

Reduction during π -(cyclopentadienyliron) complexation of 1,8-dichloroanthracene

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Abstract

Reaction of 1,8-dichloroanthracene with ferrocene and $\text{AlCl}_3 - \text{Al}$ at 81 or 101 °C affords $[\eta^6\text{-(1,8-dichloro-9,10-dihydroanthracene)FeCp}](\text{PF}_6)$ (I) and $[\eta^6:\eta^6\text{-(1,8-dichloro-9,10-dihydroanthracene)(FeCp)}_2](\text{PF}_6)_2$ (II). NMR spectral analysis of I and II, isolation of 1,8-dichloro-9,10-dihydroanthracene by pyrolytic sublimation, and X-ray analysis of two crystal forms of I show that the central ring of 1,8-dichloroanthracene is reduced. This agrees with the behavior previously reported for anthracene. NMR supports a trans configuration for dication II.

Keywords: Iron; Arene; Anthracene; Cyclopentadienyls; Activation; Hydroaromatics; Group 8

1. Introduction

Following our studies of cofacial binuclear transition metal complexes, such as $\text{Cu}_2(\text{XBA})_2 - \text{XBAH}_2 = m\text{-xylylenebis(acetylacetonate)}$ (3,3'-[1,3-phenylenebis(methylene)-bis(2,4-pentanedione)]—(see below) [1–3], we became interested in the synthesis of a more rigid ligand based on 1,8-anthracenediylbis(acetylacetonate) (3,3'-anthracenediylbis(2,4-pentanedione)) (ABAH_2). This new ligand, with its β -diketone moieties constrained to be cofacial, should enable us to obtain a wide variety of cofacial bimetallic complexes such as 1, with controllable environments around the metal centers, for synthesis of multi-metal redox active catalysts.

We have been exploring the preparation of ABAH_2 from 1,8-dichloroanthracene (ACl_2). Although aryl halides are not ordinarily susceptible to attack by nucleophiles such as 2,4-pentanedionate (acac^-), they can be activated by π complexation of the arene to a metallic moiety. Sutherland and coworkers [4,5] have reported the use of π complexation to CpFe^+ (see Scheme 1 to convert chlorobenzene into 3-phenyl-2,4-pentanedione.

Scheme 2 contains our proposed strategy for extending this synthesis to ABAH_2 from ACl_2 .

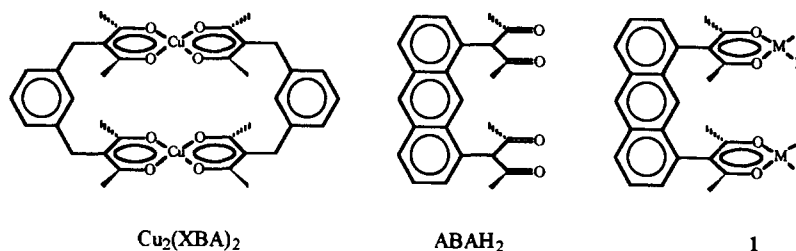
Following this approach, we now report the preparation (see Eq. (1) of the mono- and bis(cyclopentadienyliron) complexes of 1,8-dichloro-9,10-dihydroanthracene ($[(\text{AH}_2\text{Cl}_2)\text{FeCp}](\text{PF}_6)$ (I) and $[(\text{AH}_2\text{Cl}_2)_2(\text{FeCp})_2](\text{PF}_6)_2$ (II)), obtained from the ligand-substitution reaction of ferrocene with ACl_2 . In this reaction, π complexation of ACl_2 is accompanied by reduction of its central ring in forming the two Fe complexes.

2. Results and discussion

2.1. Synthesis and NMR characterization

One of the most extensively studied families of metal π -arene complexes for the formation of C–C bonds is (η^6 -haloarene) $\text{Cr}(\text{CO})_3$ [6]. In the early stages of this investigation, we pursued the π complexation of ACl_2 to this $\text{Cr}(\text{CO})_3$ moiety, by reaction of $\text{Cr}(\text{CO})_6$ with ACl_2 in *n*-butyl ether and THF. However, the reaction mixture changed color from yellow to green after a few hours, and no product could be isolated. We later found that although (η^6 -anthracene) $\text{Cr}(\text{CO})_3$ has been reported

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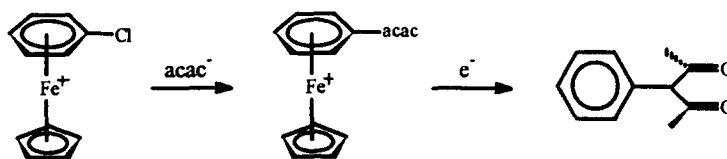


[7], it is very unstable. Also, no bis-coordinated $(\eta^6:\eta^6\text{-anthracene})[\text{Cr}(\text{CO})_3]_2$ appears to have been prepared.

