)$ and $166.2(4)^\circ$ are close to 180° . We found that only **3a**, among all other species derived from the coupling with benzene-1,2-diamine, gives dichloromethane solvate with XB. We believe that this is due to the crucial role of the shape of the molecular cation of **3a** in the crystal packing and, consequently, in the formation of XB. The replacement of cyclohexyl substituents to aryls in the starting complex and methyl substituents to chlorine atoms in the starting nucleophile lead to another environment of the chloride anion (**Figure 2**, left) and even to another complex:dichloromethane ratio in **3c**• $1\frac{1}{2}\text{CH}_2\text{Cl}_2$ and to the inclusion of water in **3d**• CH_2Cl_2 • H_2O .

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3 We also succeeded to perform the $\text{CH}_2\text{Cl}_2/\text{CH}_2\text{Br}_2$ isostructural exchange^{53,54} with
4 complete preservation of the solvent environment in $3\mathbf{a}\cdot\text{CH}_2\text{Br}_2$.^{32,36,55} In the X-ray structure of
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8 $3\mathbf{a}\cdot\text{CH}_2\text{Br}_2$, the $\text{H}_2\text{C}(\text{Br})\text{--Br}\cdots\text{Cl}^-$ XBs were found ($d(\text{Br}\cdots\text{Cl}) = 3.1911(11)$ Å is less than
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10 Rowland's $R_{\text{vdW}}(\text{Cl}) + R_{\text{vdW}}(\text{Br}) = 3.63$ Å, and $\angle(\text{C--Br}\cdots\text{Cl})$ is $167.3(2)^\circ$). Despite significant
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12 difference in the cell parameters of $3\mathbf{a}\cdot\text{CH}_2\text{Cl}_2$ and $3\mathbf{a}\cdot\text{CH}_2\text{Br}_2$, these two species demonstrate
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14 similar crystal structures, and positions of each complex cation, chloride anion, and solvent
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16 molecule are almost the same (**Figure 3, a–b**).

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21 To expand a number of dihalomethane–halide clusters, complex **4** was obtained by the
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23 metathetical reaction of **3a** with KBr (**Scheme 1**), whereupon **4** was co-crystallized with CH_2Cl_2
24
25 and CH_2Br_2 forming solvates $4\cdot\text{CH}_2\text{Cl}_2$ and $4\cdot\text{CH}_2\text{Br}_2$, respectively. In the structure of $4\cdot\text{CH}_2\text{Cl}_2$,
26
27 the positions of the complex cations and bromide counterions are close to those found for
28
29 $3\mathbf{a}\cdot\text{CH}_2\text{Cl}_2$, but solvent molecules are arranged differently and the $\text{Cl}_2\text{C}(\text{H})\text{--H}\cdots\text{Br}^-$ HBs were
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31 found instead XBs (**Figure 3, c**). This observation can be accounted for by the lower XB energy
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33 in the case of CH_2Cl_2 than that in CH_2Br_2 (see theoretical considerations for details later). The
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35 difference between $3\mathbf{a}\cdot\text{CH}_2\text{Cl}_2$ and $4\cdot\text{CH}_2\text{Cl}_2$ in terms of their ability of forming XBs vs. HBs,
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37 were also indirectly observed by IR spectroscopy in the solid state (see SI, **Figure SIV4**), when
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39 we found a change of shapes of the antisymmetric C–Cl stretches. The high temperature (300 K)
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41 XRD experiment for $4\cdot\text{CH}_2\text{Cl}_2$ indicated that CH_2Cl_2 is fully disordered, occupying at least three
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43 different positions and therefore reliable information on solvent-involved weak interactions
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45 could not be obtained.

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53 In the case of $4\cdot\text{CH}_2\text{Br}_2$, the released single-crystals are unstable at 100 K probably due
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55 to a phase transition and data collection was performed at 200 K. The structure of $4\cdot\text{CH}_2\text{Br}_2$ is
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57 close to $3\mathbf{a}\cdot\text{CH}_2\text{Br}_2$ (**Figure 3, d** and **Figure 4, d**), and the $\text{H}_2\text{C}(\text{Br})\text{--Br}\cdots\text{Br}^-$ short contacts
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referred to XB insofar as $d(\text{Br}\cdots\text{Br}) = 3.3137(8) \text{ \AA}$ is less than Rowland's $2R_{\text{vdW}}(\text{Br}) = 3.74 \text{ \AA}$, and $\angle(\text{C}-\text{Br}\cdots\text{Br})$ is $169.4(2)^\circ$. These values agree well with both geometrical IUPAC criteria⁵¹ for XB.

In $3\mathbf{a}\cdot\text{CH}_2\text{Cl}_2$, $3\mathbf{a}\cdot\text{CH}_2\text{Br}_2$, $4\cdot\text{CH}_2\text{Cl}_2$, and $4\cdot\text{CH}_2\text{Br}_2$, apart from XBs numerous $\text{N}-\text{H}\cdots\text{X}^-$, $\text{C}-\text{H}\cdots\text{X}^-$, $\text{N}-\text{H}\cdots\text{X}-\text{Pd}$, and $\text{C}-\text{H}\cdots\text{X}-\text{Pd}$ ($\text{X} = \text{Cl}, \text{Br}$) HB's were identified (see Supporting information).

