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Coordination chemistry of perhalogenated cyclopentadienes and alkynes. XXVIII [1] new high-yield synthesis of monobromoferrocene and simplified procedure for the synthesis of pentabromoferrocene. Molecular structures of 1,2,3-tribromoferrocene and 1,2,3,4,5-pentabromoferrocene

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ABSTRACT

Monobromoferrocene (**1**) was obtained in 95% yield from ferrocene via lithiation with *tert*-BuLi/KO-*tert*-Bu and bromination with dibromotetrachloroethane. Starting from **1** mixtures of 1,2-dibromoferrocene (**2**) and apparently unreacted **1** (ranging from 80:20 to 50:50, depending on the reaction conditions) can be obtained via a lithiation- zincation- bromination sequence. These mixtures can be transferred directly with a tenfold excess of Lithium-tetramethylpiperidinide, followed by bromination with 1,1,2,2-tetrabromoethane to pentabromoferrocene (**3**), in an overall yield of 36% starting from ferrocene. The molecular structures of **3** and of 1,2,3-tribromoferrocene (**4**) have been determined by X-Ray diffraction.
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1. Introduction

The lithium-halogen-exchange reaction on halogenated metallocenes has proven to be a valuable synthetic tool for the introduction of a large number of functional groups into the cyclopentadienyl ring. [2] This could be shown impressively at the perhalocymantrenes $[(C_5X_5)Mn(CO)_3]$ [3]. Although there are meanwhile quite a number of perhalocyclopentadienyl complexes available, it was only until recently that pentabromoferrocene could be prepared [4]. The analogous pentachloroferrocene was prepared already nearly 40 years ago, [5] however, in a rather low overall yield, and several preliminary examinations of its reactivity by one of us showed it to be too stable to be a useful starting material for systematic functionalization. [6] The key step in the recent synthesis of the bromo derivative was Butler's discovery [7] that 1,1′-dibromoferrocene could be easily transferred to its 1,2 regioisomer. Unfortunately, the bromination reagent used by Butler, dibromotetrafluoroethane, is due to EU regulations no longer available in continental Europe. Attempts to repeat Butler's synthesis with other bromination reagents like tetrabromoethane or dibromotetrachloroethane lead in our hands to a marked decrease from the reported 85% yield in the isomerization step to 36–46% with the consequence of a rather low overall yield of 5.2% for pentabromoferrocene starting from ferrocene. We reasoned that another synthetic alternative might be the synthesis of the "key intermediate" 1,2-dibromoferrocene starting from monobromoferrocene via directed lithiation-bromination. A literature survey shows for all of the known preparations of monobromoferrocene rather low yields [8], under the aspect of a needed starting material for a multi-step synthesis (Scheme 1).

We decided therefore to devise a new synthetic procedure for monobromoferrocene and examine its transformation to 1,2-dibromoferrocene and further to pentabromoferrocene.

2. Experimental

2.1. General remarks

Reactions were performed either under dry nitrogen or argon, using standard Schlenk techniques. Absolute dry solvents were purchased from Aldrich and used without further purification. As the reaction products are generally air-stable, isolation and purification steps were performed in air. Ferrocene and the reagents (*n*-BuLi solution, 2.5 M in hexane; *tert*-BuLi solution 1.7 M in hexane; $ZnCl_2$ solution, 1.9 M in Me-THF; KO(*tert*-Bu), $C_2Cl_4Br_2$; $C_2H_2Br_4$; TMP) were commercially available (Aldrich) and used without further purification. The alumina for chromatography was obtained from VWR (Al_2O_3 90 "standardized").

