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# Self-Assembly of Halogenated Cobaltacarborane Compounds: Boron-Assisted C−H···X−B Hydrogen Bonds?

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*Dedicated to Professor Dr. Jaume Casabó i Gispert on the occasion of his 65th birthday in recognition of his great contribution to the field of inorganic chemistry*

**Abstract:** Full structural characterisation and complete synthetic procedures for three monohalogenated cobaltacarborane compounds *closo*-[3-Co($\eta^5$-$C_5H_5$)-8-X-1,2-$C_2B_9H_{10}$] (X = Cl (**1**), Br (**2**), I (**3**)) and the dibromo derivative *closo*-[3-Co($\eta^5$-$C_5H_5$)-8,9-$Br_2$-1,2-$C_2B_9H_9$] (**4**) are reported. The supramolecular structures of **1**, **3**, and **4** reveal the existence of intermolecular C−H···X−B interactions. The role of these interactions has been investigated through a CSD search and subsequent analysis of the reported crystalline compounds. The results show that halogens become reasonably good hydrogen-bond acceptors when bonded to boron and, in this respect, are comparable in strength to metal-bound halogens.

**Keywords:** boron · crystal engineering · metallacarboranes · self-assembly · weak hydrogen bonds · weak interactions

## Introduction

Non-bonding intra- and intermolecular interactions are of fundamental importance for understanding molecular recognition phenomena, biological processes, and the physical and chemical properties of new materials.[1] The understanding and control of these forces and of the supramolecular self-assembly process is a prerequisite for the progress of crystal engineering.[1,2] In recent years, crystal engineers have begun to explore the potential of interactions other than classical hydrogen bonds as directors of molecular association. Interactions such as C−H···X (X = halogen) have often been considered as van der Waals (vdW) interactions.[3] This common view is now changing due to the evidence that halogens can give rise to true C−H···X hydrogen bonds (of relatively weak character), especially when the acceptor X bears a full or partial negative charge (halide anions or M−X bonds, respectively).[3,4] For example, halogens bonded to transition metals (X−M) are known to be better hydrogen-bond acceptors than when they are present in classical organic halides (X−C). This property arises from the strongly polarised character of the X−M bond, which generally results in an enhanced partial negative charge on the halogen. This phenomenon is known as *metal-assisted* hydrogen bonding and is now well documented, with the overall order of hydrogen-bond strengths for C−H···X−M decreasing from X = F to I.[4b,e]

Carbon-containing polyhedral boranes, *carboranes*, and their metal complexes, *metallacarboranes*, are extremely stable cage molecules that have been known for over 30 years (Scheme 1). Heteroboranes[5] containing organic functional groups have applications in a number of diverse fields, such as material science, as boron carriers for boron neutron capture therapy, as agents for the extraction of metal ions, in conducting organic polymers, as ligands for metals, and, more recently, in supramolecular chemistry.[6,7] It has been predicted that icosahedral carborane *closo*-($C_2B_{10}H_{12}$) cages could have great potential as building blocks in supramolecular systems as a result of their three-dimensional nature.[8] The supramolecular chemistry of car-

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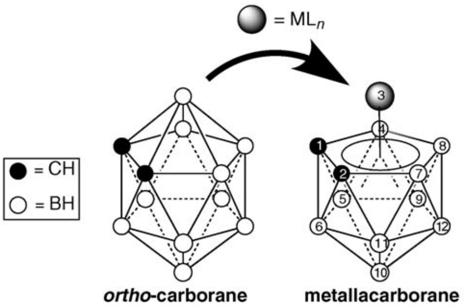
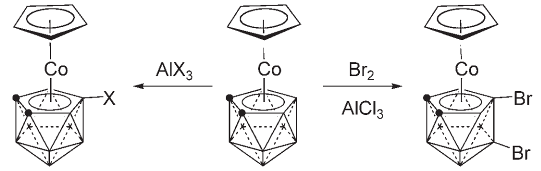
Supporting information for this article (plots of intermolecular distances versus angles and frequency distributions versus angles for C−H···X−B interactions) is available on the WWW under http://www.chemeurj.org/ or from the author.



Scheme 1. Common heteroboranes showing the atom-numbering scheme.

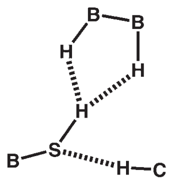


X = Cl (**1**)
Br (**2**)
I (**3**)

(**4**)

Scheme 3. Synthetic routes to **1**–**4**

boranes is mainly directed by interactions of the type C*c*—H···X between their acidic C*c*—H (C*c* = cage carbon) vertices as proton donors and classical (X = O, N, S, F, Cl, Br, I)[7,9] and weak non-classical (X = alkynes, arenes)[7,10] proton acceptors. In an attempt to relate the field of molecular crystal engineering with that of icosahedral heteroborane clusters, we have recently prepared such solids and have studied their solid-state architectures.[11] Of interest with regard to the present work is our report of the first example of an intermolecular dihydrogen bond (S—H···H—B) and its combination with a C—H···S hydrogen bond in a cooperative effect of the type C*c*—H···S—H···(H—B)$_2$ in crystalline *closo*-[3-M($\eta^n$-C$_n$H$_n$)-8-HS-1,2-C$_2$B$_9$H$_{10}$] compounds.[11a] The presence of an S—H···H—B dihydrogen bond in these complexes can be attributed to the enhanced polarisation of the HS—B bond (as compared to an HS—C bond).[12] The greater polarisation makes the sulfur atom a better acceptor for a C*c*—H donor (Scheme 2) and, as a consequence, the S—H becomes a better donor and forms a bifurcated dihydrogen bond. Based on this principle, we expected that other classical hydrogen-bond acceptors could also become better acceptors when attached to boron (hence the term *boron-assisted hydrogen bond*). The primary aim of this work is to explore these ideas as a strategy for metallacarborane crystal engineering. Thus, we report here full structural characterisation and complete synthetic procedures for four halogenated cobaltacarborane molecules (**1**–**4**, Scheme 3), which complete previous partial reports.[13] The crystal structures of **1**, **3** and **4** have been solved and their solid-state structures have been analysed. The existence of intermolecular C—H···X—B (X = Cl, Br, I) contacts in these molecules is discussed and further assessed through a CSD search and subsequent statistical analysis.



Scheme 2. Unconventional cooperative effect in mercaptan metallacarboranes.

## Results and Discussion

**Synthesis of halogenated cobaltacarboranes 1–4**: Halogenation at the boron atoms of neutral cobaltacarborane complexes has been much less well studied than that of the related anionic complexes.[14] Among the few examples, monohalogenation has been reported to take place on refluxing the complex *closo*-[3-Co($\eta^5$-C$_5$H$_5$)-1,2-C$_2$B$_9$H$_{11}$] in benzene with an excess of AlX$_3$ (X = Cl, Br, I).[13a] However, only partial characterisation of the chloro derivative was presented in the original publication and the position of attachment of the halogen atom could not be established. The corresponding bromo and iodo derivatives were identified on the basis of their mass spectra and elemental analyses, and no details regarding their syntheses were reported. With the aim of obtaining the X-ray structures of the monohalogen derivatives, we have synthesised these compounds and report here full details of the previously unreported synthetic methods used to obtain them as well as their characterisation (see Experimental Section). NMR data clearly show that halogenation of *closo*-[3-Co($\eta^5$-C$_5$H$_5$)-1,2-C$_2$B$_9$H$_{11}$] takes place at boron B(8) in all cases, affording the symmetrical monohalogenated complexes *closo*-[3-Co($\eta^5$-C$_5$H$_5$)-8-X-1,2-C$_2$B$_9$H$_{10}$] (X = Cl (**1**), Br (**2**), I (**3**)), as shown in Scheme 3. The structures of compounds **1** and **3** have been confirmed by X-ray diffraction analysis (Figure 1 and 2, respectively).