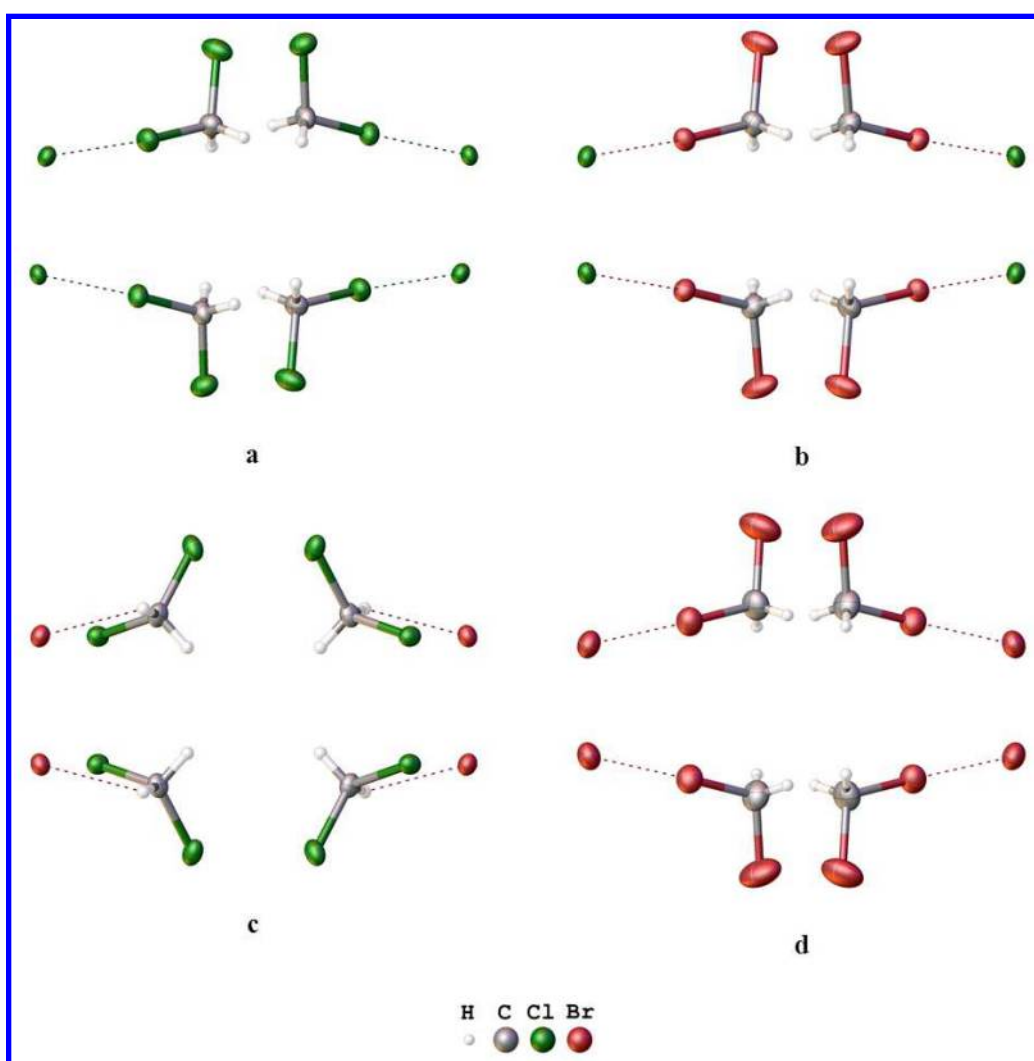
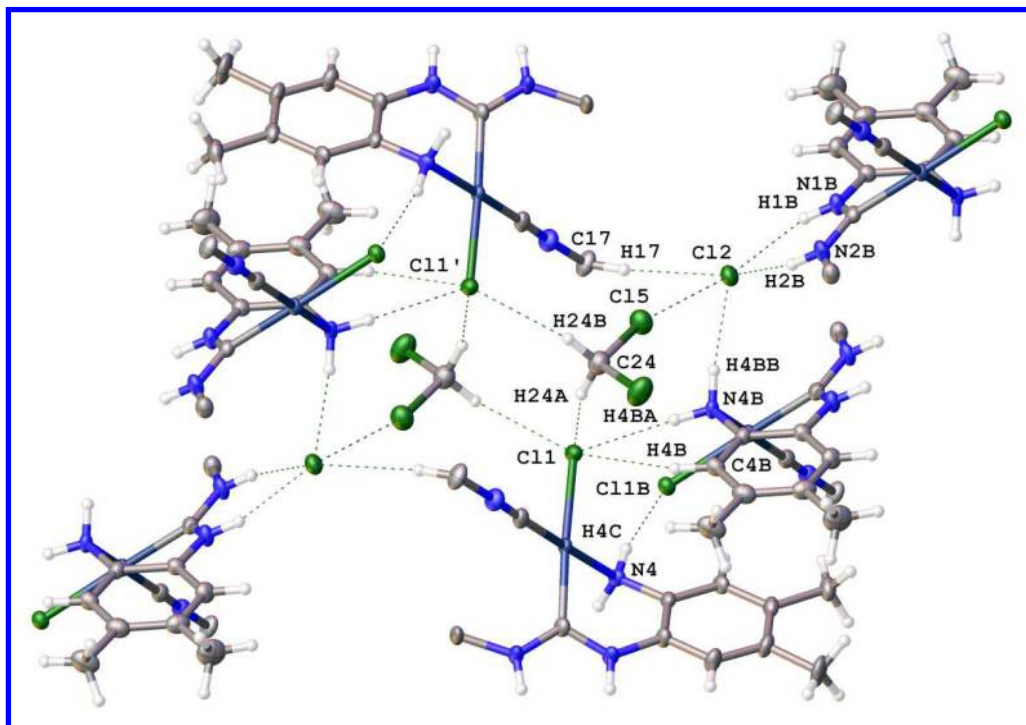
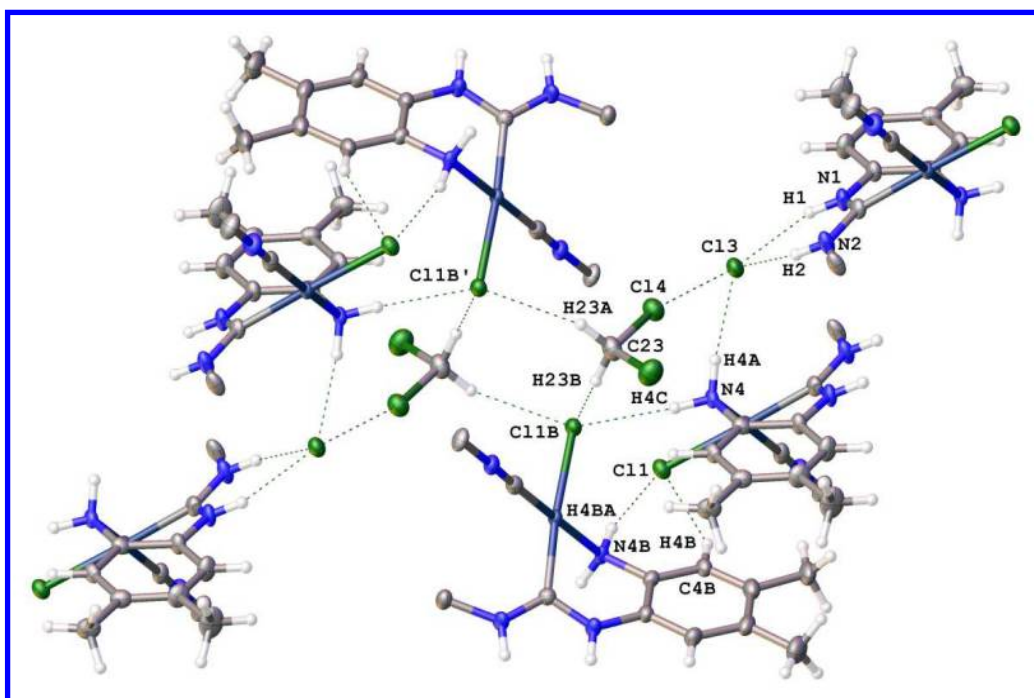


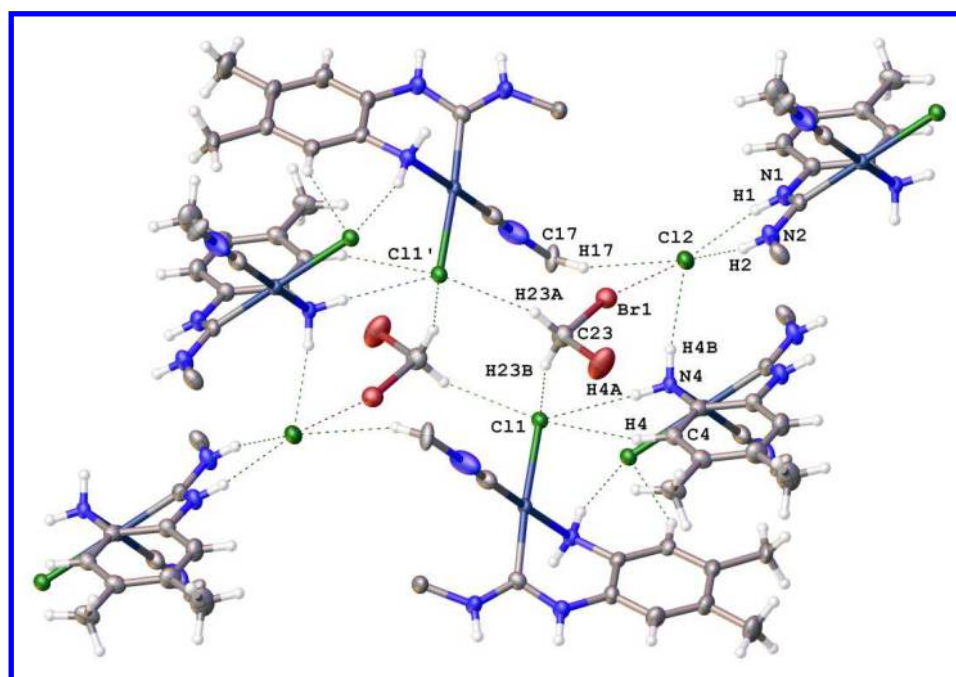
Figure 3. Packing of dihalomethane molecules and halide anions in $3\mathbf{a}\cdot\text{CH}_2\text{Cl}_2$ (a), $3\mathbf{a}\cdot\text{CH}_2\text{Br}_2$ (b), $4\cdot\text{CH}_2\text{Cl}_2$ (c), and $4\cdot\text{CH}_2\text{Br}_2$ (d). Thermal ellipsoids are given at the 50% probability level.



