Article

The Isocyanide Complexes *cis*-[MCl₂(CNC₆H₄-4-X)₂] (M = Pd, Pt; X = Cl, Br) as Tectons in Crystal Engineering Involving Halogen Bonds

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S1. X-ray Diffraction Studies

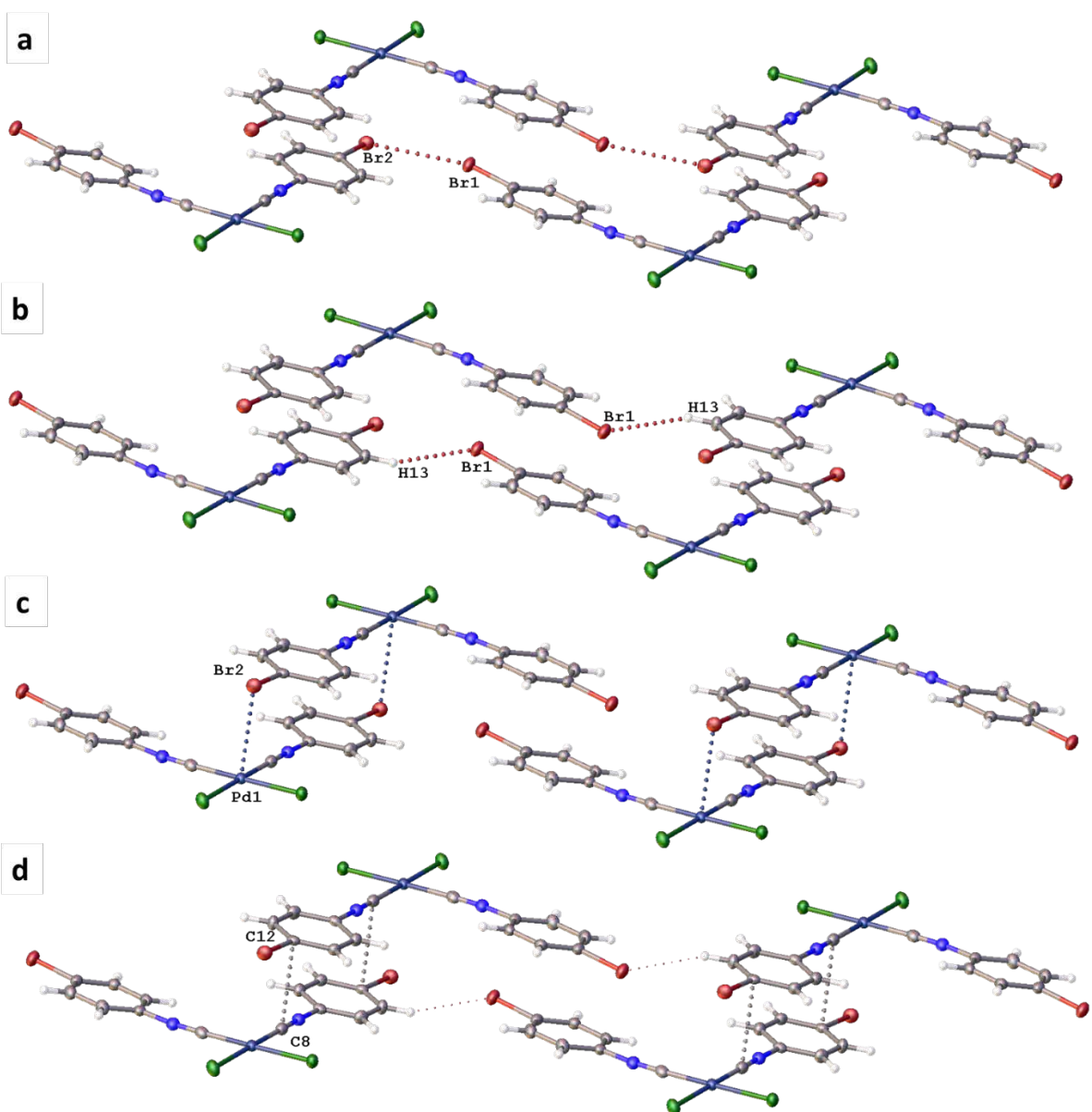**Table S1.** Crystal data and structure refinement for **1–3**.

