Synthesis and Spectroscopic Characterization of the Four Complete Series [(C$_5$X$_n$H$_{5-n}$)Fe(CO)$_2$R] (X = Cl, Br; R = Me, Ph; n = 1–5). Molecular and Crystal Structures of [(C$_5$X$_5$)Fe(CO)$_2$R]

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Dedicated to Prof. Hans-Christian Böttcher on the occasion of his 65th birthday

The complete series of chloro- and bromo-cyclopentadienyl carbonyl complexes [(C$_5$X$_n$H$_{5-n}$)Fe(CO)$_2$R] (n = 1–5, R = Me, Ph) could be prepared from the unsubstituted parent compounds via a sequence of lithiations and electrophilic halogenations. All four pentahaloyclopentadienyl complexes were studied by X-ray diffraction and show an interplay of weak intermolecular X…X, X…O and X…H interactions.

Introduction

Half-sandwich complexes (sometimes also called "piano-stool complexes) are coordination compounds, where the metal is coordinated to one aromatic cyclic ligand (like cyclopentadienyl or benzene) and one to four σ-donor ligands (like carbonyl, phosphine, halides). A search in SciFinder (accessed on June 14, 2022) gave 3531 entries for the concept "half-sandwich compounds". Compounds of this type were first synthesized and characterized in the 1950's, with "cymantrene" ([CpMn(CO)$_3$], first described in 1954[1]), the "Fp"-system ([CpFe(CO)$_2$-R], first described in 1955/6[2]) and "benchrotrene" ([(C$_6$H$_6$)Cr(CO)$_3$], first described in 1957[3]) being the most prominent members at the time, and -in retrospect- up to now. A search in SciFinder® shows 3628 results for the cymantrene system, 6101 results for the Fp system and 3978 entries for the benchrotene system, always including the "substructures" as well. Although nowadays derivatives of other metals, particularly the platinum group metals, have come into the focus of research,[4] there is still a continuing interest in these "old" systems, especially the Fp-system.[5–9] The dominance of the Fp system in the literature is certainly due to its large variability: in "CpFe(CO)$_2$-R" one or both carbonyl ligands can be replaced by other two electron donors like phosphines, the "R" can be

either another Fp fragment, a halide, an alkyl, alkynyl, aryl, silyl group and so on, or either just an electron pair or a neutral molecule, opening up the door to anionic and cationic complexes as well.[10–12] In principle, also the Cp ligand is prone to modification, however, besides mono-substituted (C$_5$H$_4$R) and (C$_5$Me$_5$) systems, this has hardly ever been tried. Aromatic halides are a very important substance class, as they allow a large variety of functional derivatizations, in particular C−C coupling reactions.[13] It could also be shown, that many of these aromatic reactions can be activated by π- coordination to transition metals.[14,15] Starting from tetraiodo-cyclobutadienyliron- or pentaiodocyclopentadienylmanganese half-sandwich complexes star-shaped polyalkynylated complexes were obtained by Stille coupling reactions.[16] While the monoiodocyclopentadienyl complex [(C$_5$H$_4$I)Fe(CO)$_2$Me] has been used in several Pd-catalyzed C−C coupling reactions,[17] there is only one other report on bromo- and iodocyclopentadienyl derivatives including the complexes [(C$_5$X$_4$I)Fe(CO)$_2$C$_3$F$_7$] (X = Cl, Br).[18] Since our group has been working for a while on perhalogenocyclopentadienyl complexes, their synthesis and post-synthetic modifications,[19] we found it worthwhile to look into the feasibility of polyfunctionalization of the cyclopentadienyl ring of the FpMe and FpPh systems, and thus add another facet of functionality to this fascinating compound class. Here we report on our studies towards the synthesis and characterization of [(C$_5$X$_5$)Fe(CO)$_2$R] (X = Cl, Br; R = Me, Ph). Once these compounds have been prepared, they might be used as starting materials for further functionalization and open up a new field of useful iron half-sandwich complexes.

Results and Discussion

Our basic approach towards the synthesis of perhalocyclopentadienyl complexes always starts with the introduction of just one halogen into the coordinated unsubstituted cyclopentadienyl ring. For this purpose, the substrate has to be metalated

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by an alkyl lithium reagent first and then be treated with an electrophilic halogenation reagent. In the literature, there are two examples of metalation of FpMe with s-BuLi,[20] and two reports on the metalation of FpPh using n-BuLi.[21] There are also two reports of using LDA with FpMe in THF.[22] We therefore decided to use s-BuLi for the deprotonation of FpMe and n-BuLi for FpPh. For the introduction of chlorine, we used hexachloroethane, while for the introduction of bromine either tetra- or pentabromoethane were used.