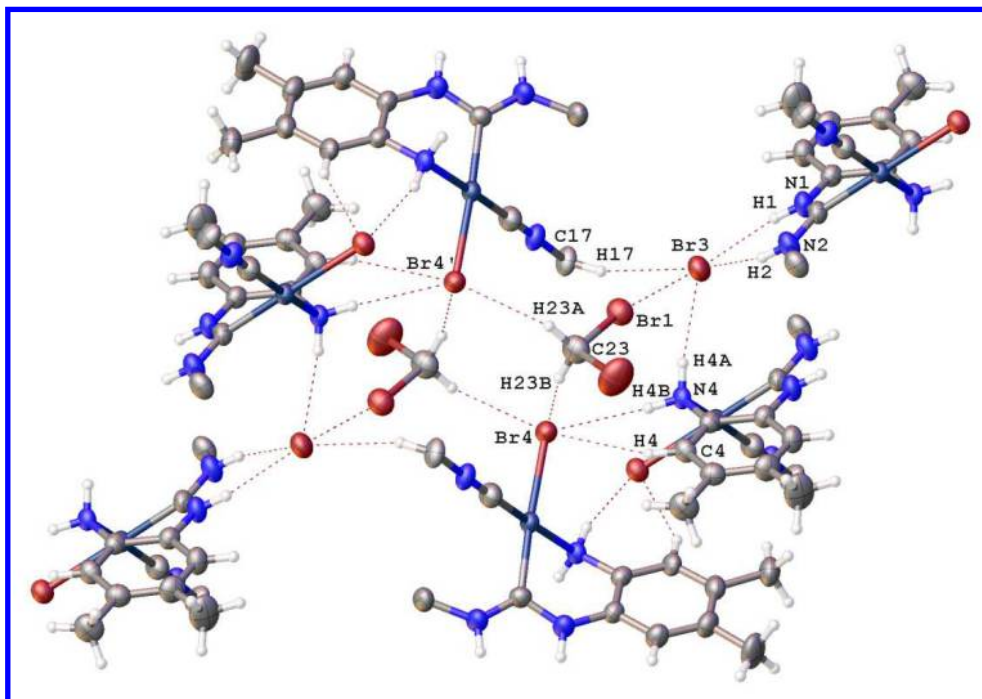
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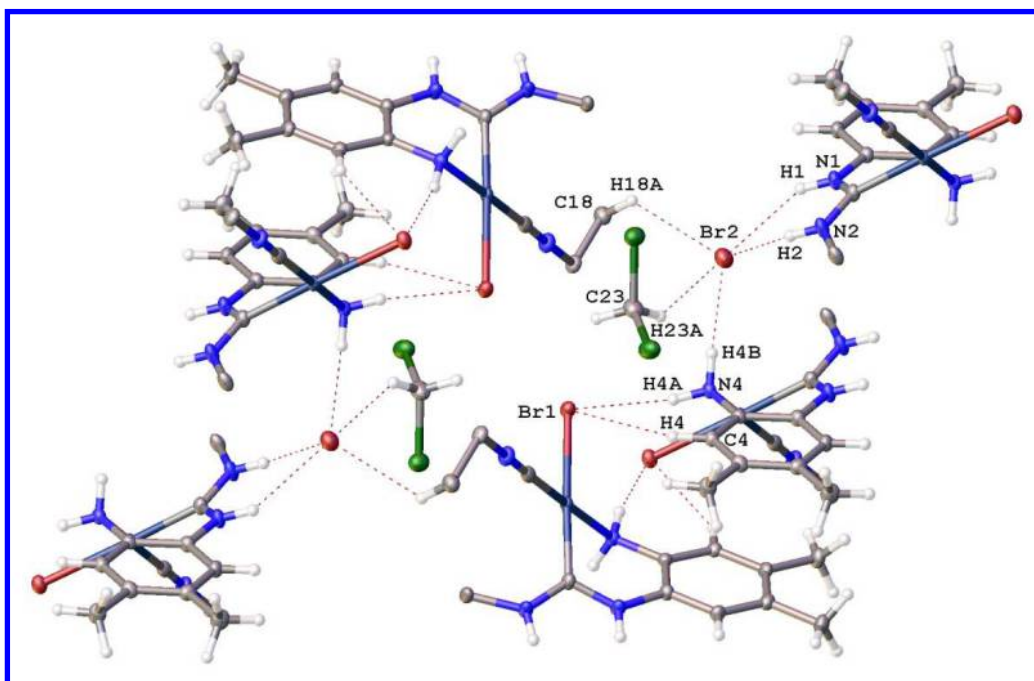
a2



b



c



d

Figure 4. Two types of isostructural fragments in $3\mathbf{a}\cdot\text{CH}_2\text{Cl}_2$ (**a1**, **a2**) and analogous fragments in $3\mathbf{a}\cdot\text{CH}_2\text{Br}_2$ (**b**), $4\cdot\text{CH}_2\text{Br}_2$ (**c**), and $4\cdot\text{CH}_2\text{Cl}_2$ (**d**). Cyclohexyl rings were omitted for clarity. Thermal ellipsoids are given at the 50% probability level.

