## **ORIGINAL PAPER**



# Molecular and Crystal Structures of Some Bromocymantrenes

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# Abstract

Crystals of mono- and dibromo as well as two isomeric tribromocymantrenes  $[Mn(C_5H_{5-n}Br_n)(CO)_2(PPh_3)]$  (n = 1–3) were obtained and examined by X-ray diffraction. The degree of substitution has only minor influence on bond lengths and angles. However, the relative orientations of bromo substituents and PPh<sub>3</sub> ligand as well as relative orientation of the cyclopentadienyl ring and the MnC<sub>2</sub>P tripod are sensitive to the number and position of bromines. All compounds show weak Br...O interactions, mostly combined with hydrogen bonds, while Br...Br interactions are unimportant. These interactions lead to sometimes complicated chain structures.

### **Graphical Abstract**

In the crystal structures of the bromocymantrenes  $[Mn(C_5H_{5-n}Br_n)(CO)_2(PPh_{3)}]$  (n = 1–3) a combination of H bonds and Br...O/Br...Br interactions leads to one-dimensional molecular chains or double-chains, which are not further connected in the other dimensions.



Keywords Cymantrene · Bromocyclopentadienyl complexes · Halogen bonding

# Introduction

Aromatic bromides belong to the most important subclasses of aromatic compounds [1]. This is due to the fact that on one hand they are omnipresent as well in natural products as in pharmaceuticals [2], and on the other hand they are

Karlheinz Sünkel suenk@cup.uni-muenchen.de valuable starting materials for C–C coupling reactions like the Stille [3], Sonogashira-Hagihara [4], Suzuki–Miyaura [5], or Mizoroki–Heck reactions [6, 7]. They are also used in C–N couplings like the Buchwald-Hartwig amination [8], C–O couplings [9] or electrocatalytic carboxylation [10]. While usually only mono-brominated arenes are employed, these reactions can also work with polyhalogenated arenes [11]. Rather new is the application of brominated arenes as single electron oxidants [12]. With this broad spectrum of applications in mind, it is quite expectable that brominated arenes are also known as ligands in organometallic

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Scheme 1 Structural formulae of compounds 1-4

chemistry, especially in metallocene compounds. While C-C coupling reactions have rather rarely been used with bromocyclopentadienyl complexes, [13, 14] there is a large number of examples, where they were used as starting materials in bromine-lithium exchange reactions coupled with electrophilic quench reactions [15–19]. When it comes to structural chemistry, aryl bromides have traditionally been studied as H bond acceptors, but during the last decades it was shown that they also take part in halogen bond(ing) interactions [20–22]. While there are numerous studies on this topic for purely "organic" compounds, the occurrence of halogen bonding in halometallocenes has rarely been discussed [23–25]. We have been studying all kinds of halometallocenes for a long time, originally only synthetic and reactivity studies (e.g. halocymantrenes [15-17], haloferrocenes [26, 27], halo-cobaltocenes [28]), later on also structural studies [24, 25]. Now we found it worthwhile to look at the crystal structures of bromocymantrenes  $[Mn(C_5H_{5-n}Br_n)]$  $(CO)_2L$  (L = CO, PPh<sub>3</sub>) with a focus on halogen- and hydrogen-bonding.

# Experimental

Scheme 1 depicts the structural formulae of all compounds described here. The synthesis and characterization of compounds 1–3 as well as  $[Mn(C_5Br_5)(CO)_2(PPh_3)]$  was reported by us recently [29]. Single crystals of all compounds were obtained from petroleum ether/Et<sub>2</sub>O 85:15 mixtures by slowly evaporation of solvent in an open vial at +5 °C in

a refrigerator. X-ray data collections were measured on a BRUKER D8 Venture system. Data were corrected for absorption effects using the Multi-Scan method (SADABS) All structures were solved with SHELXT and refined using SHELXL 2019/3 [30, 31]. Further details of the structure determinations are collected in Table 1.

# Synthesis of 1,2,4-Tribromocyclopentadienyl-Dicarbonyl-Triphenylphosphine Manganese (4)

A solution of  $[Mn(C_5Br_5)(CO)_2(PPh_3)]$  (30 mg, 36 µmol) in THF (5 mL) was treated at -78 °C with 2.5 m *n*BuLi solution (30 µL, 75 µmol) with stirring for 30 min. Then methanol (100 µL) was added, and the solution was warmed to r.t. within 60 min. After evaporation of the solvents, the residue was dissolved in the minimum amount of petroleum ether (PE) and placed on top of a silica gel column. Elution with PE/Et<sub>2</sub>O 85:15 yielded compound **4** as a yellow powder (20 mg, 30 µmol, 83% yield).