Thus, we obtained the monohalocyclopentadienyl complexes **1a–4a** as yellow oils in yields of 46%, 57%, 73% and 35%, respectively (Scheme 1; entries 1, 4, 8, 9, 14, 15 in Table S1 of the Supporting Information). It should be noted, that the yield of **3a** is an NMR yield only, since it was not possible to isolate it in a pure form. While in both reactions of FpMe the only identified product besides **1a/2a** was apparently unreacted FpMe, the outcome of the reactions with FpPh depended on the electrophile: with C_2Cl_6 besides the desired product **3a** and unreacted FpPh also the 1,2-disubstitutet compound **3b** was obtained; with $C_2H_2Br_4$ a mixture of unsubstituted, mono-, di- and trisubstituted products FpPh, **4a**, **4b**-1.2+1,3 and **4c**-1.2.3 was isolated, while with C_2HBr_5 only the desired **4a** together with unreacted FpPh was identified.

We could also prepare the monofluoro- and iodo complexes **5a** and **6a** via this synthetic approach. Both compounds, however, turned out to be rather unstable and decomposed upon attempted chromatographic purification, and were therefore not further studied.

Having now the monohalocyclopentadienyl complexes at hand, we started to introduce more halogen substituents. For this purpose, we treated **1a** and **2a** with a slight excess of LiTMP as base and C_2Cl_6 or $C_2H_2Br_4$ as electrophiles (entries 2 and 5 in Table S1). For **3a** and **4a** we used LDA as base and the same electrophiles (entries 10 and 17 in Table S1). The disubstituted complexes **1b–4b** (in both regioisomers except for **4b**) were obtained besides apparently unreacted **1a–4a** and FpR (except for **1b**) and traces of the trisubstituted complexes **3c/4c**. The 1,3 regioisomers were usually obtained in rather small (NMR-)yields (6.6, 1.6 and 0% for **1b**, **3b** and **4b**, respectively) except for **2b** (NMR yield 24%). In all cases, it was not possible
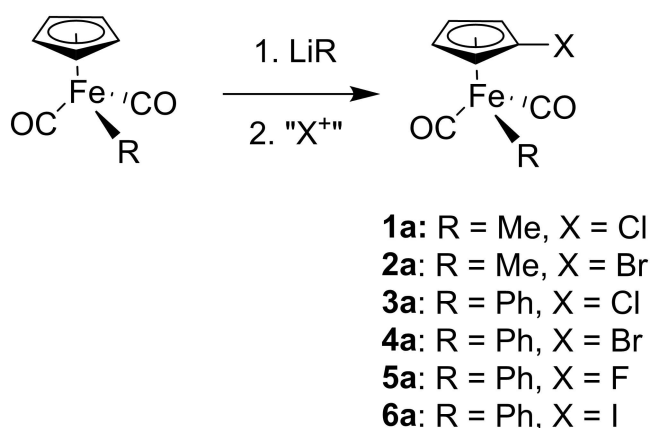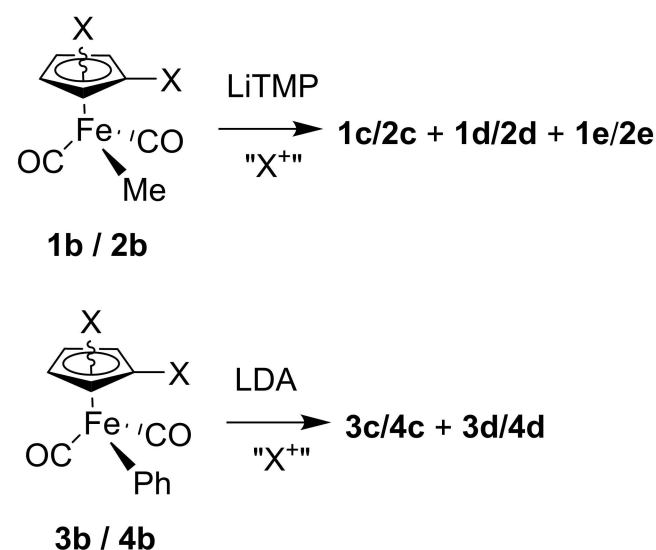
to isolate the desired products without substantial losses in yield, and therefore it was decided, to use impure materials for the next step.