Identification code	1	2	3
CCDC	2089928	2089926	2089927
Empirical formula	$C_{14}H_8Cl_4N_2Pd$	$C_{14}H_8Br_2Cl_2N_2Pd$	$C_{14}H_8Br_2Cl_2N_2Pt$
Formula weight	452.42	541.34	630.03
Temperature/K	100(2)	100(2)	100(2)
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a/Å	10.9891(7)	11.4727(4)	11.4780(3)
b/Å	10.3342(4)	10.1527(5)	10.3393(3)
c/Å	14.8501(7)	14.8165(7)	14.6156(6)
α/°	90	90	90
β/°	94.751(5)	93.068(4)	93.753(3)
γ/°	90	90	90
Volume/Å^3	1680.64(15)	1723.34(13)	1730.78(10)
Z	4	4	4
ρ_{calc}g/cm^3	1.788	2.086	2.418
μ/mm^{-1}	1.732	6.017	13.026
F(000)	880.0	1024.0	1152.0
Crystal size/mm^3	$0.21 \times 0.12 \times 0.09$	$0.21 \times 0.1 \times 0.09$	$0.2 \times 0.1 \times 0.08$
Radiation	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	5.506 to 61.874	5.362 to 61.88	5.308 to 61.992
Index ranges	$-14 \leq h \leq 13, -13 \leq k \leq 12, -11 \leq l \leq 21$	$-16 \leq h \leq 10, -14 \leq k \leq 13, -21 \leq l \leq 18$	$-16 \leq h \leq 16, -14 \leq k \leq 14, -20 \leq l \leq 17$
Reflections collected	8734	10917	21251
Independent reflections	4672 [R_{int} = 0.0297, R_{sigma} = 0.0497]	4849 [R_{int} = 0.0293, R_{sigma} = 0.0457]	4984 [R_{int} = 0.0468, R_{sigma} = 0.0399]
Data/restraints/parameters	4672/0/190	4849/0/190	4984/0/190
Goodness–of–fit on F^2	1.061	1.034	1.122