<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta = 7.56$ —7.46, 7.43— 7.35, 4.48. – <sup>31</sup>P{<sup>1</sup>H}-NMR (CDCl<sub>3</sub>, 109 MHz):  $\delta = 87.1$ .

### **Special Remarks on the Structure Determinations**

#### **General Remarks**

Some low-angle reflections were apparently affected by the beam-stop and showed therefore zero or even negative intensities. They were consequently removed from the dataset. Checkcif examination of the original cif-files showed also some other reflections, for which  $I_{obs}$  and  $I_{calc}$  differed by more than 10 standard deviations. No reason for this could be found. Nevertheless, these reflections were also removed from the datasets. It was checked, that the obtained results of the bond parameters were not changed by this "manipulation".

**Compound** 1: The compound crystallized as a racemic twin and was refined using the SHELXL TWIN card with a scale factor of 0.053. Six low-angle reflections had to be omitted from the final refinements. Examination of the structure by PLATON [32] showed that the unit cell contained solvent-accessible voids of 52.8 Å<sup>3</sup>, corresponding to 2.4% of the cell volume.

**Compound** 2: 12 low-angle reflections had to be omitted from the final refinements. The unit cell contained two symmetry-independent molecules of **2** together with half a molecule cyclohexane (most likely originating from the petroleum ether used for chromatography and recrystallization). PLATON AutoMolFit, which compares the two independent molecules, showed no indication of higher symmetry. Further examination of the structure by PLATON showed no other solvent-accessible voids.

Table 1Experimental dataof the crystal structuredeterminations

	1	2	3	4	
Empirical formula	nula C <sub>25</sub> H <sub>19</sub> BrMnO <sub>2</sub> P		$\mathrm{C}_{25}\mathrm{H}_{17}\mathrm{Br}_{3}\mathrm{MnO}_{2}\mathrm{P}$	C <sub>25</sub> H <sub>17</sub> Br <sub>3</sub> MnO <sub>2</sub> P	
Formula weight	517.22	1234.32	675.02	675.02	
Temperature [K]	293(2)	103(2)	293(2)	298(2)	
Crystal system	Orthorhombic	Triclinic	Orthorhombic	Triclinic	
Space group	$P c a 2_1$	P -1	Pbca	P -1	
Unit cell dimensions					
<i>a</i> [Å]	17.4925(17)	10.5511(7)	20.2767(6)	9.3798(5)	
b	7.7397(8)	12.6552(8)	10.8037(3)	16.3930(8)	
С	16.1284(17)	18.7305(11)	22.4515(7)	16.6604(7)	
α [°]		92.830(2)		101.2950(10)	
ß		103.940(2)		101.8700(10)	
γ		101.631(2)		96.892(2)	
V [Å <sup>3</sup> ]	2183.6(4)	2364.9(3)	4918.3(3)	2423.9(2)	
Ζ	4	2	8	4	
$\rho_{ca \ddot{o} c} [g \ cm^{-3}]$	1.573	1.733	1.823	1.850	
$\mu [mm^{-1}]$	2.527	4.028	5.497	5.577	
Crystal size [mm <sup>3</sup> ]	$0.04 \times 0.03 \times 0.03$	$0.04 \times 0.03 \times 0.02$	$0.07 \times 0.05 \times 0.04$	$0.07 \times 0.02 \times 0.02$	
$\Theta$ range	2.329-26.404°	2.039-26.393°	2.321-26.407°	2.250-26.392°	
Refl. Coll	24,986	44,319	86,992	45,719	
Indep. Refl. [R <sub>int</sub> ]	4396 [0.0391]	9678 [0.0422]	5026 [0.0527]	9916 [0.0547]	
$T_{max}/T_{min}$	0.7454/0.672	0.7454/0.6826	0.7454/0.6663	0.6465/0.5684	
Data/restraints/parameters	4396/1/271	9678/3/586	5026/0/289	9916/0/580	
GOOF	1.052	1.028	1.067	1.022	
R1/wR2 [I> $2\sigma(I)$ ]	0.0389/0.1035	0.0321/0.0696	0.0331/0.0698	0.0522/0.1194	
R1/wR2 (all data)	0.0478/0.1098	0.0457/0.0751	0.0481/0.0782	0.0794/0.1358	
$(\Delta e)_{\text{max/min}} [e \text{ Å}^{-3}]$	0.365/-0.850	1.102/-1.055	0.936/-1.015	2.463/-1.751	
CCDC-#	2,349,803	2,349,804	2,349,805	2,349,806	

**Compound** 3: Six low-angle reflections and four further reflections (5 2 2/7 2 2/5 1 3/6 3 3) had to be omitted from the final refinements. No solvent-accessible voids could be detected.