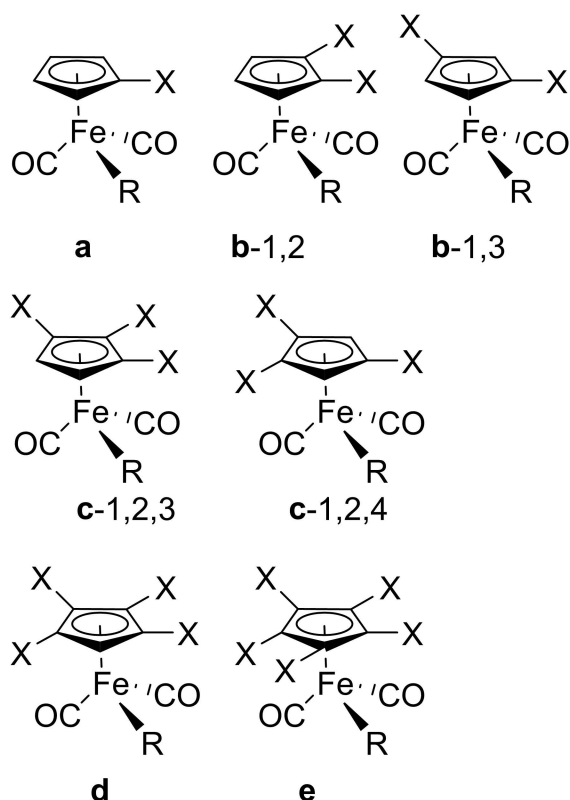When **1b** (purity ca. 93%) was treated with ca 1.11 equivalents of LiTMP and C_2Cl_6, a mixture of di-, tri-, tetra- and pentachlorocyclopentadienyl complexes **1b–e**, in all possible regio-isomers, was obtained. Repeated chromatography allowed the isolation of **1e** (in very low yield) and the 1,2,4 trichlorocyclopentadienyl complex **1c**. It was not possible to isolate **1c**-1,2,3 and **1d** in a pure form (Scheme 2 and entry 3 of Table S1). Treatment of **2b** (purity >95%) with ca. 1.2 equivalents of LiTMP and 1.33 equivalents of $C_2H_2Br_4$ yielded a mixture of **2c**-1,2,4, **2d** and **2e** which could be separated by chromatography and isolated in yields of 24, 2 and 16%, respectively (Scheme 2 and entry 7 of Table S1).

The reaction of **3b** (purity ca.93%) with ca. 1.11 equivalents of LDA and 1.27 equivalents of C_2Cl_6 produced a mixture of both dichlorocyclopentadienyl complexes with **3c**-1,2,3 and **3d**. It was not possible, to isolate any of the products in a pure form, but from NMR, **3c**-1,2,3 could be identified as the main product (Scheme 2 and entry 11 of Table S1). Finally, treatment of rather impure **4b** (purity ca 67%) with ca. 50% excess of LDA and $C_2H_2Br_4$ produced a mixture of both dibromo- and both tribromocyclopentadienyl complexes **4b** and **4c** with the tetrabromocyclopentadienyl complex **4d**. Repeated chromatography allowed isolation of **4c**-1,2,3 as main product in ca. 75% yield, and **4d** in only 4% yield (Scheme 2 and entry 18 of Table S1). The structural formulae of all new compounds are depicted in Scheme 3.

Apparently, the reactivity of the trihalocyclopentadienyl complexes is higher than that of the dihalocyclopentadienyls and thus the reaction goes further to the tetrahalo- (in case of the FpPh derivatives) or even to the pentahalocyclopentadienyl complexes.

Treatment of **3b** (purity 80%) with 6 equivalents of LDA and C_2Cl_6 allowed the isolation of **3e** in low yield (entry 13 of

1a: R = Me, X = Cl
2a: R = Me, X = Br
3a: R = Ph, X = Cl
4a: R = Ph, X = Br
5a: R = Ph, X = F
6a: R = Ph, X = I

Scheme 1. Synthesis of **1a–6a**.

Scheme 2. Electrophilic halogenation of **1b–4b**

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Scheme 3. Structural formulae of all new compounds. The compound numbers have been omitted; thus, "**a**" stands for **1a–4a**, "**b**" for **1b–4b**, and so on. R = Me for **1** and **2**, R = Ph for **3** and **4**, X = Cl for **1** and **3**, X = Br for **2** and **4**.

Table S1). Reaction of **4c**-1,2,3 (purity > 95%) with ca. 1.2 equivalents of LDA and 1.34 equivalents $C_2H_2Br_4$ yielded a mixture of **4d** and **4e**, which could be separated by chromatography (entry 19 of Table S1).