As regards the synthesis of multi-halogenated derivatives of the cobaltacarborane *closo*-[3-Co($\eta^5$-C$_5$H$_5$)-1,2-C$_2$B$_9$H$_{11}$], mono-, di-, and tribromo compounds have been reported to be formed upon treatment of the parent compound with bromine in the presence of AlCl$_3$.[13b] The authors claimed to have prepared the tribromo derivative when using an excess of bromine in the presence of a catalytic amount of AlCl$_3$, based on partial characterisation of the compounds. However, we have found that the reported tribromo compound was in fact the dibromo derivative *closo*-[3-Co($\eta^5$-C$_5$H$_5$)-8,9-Br$_2$-1,2-C$_2$B$_9$H$_9$] (**4**), as shown in Scheme 3. $^1$H NMR data and $R_F$ values for **4** are identical to those reported for the supposed tribromo derivative.[13b] However, the asymmetry of this compound is evident from the $^{11}$B NMR data (see Experimental Section), and by X-ray diffraction analysis we have now confirmed that the structure corresponds to the dibromo compound **4** (Figure 3).

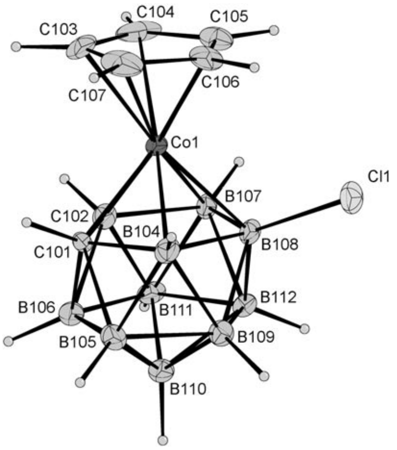


Figure 1. Molecule 1 of the two in the asymmetric unit of *closo*-[3-Co($\eta^5$-$C_5H_5$)-8-Cl-1,2-$C_2B_9H_{10}$] (**1**); thermal ellipsoids drawn at the 50 % probability level. Selected interatomic distances [Å]: C101–C102 1.640(4), Co1–C101 2.015(3), Co1–C102 2.001(3), Co1–B104 2.074(4), Co1–B107 2.067(4), Co1–B108 2.097(3).

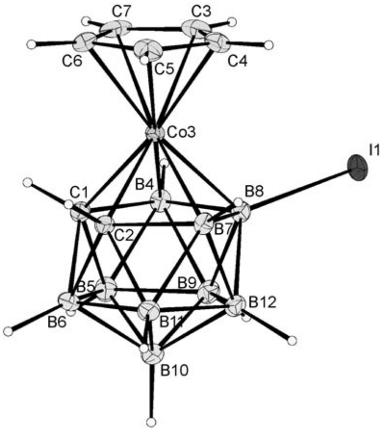


Figure 2. Molecular structure of *closo*-[3-Co($\eta^5$-$C_5H_5$)-8-I-1,2-$C_2B_9H_{10}$] (**3**); thermal ellipsoids drawn at the 35 % probability level. Selected interatomic distances [Å]: C1–C2 1.642(5), Co3–C1 2.004(4), Co3–C2 2.004(4), Co3–B4 2.075(4), Co3–B7 2.072(4), Co3–B8 2.096(4).

**Molecular structures**: Crystals of **1** and **3** suitable for X-ray analysis were obtained from solutions in acetone. Figures 1 and 2 show comparative perspective views of **1** and **3**. The asymmetric unit of **1** contains two chemically identical but crystallographically independent molecules, related by a pseudo centre of inversion. In both cases, the cobalt atom is sandwiched between a $[C_5H_5]^-$ ligand and a [10-X-7,8-*nido*-$C_2B_9H_{10}]^{2-}$ ligand and the $C_5$ ring of the hydrocarbon ligand is staggered with respect to the $C_2B_3$ carborane face. The average Co–C($C_2B_3$ face), Co–B($C_2B_3$ face), and Co–C($C_5H_5$) bond lengths are very similar in both cases (2.01, 2.08, and 2.05 Å, respectively), and are also similar to those in other neutral cobaltacarborane complexes.[15]

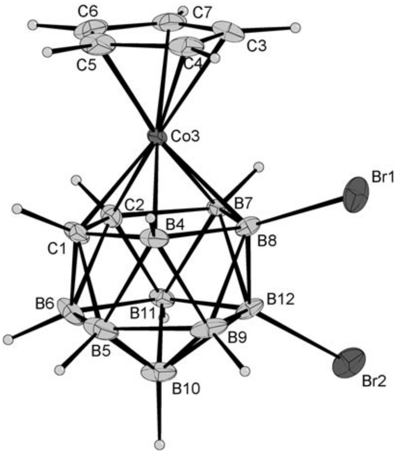


Figure 3. Molecular structure of *closo*-[3-Co($\eta^5$-$C_5H_5$)-8,9-$Br_2$-1,2-$C_2B_9H_9$] (**4**); thermal ellipsoids drawn at the 35 % probability level. Selected interatomic distances [Å]: C1–C2 1.630(15), Co3–C1 2.022(10), Co3–C2 2.014(10), Co3–B4 2.062(12), Co3–B7 2.055(11), Co3–B8 2.069(11).

The molecular geometry of compound **4** is very similar to those of **1**–**3**. The average Co–C($C_2B_3$ face), Co–B($C_2B_3$ face), and Co–C($C_5H_5$) bond lengths are 2.02, 2.06, and 2.04 Å, respectively, and the $C_5$ ring of the $C_5H_5$ ligand is again staggered with respect to the $C_2B_3$ carborane face.

**Molecular packings**: All three halogenated cobaltacarborane compounds **1**, **3** and **4** form layers sustained by intermolecular C–H···X interactions along the shortest crystallographic axes (Figures 4–6, respectively). Table 1 lists the salient intermolecular distances and angles. Figure 4 shows two pro-

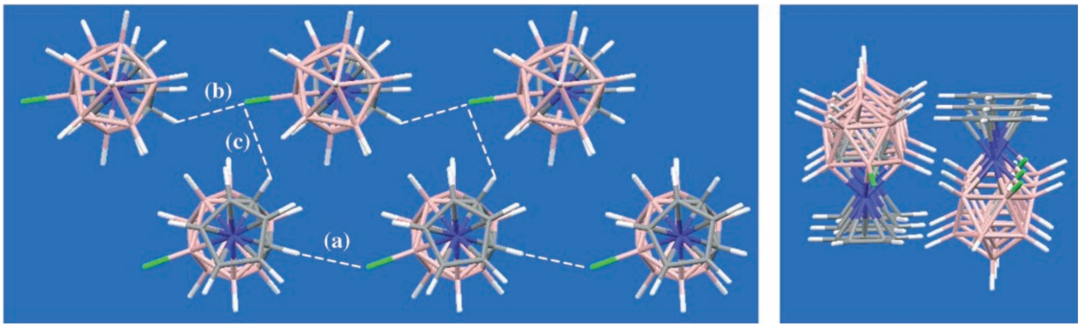


Figure 4. Left: A crystal packing diagram of the X-ray structure of *closo*-[3-Co($\eta^5$-$C_5H_5$)-8-Cl-1,2-$C_2B_9H_{10}$] (**1**) showing the planar two-dimensional sheet structure along the crystallographic *c* axis. Right: Crystal packing of **1** along a perspective between the crystallographic *a* and *c* axes showing the head-to-tail arrangement of molecules. Color code: B pink; C grey; H white; Co blue; Cl green.