**Compound** 4: Ten low-angle reflections and two further reflections (1 5 2/2 -1 2) had to be omitted from the final refinements. PLATON detected solvent-accessible voids of 12.3 Å<sup>3</sup>, corresponding to 0.5% of the cell volume. However, no particular solvent could be localized. The unit cell contains two symmetry independent molecules; PLATON AutoMolFit, showed no indication of higher symmetry.

# **Results and Discussion**

# Molecular Structure of [Mn(C<sub>5</sub>H<sub>4</sub>Br)(CO)<sub>2</sub>(PPh<sub>3</sub>)], 1

Compound 1 crystallizes in the orthorhombic space group  $Pca2_1$  with one molecule in the asymmetric unit (Fig. 1). Important bond parameters are collected in Table 2.



Fig. 1 Molecular structure of compound 1. Displacement ellipsoids are shown at the 30% probability level

Comp	1	2/Mol.A	2/Mol.B	3	4/Mol. A	4/Mol. B
Mn–P [Å]	2.229 (2)	2.245 (1)	2.242 (1)	2.248 (1)	2.253 (1)	2.252 (1)
(Mn-CO) <sub>av</sub> [Å]	1.759 (7)	1.781 (3)	1.777 (3)	1.774 (3)	1.775 (7)	1.775 (6)
Mn–Ct <sub>cp</sub> [Å]	1.782 (3)	1.779 (1)	1.772 (2)	1.776 (2)	1.776 (3)	1.783 (2)
(C–Br) <sub>av</sub> [Å]	1.851 (7)	1.874 (2)	1.873 (3)	1.870 (3)	1.874 (5)	1.873 (5)
MnBr [Å]	3.579 (1)	3.621 (1) 3.663 (1)	3.615 (1) 3.661 (1)	3.620 (1)/3.608 (1)/3.649 (1)	3.674 (1)/3.583 (1) 3.611 (1)	3.736 (1)/3.662 (1) 3.618 (1)
(C <sub>H</sub> -Ct <sub>cp</sub> -Mn-P) <sub>min</sub> [°]	14.6	18.6	19.2	16.8	53.1	50.4
Br–Ct <sub>cp</sub> –Mn–P [°]	158.1	162.6 91.1	163.6 91.9	161.0/127.0/89.4	163.0/125.6 19.4	122.7/93.6 21.4

Comparisons of the Mn–P bond lengths in [Mn(C<sub>5</sub>H<sub>4</sub>X) (CO)<sub>2</sub>(PPh<sub>3</sub>)] (X = H, [33], F, [34], Cl [35], Br (1)): 2.226(1)/2.242(1) (X = H), 2.235(1)/2.245(1) (X = F), 2.240(1) (X = Cl), 2.229(2) (X = Br) and of the Mn–ring centroid (CT) distances: 1.777(1)/1.778(1) (X = H), 1.773(2) (X = F), 1.786(2) (X = Cl), 1.782(3) (X = Br) show no recognizable influence of the substituent X. However, there are large differences in the orientations of the C–X bond with respect to the Mn–P bond: for X = F, the torsion angle X-CT-Mn-P in one of the two independent molecules is ca. 7° (and ca. 138° in the other), while for X = Cl it is ca. 78° and for X = Br it is 158°.

## Molecular Structure of [Mn(C<sub>5</sub>H<sub>3</sub>Br<sub>2</sub>-1,2)(CO)<sub>2</sub>(PPh<sub>3</sub>)], 2

Compound **2** crystallizes in the triclinic space group P-1 with two molecules in the asymmetric unit (Fig. 2).

There are only minor differences between the two independent molecules on first sight (Table 2). However, a closer look shows subtle differences between the relative orientations of the phenyl rings (for example, the torsional angle Mn1-P1-C121-C122 is 26.9°, while the corresponding Mn2-P2-C201-C202 is 16.7°). In comparison with compound 1, the Mn-P bond is slightly longer, while the distances between the metal and the cyclopentadienyl ring centroid are identical within 2o. One C-Br bond in both molecules is, similar to compound 1, in relative trans-orientation with respect to the  $Mn \rightarrow P$  vector, which is also half way between a staggered and an eclipsed conformation with respect to the cyclopentadienyl ring. The Mn... Br intramolecular distances are in both molecules of 2 as well as in compound 1 shorter than the sum of their van der Waals radii (3.85 Å).