Although it might be expected, that the lithiation reactions of compounds **3** and **4** would also lead to deprotonation of the phenyl ring, we observed no indication of such a reaction— still, we cannot fully exclude this possibility. A general observation in the performed reactions was that the FpPh compounds were more prone to the formation of side products and contamination with impurities. The reaction of FpPh with butyl lithium always led to the formation of valerophenone (see for example, NMR 17 or NMR 29 of the SI). This product most likely results from initial attack of butyl anion on a coordinated CO ligand, yielding an acyl complex, which then eliminates valerophenone, leaving back a "[CpFeCO]⁻" fragment, which presumably then decomposes. In the two publications reporting the reaction of FpPh with *n*BuLi such an observation was not reported.[17] If valerophenone was not carefully removed (which is possible by chromatography), it could be carried on to the next reaction steps. Another impurity found in the FpPh reactions, which was however very difficult to be removed by chromatography, was "BHT" (ButylHydroxiToluene), a common stabilizer of THF, in which the reactions were performed.

Apparently, this compound has high affinity for the phenyl ring of the FpPh derivatives (π-π interactions?).

We also performed a short study on the feasibility of carbonyl-phosphine substitutions. For this purpose, we irradiated compound **3a** in the presence of PPh_3 and treated compounds **3c**, **3e** and **4d** with NMe_3O and PPh_3. While the irradiation of **3a** rather cleanly yielded the chiral-at-metal complex $[(C_5H_4Cl)Fe(CO)(PPh_3)Ph]$, the other reactions led only to intractable mixtures or complete decomposition.

All compounds could be characterized by ¹H and/ or ¹³C NMR spectroscopy as well as by IR and MS spectrometry (Tables S2–S5 of the Supporting Information). The ¹H and ¹³C NMR signals for the methyl groups in the series **1a–e** and **2a--e** show the (expected) trend towards lower field upon increasing halogen content, while there is only a small difference between corresponding chloro and bromo compounds. Similarly, the carbonyl-C signals shift to lower field in all four series **a→e**, with only small differences between both analogous chloro and bromo compounds and methyl and phenyl complexes. Also, in the IR spectra the metal carbonyl frequencies show the expected shifts to higher wavenumbers upon increasing halogen content. The differences between corresponding chloro and bromo compounds are small; however, the phenyl compounds, absorb at significantly higher wavenumbers than their methyl counterparts. In the EI mass spectra, the molecular ions can only rarely be observed. The base peak is usually the $[M^+-2CO]$ ion, and also the $[M^+-CO]$ can be observed. The loss of a methyl group can be observed from the M^+, $[M^+-CO]$ and $[M^+-2CO]$ ions, while the loss of phenyl groups is not observed. Common to most spectra is the occurrence of the free substituted cyclopentadienyl ligand and of the $[RC_5X_{n-m}H_{5-n}]$ fragments arising from the formal loss of $[(OC)_2FeX_m]$ ($m = 1-4$).

Crystal and Molecular Structures

$[(C_5Cl_5)Fe(CO)_2Me]$ (**1e**) crystallizes as a racemic twin in the monoclinic space group $P2_1/c$ with one molecule in the asymmetric unit, together with half a molecule hexachloroethane (Figure 1). The methyl group is evenly disordered over the three basement positions of the piano-stool tripod; thus, each corner consists of 2/3 "CO" and 1/3 "CH₃". The figure shows only the highest symmetry conformation with the methyl group "trans" to one C–Cl bond; however, the less symmetric forms with one carbonyl group in this trans-position are evenly populated. Due to this disorder, nothing can be said about the "real" length of the $Fe–C_{Me}$ bond

There are no Cl…Cl contacts shorter than the sum of van der Waals radii, however, there are Cl…O contacts between the co-crystallized hexachloroethane and the metal carbonyl oxygens. Increasing the upper limit for Cl…Cl contacts by 0.1 Å, very weak interactions between two cyclopentadienyl chlorines and several hexachloroethane chlorines appear (Figure S1 of the Supporting Information).

$[(C_5Br_5)Fe(CO)_2Me]$ (**2e**) crystallizes in the monoclinic space group $P2_1/n$ with one molecule in the asymmetric unit (Figure 2). In this compound, there is no disorder of the methyl
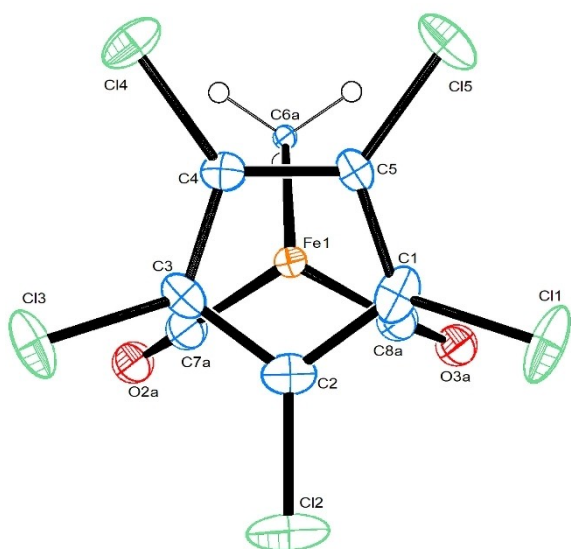
Figure 1. Molecular structure of **1e** (one of three orientations of the [(CO)$_2$CH$_3$] tripod). Co-crystallized C$_2$Cl$_6$ not shown. Displacement ellipsoids at the 30% probability level