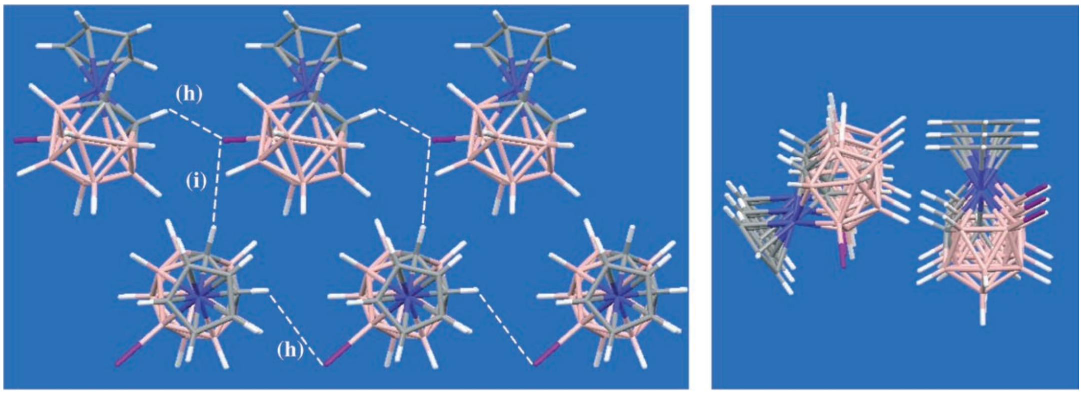


Figure 5. Left: A crystal packing diagram of the X-ray structure of *closo*-[3-Co($\eta^5$-$C_5H_5$)-8-I-1,2-$C_2B_9H_{10}$] (**3**) showing the planar two-dimensional sheet structure along a perspective between the crystallographic *a* and *c* axes. Right: Crystal packing of **3** along a perspective between the crystallographic *a*, *b*, and *c* axes showing the herringbone arrangement of molecules. Color code: B pink; C grey; H white; Co blue; I purple.

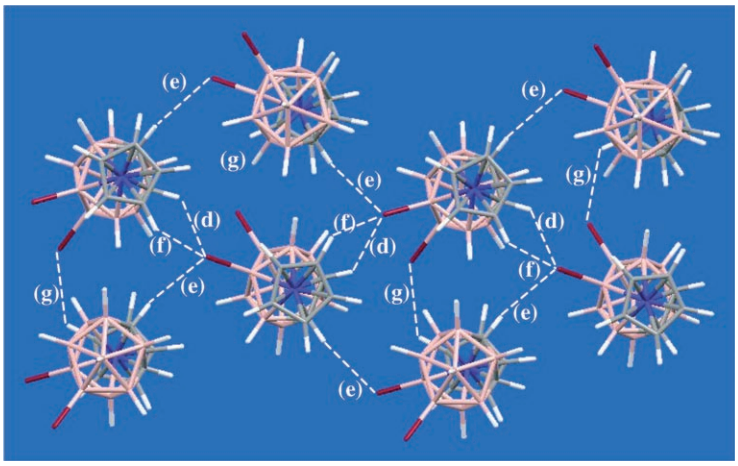


Figure 6. A crystal packing diagram of the X-ray structure of *closo*-[3-Co($\eta^5$-$C_5H_5$)-8,9-$Br_2$-1,2-$C_2B_9H_9$] (**4**) showing the planar two-dimensional sheet structure along the crystallographic *c* axis. Color code: B pink; C grey; H white; Co blue; Br red.

jections of the solid-state structure of *closo*-[3-Co($\eta^5$-$C_5H_5$)-8-Cl-1,2-$C_2B_9H_{10}$] (**1**). It can be seen that the molecules are held together by a network of hydrogen bonds. The solid-state structure of **1** consists of one-dimensional (1D) polymeric networks held together by intermolecular C*c*–H···Cl hydrogen-bond interactions along the shortest *a*-axis (Figure 4; interactions a and b). Interestingly, these interactions show different C*c*–H···Cl distances along the *a* axis (Table 1; interactions a and b). These 1D arrays then stack along the *b* direction with alternate rows in a head-to-tail arrangement to form layers (Figure 4, right). In addition, weaker C*c*–H···Cl intermolecular interactions are observed between cobaltacarborane cage hydrogens and chlorides of alternate rows (interaction c in Figure 4 and Table 1), giving rise to the observed 2D structure (layer). The distances of all of the observed intermolecular C*c*–H···Cl contacts are substantially shorter than the distance of 2.95 Å that corresponds to the sum of the van der Waals radii (ΣvdW) of hydrogen and chlorine atoms

Table 1. Geometrical parameters of C–H···X (X = Cl, Br, I) contacts (Å, °) involved in the supramolecular construction in **1**, **3**, and **4**.

| Compound | C–H···X–B[a] | $d$(H···X) | $R_{HX}$[b] | $d$(C···X) | ∡(CHX) | ∡(HXB) |
|---|---|---|---|---|---|---|
| **1** | (a) C*c*–H(307)···Cl(01)–B | 2.597 | 0.880 | 3.658 | 166.06 | 136.79 |
| | (b) C*c*–H(202)···Cl(02)–B | 2.655 | 0.900 | 3.519 | 136.34 | 148.39 |
| | (c) C*c*–H(201)···Cl(01)–B | 2.811 | 0.953 | 3.593 | 129.07 | 86.35 |
| **4** | (d) C*c*–H(2)···Br(1)–B | 2.731 | 0.895 | 3.586 | 135.63 | 116.12 |
| | (e) C*c*–H(1)···Br(1)–B | 2.886 | 0.946 | 3.903 | 156.44 | 116.73 |
| | (f) Cp–H(7)···Br(1)–B | 2.912 | 0.955 | 3.700 | 129.79 | 164.42 |
| | (g) Cp–H(4)···Br(2)–B | 2.955 | 0.969 | 3.670 | 123.79 | 131.30 |
| **3** | (h) C*c*–H(2)···I(1)–B | 3.255 | 1.030 | 3.978 | 125.12 | 86.20 |
| | (i) C*c*–H(1)···I(1)–B | 3.228 | 1.022 | 4.014 | 130.16 | 81.89 |

[a] C*c* = cage carbon; Cp = cyclopentadienide carbon; B = boron; C–H bond lengths are normalised to neutron distances; see interactions (a) to (i) in Figure 4, Figure 5, Figure 6. [b] Normalised hydrogen-bonding distances $R_{HX} = d(H\cdots X)/(r_H + r_X)$, where $r_H$ and $r_X$ are the vdW radii of H and X, respectively ($r_H$ = 1.2 Å; $r_X$ = 1.75 (Cl), 1.85 (Br), 1.96 Å (I)).[16] Symmetry codes: (a) 1−*x*, 1/2+*y*, 1−*z*; (b and c) *x*, *y*, *z*; (d and f) 1/2+*x*, 1/2−*y*, 1−*z*; (e) *x*, 1/2−*y*, 1/2+*z*; (g) *x*, −1/2−*y*, 2+*z*; (h) 1−*x*, 1−*y*, 1−*z*; (i) 1.5−*x*, 1/2+*y* , 1.5−*z*.