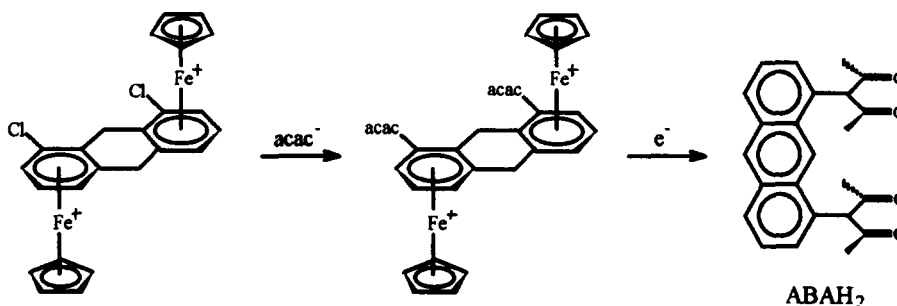
We then turned our attention to the $(\eta^6\text{-haloarene})[\text{FeCp}]^+$ system, owing to its ease of formation and the greater susceptibility of its coordinated arene to nucleophilic attack. Following the method of Nesmeyanov et al. [8], we prepared the cationic complexes $(\text{AH}_2\text{Cl}_2)[\text{FeCp}]^+$ and $(\text{AH}_2\text{Cl}_2)[\text{FeCp}]_2^{2+}$ by AlCl_3 -induced cleavage of ferrocene in the presence of

AlCl_2 and Al in refluxing cyclohexane or methylcyclohexane. Further treatment with NH_4PF_6 led to the precipitation of the hexafluorophosphate salts **I** and **II**. No dehalogenation of the arene occurred under our reaction conditions ($T = 81$ or 101°C). However, when we increased the reaction temperature to $135\text{--}155^\circ\text{C}$, using decalin as the solvent, no product could be obtained; this may be due to decomposition of AlCl_2 under the more vigorous conditions.

Our initial experiments, using a 1:1 molar ratio of



Scheme 1.



Scheme 2.

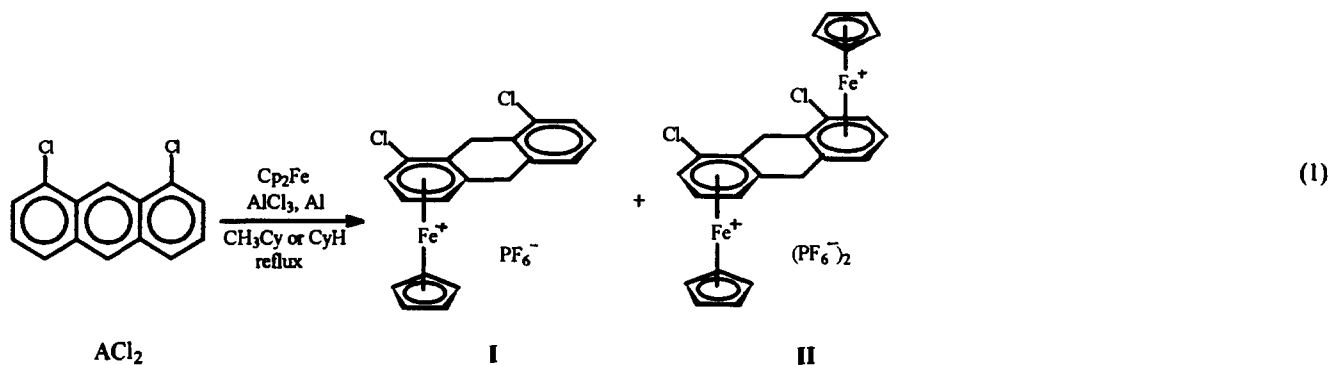


Table 1
¹H NMR data ^a

Compound	Uncomplexed arene	Complexed arene	Cp	CH ₂ or CH
I	7.53 (m,3H)	6.92 (t,1H,3.8) 6.65 (d,2H,3.9)	4.91 (s,5H)	4.86 (d,1H,19.6) 4.43 (d,1H,18.5) 4.31 (dd,1H,18.4,2.6) 4.07 (dd,1H,19.6,2.5)
II		7.03 (t,2H,3.6) 6.74 (d,4H,3.6)	5.25 (s,10H)	4.97 (s,2H) 4.94 (s,2H) 4.12 (m,4H) 9.17 (s,1H) 8.72 (s,1H)
AH ₂ Cl ₂	7.29 (m,6H)			
AlCl ₃	8.15 (br d,2H,8.5 ^b) 7.77 (dd,2H,0.9,7.3) 7.56 (dd,2H,8.5,7.3)			
(AH ₂)[FeCp] ⁺ ^c	7.51 (m,4H)	6.51 (m,4H)	4.67 (s,5H)	4.12 (s,4H)
(AH ₂)[FeCp] ₂ ²⁺ ^c		6.60 (m,8H)	5.02 (s,10H)	4.55 (s,4H)