Figure 3. ORTEP3 view of **3e**, molecule I (displacement ellipsoids at the 30% probability level)
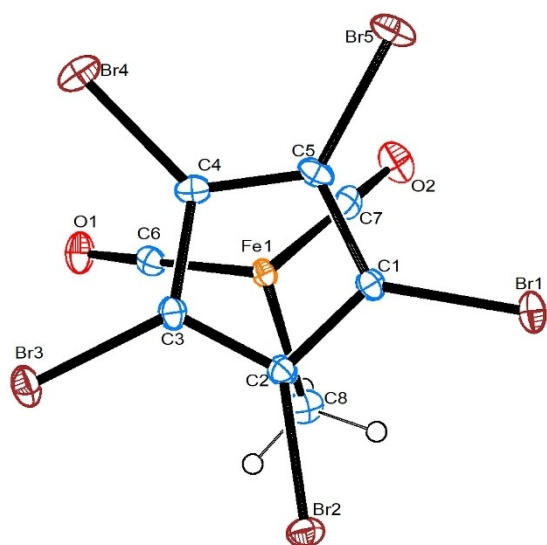

Figure 2. Molecular structure of **2e**. Displacement ellipsoids at the 30% probability level

group, which is in an eclipsed conformation with respect to one carbon–bromine bond (C2–Br2).

There are weak intermolecular Br…Br contacts between atoms Br1 and Br5, which lead to the formation of helices in the crystallographic *b* direction. These helices are interconnected in *c* direction via weak Br…O contacts between atom pairs Br1/ O1 and Br3/ O2 (Figures S2 and S3).

[(C$_5$Cl$_5$)Fe(CO)$_2$Ph] (**3e**) crystallizes in the monoclinic space group *P*2$_1$/*n* with two molecules in the asymmetric unit. Figure 3 shows a view of one of these molecules, while Figure S4 in the Supporting Information shows the other.
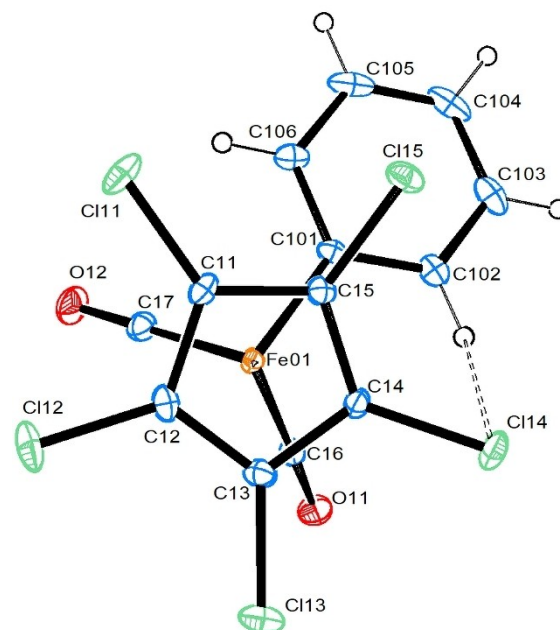
Application of the program PLATON *AutoMolFit* shows that there are rather large differences between both molecules, mostly in the relative orientation of the cyclopentadienyl and phenyl rings (Figure S5), while the corresponding bond lengths are identical within 2σ. The Fe–C$_{Ph}$ bond eclipses one C–Cl bond. The plane containing this C–Cl bond, the iron atom and the phenyl ipso carbon is almost orthogonal to the phenyl ring plane in both molecules. As Figures 3 and S4 show also, there is one very weak intramolecular C–H…Cl bond in both molecules. There is also a weak π-interaction between one chlorine atom and the phenyl ring in both molecules (Cl15–Ct$_{Ph,I}$ 3.526 Å and Cl24–Ct$_{Ph,II}$ 3.570 Å).