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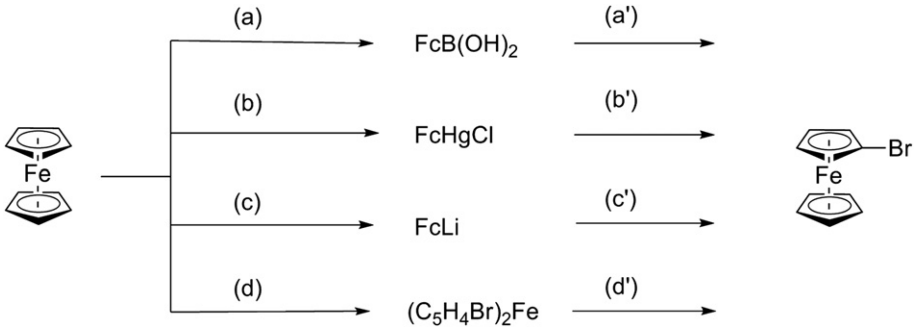


Scheme 1. Known preparations of **1** starting from ferrocene: (a): 1. ^{n}BuLi, 2. $B(OBu)_3$, 26%; (a'): $CuBr_2$, 80%, [8a]; (b): $Hg(OAc)_2$/LiCl,73%; (b'): N-Bromosuccinimide, 57%, [8b]; (c) ^{t}BuLi, 77%; (c'): Br_2 , 66%, [8c]; (d): 1. ^{n}BuLi/TMEDA, 2. $C_2Br_2F_4$, 60% [8e]; (d'): 1. ^{n}BuLi 2. H_2O, 95% [8d].

2.2. Monobromoferrocene, $[(C_5H_4Br)(C_5H_5)Fe]$, (**1**)

Ferrocene (2.00 g, 10.8 mmol) and potassium *tert*-butoxide (150 mg, 1.34 mmol) were dissolved in 100 mL THF and the solution was cooled to −78 °C. Over a period of 15 min, 12.7 mL (21.6 mmol) of *tert*-BuLi were added dropwise, while ensuring the temperature remained below −70 °C. The mixture was stirred at this temperature for 1.5 h. 1,2-dibromotetrachloroethane (5.25 g, 16.1 mmol) was added and the mixture was stirred for 30 min at −78 °C. The cooling bath was removed and the solution was allowed to warm to room temperature and quenched with water. The product was extracted two times with CH_2Cl_2 and the organic layers were washed with water and dried over $MgSO_4$. The solvent was removed under vacuum and the residue was purified by flash column chromatography using neutral alumina as the stationary phase and hexane as solvent. Yield: 2.74 g (10.3 mmol, 95%). ^{1}H NMR (400 MHz, $CDCl_3$): 4.41 (t, 2H), 4.22 (s, 5H), 4.09 (t, 2H). ^{13}C NMR (100.5 MHz, $CDCl_3$): 77.8 (CBr), 70.7 (C_5H_5), 70.2 (CH), 67.2 (CH).

2.3. 1,2-Dibromoferrocene, $[(C_5H_3Br_2)(C_5H_5)Fe]$, (**2**)

2.3.1. Isolation of pure 1,2-dibromoferrocene

A solution of **1** (0.63 g, 2.38 mmol) in 14 mL THF was added at −30 °C to freshly prepared LiTMP (2.62 mmol) in 4 mL THF. After aging for 3 h at −30 °C, $ZnCl_2$ solution (1.40 mL, 2.66 mmol) was added dropwise and the mixture stirred for additional 30 min at −30 °C. The solution was cooled to −78 °C and bromine (0.18 mL, 3.50 mmol) was added dropwise, while ensuring the temperature remained below −50 °C. After 45 min, the cooling bath was removed and the solution was allowed to warm to room temperature and quenched with water. The product was extracted two times with CH_2Cl_2 and the organic layers were washed with 1 M HCl followed by water and dried over $MgSO_4$. The solvent was removed under vacuum and the residue was purified by flash column chromatography using hexane as solvent. Yield: 0.43 g (1.25 mmol, 53%). ^{1}H NMR (270 MHz, $CDCl_3$): 4.43 (d, 2H), 4.25 (s, 5H), 4.11 (t, 1H). ^{13}C NMR (100.5 MHz, $CDCl_3$): 80.4 (CBr), 73.3 (C_5H_5), 69.0 (CH), 66.1 (CH).