Fig. 2 The two independent molecules of compound 2 in the crystal. Displacement ellipsoids are shown at the 30% probability level

# Molecular Structure of [Mn(C<sub>5</sub>H<sub>2</sub>Br<sub>3</sub>-1,2,3) (CO)<sub>2</sub>(PPh<sub>3</sub>)], 3

Compound **3** crystallizes in the orthorhombic space group *Pbca* with one molecule in the asymmetric unit (Fig. 3). In comparison with the structures of **1** and **2**, the main metrical parameters are the same, with another slight increase in



Fig. 3 Molecular structure of compound 3. Displacement ellipsoids are shown at the 30% probability level

the Mn–P bond length (Table 2). The middle C–Br bond is nearly in a transoid position with respect to the Mn–P vector, which is again half way between staggered and eclipsed conformation relative to the cyclopentadienyl ring. The structure of **3** can also be compared with its tricarbonyl analog,  $[Mn(C_5H_2Br_3)(CO)_3]$  (**5**) [35]. In this compound the metalcentroid distance is shorter (1.766 Å), the average C–O bond length longer (1.800 Å), while the average C–Br bond length is the same (1.871 Å).

# Molecular Structure of [Mn(C<sub>5</sub>H<sub>2</sub>Br<sub>3</sub>-1,2,4) (CO)<sub>2</sub>(PPh<sub>3</sub>)], 4

Compound 4 crystallizes in the triclinic space group P-1 with two molecules in the asymmetric unit (Fig. 4).

The two molecules differ in the relative orientation of the C–Br bonds with respect to the  $MnC_2P$  tripod. In both molecules, and in significant difference with the structures of **1–3**, two C–Br bond nearly eclipse the Mn  $\rightarrow$  P vector and one of the Mn  $\rightarrow$  CO vectors. The third C–Br bond, however, is in molecule A in relative transoid position with respect to the Mn  $\rightarrow$  P vector, while in molecule B it is at a right angle with it. Another difference between the two molecules is the relative orientation of the phenyl rings that are furthest away from the cyclopentadienyl ring: the corresponding torsion angles Mn1-P1-C111-C116 and Mn2-P2-C201-C206 are 107.6° and 136.1°, respectively. The Mn–P bonds continue the trend of increased length with increasing number



Fig. 4 The two independent molecules in the crystal of compound 4. Displacement ellipsoids are shown at the 30% probability level

of bromine substituents, while this change has no effect on the metal-ring centroid distance.

# Intra- and Intermolecular Hydrogen Bonding

The following discussion includes only such contacts that are shorter than the sum of van-der-Waals radii (H...Br 3.05 Å, H...O 2.72 Å). There are no "classical" H bonds, since there are only C-H donors. In compound 1 there are neither intra- nor intermolecular H bonds. In each of the independent molecules of compound 2 is one intramolecular H-bond between a phenyl C-H bond and a bromine atom (Br12 and Br21, respectively). Carbonyl oxygen atom O21 accepts two intermolecular H bonds: one from a phenyl C-H and one from a cyclopentadienyl C-H group. In addition, carbonyl oxygen atom O12 accepts one intermolecular H bond from a phenyl C–H group (Table 3). In compound 3 bromine atom Br1 accepts one intramolecular H-bond from a phenyl C-H group, while Br3 accepts an intermolecular H bond from another phenyl C-H group. In addition, carbonyl oxygen atom O1 accepts an intermolecular H bond from a cyclopentadienyl C–H group (Table 3). In compound 4, there is one "true" intramolecular H bond involving bromine atom Br21 and one phenyl C-H group, and two "pseudointramolecular" H bonds (between different independent molecules of the asymmetric unit) involving oxygen atom O21: one from a cyclopentadienyl C-H group and one from a phenyl C-H group. In addition, there are intermolecular H bonds between phenyl C-H groups and oxygen atom O12 and bromine atom Br21, respectively (Table 3). For all compounds, neither all oxygen nor all bromine atoms are involved in H bonding. In each of the compounds 2-4 there is one intramolecular C-H...Br bond involving a phenyl C-H bond, with C...Br distances between 3.77 and 3.84 Å. In both compounds 2 and 4 one carbonyl oxygen accept two H bonds each.