(Table 1, entries a–c) and, in general, these contacts are close to linear. Thus, they qualify as hydrogen bonds.[1]

The layers of **3** can best be understood by comparison with those of **1** (Figure 4 and Figure 5). As in the case of **1**, the molecules of **3** align in rows with perfect translational symmetry along the *a* axis. However, alternate rows are not arranged in a head-to-tail fashion, but rather adopt a herringbone arrangement (Figure 5). Although longer, intermolecular C*c*–H···I contacts are found between molecules in the 2D structure of **3**, as shown in Figure 5 and Table 1. In this case, the intermolecular contacts (3.23–3.26 Å) exceed the ΣvdW distance (3.16 Å).

Compound **4** shows a more complex layer structure, which includes many intermolecular C–H···Br contacts (Figure 6 and Table 1). Sheets are formed in the *ab* plane through trifurcated $(C–H)_3$···Br interactions involving Br1. The arrangement of the molecules in the sheet can best be described as zigzag chains along the *b* direction, with alternate molecules being inverted along the *a* direction. The sheets are stacked in an offset manner in the *c* direction and linked by C–H···Br2 contacts. Unlike in the iodo compound **3**, the intermolecular C–H···X contacts in **4** (X = Br) are substantially shorter that the ΣvdW limit. The observed C–H···Br contacts are also directional and consequently attractive in nature and are thus best described as weak hydrogen bonds.[1c]

It is clear that whereas the chloro and dibromo derivatives (**1** and **4**) show intermolecular C*c*–H···Cl/Br contacts shorter than the ΣvdW distances, those for the iodo compound **3** exceed the ΣvdW limit. A useful way to compare the relative hydrogen-bond acceptor capabilities of different halogens and to establish a qualitative assessment of the relative strengths of the different hydrogen-bond types is to normalise the H···X distances ($R_{HX} = d(H\cdots X)/(r_H + r_X)$).[17] The $R_{HX}$ values for the C–H···X–B contacts in **1**–**4** are summarised in Table 1. The mean $R_{HX}$ values are 0.911, 0.941, and 1.026 for the Cl (**1**), $Br_2$ (**4**), and I (**3**) compounds, respectively (note that $R_{HX} = 1$ corresponds to the ΣvdW limit). Although the crystal structure of the monobromo derivative **2** could not be satisfactorily refined due to a persistent severe disorder, the solid-state structure of the dibromo derivative **4** shows that the bromine atom bound to boron atom B(9)—the same as that in **2**—is the most "active" in the hydrogen-bond network (Figure 6). Thus, we can establish that the hydrogen-bond strengths increase in the order I < Br < Cl. The order of the hydrogen-bond strengths observed for the present halogenated cobaltacarboranes correlates well with that seen for C–H···X–M(or C) interactions.[3,4] This is clearly associated with the electronegativities of the halogens and thus the polarities of the X–Y bonds (Y = M, B, C) and suggests that boron-bound halogens are reasonably good hydrogen-bond acceptors. Several questions then arise. Are these C–H···X–B contacts present in other boron compounds besides the icosahedral metallacarboranes? If so, are they true hydrogen bonds? Can they be considered as weak hydrogen bonds as seen with metal-bound halogens (C–H···X–M) or are they closer to the vdW contacts seen with some carbon-bound halogens (C–H···X–C)? Chemical intuition tells us that the intermediate electronegativity of boron, which lies between that of carbon and those of most transition metals, will polarise the X–B bond, leading to a greater accumulation of negative charge on a given halogen than in the case of the corresponding X–C bond, but lower than in the case of the corresponding X–M bond. According to this reasoning, the expected order of acceptor strengths would be X–M > X–B > X–C. To address these questions, we have carried out a search of the Cambridge Structural Database (CSD). Statistical analysis of a significant number of crystal structures from the CSD has made it possible to draw chemical conclusions, as discussed in the following section.

**CSD database analysis**: Traditionally, the distinction between hydrogen bonds and vdW interactions has been based on the vdW cut-off criterion, requiring that the H···acceptor distance be substantially shorter than the sum of the vdW radii of H and the acceptor (ΣvdW).[18] This cut-off criterion has been strongly criticised as being far too restrictive and misleading.[3,4] In fact, the forces establishing hydrogen-bond interactions do not terminate at any given cut-off distance, hence there can be no sharply defined border between hydrogen bonds and vdW interactions. Rather, H···acceptor distances near the ΣvdW distance should be considered as hydrogen bonds if their directionality is also appropriate (D–H···A close to 180°; D = donor; A = acceptor), as distinct from vdW contacts, for which no directionality is required.[19] Thus, we have searched the structures deposited in the Cambridge Structural Database (CSD)[20] to assess the role of C–H···X–B (X = Cl, Br, I) interactions in determining crystal structures.[21] The search was restricted to C–H···X–B contacts with H···X distances within ΣvdW + 0.2 Å, but with unrestricted angles (see Experimental Section). In total, 2511 C–H···X–B contacts were retrieved, which occurred in 459 different crystal structures (see Experimental Section for details). As noted above, the H···X distances were normalised to take into account the different sizes of the halogens to permit direct comparison of the distance distributions for the different halogens. The mean $R_{HX}$ values for C–H···X–B contacts are summarised in Table 2,

Table 2. Mean $R_{HX}$ normalised distances (number of observations) of H···X contacts with $R_{HX} < 1.048$ and C–H···X > 110°.

| X[a] | C–H···X | |
|---|---|---|
| | From ref. [4c] | This work |
| Cl–M | 0.975 (7943) | 0.972 (87971) |
| Cl–B | – | 0.989 (896) |
| Cl–C | 0.995 (7729) | 0.995 (53288) |
| Br–M | 0.982 (3269) | 0.980 (13604) |
| Br–B | – | 0.992 (792) |
| Br–C | 0.998 (4018) | 0.997 (11739) |
| I–M | 0.997 (2429) | 0.999 (8842) |
| I–B | – | 1.002 (255) |
| I–C | 1.006 (603) | 1.006 (2020) |

[a] M = any transition metal; B = boron; C = carbon. See text and ref. [22] for details).

where they are also compared with previous results obtained by Brammer et al. for C–H···X–Y (Y = M, C) contacts.[4c] For comparison purposes, the mean $R_{HX}$ values of the C–H···X–B contacts in Table 2 have been calculated according to the same criteria as employed by Brammer et al.[22] The normalised data give a qualitative comparison of the strengths of the interactions. As might be anticipated, the mean $R_{HX}$ values for the C–H···X–B contacts follow the same trends as those for the related C–H···X–M (or C) contacts. Thus, the lowest mean $R_{HX}$ value corresponds to the combination of the most polar bonds in the donor–acceptor pairs (C–H···Cl), while the highest $R_{HX}$ value corresponds to a combination of the least polar bonds (C–H···I). Moreover, the mean $R_{HX}$ ratio increases in the order H···X–M < H···X–B < H···X–C, as expected in view of the decreasing polarisation of the acceptor groups.