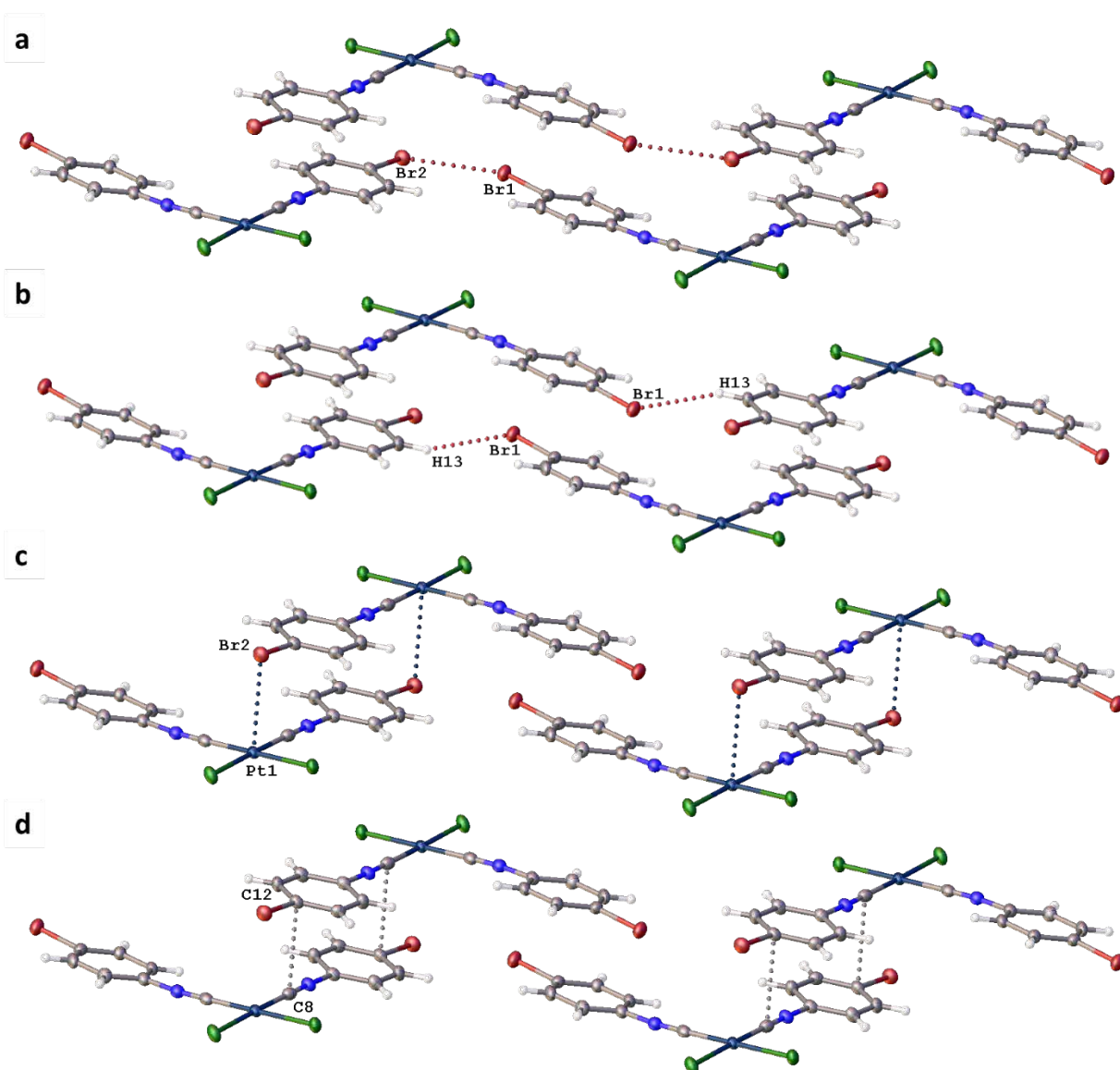|			
Final R indexes [I≥2σ (I)]	$R_1 = 0.0360$, $wR_2 = 0.0717$	$R_1 = 0.0321$, $wR_2 = 0.0572$	$R_1 = 0.0361$, $wR_2 = 0.0784$
Final R indexes [all data]	$R_1 = 0.0543$, $wR_2 = 0.0836$	$R_1 = 0.0493$, $wR_2 = 0.0623$	$R_1 = 0.0481$, $wR_2 = 0.0830$
Largest diff. peak/hole /e·Å^{-3}	1.07/-1.03	0.67/-0.62	2.30/-1.21

Table S2. Selected bond lengths (Å) and angles (°) in **1–3**.

	1	2	3
Bond lengths, Å			
M1—Cl1	2.2991(8)	2.3006(7)	2.3096(13)
M1—Cl2	2.3141(8)	2.3124(8)	2.3221(14)
M1—C1	1.941(4)	1.935(3)	1.918(6)
M1—C8	1.938(3)	1.930(3)	1.905(6)
N1—C1	1.138(4)	1.142(4	1.142(7)
N1—C2	1.411(4)	1.398(4)	1.396(7)
N2—C8	1.145(4)	1.147(4)	1.150(7)
N2—C9	1.409(4)	1.403(3)	1.403(7)
Angle, °			
C1—M1—Cl1	88.01(9)	88.45(9)	88.85(17)
C1—M1—C8	90.09(13)	89.36(12)	90.5(2)
Cl1—M1—Cl2	93.53(3)	93.33(3)	91.43(5)
C8—M1—Cl2	88.36(10)	88.85(9)	89.25(17)
M1—C1—N1	178.5(3)	178.2(3)	178.9(5)
M1—C8—N2	177.5(3)	177.1(3)	177.6(5)
C1—N1—C2	173.7(3)	174.4(3)	174.6(6)
C8—N2—C9	179.3(3)	178.5(3)	178.1(6)