2.3.2. Treatment of a 1:1 mixture of **1** and **2** with 0.5 equivalents of LiTMP

A mixture of 48% 1,2-dibromoferrocene and 52% bromoferrocene (3.65 g, 12.0 mmol, obtained by a procedure similar to 2.3.1., starting from 4.44 g **1**, 3.12 mL TMP and 7.38 mL BuLi solution in a total of 80 mL THF, with no chromatography step) was dissolved in 50 mL THF. At −30 °C, this solution was added to freshly prepared LiTMP (6.00 mmol) in 10 mL THF. After aging for 4 h at −30 °C, the mixture was cooled to −78 °C and 1,1,2,2-tetrabromoethane (0.71 mL, 6.09 mmol) was added. The solution was allowed to warm to room temperature over a period of 16 h and quenched with water. The product was extracted two times with CH_2Cl_2 and the organic layers were washed with water and dried over $MgSO_4$. The solvent was removed under vacuum and the residue was purified by flash column chromatography using hexane as solvent. Yield: 3.67 g of a mixture of 1,2,3,4-tetrabromoferrocene (7%), 1,2,3-tribromoferrocene (18%), 1,2-dibromoferrocene (24%) and bromoferrocene (51%).

2.4. 1,2,3,4,5-Pentabromoferrocene, $[(C_5Br_5)(C_5H_5)Fe]$, (**3**)

2.4.1. Preparation from a mixture containing **1**, **2**, **4** and **5**

The mixture from experiment 2.3.2. (3.60 g, corresponds to 10.8 mmol) was dissolved in 15 mL THF. At −30 °C, this solution was added to freshly prepared lithiated TMP (100 mmol) in 100 mL THF. After aging for 5 h at −30 °C, the mixture was cooled to −78 °C and 1,1,2,2-tetrabromoethane (11.7 mL, 100 mmol) was added. The solution was allowed to warm to room temperature over a period of 16 h and quenched with water. The product was extracted two times with CH_2Cl_2, the organic layers were washed with 1 M HCl followed by water and dried over $MgSO_4$. The solvent was removed under vacuum and the residue was purified by flash column chromatography using hexane as solvent. The solution was concentrated and allowed to stand at 5 °C for 16 h. Brown crystals of the product were formed. Yield: 3.59 g (6.18 mmol, 57%). ^{1}H NMR (400 MHz, $CDCl_3$): 4.30; (270 MHz, C_6D_6): 3.88. ^{13}C NMR (100.5 MHz, $CDCl_3$): 80.9 (CBr), 80.8 (C_5H_5); (67.9 MHz, C_6D_6): 81.0 (CBr), 80.5 (C_5H_5). EA (calc./found): C: 20.69/20.72; H: 0.87/0.84; Br: 68.82/68.79; Fe: 9.62/10.26%. HRMS: calc: 579.5618, found: 579.5634.

2.4.2. Preparation from bromoferrocene

A solution of **1** (1.26 g, 4.76 mmol) in 7 mL THF at −30 °C was added to freshly prepared LiTMP (47.5 mmol) in 48 mL THF. After stirring for 5 h at −30 °C, the mixture was cooled to −78 °C and 1,1,2,2-tetrabromoethane (5.54 mL, 47.5 mmol) was added. The solution was allowed to warm to room temperature over a period of 16 h and quenched with water. The product was extracted two times with CH_2Cl_2, the organic layers were washed with 1 M HCl followed by water and dried over $MgSO_4$. The solvent was removed under vacuum and the residue was purified by flash column chromatography using hexane as solvent. The solution was concentrated and allowed to stand at 5 °C for 16 h. Brown crystals of the product were formed. Yield: 0.31 g (0.53 mmol, 11%). The solvent was removed under vacuum because no more crystals were formed from the solution. Yield: 3.18 g of a mixture of 1,2,3,4,5-pentabromoferrocene (7%, corresponds to 0.72 mmol, 15% yield based on **1**), 1,2-dibromoferrocene (28%, corresponds to 2.9 mmol, 61% yield based on **1**) and Tribromoethylene (65%).