There are no intermolecular Cl…Cl contacts involving molecule I. However, individual molecules II are joined in *b* direction via the atom pair Cl21/Cl24 and in *c* direction via Cl25/O21. Molecules I and II are connected in *c* direction by two Cl…O contacts, using the atom pairs Cl11/ O22 and Cl22/ O12 (Figure S6).

Also [(C$_5$Br$_5$)Fe(CO)$_2$Ph] (**4e**) crystallizes in the monoclinic space group *P*2$_1$/*n* with two molecules in the asymmetric unit. Figure 4 shows an ORTEP3 view of one of the molecules, while Figure S7 in the Supporting Information shows the other. An analysis by the program PLATON *AutoMolFit* shows hardly any difference between both molecules (Figure S8), however a closer look at the ORTEP3 plots shows, that molecule I employs weak intramolecular hydrogen bonds C–H…Br and a C–H…O, respectively, while molecule II shows only two C–H…Br bonds. Besides that, all averaged bond lengths are identical between both molecules within 2σ. The Fe–C$_{Ph}$ bond eclipses one C–Br bond in both molecules, and as in compound **3e** the plane through this C–Br bond, the Fe atom and the phenyl ipso carbon is nearly orthogonal to the phenyl ring. Also similar to
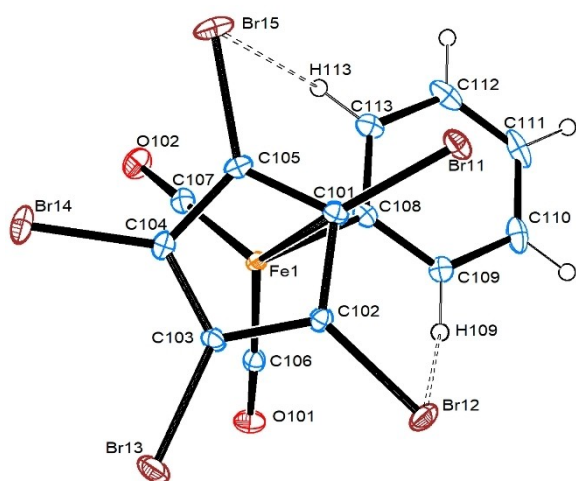
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Figure 4. ORTEP3 view of **4e**, molecule I (displacement ellipsoids at the 30% probability level)

compound **3e**, there are weak π interactions between one bromine atom and the phenyl ring (Br11–Ct$_{Ph,I}$ 3.518 Å and Br21–Ct$_{Ph,II}$ 3.591 Å).

There are no intermolecular Br…Br contacts between molecules I; however, individual molecules I are linked in *c* direction via Br…O contacts using the atom pairs Br15/ O101. Molecules II form "dimers" by cooperative action of H…Br and Br…O contacts using the atom pairs H209/Br25 and O202/Br25, respectively. These dimers are joined in *b* direction through Br…Br contacts via the atom pairs Br21/Br24 (Figure S9). Molecules I and II are joined via two Br…O contacts, using the atom pairs O102/Br23 and O201/Br15. (Figure S10).

Table 1 collects the most important bond lengths of all four compounds. A comparison shows that except for the element-specific C–X bond lengths there are hardly any differences between the corresponding chloro and bromo compounds. However, the distances from Fe to the cyclopentadienyl ring centroids as well as the carbonyl C–O bonds are slightly longer in the phenyl compounds. There are no other crystal structures containing a [Fe(C$_5$Cl$_5$)] unit, however, there is a gas phase electron diffraction study of [(C$_5$Cl$_5$)$_2$Fe].[23] In this compound

the average C–Cl distance is 1.702(4) Å and the iron-centroid distance is 1.648 Å. Two different studies describe crystal structures containing a [Fe(C$_5$Br$_5$)] unit: one is about pentabromoferrocene,[19d] the other on nona- and decabromoferrocene.[24] In these compounds, the C–Br distances are around 1.869 Å, while the iron centroid distance is in pentabromoferrocene significantly shorter than in the decabromo compound (1.609(3) Å vs. 1.644(1) Å). These distances show, that the C–X distances do not depend on the nature of the coordinated metal fragment, while– not unexpectedly– the iron centroid distance does.

More differences between the compounds can be seen in the intermolecular non-covalent interactions, which are collected in Table 2.

Most of these interactions are rather weak, being only shorter than the sum of van der Waals radii by less than 0.1 Å. A few of the O…Br contacts are more significantly shortened, but only one X…X contact, namely Br21…Br24 in compound **4e** can be regarded as strong.