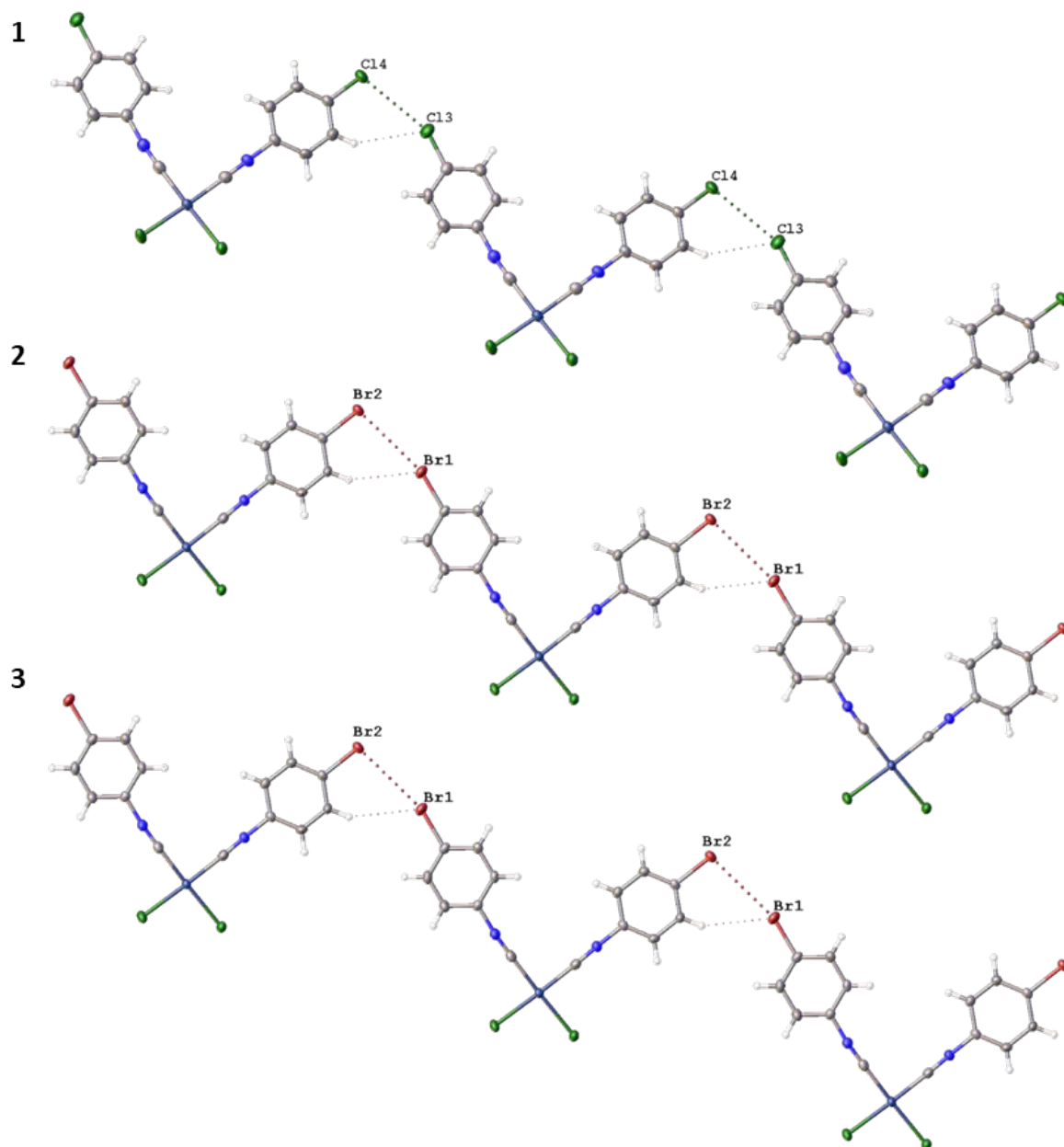**S2. Noncovalent Interactions**

Figure S1. Noncovalent interactions in **2**. Dotted line indicates the C–Br···Br′–C HaBs (**a**), C–H···Br–C hydrogen bonds (**b**), Br···Pd semicoordination (**c**), and C···C′ contacts (**d**).