2.5. 1,2,3-Tribromoferrocene [$(C_5Br_3H_2)(C_5H_5)Fe$], (**4**)

A solution of 1,1′-dibromoferrocene (8.60 g, 25.0 mmol) in THF (150 mL) was treated at −70 °C with *n*-BuLi solution (10.0 mL, 25.0 mmol), and after 30 min stirring with TMP (4.22 mL, 25.0 mmol). Stirring was continued for 3 h at −30 to −40 °C. After cooling to −70 °C 1,1,2,2-tetrabromoethane (2.92 mL, 25.0 mmol) was added. The temperature was raised to ambient over the course of 18 h, when 50 mL water was added. The aqueous phase was separated and extracted with 50 mL Et_2O. The combined organic phases were dried over $MgSO_4$. Evaporation of the filtered extract and chromatography on alumina gave an orange solid, which contained ferrocene and **2**. Ferrocene could be removed from this mixture by sublimation, yielding pure **2** (3.09 g, 8.99 mmol, 36%).

A solution of TMP (1.51 mL, 8.96 mmol) in THF (15 mL) was treated at −30 °C with *n*-BuLi solution (3.58 mL, 8.96 mmol). After stirring for 15 min at 0 °C this solution was added to **2**, dissolved in 60 mL THF, at −30 °C. Stirring was continued at this temperature for 3 h. After cooling to −70 °C, this solution was treated with 1,1,2,2-tetrabromoethane (1.05 mL, 8.96 mmol). Again, the reaction mixture was brought to room temperature within 18 h, water (50 mL) was added, the aqueous phase extracted with ether (50 mL), the combined organic phases dried over $MgSO_4$ and the filtered solution evaporated in vacuo. The residue was taken up in petrol ether and filtered through a 3 cm plug of alumina. Partial evaporation of the solvent and cooling to 4 °C left **4** as light brown needles (2.63 g, 6.23 mmol, 69%). Another recrystallization gave crystals suitable for X-ray determination. ^{1}H NMR (400 MHz, $CDCl_3$): 4.27 (5H), 4.49 (2H). ^{13}C NMR (100.5 MHz, $CDCl_3$): 83.2 (CBr), 78.8 (CBr), 75.9 (C_5H_5), 67.8 (CH).

2.6. 1,2,3,4-Tetrabromoferrocene, [$(C_5Br_4H)(C_5H_5)Fe$], (**5**)

A solution of TMP (2.67 mL, 15.8 mmol) in THF (25 mL) was treated at −30 °C with *n*-BuLi solution (6.32 mL, 15.8 mmol) and stirred for 15 min at 0 °C. This solution was then added to a solution of **4** (2.68 g, 6.34 mmol) in 40 mL THF at −30 °C. Stirring was continued for 3 h at this temperature. After cooling to −70 °C, 1,1,2,2-tetrabromoethane (1.84 mL, 15.8 mmol) was added, and then the reaction mixture was allowed to reach room temperature within 18 h, followed by standard work-up. Careful recrystallization from petrol ether/Et_2O at 4 °C gave first **3** (0.65 g, 1.12 mmol, 18%) as dark brown crystals, suitable for X-ray determination, and then **5** (1.41 g, 2.81 mmol, 44%) as light brown powder. ^{1}H NMR (400 MHz, $CDCl_3$): 4.30 (5H), 4.93 (1H); (270 MHz, C_6D_6): 3.91 (5H), 4.31 (1H); ^{13}C NMR (67.9 MHz, C_6D_6): 82.1 (CBr), 78.1 (C_5H_5), 77.9 (CBr), 69.5 (CH). EA: (calc/found): C: 23.94/23.96; H: 1.21/1.15; Br: 63.72/63.45; Fe: 11.13/11.00%. HRMS: calc.501.6513/found: 501.6505.

2.7. Experimental details of the crystal structure determinations of **3** and **4** [9]

An X-ray quality crystal of **3** was mounted on a glass fiber and cooled to 173(3) K during measurement. The data were collected on an Oxford Xcalibur3 CCD diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$). A multi-scan absorption correction was applied using the *ABSPACK* [9a] program. The structure was solved with the SIR-97 software [9c] as implemented in the WinGX software package [9e]. Refinement (full matrix least square on F^2) was done with SHELXL 97 [9d], also as implemented in WinGX. Further details can be seen in Table 1.