For the subsequent directionality analysis of the intermolecular C–H···X–B contacts, we employed all data retrieved from the CSD with a liberal distance cut-off (ΣvdW + 0.2 Å). Although no angle cut-off was imposed in the searches, very few C–H···X angles smaller than 90° were found and the angular distributions are centred around mean values of 140° (Figure 7). Moreover, the cone-corrected[23] angular distribution graphs show a more pronounced preference for linearity (Figure 7, right). Comparison of cone-corrected graphs for the studied halogens (Figure 7a–c, right) shows that the preference for linearity decreases in the order Cl ≈ Br > I. The experimental distribution of H···X–B angles (see Supporting Information) shows similar behaviour to that of the (C)H···X–Y contacts (90–130°).[4c]

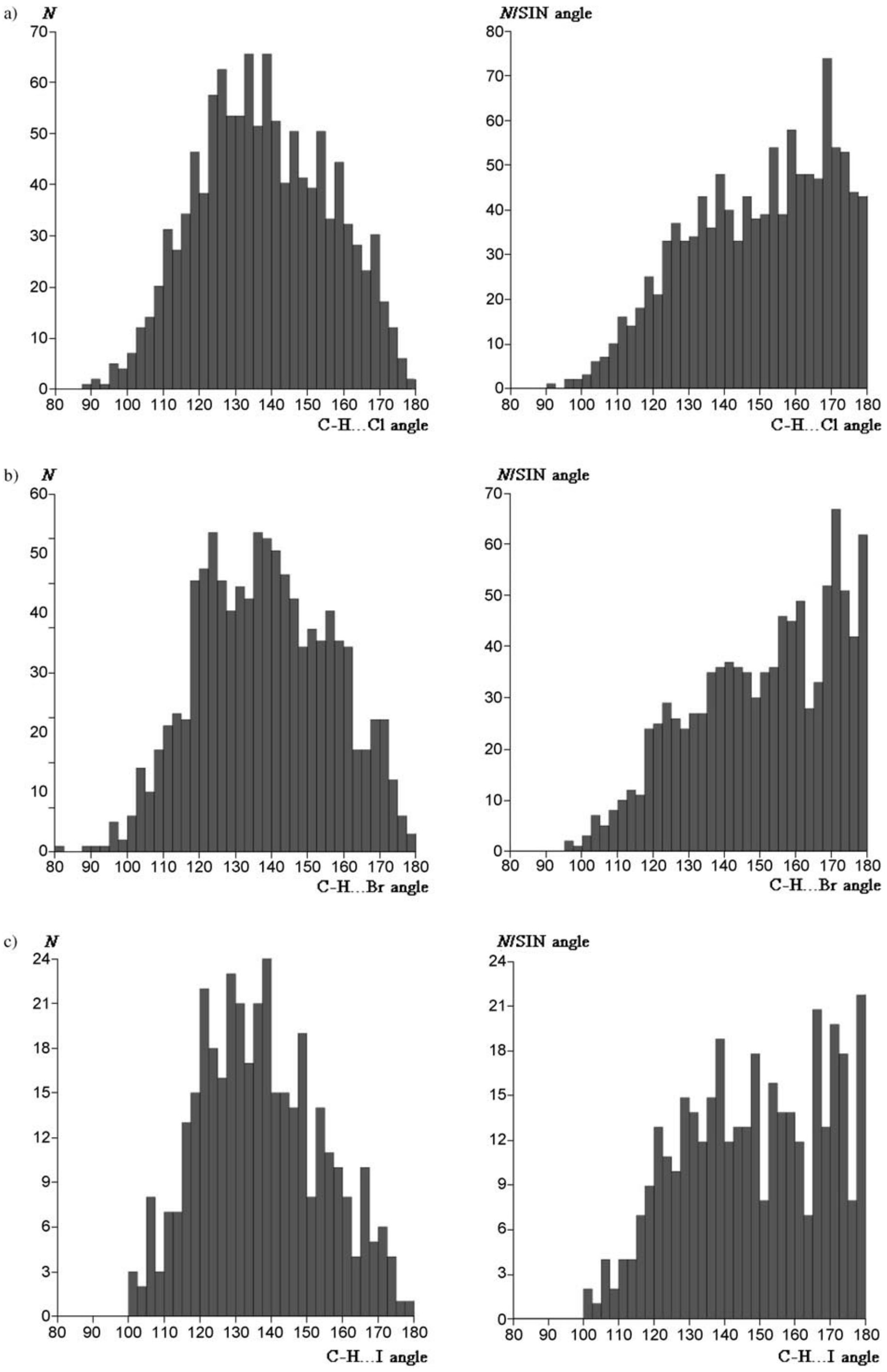


Figure 7. Frequency distributions of C–H···X angles (left) and cone-corrected[23] angles (right) for C–H···X–B contacts (X = Cl (a), Br (b), I (c)) in the retrieved crystal structures.

Normalised distance ($R_{HX}$)–angle scatter plots for C–H···X–B interactions are shown in Figure 8.[24] The shortest of these contacts show a preference for approximate linearity, that is, typical distributions for hydrogen bonds.[1c] At increasing distances, the directionality becomes more flexible, with a regular angular distribution being observed beyond $R_{HX} \approx 1$. This regular distribution at longer distances re-

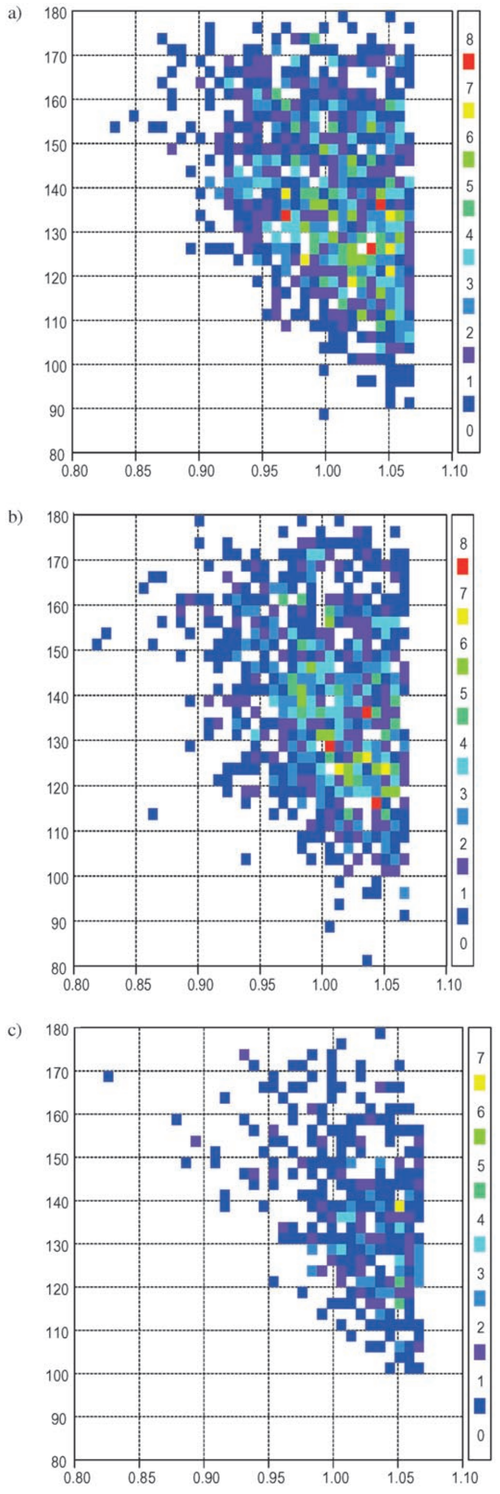


Figure 8. Plots of intermolecular distances (represented as $R_{HX}$) versus angle (C–H···X, °) for C–H···X–B interactions (X = Cl (a), Br (b), I (c)).

flects the weakness of these interactions.[1c] It is well known that weak hydrogen bonds are easily bent and so directionality is often blurred by steric hindrance and competition with other hydrogen-bonding groups. The C–H···I–B interactions follow a similar trend, but this is not so clear-cut as with the other interactions (Cl and Br) due to the smaller set of contact data.