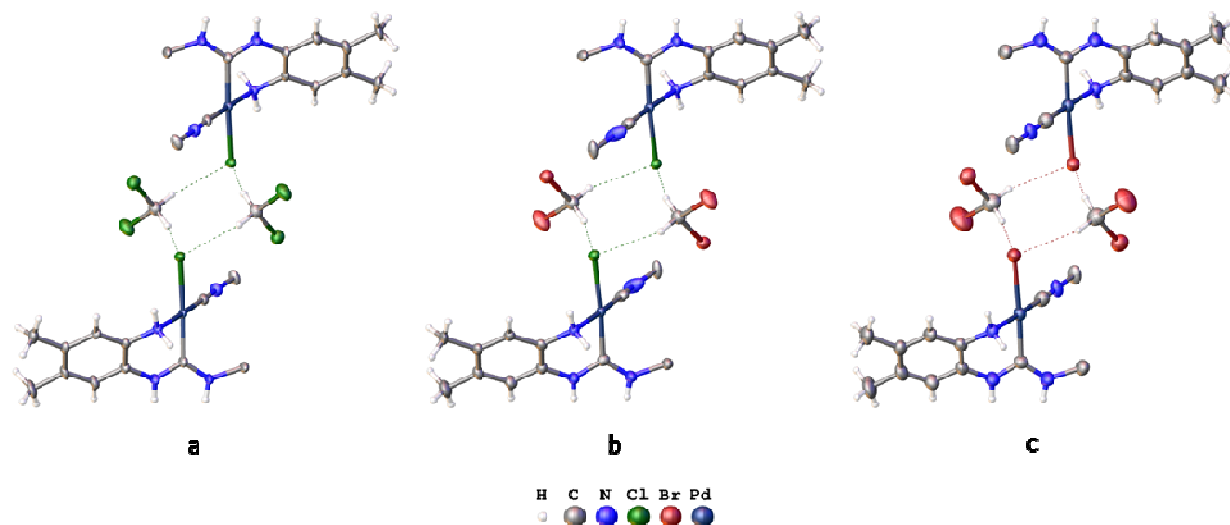


Figure 5. One of the heterotetrameric clusters in $3\mathbf{a}\cdot\text{CH}_2\text{Cl}_2$ (**a**) and the analogous clusters in $3\mathbf{a}\cdot\text{CH}_2\text{Br}_2$ (**b**), and $4\cdot\text{CH}_2\text{Br}_2$ (**c**). Cyclohexyl rings were omitted for clarity. Thermal ellipsoids are given at the 50% probability level.

Noteworthy that in $3\mathbf{a}\cdot\text{CH}_2\text{Cl}_2$, $3\mathbf{a}\cdot\text{CH}_2\text{Br}_2$, and $4\cdot\text{CH}_2\text{Cl}_2$, we observed the heterotetrameric clusters (**Figure 5**) that consist of two complex cations and two solvent molecules with two types of the $\text{X}_2\text{C}(\text{H})\text{--H}\cdots\text{X}\text{--Pd}$ ($\text{X} = \text{Cl}, \text{Br}$) HB's. Electrostatic repulsion between the negatively charged halide ligands is shielded by two solvent molecules. Similar clusters were previously reported by us,³⁶ and these species contain two neutral chloride platinum(II) complexes and two dihalomethane molecules, simultaneously linked by two $\text{X}_2\text{C}(\text{H})\text{--H}\cdots\text{Cl}\text{--Pt}$ HB's and two $\text{H}_2\text{C}(\text{X})\text{--X}\cdots\text{Cl}\text{--Pt}$ ($\text{X} = \text{Cl}, \text{Br}$) XB's.

Table 3. The parameters of the H₂C(X)–X•••Cl[−] (X = Cl, Br) XBs.

Solvate	C–X•••Cl [−]	<i>d</i> (X•••Cl), Å	<i>R</i> _{ClX}	∠(C–X•••Cl), °	<i>E</i> _{int} ^{a*}	<i>E</i> _{int} ^{b*}
3a •CH ₂ Cl ₂	C24–Cl15•••Cl2 [−]	3.276(3)	0.93	166.3(3)	1.9	2.2
	C23–Cl14•••Cl3 [−]	3.236(2)	0.92	166.2(4)	2.2	2.2
3a •CH ₂ Br ₂	C23–Br1•••Cl2 [−]	3.1911(11)	0.88	167.3(2)	2.8	2.7
4 •CH ₂ Br ₂	C23–Br1•••Br3 [−]	3.3137(8)	0.89	169.4(2)	2.5	2.4
	Comparison ^{**}	3.52 (Cl•••Cl)	1.00	180		
		3.63 (Br•••Cl)				
		3.74 (Br•••Br)				

* The strength of these weak interactions (in kcal/mol) has been defined according to the procedures proposed by Espinosa et al. ($E_{int}^a = -V(\mathbf{r})/2$)⁵⁶ and Vener et al. ($E_{int}^b = 0.429G(\mathbf{r})$),⁵⁷ these approaches considered explore linear relationships between potential energy $V(\mathbf{r})$ and Lagrangian kinetic energy $G(\mathbf{r})$ densities at the bond critical points and energies of appropriate contacts.

** “Comparison” is the sum of Rowland’s vdW radii and the classic XB angle.

Theoretical considerations. Inspection of the crystallographic data for dihalomethane solvates **3a**•CH₂Cl₂, **3a**•CH₂Br₂, and **4**•CH₂Br₂ suggests the availability of Cl•••Cl[−] and Br•••Cl[−] XBs and along with the presence different types of HBs. To confirm the existence of these weak XB interactions from theoretical viewpoint and evaluate their energies, we performed DFT calculations followed by Bader’s QTAIM analysis.⁵⁸ We have successfully used this approach upon studies of non-covalent interactions and properties of coordination bonds in various transition metal complexes.^{36,40,59–65} The model systems were isolated from the experimental X-ray data as three large clusters (*cis*-[PdCl(CNCy){C(NHCy)=NHC₆H₂Me₂NH₂}]⁺)₆•(Cl[−])₂•(CH₂X₂)₂ (X = Cl, two types, see

Figure 2, a–b; X = Br, **c**), which include all types of short contacts. Results of QTAIM analysis are summarized in **Table 4** (XBs) and **Table SV2** (HBs).

Table 4. Values of the density of all electrons – $\rho(\mathbf{r})$, Laplacian of electron density – $\nabla^2\rho(\mathbf{r})$, energy density – H_b , potential energy density – $V(\mathbf{r})$, and Lagrangian kinetic energy – $G(\mathbf{r})$ (Hartree) at the bond critical points (3, –1), corresponding to the $H_2C(X)-X\cdots Cl^-$ (X = Cl, Br) XBs.

Solvate	C–X \cdots X [–]	type ^{**}	d(X \cdots X [–])	$\rho(\mathbf{r})$	$\nabla^2\rho(\mathbf{r})$	H_b	$V(\mathbf{r})$	$G(\mathbf{r})$	E_{int}^{a*}	E_{int}^{b*}
3a •CH ₂ Cl ₂	C24–Cl5 \cdots Cl2 [–]	exp.	3.276	0.011	0.037	0.002	–0.006	0.008	1.9	2.2
		free	3.276	0.012	0.035	0.001	–0.006	0.007	1.9	1.9
		opt.	2.963	0.020	0.062	0.002	–0.012	0.014	3.8	3.8
	C23–Cl4 \cdots Cl3 [–]	exp.	3.236	0.011	0.040	0.002	–0.007	0.008	2.2	2.2
		free	3.236	0.013	0.037	0.001	–0.007	0.008	2.2	2.2
		opt.	2.966	0.020	0.061	0.002	–0.012	0.014	3.8	3.8
3a •CH ₂ Br ₂	C23–Br1 \cdots Cl2 [–]	exp.	3.191	0.014	0.048	0.002	–0.009	0.010	2.8	2.7
		free	3.191	0.016	0.044	0.001	–0.008	0.010	2.5	2.7
		opt.	2.941	0.024	0.071	0.001	–0.015	0.016	4.7	4.3
	***C–Cl \cdots Br [–]	opt.	3.072	0.021	0.050	0.000	–0.012	0.012	3.8	3.2
4 •CH ₂ Br ₂	C23–Br1 \cdots Br3 [–]	exp.	3.314	0.014	0.038	0.001	–0.008	0.009	2.5	2.4
		free	3.314	0.016	0.034	0.000	–0.008	0.008	2.5	2.2
		opt.	3.016	0.025	0.060	0.000	–0.015	0.015	4.7	4.0

* The strength of these weak interactions (in kcal/mol) has been defined according to the procedures proposed by Espinosa et al. ($E_{int}^a = -V(\mathbf{r})/2$)⁵⁶ and Vener et al. ($E_{int}^b = 0.429G(\mathbf{r})$),⁵⁷ these approaches considered explore linear relationships between potential energy $V(\mathbf{r})$ and Lagrangian kinetic energy $G(\mathbf{r})$ densities at the bond critical points and energies of appropriate contacts.