Hirshfeld Analyses

In order to get some information on the energetics of the weak interactions as well as on the relative importance of the individual interactions, a Hirshfeld analysis was undertaken, using the program *CrystalExplorer*.[25] Figures S11 and S12 show the Hirshfeld surfaces of **1e**, **2e**, **3e** and **4e**. As usual, red spots mark those points where very close contacts exist between atoms inside and outside the surface. "Fingerprint plots" of these four compounds are depicted in Figure S13. A detailed analyses of all contacts yields the distribution of individual contributors (in %) and is shown in Table 3. As can be seen, there are large differences in the percentages between the four

Table 1. Important bond lengths in **1e–4e**				
Compd	**1e**	**2e**	**3e**	**4e**
Fe–Ct[a] [Å]	1.725(5)	1.722(2)	1.7296(10)/ 1.7316(10)	1.734(2)/ 1.735(2)
Fe–CR	–	2.038(4)	2.001(2)/ 2.007(2)	1.999(3)/ 2.007(4)
(C–O)av	(1.084)	1.111(5)	1.138(3)/ 1.142(3)	1.139(5)/ 1.141(5)
(C–X)av	1.698(10)	1.863(3)	1.705(2)/ 1.704(2)	1.861(3)/ 1.861(4)
(C–C)cp,av	1.423(13)	1.425(4)	1.419(3)/ 1.417(3)	1.426(4)/ 1.418(6)
[a] "Ct" is the centroid of the cyclopentadienyl ring.				

Table 2. Parameters of the non-covalent intermolecular interactions in **1e–4e**				
Comp	Atom pairs	distance	distance-VdW	Symm. op.
1e	Cl2…Cl2H	3.590	0.090	x, y, z
	Cl5…Cl1H	3.595	0.095	x, y, z
	Cl3…Cl2H	3.522	0.022	1−x,1−y, 2−z
	O2 A…Cl1H	2.962	−0.308	1+x, y, z
	O3 A…Cl2H	3.126	−0.144	x, 1.5−y, −1/2+z
2e	Br1…Br5	3.625	−0.075	1/2−x, −1/2+y, 1/2-z
	Br3…O2	3.320	−0.050	1/2+x, 1.5−y, 1/2+z
	O1…Br1	3.156	−0.214	1/2+x, 1.5−y, 1/2+z
3e	Cl21…Cl24	3.415	−0.085	1/2−x, −1/2+y, 1/2−z
	Cl11…O22	3.212	−0.058	x, y, z
	O12…Cl22	3.223	−0.047	x, y, z
	Cl25…O21	3.165	−0.105	−x, 1−y, −z
4e	H209…Br25	3.032	−0.019	2−x, 1−y, 1−z
	Br15…O101	3.349	−0.021	x−1/2, 1/2−y, z−1/2
	Br15…O201	3.283	−0.087	1−x, 1−y, −z
	O102…Br23	3.346	−0.024	1−x, 1−y, −z
	Br25…O202	3.223	−0.147	2−x, 1−y, 1−z
	Br11…Br25	3.673	−0.027	1−x, 1−y, 1−z
	Br21…Br24	3.479	−0.221	1.5−x, y−1/2, 1/2−z

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Table 3. Individual contributions of contacts in the structures of **1 e–4 e**.

	1 e[a]	**2 e**	**3 e**	**4 e**
C…C	0.1	0.8	5.4	5.0
H…H	0.6	3.5	7.8	8.4
X…X	33.8	23.8	12.7	12.8
O…O	2.4	0	3.5	2.4
C…H	0.7	0	5.0	4.9
C…X	9.9	12.5	7.9	6.8
C…O	0	2.0	3.8	2.7
H…X	19.7	24.7	31.6	32.1
H…O	8.4	6.8	3.8	3.6
X…O	24.5	32.3	18.5	22.3

[a] without C2Cl6.

structures. While the Cl…Cl contacts are the most important for compound **1 e**, the Br…O contacts take the first place for **2 e**, while the H…X contacts are the most important for both phenyl complexes. However, for all four compounds the X…X, X…O and H…X contacts are the three most important ones, making up for 78 % (**1 e**), 81 % (**2 e**), 63 % (**3 e**) and 67 % (**4 e**). The low percentages of the contacts containing carbon show, that π interactions are of no or rather low importance.

Electron density calculations on the HF/3-21G level (*CrystalExplorer* also allows also calculations at the B3LYP/6-31G(d,p) level,[25] however with so many heavy atoms this uses a lot of CPU time on smaller personal computers, without changing the general outcome of the calculations) give an impression of the interaction energies giving rise to the observed crystal packings. The results of these calculations are depicted in Figures S14 and S15. All calculated total energies are negative, i.e., attractive. The absolute values are larger for the phenyl compounds, and for all compounds the dispersion terms are the dominant ones.