We also had a look at the intermolecular C-H...C interactions (not contained in Table 3). Compounds 1-4 contain only interactions between phenyl H atoms and phenyl carbons, and none are of the C-H... $\pi$  type. This is quite different in compounds 6 and 7, where many other kinds of C-H...C interactions, including the C-H... $\pi$  type are found.

For comparison, Table 3 includes the corresponding data from the structurally related compounds  $[Mn(C_5H_2Br_3, 1, 2, 3)]$  $(CO)_{3}$  (5),  $[Mn(C_{5}HBr_{4})(CO)_{2}(PPh_{3})]$  (6) and  $[Mn(C_{5}Br_{5})]$  $(CO)_2(PPh_3)$ ] (7), which were extracted from the cif-files

Table 3H bond parameters incompounds 2–4	Compound	CHX	HX [Å]	CX [Å]	C–HX [°]	Reference
1	2	C122-H122Br12	2.91	3.816 (4)	160	This work
		C202-H202Br21	2.91	3.842 (4)	168	
		C114-H114O21'	2.60	3.481 (4)	155	
		С205-Н205О21'	2.54	3.199 (4)	127	
		С125-Н125О12'	2.58	3.236 (4)	126	
	3	C32-H32Br1	2.95	3.775 (4)	148	
		C5-H5O1'	2.58	3.373 (4)	144	
		C33–H33Br3'	2.98	3.698 (4)	136	
	4	C216-H216Br21	2.93	3.824 (7)	163	
		C13-H13O21	2.63	3.429 (9)	144	
		C102-H102O21'	2.67	3.441 (8)	141	
		C125-H125O11'	2.63	3.335 (7)	133	
		C113-H113Br21'	2.95	3.620 (7)	130	
	5	C15-H15O3'	2.66 (6)	3.60(1)	160 (5)	FOFROI [35]
	6	C26-H26Br4	3.04	3.952 (2)	169	IRIYOA [29]
		С36-Н36О2	2.71	3.606 (3)	161	
		C13-H13O1'	2.69	3.398 (3)	133	
	7	C126-H126O11	2.64	3.522 (7)	155	IRIYUG [29]
		C212-H212O22	2.70	3.444 (5)	135	
		C226–H226Br22	2.91	3.527 (4)	124	
		C236-H236Br21	3.03	3.805 (5)	140	
		C114–H114O21'	2.61	3.327 (6)	132	
		C225-H225Br12'	3.03	3.882 (6)	150	
		C234–H234Br15'	2.95	3.702 (4)	138	
		C234–H234O21'	2.64	3.274 (6)	125	
		C235-H235O11'	2.55	3.196 (6)	125	

FOFROI, IRIYOA and IRIYUG, distributed at the CSD, as they were not discussed in the original publications. As these data for compounds 2–7 show, C–H...O distances range from 2.54 to 2.71 Å and C–H...Br distances from 2.91 to 3.04 Å. Compound 5 is the only one (besides compound 1) that contains no C–H...Br bonds, which shows the importance of the presence of the PPh<sub>3</sub> ligand for this kind of interaction (see, however, the different outcome of the Hirshfeld Analysis with respect to the fingerprint plots, discussed further down).

#### Halogen Bonds: Br...Br and Br...O Interactions

As was mentioned in the Introduction, the importance of halogen bonds for the particular arrangements of molecules in a crystal structure has been revealed only within the last few decades. The vast majority of the discussed compounds was purely "organic", and only recently organometallic compounds were studied as well [23, 24]. Apparently, so far, no metal carbonyls except for [Fe(C<sub>5</sub>H<sub>5-n</sub>X<sub>n</sub>)(CO)<sub>2</sub>R] have been studied in this context [25]. In the compounds reported in the present study, besides the H...Br interactions discussed in the previous section, mainly interactions of the type Br... Br, Br...O, Br...Mn and Br... $\pi$  can be expected [23]. No significant interactions of the latter two types were found. For further discussion and classification, the angles  $\Theta 1/\Theta 2$  are defined as shown in Scheme 2.

The most common classifications are "Type I" (with  $|\Theta 1-\Theta 2| < 15^{\circ}$ ) and "Type II" (with  $30^{\circ} < |\Theta 1-\Theta 2| < 90^{\circ}$ ), [20, 23], although other definitions exist. With these



Scheme 2 Definition of the angles  $\Theta 1$  and  $\Theta 2$ 

Table 4 Important parameters of Br...X interactions in compounds 1-7

definitions in mind, the situation found in compounds 1 - 7 is described in Table 4.