Figure S2. Noncovalent interactions in **3**. Dotted line indicates the C–Br···Br′–C HaBs (**a**), C–H···Br–C hydrogen bonds (**b**), Br···Pt semicoordination (**c**), and C···C′ contacts (**d**).

Figure S3. 1D chains of HaB-bonded hexagon-like structures of **1–3**.

S2.1. C–H⋯Cl–M Hydrogen Bonding

The intermolecular C–H⋯Cl–M contacts bind the 1D layers of the complex molecules complementing a 3D crystal packing (**Figure S4**). The C–H⋯Cl–M interactions in structures **1–3** correspond to the IUPAC criteria for hydrogen bonding [1]: the distances C–H⋯Cl between hydrogen atoms in benzene rings and chloride ligand comprise 91–92% of the sum of the Bondi vdW radii [2]; the corresponding angles around the H center are close to 180° (C–H⋯X = 146.87(17)–162.8(4)°; **Table S3**).

Figure S4. 1D chains of **1**–**3** complex molecules bound by C–H···Cl–M hydrogen bonds.

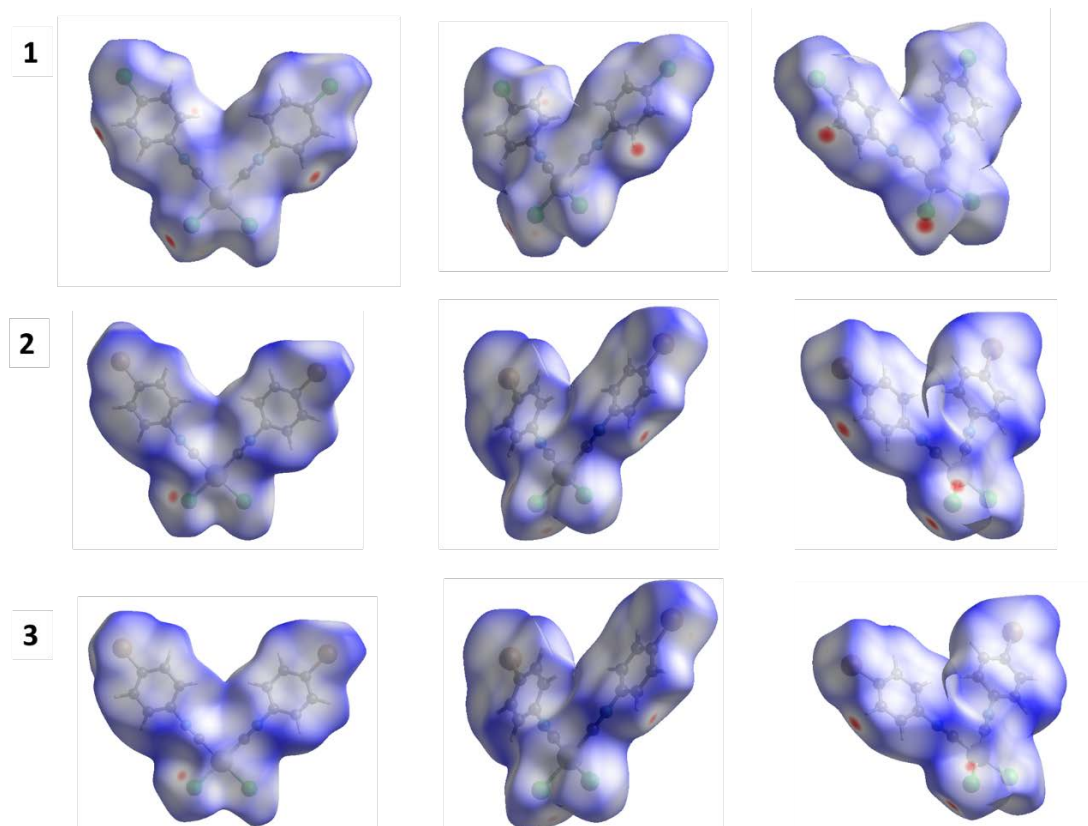**Table S3.** Characteristic parameters of C–H⋯Cl–M hydrogen bonds in **1–3**.