** Type of calculations: exp. – single point calculations based on the experimental X-ray geometries for the large clusters (*cis*-[PdX(CNCy){C(NHCy)=NHC₆H₂Me₂NH₂}]⁺)₆•(X[–])₂•(CH₂X₂)₂, free – single point calculations based on the experimental X-ray geometries for

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3 *the small clusters $(X^-) \cdot (CH_2X_2)$, opt. – single point calculations based on the optimized gas*
4 *phase geometries for the small clusters $(X^-) \cdot (CH_2X_2)$.*

5 **** Only the optimized structure for $C-Cl \cdots Br^-$.*
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11 The QTAIM analysis allows the verification of several bond critical points (BCP's)
12 (3, -1) for XBs $C-X \cdots X^-$ (X = Cl, Br) (**Table 4**) and different HB's (**Table SV2**). The low
13 magnitude of the electron density, positive values of the Laplacian, and very close to zero energy
14 density in these BCP's are typical for non-covalent interactions. The relation $-G(\mathbf{r})/V(\mathbf{r}) \geq 1$ for
15 all BCP's listed in **Tables 4** and **SV2**, and points out that the nature of these interactions is
16 purely non-covalent.⁶⁶ The small values of the Wiberg bond indices for $C-X \cdots X^-$ contacts in the
17 optimized structures (viz. 0.08–0.18) computed by using the natural bond orbital (NBO)
18 partitioning scheme additionally confirm the electrostatic nature of these non-covalent
19 interactions.
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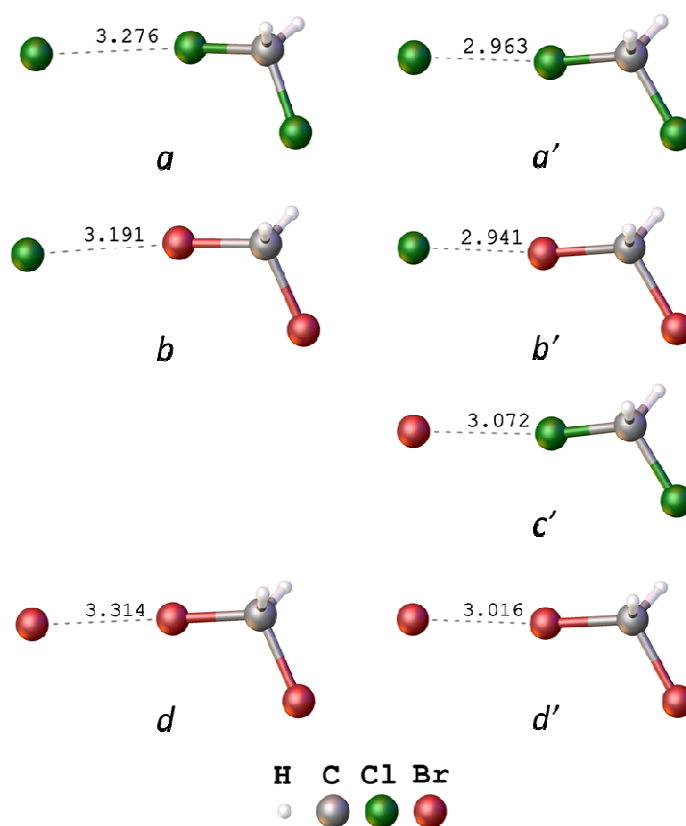


Figure 6. Experimental (left) and optimized (right) structures of the $(X^-)\cdot(\text{CH}_2\text{X}_2)$ clusters, length unit – Å.

We attempted to estimate the effect of short-range environment and crystal packing on the energies of XBs in the studied systems. For these purposes we isolated the small clusters $(\text{Cl}^-)\cdot(\text{CH}_2\text{Cl}_2)$ (**Figure 6, a**), $(\text{Cl}^-)\cdot(\text{CH}_2\text{Br}_2)$ (**b**), and $(\text{Br}^-)\cdot(\text{CH}_2\text{Br}_2)$ (**d**) from the experimental X-ray geometries of $\mathbf{3a}\cdot\text{CH}_2\text{Cl}_2$, $\mathbf{3a}\cdot\text{CH}_2\text{Br}_2$, and $\mathbf{4}\cdot\text{CH}_2\text{Br}_2$, respectively, and carried out single point calculations and QTAIM analysis (in this case only short-range environment effect is excluded from the consideration). Then we performed geometry optimization procedure followed by the single point calculations and QTAIM analysis (in that case both effects are not taking into account). For the cluster $(\text{Br}^-)\cdot(\text{CH}_2\text{Cl}_2)$, the starting $(\text{Cl}^-)\cdot(\text{CH}_2\text{Cl}_2)$ geometry followed by the Cl^-/Br^- exchange was used (**Figure 6, c**). Our results are presented in **Table 4**

(“free” for the starting experimental geometries, “opt.” for the optimized geometries). It is clear that short-range environment virtually does not affect the energies of XBs, but the influence of crystal packing is much more significant. Indeed, geometry optimization leads to shortening of the $\text{Br}\cdots\text{Cl}^-$, $\text{Cl}\cdots\text{Cl}^-$, and $\text{Br}\cdots\text{Br}^-$ contacts by 0.250–0.313 Å and to their approximately two-fold strengthening. Noteworthy that the optimized structures *a–d* exhibit similar structural motifs. The contour line diagrams of the Laplacian distribution $\nabla^2\rho(\mathbf{r})$, bond paths and selected zero-flux surfaces for the optimized $(\text{X}^-)\cdot(\text{CH}_2\text{X}_2)$ clusters are shown in **Figure 7**. To visualize XBs in the studied systems, reduced density gradient (RDG) analysis⁶⁷ was carried out. The RDG isosurfaces reveal the presence of $\text{H}_2\text{C}(\text{X})-\text{X}\cdots\text{X}^-$ ($\text{X} = \text{Cl}, \text{Br}$) non-covalent interactions in optimized structures of $(\text{Cl}^-)\cdot(\text{CH}_2\text{Cl}_2)$, $(\text{Cl}^-)\cdot(\text{CH}_2\text{Br}_2)$, $(\text{Br}^-)\cdot(\text{CH}_2\text{Cl}_2)$, and $(\text{Br}^-)\cdot(\text{CH}_2\text{Br}_2)$.