Most compounds show Br...O interactions except for **5**, and also in **4** the Br...O distance is larger than the sum of van-der-Waals radii of O and Br (3.37 Å). On the other hand, in compound **1** the distance between Br1 and O2 is significantly shorter (by 0.22 Å). Br...O contacts of Type I are found in compounds **1** and **6**, while compounds **2**, **3** and **7** show Type II behaviour, or in other words, have "true" halogen bonds. Br...Br contacts below the sum of van-der-Waals radii (3.70 Å) are found in the present study only for compound **2** and are of Type I only. However, the literature compounds **5** and **6** show Br...Br contacts of Type II, while compound **7** contains a Br...Br contact

It is also possible to compare the number of Br and O atoms involved in either H bonds, Br...O or Br...Br interactions. In compound 1, the only Br atom is involved in a Br...O interaction with one carbonyl oxygen. The other carbonyl oxygen is not involved in any interactions. In compound 2 all Br atoms are involved either in H bonds (Br12, Br21), in Br...O (Br11) or Br...Br (Br11, Br22) interactions. Three out of four carbonyl oxygen atoms are also involved in either H bond (O12, O21) or Br...O interaction (O22). Oxygen atom O11 does not participate in any non-covalent interactions. In compound 3 Br atoms are involved in H bonds (Br1, Br3) and/or Br...O interactions (Br3), while one carbonyl oxygen atom is involved in both H bonding and Br...O interactions (O1). Neither Br2 nor O2 participate in any non-covalent interactions. In compound 4 two Br atoms take part in either H bonding (Br21) or Br...O interactions (Br4), while the remaining four Br atoms take part in no non-covalent interactions. One carbonyl oxygen is part of both H bonding and Br...O interactions (O11) and another only in H bonding (O21). The remaining two oxygen atoms don't take part in any non-covalent interactions.

Comp	C–BrX–C	Symm. Op. atom X	BrX [Å]	<b>Θ</b> 1 [°]	Θ2 [°]	<b>Θ</b> 1− <b>Θ</b> 2  [°]	XB-Type
1	C1–Br1O2'–C7'	1.5-x,y,z-0.5	3.154 (6)	148.6 (2)	148.0 (5)	0.6	I
2	C11-Br11O22'-C27'	<i>x</i> , <i>y</i> , <i>z</i>	3.242 (7)	158.6(1)	121.7 (2)	36.9	II
	C11-Br11Br21'-C21'	<i>x</i> , <i>y</i> , <i>z</i>	3.7346 (6)	128.7 (1)	119.1 (1)	9.6	Ι
3	C3-Br3O1'-C6'	0.5-x,y-0.5,z	3.164 (2)	160.0(1)	93.5 (2)	66.5	II
4	C14-Br4O11'-C16'	l+x,y,z	3.464 (6)	117.8 (2)	142.4 (5)	24.6	I/II
5	C11-Br11Br13'-C13'	x,0.5-y,z-0.5	3.647 (1)	155.5 (2)	94.5 (2)	61.0	II
	C12-Br12Br13'-C13'	1-x,y-0.5,1.5-z	3.613 (1)	130.2 (2)	160.0 (2)	29.8	II
6	C4-Br4O1'-C6'	x,1.5-y,z-0.5	3.285 (2)	134.7 (1)	146.1 (2)	11.4	Ι
	C1-Br1Br3'-C3'	1-x,y-0.5,1.5-z	3.4382 (4)	97.4 (1)	161.2 (1)	63.8	II
7	C14-Br14O12'-C17'	1-x,-y,2-z	3.217 (4)	174.2 (2)	97.6 (3)	76.6	II
	C13-Br13Br21'-C21'	1-x,-y,2-z	3.530(1)	143.6 (2)	131.2 (2)	12.4	Ι



**Fig. 5** Packing plot of compound **1**, viewed along *b*. The "central" molecule has symm.op. x, y, z



**Fig. 6** Packing plot of compound **2**, viewed along *a*. MERCURY colour code: "by symmetry equivalence" (red: Molecules B, dark blue: molecules A; green: lattice cyclohexane; the "left" blue, the "bottom" green and the "bottom right" molecules correspond to symmetry operator: *x*, *y*, *z*; the other molecules are created by combinations of inversion and translations along *b* and *c* (Color figure online)

## **Packing Plots**

The interplay of H bonds and Br...O and Br...Br interactions lead to the crystal packing shown in Figs. 5, 6, 7, 8, 9.