Structure	d(H⋯X), Å	d(C(–H) and X), Å	∠(C–H⋯X), °	**R**^{1}	**R**^{2}
1	2.6934(9)	3.545(3)	146.87(17)	*0.91*	*0.94*
2	2.6899(8)	3.597(4)	160.14(19)	*0.91*	*0.94*
3	2.7041(15)	3.623(6)	162.8(4)	*0.92*	*0.95*

[1] R is the ratio of the D⋯A distance to the sum of Bondi vdW radii [2].
[2] R is the ratio of the D⋯A distance to the sum of Rowland vdW radii [3].

S3. Hirshfeld analysis

The molecular Hirshfeld surface represents an area in which molecules come into contact, and its analysis gives the possibility of an additional insight into the nature of intermolecular interactions in the crystal state. We carried out a Hirshfeld surface analysis for the X-ray structures of complexes **1–3** and systematized types of short contacts to verify what kind of intermolecular forces contribute to the crystal packing (**Table S4** and **Figure S5**). The Hirshfeld molecular surfaces were generated by CrystalExplorer17 program [4,5]. The normalized contact distances, d_{norm} [6], based on Bondi's van der Waals radii [2], 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 that are 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 with blue.

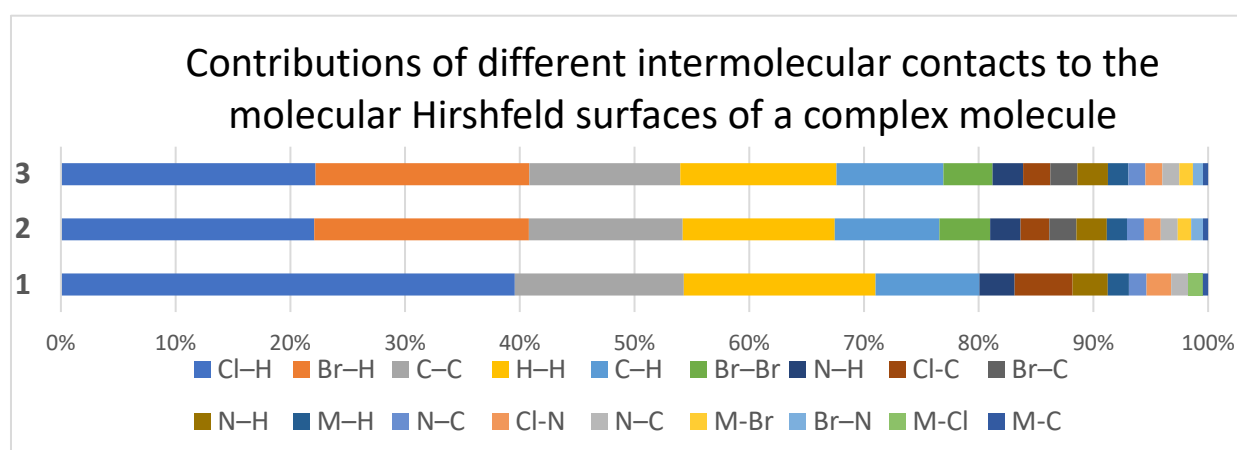**Figure S5.** Hirshfeld surfaces for **1–3**.
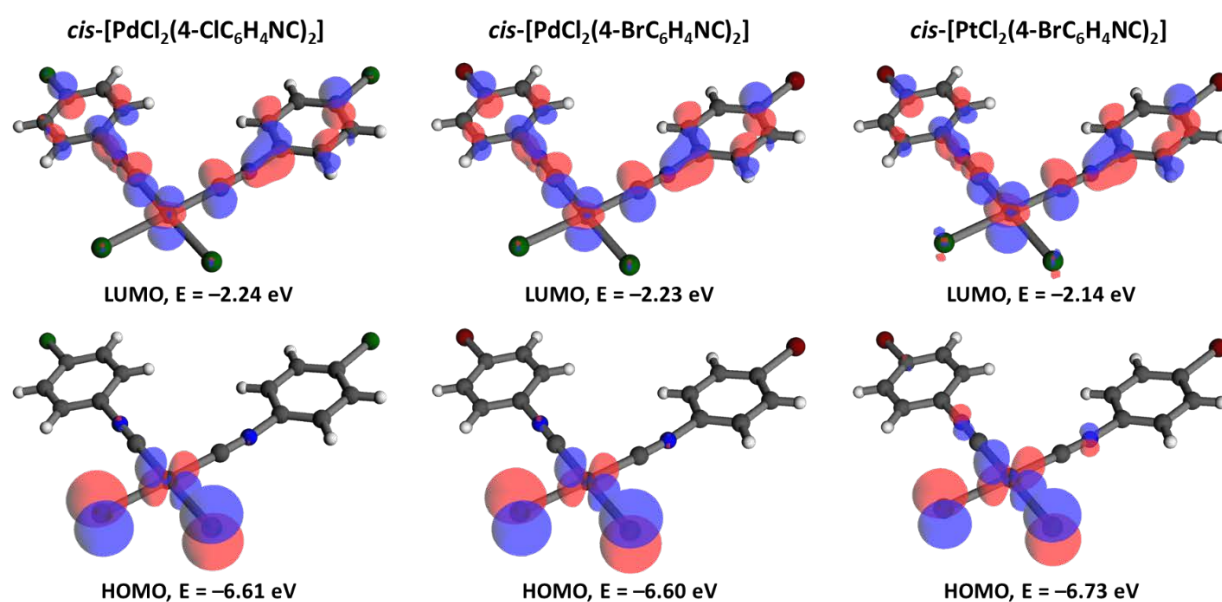
Table S4. Results of the Hirshfeld surface analysis.