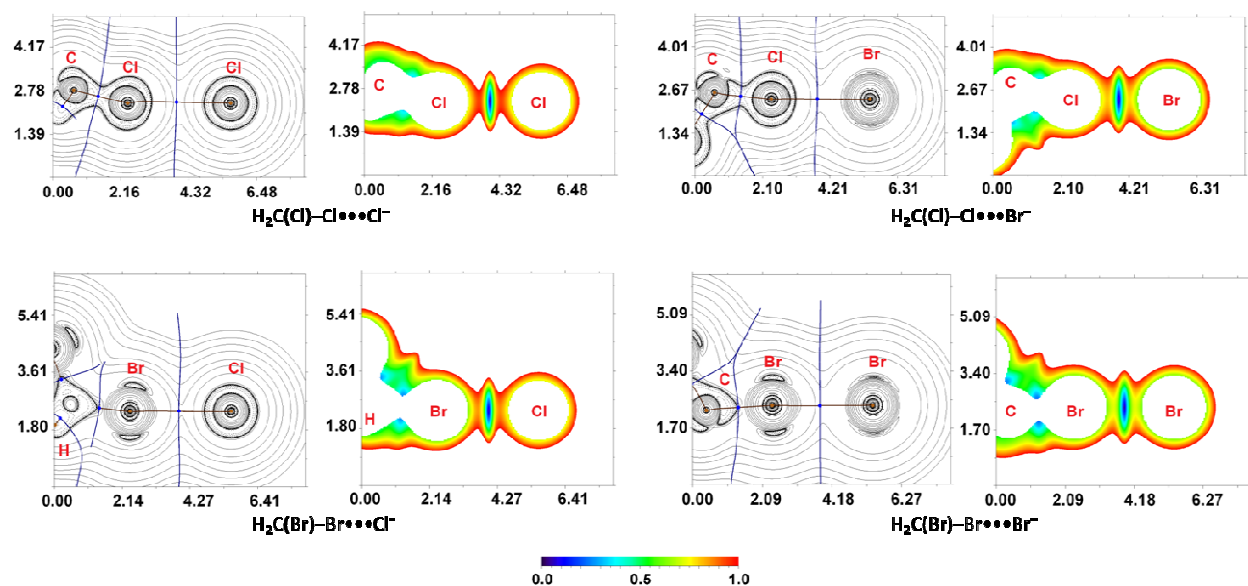


Figure 7. Contour line diagrams of the Laplacian distribution $\nabla^2\rho(\mathbf{r})$, bond paths, and selected zero-flux surfaces (left) and RDG isosurfaces referring to the XBs (right) for the optimized structures of $(\text{Cl}^-)\cdot(\text{CH}_2\text{Cl}_2)$, $(\text{Cl}^-)\cdot(\text{CH}_2\text{Br}_2)$, $(\text{Br}^-)\cdot(\text{CH}_2\text{Cl}_2)$, and $(\text{Br}^-)\cdot(\text{CH}_2\text{Br}_2)$. Bond critical

points (3, -1) are shown in blue, nuclear critical points (3, -3) – in pale brown. Length units – Å, RDG isosurface values are given in Hartree.

We additionally evaluated the magnitude of intermolecular interaction energies in the XBs linked clusters $(\text{Cl}^-)\cdot(\text{CH}_2\text{Cl}_2)$, $(\text{Cl}^-)\cdot(\text{CH}_2\text{Br}_2)$, $(\text{Br}^-)\cdot(\text{CH}_2\text{Cl}_2)$, and $(\text{Br}^-)\cdot(\text{CH}_2\text{Br}_2)$ by supermolecule method using both coupled cluster approach and second order Møller–Plesset perturbation theory at the CCSD(T)/aug-cc-pVDZ//M06/DZP-DKH and MP2/aug-cc-pVDZ//M06/DZP-DKH computational levels. The obtained values of intermolecular interaction energies are higher than those obtained from QTAIM analysis, but lower than calculated vertical dissociation energies at the M06/aug-cc-pVDZ//M06/DZP-DKH level of theory (**Table 5**). The intermolecular interaction energy turns larger with the increase of σ -hole on XB donor and the polarizability decrease of the XB acceptors along the following series $\text{H}_2\text{C}(\text{Cl})\text{--Cl}\cdots\text{Br}^- < \text{H}_2\text{C}(\text{Cl})\text{--Cl}\cdots\text{Cl}^- < \text{H}_2\text{C}(\text{Br})\text{--Br}\cdots\text{Br}^- < \text{H}_2\text{C}(\text{Br})\text{--Br}\cdots\text{Cl}^-$.

Table 5. The calculated vertical dissociation energies ΔE_1 (CCSD(T)/aug-cc-pVDZ//M06/DZP-DKH), ΔE_2 (MP2/aug-cc-pVDZ//M06/DZP-DKH), and ΔE_3 (M06/aug-cc-pVDZ//M06/DZP-DKH) of XBs linked optimized clusters $(\text{Cl}^-)\cdot(\text{CH}_2\text{Cl}_2)$, $(\text{Cl}^-)\cdot(\text{CH}_2\text{Br}_2)$, $(\text{Br}^-)\cdot(\text{CH}_2\text{Cl}_2)$, and $(\text{Br}^-)\cdot(\text{CH}_2\text{Br}_2)$ (in kcal/mol).

Process	ΔE_1	ΔE_2	ΔE_3
$(\text{Cl}^-)\cdot(\text{CH}_2\text{Br}_2) \rightarrow \text{CH}_2\text{Br}_2 + \text{Cl}^-$	9.5	10.0	12.5
$(\text{Br}^-)\cdot(\text{CH}_2\text{Br}_2) \rightarrow \text{CH}_2\text{Br}_2 + \text{Br}^-$	8.2	8.9	11.0
$(\text{Cl}^-)\cdot(\text{CH}_2\text{Cl}_2) \rightarrow \text{CH}_2\text{Cl}_2 + \text{Cl}^-$	3.9	4.2	5.6
$(\text{Br}^-)\cdot(\text{CH}_2\text{Cl}_2) \rightarrow \text{CH}_2\text{Cl}_2 + \text{Br}^-$	3.0	3.4	4.4

We have defined energies for all these contacts according to the procedures proposed by Espinosa et al.⁵⁶ and Vener et al.,⁵⁷ and one can state that: (i) strengths of XBs in these systems varies from 1.9 to 2.8 kcal/mol; (ii) the energies of C–X•••Cl[−] XBs for X = Br in all cases are higher than those for X = Cl by 13–47%. This observation agrees well with the previously reported¹⁷ and calculated (**Table 1**) electrostatic potentials on the halogen atoms in CH₂Br₂ and CH₂Cl₂; (iii) the strongest N–H•••Cl[−] HB's may be classified as moderate force contacts (> 4 kcal/mol) mainly due to electrostatics following the classification of Jeffrey (“strong” H-bonds: 40–15 kcal/mol, “moderate” H-bonds: 15–4 kcal/mol, “weak” H-bonds: <4 kcal/mol).⁶⁸ Thus, results of our theoretical calculations confirm the presence and provide the energies of the previously unreported H₂C(X)–X•••X[−] (X = Cl, Br) XBs involving uncomplexed halides. Results of our calculations can be compared with the data obtained at the MP2/aug-cc-pVDZ level of theory for XBs in TEMPO•CH₂Cl₂ (2.5 kcal/mol) and TEMPO•CH₂Br₂ (3.7 kcal/mol) supramolecular clusters.¹⁷ The larger evaluated energies of XBs in cases of anions as XB acceptors (3.4 and 4.2 kcal/mol for CH₂Cl₂ as XB donor; 8.9 and 10.0 kcal/mol for CH₂Br₂ as XB donor) can be explained by charge reasons.