An X-ray quality crystal of **4** was mounted on a glass fiber and cooled to 173(3) K during measurement. The data were collected on a Nonius KappaCCD diffractometer using Mo Kα radiation ($\lambda = 0.71073$, graded multilayer X-ray optics). A multi-scan absorption correction was applied using the *SADABS* [9b] program. The structure was solved with the SIR-97 software as implemented in the WinGX software package. Refinement (full matrix least square on F^2) was done with SHELXL 97, also as implemented in WinGX. Further details can be seen in Table 1.

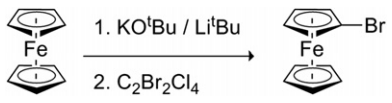
Table 1
Experimental parameters of the crystal structure determinations.

Identification code	**3**	**4**
Empirical formula	$C_{10}H_5Br_5Fe$	$C_{10}H_7Br_3Fe$
Formula weight	580.54	422.74
Crystal system	Triclinic	Monoclinic
Space group	P -1	P2(1)/*n*
Unit cell dimensions	a = 829.0(5) pm *b* = 1222.0(5) pm *c* = 1403.9(5) pm α = 106.329(5)° β = 96.166(5)° γ = 97.007(5)°	a = 693.0(5) pm *b* = 1048.6(5) pm *c* = 1540.7(5) pm α = 90.000(5)° β = 90.677(5)° γ = 90.000(5)°
Volume	1.3396(11) nm^3	1.1195(10) nm^3
Z	2 × 2 indep. Mol.	4
Density (calculated)	2.879 Mg/m^3	2.508 Mg/m^3
Absorption coefficient	16.008 mm-1	12.009 mm^{-1}
F(000)	1064	792
Crystal size	0.24 × 0.2 × 0.15 mm^3	0.15 × 0.14 × 0.13 mm^3
Theta range for data collection	4.24–26.34°	3.21–27.54°
Index ranges	$-10 \le h \le 10$, $-12 \le k \le 15$, $-17 \le l \le 17$	$-9 \le h \le 8$, $-13 \le k \le 13$, $-20 \le l \le 20$
Reflections collected	10007	30867
Independent reflections	5418 [R(int) = 0.0276]	2562 [R(int) = 0.0804]
Completeness to theta = 26.34°	99.0%	99.5%
Max. and min. transmission	1 and 0.47567	0.2494 and 0.1180
Data/restraints /parameters	5418/0/289	2562/0/148
Goodness-of-fit on F^2	868	1078
Final R indices [I > 2sigma(I)]	R1 = 0.0330, wR2 = 0.0716	R1 = 0.0267, wR2 = 0.0626
R indices (all data)	R1 = 0.0587, wR2 = 0.0744	R1 = 0.0311, wR2 = 0.0645
Largest diff. peak and hole	0.727 and −1.407 e.Å^{-3}	0.690 and −0.682 e.Å^{-3}
CCDC numbers	79126	79127

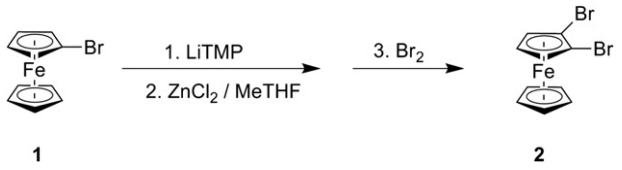
3. Results and discussion

After a decades long search for a clean high-yield preparation of monolithioferrocene Kagan's procedure in the modification by Mueller- Westerhoff [10] using a combination of *tert*-butyllithium and potassium *tert*-butylate has been established as the method of choice. Using the same lithiation procedure, followed by bromination with 1,2-dibromotetrachloro-ethane, we obtained the desired monobromoferrocene (**1**) in 95% yield. NMR analysis showed no traces of unreacted ferrocene or higher brominated ferrocenes. (Scheme 2)

For the preparation of 1,2-dibromoferrocene (**2**) we used a recent synthetic protocol for 1,2-dibromoarenes via a lithium-zinc transmetallation, published by Menzel et al [11]. **1** was selectively orthometalated with LiTMP followed by lithium- zinc- exchange



Scheme 2. Preparation of **1**.