^a In acetone-*d*₆, unless otherwise noted, δ /ppm vs. TMS (*J*/Hz in parentheses). ^b The expected second coupling constant (*J* = 0.9 Hz) is unresolved. ^c In DMSO-*d*₆, from Ref. [9].

AlCl₃ and FeCp₂, led to compound **I** in 6% yield. Better yields were obtained by using a large excess of FeCp₂, AlCl₃ and Al, leading to **I** and **II** in 13% and 26% yields respectively. Separation of these compounds was possible on the basis of their solubilities. Both of them are soluble in polar solvents, such as acetone, CH₃CN and CH₃OH, but only **I** is soluble in CHCl₃. Thus, treating the crude product with CHCl₃, followed by acetone, afforded pure mono- (**I**) and diiron (**II**) salts respectively. Both salts decompose in aerated solution after 1–2 days, but the solids are stable in air for several months.

Demetalation of both the mono- and diiron salts by pyrolytic sublimation yielded AH₂Cl₂ with small traces of AlCl₃, as identified by ¹H NMR; solid AH₂Cl₂ and its solutions slowly oxidize in air to form AlCl₃.

¹H and ¹³C NMR data for **I** and **II** and several reference compounds are presented in Tables 1 and 2. In general appearance, the spectra of **I** and **II** are similar to those of the analogous mono- and diiron complexes of 9,10-dihydroanthracene (AH₂) [9]. For both complexes **I** and **II** the ¹H and ¹³C resonances of the complexed ring(s) of AH₂Cl₂ are shifted upfield compared with those of the parent AH₂Cl₂. There is also a downfield shift of the non-coordinated ring atoms and methylene protons of AH₂Cl₂ in complex **I** compared with the free arene. Bis-coordination in complex **II** increases the downfield shift of the methylene and Cp ring protons and carbons. Reduction of AlCl₃ during π complexation is evidenced by signals in both ¹H NMR (δ 4–5 ppm) and ¹³C NMR (30–35 ppm), indicative of the methylene groups in the π -coordinated AH₂Cl₂.

Table 2
¹³C NMR data ^a

Compound	Uncomplexed arene	Complexed arene	Cp	CH ₂ or CH
I	136.9, 133.8, 131.6, 129.8(CH), 129.0(CH), 127.7(CH)	107.3, 101.0, 98.0, 88.3(CH), 87.4(CH), 87.1(CH)	79.7	34.9, 29.9
II		119.9, 107.4, 99.5, 89.0(CH), 88.2(CH), 87.4(CH)	81.2	33.2, 30.9
AH ₂ Cl ₂ ^b	127.2(CH), 127.1(CH), 125.9(CH), 125.0			36.1, 30.0
AlCl ₃	133.8, 132.5, 130.3, 129.3(CH), 128.8(CH), 127.5(CH), 127.0(CH), 120.8(CH)			
(AH ₂)[FeCp] ⁺ ^c	134.1, 127.2(CH), 126.7(CH)	102.7, 86.3(CH), 85.7(CH)	75.8	33.5
(AH ₂)[FeCp] ₂ ²⁺ ^c		99.0, 86.5(CH), 86.3(CH)	77.1	31.9

^a In acetone-*d*₆, unless otherwise noted; δ /ppm vs. TMS; assignments were made using DEPT experiment. ^b In CDCl₃. Six arene signals were expected; see Experimental part for discussion. ^c In DMSO-*d*₆, from Ref. [9].

This was confirmed in both iron compounds by using the DEPT experiment.

The ^1H NMR spectrum of compound **II** supports a trans configuration. The methylene protons appear as two singlets, which indicates that the protons in each methylene bridge are equivalent. This equivalence is likely to be due to rapid boat-to-boat interconversion of the AH_2Cl_2 ligand on the NMR time scale, generating two magnetically equivalent methylene protons. If the two CpFe groups were cis, then each of the two CH_2 groups would contain one exo and one endo proton; thus, two AB quartets should result.