Verification of H₂C(X)–X•••X[−] (X = Cl, Br) XBs in other systems. We processed available CCDC data and found nine structures exhibiting H₂C(Cl)–Cl•••Cl[−] XBs (**Table 6**) and four structures with H₂C(Cl)–Cl•••Br[−] XBs (**Table 7**) accordingly to their geometric parameters; all these contacts were overlooked in the corresponding reports. The H₂C(Br)–Br•••X[−] XBs were not found although the H₂C(Br)–Br•••Cl–Pt XBs with metal-bound chloride were previously reported by us³⁶ and the H₂C(Br)–Br•••Br–C XBs were observed in the crystalline dibromomethane.^{69,70} Remarkable that XB in **3a**•CH₂Cl₂ is the shortest chlorine•••chlorine separation involving dihalomethane so far recognized.

Table 6. The parameters of the H₂C(Cl)–Cl•••Cl[−] XBs obtained from CCDC data processing.

Structure	$d(\text{Cl}\cdots\text{Cl}), \text{Å}$	R_{ClCl}	$\angle(\text{C}-\text{Cl}\cdots\text{Cl}), ^\circ$
EZAPIE	3.3466(18)	0.95	166.84(11)
LOBGIT	3.371(6)	0.96	163.5(6)
PACVOG	3.5097(10)	1.00	174.99(12)
QACNEP	3.265(2)	0.93	173.31(14)
	3.3616(19)	0.96	167.0(2)
	3.3841(19)	0.96	170.8(2)
SUNMUL	3.4545(16)	0.98	177.32(3)
WUYSEP	3.496(2)	0.99	166.23(18)
XERTOE	3.4189(8)	0.97	161.94(9)
YEDPEC	3.4932(16)	0.99	160.33(10)
ZETBOR	3.443(2)	0.98	169.7(2)
<i>This work</i>	3.276(3)	0.93	166.3(3)
	3.236(2)	0.92	166.2(4)
<i>Comparison^a</i>	<i>3.52 (Cl•••Cl)</i>	<i>1.00</i>	<i>180</i>

^a*Comparison is the sum of Rowland's vdW radii and the classic XB angle.*

Table 7. The parameters of the H₂C(Cl)–Cl•••Br[−] XBs obtained from CCDC data processing.

Structure	$d(\text{Cl}\cdots\text{Br}), \text{Å}$	R_{ClBr}	$\angle(\text{C}-\text{Cl}\cdots\text{Br}), ^\circ$
AJUZUA	3.5493(15)	0.98	172.0(2)
BOHTIG	3.3972(18)	0.94	170.0(3)

IHUGUO	3.5284(17)	0.97	169.5(3)
MOWBEG	3.101(8)	0.85	173.8(9)
<i>Comparison^a</i>	<i>3.63 (Cl•••Cl)</i>	<i>1.00</i>	<i>180</i>

^a Comparison is the sum of Rowland's vdW radii and the classic XB angle.

Concluding Remarks

A series of the *cis*-[PdX(CNCy){C(NHCy)=NHC₆H₂Me₂NH₂}]X•CH₂X₂ (X = Cl, Br) associates with the dihalomethanes were characterized by XRD. In the structures of **3a**•CH₂Cl₂, **3a**•CH₂Br₂, and **4**•CH₂Br₂, we detected the previously unreported H₂C(X)–X•••X[–] (X = Cl, Br) contacts with uncomplexed halides that fulfill the IUPAC criteria for the halogen bonding. Results of Bader's QTAIM analysis (M06/DZP-DKH level of theory) reveal that estimated strength of these XBs varies from 1.9 to 2.8 kcal/mol and that these contacts are actually non-covalent; the crystal packing significantly affects the lengths and energies of XBs.

Our processing of the available CCDC data allowed the recognition of some more H₂C(Cl)–Cl•••X[–] (X = Cl, Br) halogen bonds, but no H₂C(Br)–Br•••X[–] (X = Cl, Br) XBs were found. All contacts presented in **Tables 6** and **7** were overlooked in the corresponding papers. It is clear that the XB in **3a**•CH₂Cl₂ is the shortest chlorine•••chlorine separation involving dihalomethane so far recognized.

The results reported in this work can be used as starting point for further studies of XBs in dihalomethane solutions, where they may be sufficiently strong to contribute, along with H-bonding, to the overall solvation. We hope that our observation will be beneficial for both crystal

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3 engineering and physical chemistry communities because it expands the arsenal of
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6 supramolecular assembly and contributes to the understanding of solvation with dihalomethanes.
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8 9 **Experimental section**