Figure 5 shows a packing plot of compound 1. As can be seen, O...Br interactions lead to parallel zigzag chains in c

direction, which are shifted with respect to each other by a/2 in *a* direction. These parallel chains are not interconnected.

Figure S1 shows a standard MERCURY packing plot of compound **2**, analogous to Fig. 5, while Fig. 6 shows a MERCURY packing plot with colour coding "by symmetry equivalence".

Since both these plots do not show well, which molecules interact, some alternative views are given in Fig. 7 (without the lattice solvent).

Each molecule interacts with four others. Four molecules form a rhomb in an approximate plane perpendicular to the *a* axis (red, dark blue, magenta and brown, or dark green, orange, violet and pink). Each rhomb is connected to two others on both sides along *a*, of which is shown only one in Fig. 7. Thus, stacks of such rhombs form along *a*, which are not connected to other stacks. One A molecule is connected to two other A molecules via H bonds (with a distance of 10.551 Å) and two B molecules via one H bond (8.452 Å between Mn centres) and one X bond (8.582 Å between Mn atoms) each, and vice versa.

Packing plots of compound **3** are shown in Figures S2 (standard MERCURY packing plot) and Fig. 8 (MERCURY plot "by symmetry operation"). As can be seen, individual molecules interact in a and b directions via H bonds (e.g., one "white molecule" interacts with two "green molecules" in b and two "magenta molecules" in a direction), while Br...O contacts join the molecules in b direction (one "white molecule" joins with two "magenta molecules", and vice versa. In addition -not shown- one "green molecule" joins with two "magenta molecules" and vice versa). There are no non-covalent interactions in c direction.

Complete packing plots for compound 4 are shown in Figure S3, and are also very unclear. Therefore, Fig. 9 shows only six selected molecules, three of molecules A and three of molecules B. Starting with the light green molecule A, it is connected via a bifurcated double H bond accepted by oxygen atom O21 on the very light blue molecule B. This molecule accepts via bromine atom Br21 a H bond from a second light green molecule A, which is translated from the first one by a one-unit shift along a. This molecule is bonded again via a bifurcated H bond with oxygen atom O21 on a second light blue molecule translated by one unit in a direction. Thus, a zig-zag line of A and B molecules extends in a direction. The second light green molecule is doubly H bonded to an inversion related dark green molecule A across the ab face. The dark green A molecule is doubly H-bonded via a bifurcated H bond with oxygen atom O21 on the dark blue B molecule. Both molecules are part of another zigzag chain, that extends in a direction, parallel to the first one. As the right side of Fig. 9 shows, the rather long Br...O contact between O11 and Br4, both on A molecules, support the H bridges between A molecules in a direction. The double zig-zag chains are not further interconnected, neither in b nor in c direction.



Fig. 7 left and middle: two packing plots of compound 2, viewed along b (left) and along a (middle), eight interacting molecules selected. Right: schematic diagram of the selected molecules, same

colour code. Light blue lines symbolize H bonding interactions, brown lines Br...O/Br...Br interactions. The numbers are distances (in Å) between the Mn centres (Color figure online)



**Fig. 8** Packing plots of compound **3**, viewed along *c*: top: H bonding; bottom: Br...O interactions. MERCURY colour coding "by symmetry operation": left: green = 1-x,  $y \pm \frac{1}{2}$ , 1.5-y; magenta =  $-x \pm \frac{1}{2}$ , y, 1.5-z; right: magenta =  $\frac{1}{2}$ -x,  $y \pm \frac{1}{2}$ , z; white: x,  $y (\pm 1)$ , z (Color figure online)

#### **Hirshfeld Analysis**

In order to get some further information on the energetics of the non-covalent interactions found in compounds 1–4, a Hirshfeld Analysis was undertaken using the program *CrystalExplorer* [36]. First, a calculation of Hirshfeld surfaces was performed for compounds 1–7 except for 5. When there were two independent molecules in the asymmetric unit, only one of them was selected for the calculation. Figure S4 shows the result for compounds 1–4. Figure S5 shows the Fingerprint plots [37] for compounds 1–3, and Figure S6 for compounds 4, 6 and 7.From these Fingerprint plots, a calculation of the relative contributions of the X…Y interactions across the Hirshfeld surface can be performed, and the results are shown in the following Table 5.