These results suggest that C–H···X–B interactions, although exceeding the classical vdW cut-off distance, can still be considered weak hydrogen bonds and not merely as vdW interactions.[1c] This conclusion is in agreement with previous work on C–H···X–Y (Y = M, C) hydrogen bonds.[3,4] The results presented in Table 2 are also in agreement with expected trends in the strengths of hydrogen bonds based on the polarities of the X–Y bonds (Y = M, B, C). The preference for C–H···X linearity at short H···X distances is found to decrease in the order C–H···Cl ≈ C–H···Br > C–H···I in the case of C–H···X–B contacts (Figure 7, Figure 8, and Supporting Information), reflecting the even weaker hydrogen-bond nature of the heavier halogen. Furthermore, the observed linearity for C–H···X–B (X = Cl, Br) contacts correlates well with that for the related weak C–H···X–M hydrogen bonds.[4c] Therefore, the combination of directionality data (Figure 7, Figure 8, and Figures S1–S3) and the mean $R_{HX}$ normalised distances in Table 2 suggests that the hydrogen-bond acceptor strength of X follows the sequence X–M > X–B > X–C. That the boron-bound halogens (X–B) have comparable acceptor strengths for hydrogen bonding as metal-bound halogens (X–M) is not surprising, since the related boron- and metal-bound hydrogens (H–B and H–M) are both good acceptors for very weak dihydrogen bonds (C–H···H–M (or B)).[25]

We can now compare our crystallographic results for the halogenated cobaltacarboranes with those obtained from the CSD search. As mentioned earlier, the mean normalised $R_{HX}$ values for the chloro, bromo, and iodo compounds (**1**, **4**, and **3**) are 0.911, 0.941, and 1.026, respectively (calculated from Table 1). It is clear that the H···Cl and H···Br intermolecular distances found in our cobaltacarboranes are among the shortest reported (especially if we compare them with the normalised values in Table 2). However, the observed H···I distances for **3** are substantially longer than the average (1.002) and so these interactions cannot be considered as hydrogen bonds. This can be explained in terms of the increasing importance of vdW forces as a result of the greater polarisability of the iodo compound as compared to those bearing the lighter halogens.[3] However, this is at variance with the solid-state structure of the related iodocarborane *closo*-[3-I-1,2-$C_2B_{10}H_{11}$] (Figure 9, top) previously reported by our group.[9d] This iodocarborane represented the first reported example of a carborane solid-state structure held together by intermolecular C–H···I–B hydrogen bonds (H···I, 3.215 Å; $R_{HI}$, 0.982; C–H···I, 133.5°). At this point, it is interesting to compare the packing of iodocarborane with that of iodobenzene (Figure 9, bottom).[26] It is important to note that the icosahedral cage of the carborane is only slightly larger than the phenyl ring rotation envelope. However, the packing of iodobenzene, which is less bulky and contains a higher number of protonic C–H hydrogens than the iodocarborane, shows exclusively intermolecular C–I···I–C contacts. Thus, it is remarkable that the iodocarborane, which is bulkier than its organic counterpart, optimizes its packing by

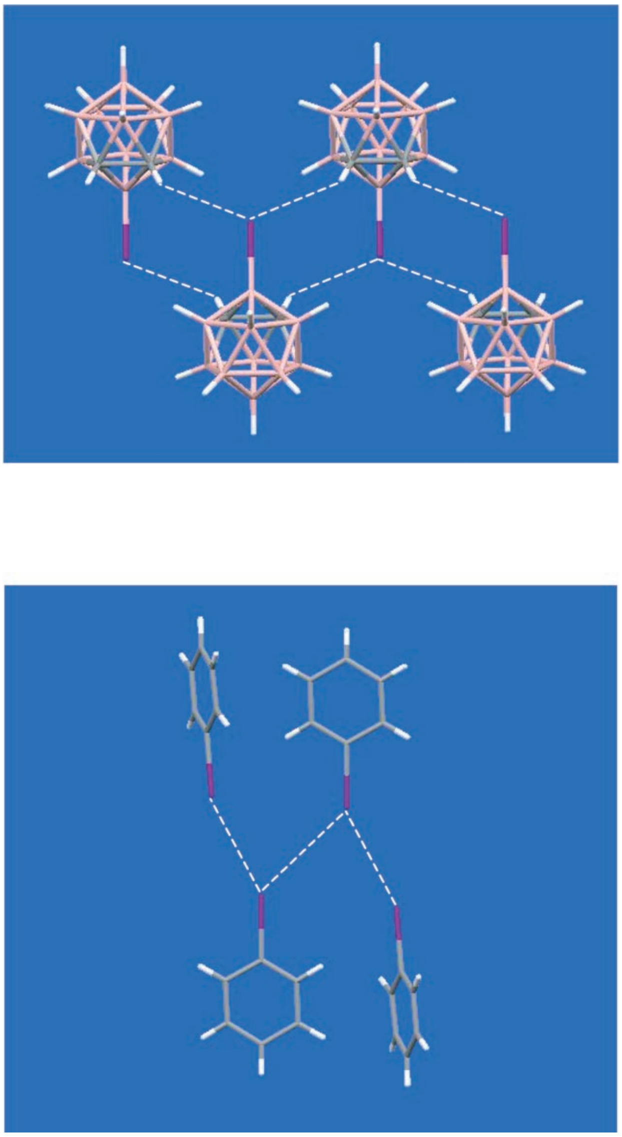


Figure 9. Crystal packing diagrams for: (top) *closo*-[3-I-1,2-$C_2B_{10}H_{11}$] showing the C–H···I–B hydrogen bonding; (bottom) $C_6H_5I$ showing the C–I···I–C interactions. Color code: B pink; C grey; H white; Co blue; I purple.

forming C–H···I–B hydrogen bonds. This particular example shows how iodine, the least electronegative and most polarizable of the common halogens, can give rise, in certain cases, to the formation of C–H···I–B hydrogen bonds.

## Conclusion

We have shown that halogens become good hydrogen-bond acceptors when bonded to boron of cyclopentadienyl cobaltacarborane compounds, giving networks that are held together by weak hydrogen bonds of the type C–H···X–B. The hydrogen-bond strength increases in the order C–H···I–B < C–H···Br–B < C–H···Cl–B, consistent with the increasing electronegativity of the halogens. These weak hydrogen bonds may play a very important role in the development of crystal engineering methods and it is crucial to recognise the relative strength of these weak forces in order to predict self-assembly. CSD searches for C–H···X–B intermolecular contacts in any boron-containing compounds and their statistical analysis clearly shows that distances and angles follow similar trends to those found for related C–H···X–M or C–H···X–C intermolecular interactions, and hence they are best described as weak hydrogen bonds. Brammer et al. have already pointed out that other main group metal halides can be expected to show similar behaviour to that seen with transition metal halides. Thus, the present study is complementary to these previous reports and focuses on the hydrogen-bond acceptor capability of halogens.[3,4] In this sense, we have disclosed a new class of "halogen acceptors", that is, boron-bound halogens (X–B). Statistical analysis of the crystal structures of boron-containing compounds retrieved from the CSD shows that the strengths of the hydrogen bonds formed follow the order X–M > X–B > X–C, consistent with the expected order of polarity of these bonds. The results are of particular relevance to the fields of crystal engineering and boron chemistry. These observations also aid our understanding of the basic principles of supramolecular chemistry of metallacarborane systems and consequently expedite the progress of crystal engineering.