In addition to the spectral data, reduction of the arene ligand was established by the X-ray analysis of **I** (see Section 2.2). The reduction of ACl_2 during π complexation to CpFe^+ is in accordance with the behavior shown by other previously reported CpFe^+ derivatives of condensed polycyclic arenes (e.g. naphthalene, anthracene, phenanthrene, and pyrene) [9–12]. For example, the mono- and diiron complexes of AH_2 have been prepared by a ligand-substitution reaction with ferrocene [9]. Other iron starting materials have also been used: reaction of $\text{Cp}^* \text{Fe}(\text{CO})_2 \text{Br}$ ($\text{Cp}^* = \eta^5\text{C}_5(\text{CH}_3)_5$) with anthracene in the presence of AlCl_3 [13] afforded a

6:4 mixture of (η^6 -1,2,3,4-tetrahydroanthracene) $[\text{FeCp}^*]^+$ and (η^6 -9,10-dihydroanthracene) $[\text{FeCp}^*]^+$. In this case, the more sterically hindered Cp^* ligand may partially inhibit the reduction of the 9 and 10 positions of anthracene, favoring reaction instead at the more remote 1–4 positions. Two radical mechanisms, involving $\text{Fe}(\text{III})$ or $\text{Fe}(\text{I})$ 17-electron intermediates, have been proposed [12–14], in which the formation of a Fe-H species leads to a stereospecific transfer (cis and endo) of the hydrogen atom to the arene. In all cases, the H atoms required for reduction of anthracene to AH_2 are believed to come from the solvent.

Reduction of both anthracene and ACl_2 occurs at low reaction temperatures, about 80°C . These mild conditions prevent dehalogenation of ACl_2 , making complexes **I** and **II** the first examples of haloanthracene derivatives coordinated to CpFe^+ moieties.

2.2. Crystal structures of mono- and diiron complexes

Complex **I** was crystallized in two forms, with space groups $Pbca$ (**Ia**) and $P\bar{1}$ (**Ib**), by layering solutions of **I** in CHCl_3 with ether and hexane respectively. The **Ia** form contains a poorly-defined CHCl_3 molecule. This

Table 3
Crystal data and summary of intensity data collection and structure refinement

Compound	$[(\text{AH}_2\text{Cl}_2)(\text{CpFe})]\text{PF}_6 \cdot \text{CHCl}_3$ (Ia)	$[(\text{AH}_2\text{Cl}_2)(\text{CpFe})]\text{PF}_6$ (Ib)
Formula	$\text{C}_{20}\text{H}_{16}\text{Cl}_3\text{F}_6\text{FeP}$	$\text{C}_{19}\text{H}_{15}\text{Cl}_2\text{F}_6\text{FeP}$
Color/shape	orange needle	orange-yellow parallelepiped
Formula weight	634.4	515.1
Space group	orthorhombic, $Pbca$	triclinic, $P\bar{1}$
Temp. ($^\circ\text{C}$)	22	26
Cell constants		
a (\AA)	10.2463(6)	8.2301(4)
b (\AA)	15.9047(8)	9.8770(6)
c (\AA)	29.882(2)	13.4623(7)
α (deg)	90	72.895(5)
β (deg)	90	72.218(4)
γ (deg)	90	77.384(5)
V (\AA^3)	4869.7(9)	985.97(4)
Z	8	2
D_{calc} (g cm^{-3})	1.731	1.735
μ (cm^{-1})	12.9	11.7
Crystal dimensions (mm^3)	$0.12 \times 0.22 \times 0.40$	$0.10 \times 0.20 \times 0.33$
Transmission coefficient	0.982–0.999	0.877–1.000
Decay of standards	< 2%	< 2%
2θ range (deg)	$2 < 2\theta < 50$	$2 < 2\theta < 50$
Range of h, k, l	12, 18, 35	9, ± 11 , ± 15
Unique reflections	4272	3472
Observed reflections ^a	2306	2660
No. of parameters varied	298	263
GOF ^b	3.454	2.297
R ^c	0.074	0.043
R_w ^d	0.085	0.051
Max. shift/esd	< 0.01	0.01
Largest feature final diff. map ($\text{e}^- \text{\AA}^{-3}$)	0.90	0.52

^a $I > 3\sigma(I)$. ^b $\text{GOF} = \{\sum w(|F_o| - |F_c|)^2 / (N_{\text{obs}} - N_{\text{param}})\}^{1/2}$. ^c $R = \sum \|F_o| - |F_c| \| / \sum |F_o|$. ^d $R_w = \{\sum w(|F_o| - |F_c|)^2 / \sum wF_o^2\}^{1/2}$; $w = 4F_o^2[\sigma^2(I) + (0.02F_o)^2]^{-1}$.