Quite unexpectedly, there are sometimes significant differences between the two molecules of a compound in one structure: for example, in the structure of compound 2 the H...H interactions are far more important for molecule B, while on the other hand the H...O interactions are more important for molecule A. Similarly, for compound 4 the C...C interactions are significantly more important for molecule A, while the H...C interactions are far more important for molecule B. For compound 7 H...H interactions in molecule A are far more important than in molecule B, while the H...O and Br...Br interactions are far more important for molecule B compared to molecule A. In order to study the influence of the number of Br atoms on these interactions, the values for compounds 2, 4 and 7 were averaged. The most important interactions are the H...H contacts, with a continuous decrease from 43% down to 27% with increasing number of Br substituents there is no obvious connection



**Fig.9** Partial packing plots of compound **4** along a (top) and b (bottom), six interconnected molecules selected. greenish colours correspond to A molecules, while bluish colours resemble B molecules (Color figure online)

between the contributions of C...C contacts and the number of Br atoms, with a maximum of 3.7% with compound 3. Closer inspection of this compound showed, that there exists a weak  $\pi$ - $\pi$  interaction between a cyclopentadienyl and a phenyl ring with their centroids 3.671 Å apart. Br...Br contacts are absolutely unimportant for all compounds with 1-4 Br substituents, but are the second most important contributors for compound 7. The importance of H...Br contacts increases when going from 1 to 3 Br atoms and decreases then again, being for compound 7 only slightly more important than for compound 1. There seems to be no correlation between degree of Br substitution and importance of H...C contacts. However, it is quite surprising that there is a significant difference between the two isomeric tribromo compounds (13.6 vs. averaged 19.2%). The importance of H...O contacts gradually decreases with increasing Br substitution, while the opposite trend is observed for the Br...O contacts. In summary it can be seen, that the cyclopentadienyl protons have a much larger impact on all H...X interactions than the phenyl protons, and, indirectly, on the Br...Br interactions.

Next, we performed a calculation of interaction energies [38, 39]. First, we looked at the differences between energy models CE-B3LYP and CE-HF for compound **1**. Figure S7 shows that there are subtle differences between the exact B3LYP/6-31G (d,p) model and the substantially faster HF/3-21G, however, usually they are smaller than 0.5 kJ/mol. Therefore, we decided to save computation time, and performed the calculations for the other compounds only based on the HF/3-21G model (Figure S8). As can be seen from these tables, total energies of individual interactions vary from +0.8 to -58.2 kJ/mol, with the largest contributions coming from the dispersion terms (variations between +0.0 and -73.8 kJ/mol).

## Conclusion

Analysis of the metrical parameters of the molecular structures of compounds 1 - 4 also in comparison with compounds **6** and **7** shows that the number of bromine atoms

Table 5Relative contributions(%) of inter-element contactsacross the Hirshfeld surfaces

Compound	НН	CC	BrBr	HBr	НС	НО	BrO
1	43.2	1.0	0.0	11.0	23.1	17.5	2.0
2/Mol A	33.6	0.5	1.5	19.6	21.7	17.2	2.1
2/Mol B	39.3	0.7	1.4	17.3	21.1	14.6	2.2
3	29.4	3.7	0.8	28.3	13.6	16.5	3.0
4/Mol. A	28.5	3.0	0.3	28.3	16.8	14.5	3.8
4/Mol. B	30.6	0.5	0.0	25.7	21.6	12.6	5.1
6	25.7	0.4	2.4	26.1	17.7	13.4	5.4
7/Mol.A	32.8	0.9	13.7	11.5	14.3	6.9	8.6
7/Mol. B	21.8	2.5	20.0	13.0	17.4	13.1	3.2

has a negligible influence on the distance of the cyclopentadienyl centroid from the manganese atom, while the Mn-P distance increases slightly when going from 1 to 4 Br substituents and then decreases slightly again. All studied compounds 1–4 (and the structurally related compounds 6 and 7) show Br...O interactions, which are supported, except for 1, by hydrogen bonding both of the C–H...O and/or the C–H...Br type. Br...Br interactions are found only in 2 (but in compound 6 and particularly in 7, where they are the second most important interaction). Both type I and Type II halogen bonds are found. These interactions lead to onedimensional chain structures (eventually double or quadruple chains), which are however never three-dimensionally interconnected. Theoretical calculations of interaction energies show that dispersion terms are the most important.

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**Data Availability** CCDC 2349803-2349806 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www. ccdc.cam.ac.uk/data\_request/cif. The authors declare that all other data supporting the findings of this study are available within the article and its supplementary information files.

### Declarations

**Conflicts of interest** The authors have no conflicts of interest to declare that are relevant to the content of this article.

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