Scheme 3. Preparation of **2**.

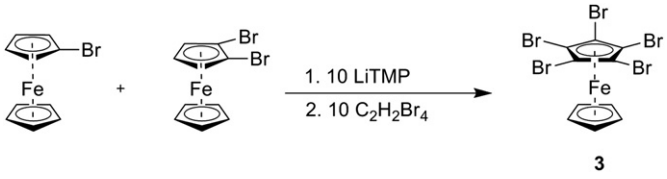
via $ZnCl_2$ and then the intermediate aryl zinc species was carefully brominated with elemental bromine. After work-up product mixtures of **2** and apparently unreacted **1** in relative proportions ranging from 1:1 to 4:1, depending on the reaction conditions, could be obtained. Isolated yields were usually around 40–45%, with a maximum of 53%. If the primary lithiation product was treated directly with 1,2-dibromotetrachloroethane, isolated yields were substantially lower. (Scheme 3)

In another experiment, we treated a 1:1 mixture of **1** and **2** with half an equivalent of LiTMP followed by bromination with 1,1,2,2-tetrabromoethane. Unexpectedly, the relative amount of **1** in the mixture didn't change, while appreciable amounts of 1,2,3-tribromoferrocene **4** and tetrabromoferrocene **5** were formed. This result suggested that the reactivity in the lithiation/bromination reaction increased with increasing bromine content. Therefore, we tried out what would happen if we treated this mixture of **1, 2, 4** and **5** with a large excess of LiTMP followed by bromination with 1,1,2,2-tetrabromoethane. To our delight we found out that after work-up a 57% yield of pentabromoferrocene **3** could be isolated, corresponding to an overall yield of 36% starting from ferrocene.

Finally, we tried what would happen, if we treated bromoferrocene **1** directly with a large excess of LiTMP followed by bromination with $C_2H_2Br_4$. After work-up and recrystallization an 11% yield of brown crystals of **3** could be isolated. NMR examination of the evaporated mother liquor showed the presence of more **3** (corresponding to a further 15% yield) besides dibromoferrocene **2** and tribromoethylene as the organic product from $C_2H_2Br_4$. In our hands, it was not possible to isolate the contained **3** from this mixture without substantial losses. (Scheme 4)

Pentabromoferrocene has a high tendency to crystallize, and thus we decided to perform an X-ray crystal structure determination. Fig. 1 shows an ORTEP view of one of the two independent molecules in the unit cell. There are only minute differences between the two molecules, except for the degree of deviation from ideal eclipsed conformation: The torsion angle between corresponding ring-centroid ring-carbon vectors is ca. 2.5° in molecule A and ca. 8° in molecule B. The other structural parameters are quite similar to other pentabromocyclopentadienyl complexes [12].

As our X-ray structure determination proved that we actually had prepared the compound, we were quite astonished to find out that our ^{13}C NMR data ($\delta = 80.9$ (CBr) and 80.8 (CH) ppm in $CDCl_3$) disagreed with the literature data ($\delta = 78.8$ and 80.8 ppm in $CDCl_3$, [4]). We had therefore a closer look at the published procedure. When we repeated the bromination step of 1,2,3-tribromoferrocene **4** by using 1,1,2,2-tetrabromoethane and carefully recrystallized the crude product, we could actually obtain two different products- the described pentabromoferrocene, in only 18% yield, and tetrabromoferrocene **5** (first identified by mass



Scheme 4. Preparation of **3**.