## Experimental Section

**General**: All manipulations were carried out under an $N_2$ atmosphere. The chemicals used were as follows: acetone, distilled from $P_2O_5$; ethanol, dichloromethane, heptane, benzene, $AlCl_3$ (99%, Fluka), $AlBr_3$ (98%, Aldrich), $AlI_3$ (95%, Aldrich), bromine (>99%, Acros), used as received; *closo*-[3-Co($\eta^5$-$C_5H_5$)-1,2-$C_2B_9H_{11}$] complex prepared according to a literature procedure.[27] NMR spectra were acquired on a Bruker ARX 300 MHz spectrometer and referenced to the solvent ($^1$H, residual [$D_5$]acetone; $^{13}$C, [$D_6$]acetone)[28] or $BF_3{\cdot}OEt_2$ ($^{11}$B NMR). Chemical shifts are reported in ppm and coupling constants in Hz; peaks are described as follows: s, singlet; d, doublet; t, triplet; sept, septet; br, broad; m, multiplet. Chromatography was performed on Acros silica gel (0.035–0.070 mm, pore diameter ca. 6 nm).

**Synthesis of *closo*-[3-Co($\eta^5$-$C_5H_5$)-8-Cl-1,2-$C_2B_9H_{10}$] (1)**: A Schlenk flask was charged with *closo*-[3-Co($\eta^5$-$C_5H_5$)-1,2-$C_2B_9H_{11}$] (98.2 mg, 0.383 mmol), $AlCl_3$ (152.1 mg, 1.141 mmol), and benzene (10 mL). The mixture was stirred under reflux conditions until completion of the reaction, as monitored by TLC (≈3 h). The flask was then placed in an ice bath and water (7 mL) was added to the reaction mixture. The resulting yellow suspension was stirred at room temperature for 2 h. The benzene phase was extracted with benzene (2×5 mL). Evaporation of the solvent afforded pure compound **1**, which was dried under oil-pump vacuum to give a crystalline yellow-orange solid (94.1 mg, 0.324 mmol, 85%). $^1$H NMR: $\delta = 5.91$ (s, 5H; $\eta^5$-$C_5H_5$), 4.52 ppm (brs, 2H; $C_c$-H); $^1$H{$^{11}$B} NMR (only the new signals due to B–H protons are listed): $\delta = 3.16$ (brs, 2H), 2.73 (brs, 1H), 2.04 (brs, 2H), 1.55 (brs, 2H), 1.40 ppm (brs, 1H); $^{11}$B NMR:[29] $\delta = 18.8$ (s, 1B; B-8), 0.2 (d, $^1J$(B,H) = 147 Hz, 1B; B-10), −3.6 (d, $^1J$(B,H) = 144 Hz, 2B; B-9 and 12), −6.4 (d, $^1J$(B,H) = 163 Hz, 2B; B-4 and 7), −17.4 (d, $^1J$(B,H) = 157 Hz, 2B; B-5 and 11), −26.2 ppm (d, $^1J$(B,H) = 172 Hz, 1B; B-6); $^{13}$C{$^1$H} NMR: $\delta = 92.6$ (s; $\eta^5$-$C_5H_5$), 47.5 ppm (brs; $C_c$-H).

**Synthesis of *closo*-[3-Co($\eta^5$-$C_5H_5$)-8-Br-1,2-$C_2B_9H_{10}$] (2)**: The general procedure described above for **1** was followed, using *closo*-[3-Co($\eta^5$-$C_5H_5$)-1,2-$C_2B_9H_{11}$] (48.8 mg, 0.190 mmol), $AlBr_3$ (156.9 mg, 0.576 mmol), and benzene (15 mL). Monitoring of the reaction by TLC showed that the starting cobaltacarborane compound was not completely consumed after refluxing for 7 h. Compound **2** was then extracted as described above and purified by preparative chromatography on silica gel using $CH_2Cl_2$/hexane (1:1) as eluent ($R_f$ = 0.27) to afford a yellow solid (33.7 mg, 0.100 mmol, 53 %). $^1$H NMR: $\delta$ = 5.94 (s, 5H; $\eta^5$-$C_5H_5$), 4.57 ppm (brs, 2H; $C_c$-H); $^1$H{$^{11}$B} NMR (only the new signals due to B–H protons are listed): $\delta$ = 3.20 (brs, 2H), 2.79 (brs, 1H), 2.19 (brs, 2H), 1.59 ppm (brs, 3H); $^{11}$B NMR:[30] $\delta$ = 12.5 (s, 1B; B-8), 2.3 (d, $^1J$(B,H) = 145 Hz, 1B; B-10), −2.0 (d, $^1J$(B,H) = 151 Hz, 2B; B-9 and 12), −4.3 (d, $^1J$(B,H) = 162 Hz, 2B; B-4 and 7), −15.4 (d, $^1J$(B,H) = 156 Hz, 2B; B-5 and 11), −23.9 ppm (d, $^1J$(B,H) = 171 Hz, 1B; B-6); $^{13}$C{$^1$H} NMR: $\delta$ = 93.3 (s; $\eta^5$-$C_5H_5$), 48.3 ppm (brs; $C_c$-H).

**Synthesis of *closo*-[3-Co($\eta^5$-$C_5H_5$)-8-I-1,2-$C_2B_9H_{10}$] (3)**: The general procedure described above was followed, using *closo*-[3-Co($\eta^5$-$C_5H_5$)-1,2-$C_2B_9H_{11}$] (50.4 mg, 0.197 mmol), $AlI_3$ (250.1 mg, 0.583 mmol), and benzene (10 mL). Monitoring of the reaction by TLC showed that *closo*-[3-Co($\eta^5$-$C_5H_5$)-1,2-$C_2B_9H_{11}$] was not completely consumed after refluxing for 24 h. Compound **3** was then separated and purified by preparative chromatography ($R_f$ = 0.22) as described above (34.7 mg, 0.09 mmol, 46 %). $^1$H NMR: $\delta$ = 5.95 (s, 5H; $\eta^5$-$C_5H_5$), 4.66 ppm (brs, 2H; $C_c$-H); $^1$H{$^{11}$B} NMR (only signals due to B–H protons are listed): $\delta$ = 3.22 (brs, 2H), 2.84 (brs, 1H), 2.45 (brs, 2H), 1.80 (brs, 2H), 1.62 ppm (brs, 1H); $^{11}$B NMR:[30] $\delta$ = 3.6 (d, $^1J$(B,H) = 144 Hz, 1B; B-10), −0.5, −2.2, −4.3 (br, 5B; B-4, B-7, B-8, B-9 and 12), −14.6 (d, $^1J$(B,H) = 159 Hz, 2B; B-5 and 11), −22.2 (d, $^1J$(B,H) = 171 Hz, 1B; B-6).