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12 **Materials and Instrumentation.** Solvents, PdCl₂, and cyclohexyl isocyanide were
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14 obtained from commercial sources and used as received, whereas CH₂Cl₂ was purified by the
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16 conventional distillation over calcium chloride. 3,4-Dimethylbenzene-1,2-diamine was
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18 synthesized from 3,4-dimethylaniline (synthetic procedure can be found in Supporting
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20 Information).⁷¹ Complex **3a** was synthesized by the reported procedure⁴⁸ and **4** was synthesized
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22 from **3a** by metathesis with KBr in acetone.⁷² C, H, and N elemental analyses were carried out on
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24 a Euro EA 3028HT CHNS/O analyzer. Mass-spectra were obtained on a Bruker micrOTOF
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26 spectrometer equipped with electrospray ionization (ESI) source; MeOH was used as the solvent.
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28 The instrument was operated both at positive and negative ion modes using *m/z* range of 50–
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30 3000. The capillary voltage of the ion source was set at –4500 V (ESI⁺) or 3500 V (ESI[–]) and the
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32 capillary exit at ±(70–150) V. The nebulizer gas pressure was 0.4 bar and drying gas flow 4.0
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34 L/min. The NMR spectra were recorded on Bruker AVANCE III 400 spectrometer at ambient
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36 temperature in CDCl₃ (at 400, and 100 MHz for ¹H and ¹³C{¹H} NMR spectra, respectively).
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38 Chemical shifts are given in δ-values [ppm] referenced to the residual signals of non-deuterated
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40 solvent (CHCl₃): δ 7.26 (¹H) and 77.2 (¹³C). ¹H and ¹³C{¹H} NMR data assignment for **4**
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42 produced by using 2D (¹H,¹³C-HMQC/HSQC and ¹H,¹³C-HMBC) NMR correlation
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44 experiments.
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54 **Synthesis, crystallization, and structure refinement.** *Synthesis of 4.* Solid KBr (480
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56 mg, 4 mmol) was added to a suspension of **3a** (53 mg, 0.1 mmol) in acetone (4 mL) at 20–25 °C
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3 and the reaction mixture was stirred at RT for 1 d. The formed suspension was evaporated at 40–
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5 45 °C under normal pressure and the product was extracted with three 2-mL portions of CH₂Cl₂.
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7 The resulting bright yellow solution was filtered off to remove some insoluble material, the
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9 filtrate was evaporated at RT to dryness, and thus formed solid was dried in air at 20–25 °C.
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14 **4•CH₂Cl₂**. Yield 93%. Calc. for C₂₃H₃₆N₄Br₂Cl₂Pd: C, 39.15; H, 5.14; N, 7.94. Found: C,
15
16 39.30; H, 5.17; N, 7.99. HRESI⁺-MS (70 V, MeOH): calc. for C₂₂H₃₄N₄BrPd⁺ 539.0996, found
17
18 *m/z* 539.1004 [M – Br]⁺. IR (KBr, selected bands, cm⁻¹): ν(N–H) 3180 (m), ν(C–H) 2930–2854
19
20 (m), ν(C≡N) 2234 (s), ν(N–C_{carbene}) 1570 (s), δ(N–H) 1514 (s). ¹H NMR (CDCl₃, δ): 0.86–1.91
21
22 (20H, m, CH₂), 2.08 (3H, s, CH₃), 2.18 (3H, s, CH₃), 3.67–3.70 (1H, m, CH), 3.83–3.86 (1H, m,
23
24 CH), 5.30 (2H, s, CH₂Cl₂), 6.71 (1H, s, H_{Ar}), 6.91 (1H, s, H_{Ar}), 9.24–9.27 (1H, m, C_{carbene}–NH–
25
26 Cy), 10.66 (1H, s, NH). ¹³C {¹H} NMR (CDCl₃, δ): 19.03 (CH₃), 19.07 (CH₃), 22.58 (2CH₂),
27
28 24.47 (CH₂), 24.71 (3CH₂), 31.77 (2CH₂), 33.88 (2CH₂), 53.39 (CH₂Cl₂), 55.68 (CH), 59.17
29
30 (CH), 122.15(CH_{Ar}), 122.77 (CH_{Ar}), 123.61 (C≡N), 124.55(C_{Ar}), 133.03 (C_{Ar}), 133.69 (C_{Ar}),
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32 135.38 (C_{Ar}), 179.06 (C_{carbene}).
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39 Crystals of **3a•CH₂Cl₂**, **3a•CH₂Br₂**, **4•CH₂Cl₂**, and **4•CH₂Br₂** were obtained upon slow
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41 evaporation of a solution of **3a** or **4•CH₂Cl₂** in CH₂Cl₂ and CH₂Br₂, respectively, in air at RT.
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43 Details of structure solutions and refinements can be found in SI.
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47 **Computational Details.** Unless otherwise indicated, the single point calculations and full
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49 geometry optimization have been carried out at the DFT level of theory using the M06
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51 functional⁷³ (this functional describes reasonably weak dispersion forces and non-covalent
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53 interactions^{74,75}) with the help of Gaussian-09⁷⁶ program package. The Douglas–Kroll–Hess 2nd
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55 order scalar relativistic calculations requested relativistic core Hamiltonian were carried out
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3 using DZP-DKH basis sets⁷⁷⁻⁸³ for all atoms based on the experimentally obtained X-ray
4 geometries ((*cis*-[PdCl(CNCy){C(NHCy)=NHC₆H₂Me₂NH₂}]⁺)₆•(Cl⁻)₂•(CH₂Cl₂)₂ (two types),
5
6 (*cis*-[PdCl(CNCy){C(NHCy)=NHC₆H₂Me₂NH₂}]⁺)₆•(Cl⁻)₂•(CH₂Br₂)₂, (Cl⁻)•(CH₂Cl₂) (two
7
8 types), and (Cl⁻)•(CH₂Br₂)) or optimized equilibrium structures ((Cl⁻)•(CH₂Cl₂) (two types) and
9
10 (Cl⁻)•(CH₂Br₂)). No symmetry restrictions have been applied during the geometry optimization.
11
12 The Hessian matrix was calculated analytically for optimized structures to prove the location of
13
14 correct minima (no imaginary frequencies). The topological analysis of the electron density
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16 distribution with the help of the atoms in molecules (QTAIM) method developed by Bader⁸⁴ has
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18 been performed by using the Multiwfn program (version 3.3.4).⁸⁵
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25 ASSOCIATED CONTENT

26 27 28 **Supporting Information.**

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31
32 The following files are available free of charge:

33
34 additional data from the literature: maximum σ -hole potentials of halomethane molecules and
35
36 geometrical parameters of the halomethane–halide XBs; full crystal data description; full HB
37
38 description; NMR and IR spectra; additional results of the theoretical calculations; and synthesis
39
40 of 1,2-diamino-4,5-dimethylbenzene from 3,4-dimethylaniline; all in one PDF file.
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ABBREVIATIONS

HB, hydrogen bonding; XB, halogen bonding; XRD, X-ray diffraction; NMR, nuclear magnetic resonance; EPR, electron paramagnetic resonance; IR, infrared; TLC, thin layer chromatography; TEMPO, 2,2,6,6-tetramethyl-1-piperidin-1-yloxy free radical; ESP, electrostatic surface potential; RDG, reduced density gradient; QTAIM, quantum theory of atoms in molecules.

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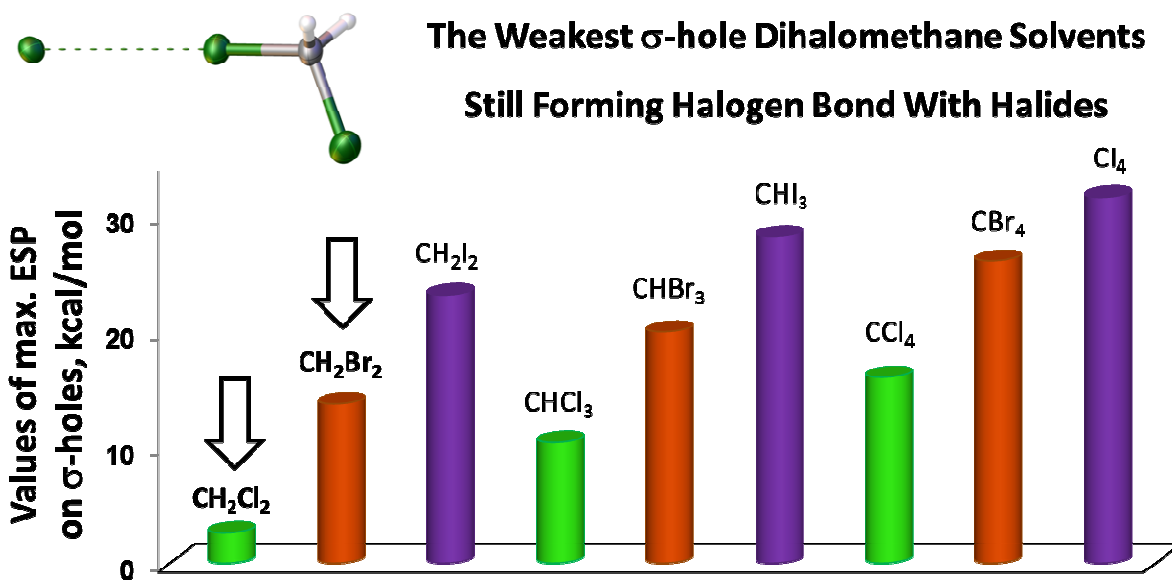
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The $\text{H}_2\text{C}(\text{X})\text{-X}\cdots\text{X}^-$ (X = Cl, Br) Halogen Bonding of Dihalomethanes

Daniil M. Ivanov, Mikhail A. Kinzhalov, Alexander S. Novikov, Ivan V. Ananyev,
Anna A. Romanova, Vadim P. Boyarskiy, Matti Haukka, and Vadim Yu. Kukushkin



SYNOPSIS

The weakest σ -hole dichloromethane and dibromomethane still form XBs with chloride in bromide in the solvates of acyclic diaminocarbene palladium(II) complex used as a scaffold. The estimated bonding energies of the $\text{H}_2\text{C}(\text{X})\text{-X}\cdots\text{X}^-$ non-covalent interactions is in the 1.9–2.8 kcal/mol range.

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