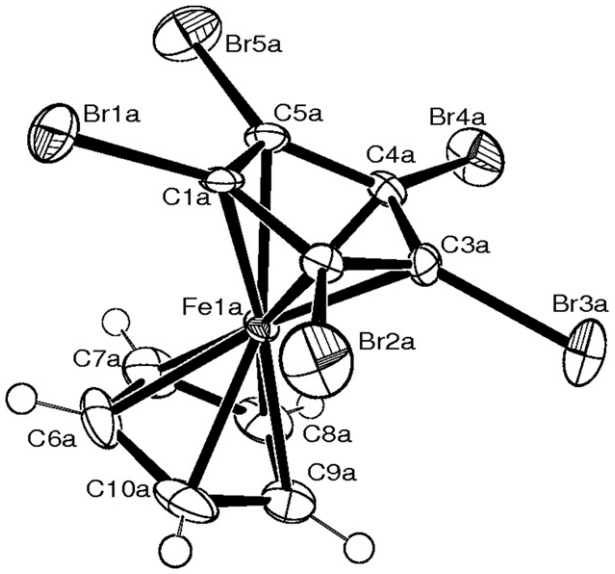


Fig. 1. Molecular Structure of **3**, Molecule A. Thermal Ellipsoids are drawn at the 50% probability level.

spectrometry) in 44% yield. Comparison of the published NMR data with our data for **3** and **5** ($\delta = 82.1$ (CBr), 78.1 (C_5H_5), 77.9 (CBr), 69.5 (CH)) suggests that the published product actually is a mixture of these latter compounds.

Also our one-pot synthesis produces minor amounts of **5**, which can be separated by careful recrystallization. However, depending on the desired further use of **3**, the mixture might be used as it is.

As, by chance, purification of tribromoferrocene **4** lead to crystals of X-ray quality, we also undertook its crystal structure determination. Fig. 2 shows an ORTEP view of its molecular structure. This shows also that the three bromine atoms are in the expected 1,2,3-orientation. Quite interestingly, there seems to be a kind of ring slippage in the $C_5Br_3H_2$ ring, as the distances from the iron atom to the bromine bearing carbon atoms are significantly shorter than to the other two (201.2(3) pm vs 205.3(3) pm). The iron ring-centroid distance to the substituted ring is approximately 3 pm shorter than the one to the unsubstituted ring. In comparison to the structure of **3**

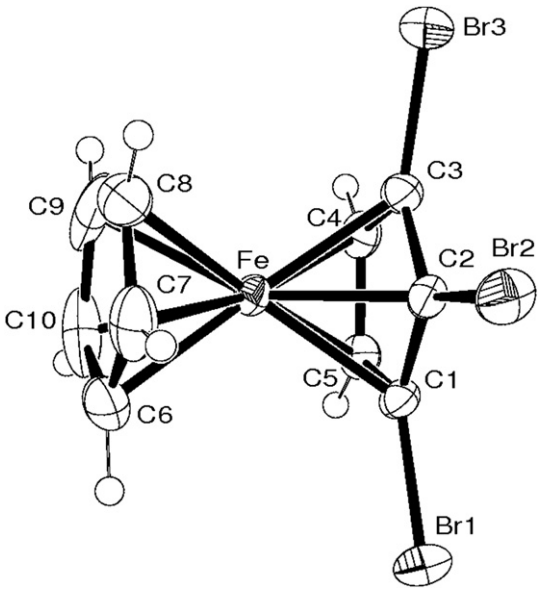


Fig. 2. Molecular Structure of **4**. Thermal Ellipsoids are drawn at the 50% probability level.

the C–Br bonds in **5** are slightly longer (on average 187.9 pm vs 186.9 pm), as well as the C–C bonds in the brominated ring (142.5 pm vs 141.9 pm) and the distance from Fe to the centroid of this ring (162.7 pm vs. 160.9 pm). The two cyclopentadienyl rings are slightly staggered (torsion angle ca. 15°). The $C_5Br_3H_2$ ring deviates only by 1.7 pm from planarity; the three bromine atoms are shifted away from the Fe side of the ring by 6 (Br3) to 12 pm (Br2).

4. Conclusion

A new high-yield preparation of monobromoferrocene has been achieved. It could be shown that for the synthesis of pentabromoferrocene the mixture of mono- and 1,2-dibromoferrocene can be directly used without the need of isolation and purification of the less substituted intermediate bromoferrocenes. Where the $C_2Br_2F_4$ is still available even higher yields might be achievable.

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