X-ray Structure	Contributions of Different Intermolecular Contacts to the Molecular Hirshfeld Surface *
1	Cl–H 25.8%, H–H 10.9%, C–C 9.6%, C–H 5.9%, Cl–Cl 5.1%, Cl–C 3.3%, N–H 2.0%, Cl–N 1.4%, Pd–H 1.2%, N–C 1.0%, Pd–Cl 0.8%, Pd–C 0.3%
2	Cl–H 15.0%, Br–H 12.7%, C–C 9.1%, H–H 9.0%, C–H 6.2%, Br–Br 3.0%, N–H 1.8%, Cl–C 1.7%, Br–C 1.6%, Pd–H 1.2%, N–C 1.0%, Cl–N 1.0%, Pd–Br 0.8%, Br–N 0.7%, Cl–Br 0.6%, Pd–C 0.3%
3	Cl–H 15.0%, Br–H 12.6%, H–H 9.2%, C–C 8.9%, C–H 6.3%, Br–Br 2.9%, N–H 1.8%, Br–C 1.6%, Cl–C 1.6%, Pt–H 1.2%, N–C 1.0%, Cl–N 1.0%, Pt–Br 0.8%, Cl–Br 0.7%, Br–N 0.6%, Pt–C 0.3%

*The contributions of all other intermolecular contacts do not exceed 0%.

Figure S6. Contributions of various intermolecular contacts to the molecular Hirshfeld surfaces of **1–3** complex molecules.

S4. HOMO and LUMO orbital diagrams

cis-[PdCl₂(4-ClC₆H₄NC)₂]

cis-[PdCl$_2$(4-ClC$_6$H$_4$NC)$_2$]   cis-[PdCl$_2$(4-BrC$_6$H$_4$NC)$_2$]   cis-[PtCl$_2$(4-BrC$_6$H$_4$NC)$_2$]

LUMO, E = −2.24 eV   LUMO, E = −2.23 eV   LUMO, E = −2.14 eV

HOMO, E = −6.61 eV   HOMO, E = −6.60 eV   HOMO, E = −6.73 eV

Figure S7. HOMO and LUMO orbital diagrams of **1–3**.

S5. References

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