**Synthesis of *closo*-[3-Co($\eta^5$-$C_5H_5$)-8,9-$Br_2$-1,2-$C_2B_9H_9$] (4)**: A Schlenk flask was charged with *closo*-[3-Co($\eta^5$-$C_5H_5$)-1,2-$C_2B_9H_{11}$] (50.3 mg, 0.196 mmol), $AlCl_3$ (3.1 mg, 0.023 mmol), $Br_2$ (220 mg, 1.38 mmol), and $CH_2Cl_2$ (20 mL). The mixture was stirred under reflux conditions for 16 h. Thereafter, TLC analysis showed the formation **2** as a minor product and **4** as the major product. Compound **4** was separated and purified by preparative chromatography on silica gel using $CH_2Cl_2$/hexane (1:1) as eluent ($R_f$ = 0.09) to afford a yellow solid (44.8 mg, 0.108 mmol, 55 %). $^1$H NMR: $\delta$ = 6.03 (s, 5H; $\eta^5$-$C_5H_5$), 4.64 ppm (brs, 2H; $C_c$-H); $^1$H{$^{11}$B} NMR (only the new signals due to B–H protons are listed): $\delta$ = 3.18 to 1.55 ppm (brm, 7H); $^{11}$B NMR:[29] $\delta$ = 10.7 (s, 1B; B-8), 2.4 (d, $^1J$(B,H) = 149 Hz, 1B; B-10), 0.1 (s, 1B; B-9), −1.8 (d, $^1J$(B,H) = 152 Hz, 1B; B-12), −4.5 (d, $^1J$(B,H) = 164 Hz, 1B; B-4), −6.2 (d, $^1J$(B,H) = 157 Hz, 1B; B-7), −15.3 (d, $^1J$(B,H) = 136 Hz, 1B; B-5), −16.5 (d, $^1J$(B,H) = 135 Hz, 1B; B-11), −24.0 ppm (d, $^1J$(B,H) = 172 Hz, 1B; B-6); $^{13}$C{$^1$H} NMR: $\delta$ = 93.7 (s; $\eta^5$-$C_5H_5$), 45.5 (brs; $C_c$-H), 43.3 (brs; $C'_c$-H).

**X-ray crystallography**: Cell dimensions and intensity data for **1**, **3**, and **4** were obtained at 120 K, using a Bruker Nonius KappaCCD area detector diffractometer mounted at the window of a rotating Mo anode ($\lambda(Mo_{K\alpha})$ = 0.71073 Å). The crystal-to-detector distance was 30 mm, and $\phi$ and $\Omega$ scans were carried out to cover the asymmetric unit. Data collection and processing were carried out using the programs COLLECT[31] and DENZO,[32] and an empirical absorption correction was applied using SADABS.[33]

The structures were solved by direct methods[34] and refined by full-matrix least-squares[34] against $F^2$. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were treated using a riding model. All crystallographic data are collected in Table 3.

**Contact searching**: The CSD[20] (version 5.27; 355 064 entries) was used to search for C–H···X–B (X = Cl, Br, I; B = boron) interactions. All searches required that the *R*-factor be less than 0.05, and that there be no disorder or errors in the crystal structures, as defined by Conquest.[35] All C–H distances were normalised to neutron lengths and the search was restricted to C–H···X–B (X = Cl, Br, I) with liberal H···X distances within ΣvdW + 0.2 Å with unrestricted C–H···X and H···X–B angles (0–180°). Both organic and organometallic compounds were considered. The program VISTA[36] was used to analyze and plot the data obtained, which were ultimately stored in a table file (.tab). A total of 2511 C–H···X–B contacts were retrieved, which occurred in 459 different crystal structures (CSD codes). Partial contacts/crystal structures: 1147/241 (Cl), 998/144 (Br), 366/74 (I). The H···X distances for all of the donor–acceptor pairs obtained in the aforementioned CSD search were set on a common scale by use of the normalised distance function $R_{HX} = d(H\cdots X)/(r_H + r_X)$.[17] To calculate $R_{HX}$ values (Table 2), we adopted the same criteria as Brammer et al., but duplicate refcodes and bifurcated hits were not removed.[22]

Table 3. Crystallographic parameters for compounds **1**, **3**, and **4**.[a]

| Compound | **1** | **3** | **4** |
|---|---|---|---|
| empirical formula | $C_7H_{15}B_9ClCo$ | $C_7H_{15}B_9ICo$ | $C_7H_{14}B_9Br_2Co$ |
| formula weight | 290.86 | 382.31 | 414.22 |
| temperature [K] | 120(2) | 120(2) | 120(2) |
| wavelength [Å] | 0.71073 | 0.71073 | 0.71073 |
| crystal system | monoclinic | monoclinic | orthorhombic |
| space group | $P2_1$ | $P2_1/n$ | *Pbca* |
| *a* [Å] | 7.8374(12) | 7.14880(10) | 13.4975(5) |
| *b* [Å] | 10.4037(6) | 16.0920(4) | 13.2571(5) |
| *c* [Å] | 15.746(3) | 11.7898(2) | 15.7528(6) |
| $\beta$ [°] | 90.935(12) | 91.1270(10) | |
| volume [Å$^3$] | 1283.7(3) | 1356.02(5) | 2818.77(18) |
| *Z* | 4 | 4 | 8 |
| $\rho_{calcd}$ [g cm$^{-3}$] | 1.505 | 1.873 | 1.952 |
| absorption coefficient [mm$^{-1}$] | 1.507 | 3.507 | 6.857 |
| *F*(000) | 584 | 728 | 1584 |
| crystal | slab; yellow | block; dark red | cut rod; yellow |
| crystal size [mm] | 0.3 × 0.2 × 0.05 | 0.3 × 0.2 × 0.2 | 0.3 × 0.1 × 0.1 |
| $\theta$ range for data collection [°] | 3.25–27.48 | 3.12–27.48 | 3.07–27.48 |
| reflections collected | 17 925 | 17 121 | 21 510 |
| independent reflections | 5850 [$R_{int}$ = 0.0407] | 3098 [$R_{int}$ = 0.0542] | 3229 [$R_{int}$ = 0.0604] |
| completeness to $\theta$ = 27.48° | 99.7 % | 99.8 % | 99.8 % |
| max. and min. transmission | 0.9284 and 0.6505 | 0.5406 and 0.4093 | 0.5472 and 0.2328 |
| data/restraints/parameters | 5850/7/337 | 3098/0/164 | 3229/162/173 |
| goodness-of-fit on $F^2$ | 1.058 | 1.061 | 1.191 |
| final *R* indices [$F^2 > 2\sigma(F^2)$] | $R1 = 0.0365$, $wR2 = 0.0781$ | $R1 = 0.0332$, $wR2 = 0.0856$ | $R1 = 0.0877$ $wR2 = 0.2404$ |
| *R* indices (all data) | $R1 = 0.0491$, $wR2 = 0.0826$ | $R1 = 0.0429$, $wR2 = 0.0905$ | $R1 = 0.1109$ $wR2 = 0.2510$ |

[a] CCDC-614752, CCDC-614753, and CCDC-614754 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.

## Acknowledgements

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[22] For the C−H···X−M and C−H···X−C results (left-hand column in Table 2), duplicate refcodes and bifurcated hydrogen bonds were removed in the original publication.[4c] We have now estimated the mean $R_{\mathrm{HX}}$ values for these contacts without removing duplicate refcodes and bifurcated hydrogen bonds and found that errors were minimal, as can be seen in Table 2 (right-hand column). Note that whereas an $R_{\mathrm{HX}}$ value of 1 corresponds to a conservative cut-off criterion (ΣvdW), a more relaxed upper limit of 1.048 (ΣvdW + 0.15 Å) was considered by Brammer et al.

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