Conclusion

The synthesis of the monohalocyclopentadienyl iron dicarbonyl complexes from the unsubstituted FpR (R= Me, Ph) could be established in moderate yields ranging from 35 % to 57 %. The introduction of further halogen substituted proceeded with more ease, and usually mixtures of products containing two to five halogens were obtained, which were difficult to separate completely. However, spectroscopic characterization by IR, NMR and mass spectrometry was possible for all compounds, and the four pentahalogencyclopentadienyl complexes were also characterized by X-ray diffraction. The crystal structures show an interplay of weak interactions, with X…X, X…O and X…H contacts being the most important.

Experimental Section

Instrumentation

NMR spectra were usually taken in CDCl$_3$ solutions, using either a *Jeol Eclipse 400 +*, a *Bruker AV400* or *AV400TR* instrument, operating at 400 MHz (^{1}H), 101 MHz (^{13}C), or a *Jeol Eclipse 270 +*, operating at

270 MHz (1H) and 67.8 MHz (^{13}C), respectively.. Mass spectra were taken in DEI mode, operating at 70 eV, using a *Finnigan MAT 95Q* or a *Jeol Mstation 700* instrument. IR spectra were measured either as KBr pellets on a *Bruker IFS 66v/S* or in ATR mode on a *Jasco FT/IR-650* spectrometer. Elemental analyses (EA) were performed at the Microanalytical Laboratory of the Chemistry Department of the Ludwig Maximilians University Munich, using either an *Elementar Vario el* or an *Elementar Vario micro* instrument. The irradiations were performed with a *Hanau Heraeus TQ 150* mercury immersion high-pressure lamp.

Chemicals and starting materials

Anhydrous THF was obtained commercially from Aldrich and was saturated with N$_2$. Other solvents were of analytical grade and used as such. *n*-butyl lithium (2.5 M in hexane), *s*-butyl lithium (1.4 M in cyclohexane), LDA (1.0 M in THF/ hexane), MeMgBr (3.0 M in Et$_2$O) and PhMgCl (2.0 M in THF) were obtained from Aldrich and used as such. LiTMP was freshly prepared from tetramethylpiperidine and *n*-BuLi in THF. Hexachloroethane and tetrabromoethane as well as iodine were obtained commercially from Aldrich, pentabromo-ethane from Columbia.

[CpFe(CO)$_2$]$_2$ ("Fp$_2$") was prepared from Fe(CO)$_5$ and dicyclopenta-diene and FpI from Fp$_2$ and I$_2$ according to literature[26] FpMe and FpPh were prepared from FpI and MeMgBr or PhMgCl in THF with Pd(OAc)$_2$/ TMEDA as catalyst in 79 % and 87 % yields, respectively, using an adapted literature procedure.[27]

General synthetic procedures

A solution of the substrate in THF was treated at −78 °C with a solution of base (ⁿBuLi, ˢBuLi, LDA, or LiTMP) with stirring for 2 h. Then the electrophile (C$_2$Cl$_6$, C$_2$HBr$_5$ or C$_2$H$_2$Br$_4$) was added at −78 °C with stirring and then the temperature was gradually raised to room temperature within 16 h. After evaporation of ca. 75 % of the solvent, Et$_2$O (10 mL) was added and the resulting suspension was filtered through a plug of silicagel. Then the residue was either directly (procedure I) or after examination by ^{1}H NMR spectroscopy (procedure II) taken up in the minimum amount of petroleum ether and placed on top of a silica gel chromatography column. Details of the individual procedures can be found in Table S1 of the Supporting Information.

Crystal structure determinations

Crystals of compounds **1 e**, **2 e**, **3 e** and **4 e** were obtained by slow evaporation of PE solutions in open vials in a refrigerator. They were mounted on top of a glass fibre and measured at ca. 100 K on a BRUKER D8Venture diffractometer. Experimental details of the structure determinations are collected in Table S6 of the Supporting Information. Structures were solved, refined and analysed by the program suite WINGX.[28]

Deposition Number(s) 2191364 (for **1 e**), 2191365 (for **2 e**), 2191366 (for **3 e**), 2191367 (for **4 e**), contain(s) the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service

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Supporting Information Summary

Supporting Information contains more experimental details, spectroscopic data, copies of NMR and mass spectra as well as more crystallographic tables, figures, including the results of Hirshfeld Analysis.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The crystal structures have been deposited with the CCDC. Spectroscopic data including reproductions of NMR and mass spectra can be found in the Supporting Information

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