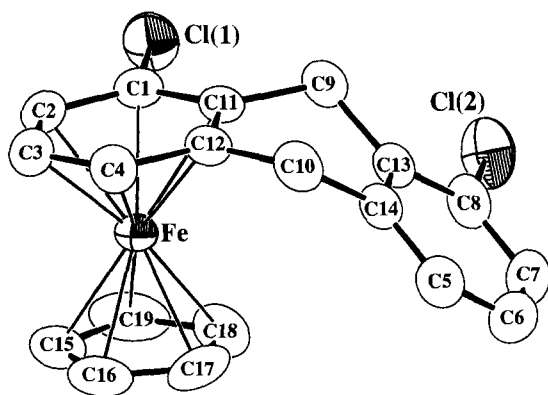


Fig. 1. Molecular structure of $[\eta^6\text{-}(1,8\text{-dichloro-}9,10\text{-dihydroanthracene})\text{FeCp}]^+$, from **Ib**, with thermal ellipsoids at the 40% probability level. Hydrogen atoms omitted for clarity.

diffuse solvent molecule may be responsible for the somewhat poorer structural results obtained for **Ia** than for **Ib** (as judged by agreement indices R , goodness of fit, and esd values for atomic coordinates and displacement parameters). A view of the cation in **Ib** with the atom labelling scheme is shown in Fig. 1. Crystallographic data are summarized in Table 3. Atomic coordinates and selected bond distances and angles of the two forms are listed in Tables 4 and 5.

Both crystal forms show an endo conformation for compound **I**, where the FeCp moiety is located inside the fold of the AH_2Cl_2 ligand. The most significant difference between the two crystal forms of **I** is the dihedral angle formed by the benzene rings of the AH_2Cl_2 ligand: the uncomplexed ring in AH_2Cl_2 is bent somewhat more strongly towards the iron atom in **Ib** (134.5°) than in **Ia** (145.6°). The latter value is very close to that reported for AH_2 (145°) [15,16]. Previous studies of CpFe^+ compounds of bent heterocyclic systems related to AH_2 , containing two heteroatoms at the 9,10-positions [17,18], have suggested that π coordination and substitution by electron-withdrawing groups on the aromatic rings may result in a flattening of the arene ligand. This proposal does not seem to apply for complex **I** where, in spite of π coordination and chlorine substituents, the AH_2Cl_2 ligand shows the same or even greater degree of folding compared with free AH_2 . The difference in the dihedral angles of the complexed AH_2Cl_2 in **Ia** and **Ib** may originate from crystal packing forces, and the energy difference between the two conformations may be small. Conformational studies of AH_2 [19] indicate that the variation of potential energy is small (ca. 4 kJ mol^{-1}) over the range of dihedral angles between about 140° and 180° .

The aromatic rings of the AH_2Cl_2 ligands are planar (no deviations larger than 0.018 \AA in either structure) in both crystal forms. Longer average carbon–carbon distances are observed in **Ib** for the complexed ring of

Table 4

Atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

Atom	x	y	z	U_{eq}^a
Ia				
Fe	0.5847(1)	0.67763(7)	0.65189(4)	0.0571(3)
Cl(1)	0.3993(3)	0.5585(2)	0.5788(1)	0.099(1)
Cl(2)	0.8436(3)	0.4621(2)	0.53422(9)	0.121(1)
C1	0.4629(9)	0.5812(5)	0.6308(3)	0.062(3)
C2	0.3933(8)	0.6372(6)	0.6587(3)	0.079(3)
C3	0.446(1)	0.6587(5)	0.7002(3)	0.078(3)
C4	0.563(1)	0.6242(5)	0.7146(3)	0.077(3)
C5	0.989(1)	0.5202(6)	0.6718(4)	0.103(4)
C6	1.073(1)	0.5087(7)	0.6375(5)	0.120(5)
C7	1.031(1)	0.4921(6)	0.5951(4)	0.105(4)
C8	0.8955(9)	0.4873(5)	0.5869(3)	0.079(3)
C9	0.6618(8)	0.4919(5)	0.6135(3)	0.061(3)
C10	0.758(1)	0.5274(6)	0.7017(3)	0.090(3)
C11	0.5834(8)	0.5464(5)	0.6443(3)	0.053(2)
C12	0.6313(8)	0.5663(5)	0.6870(3)	0.057(3)
C13	0.8054(8)	0.4994(5)	0.6215(3)	0.057(2)
C14	0.8550(9)	0.5170(5)	0.6642(3)	0.073(3)
C15	0.592(1)	0.8043(6)	0.6507(5)	0.129(5)
C16	0.707(1)	0.7752(6)	0.6636(3)	0.100(4)
C17	0.759(1)	0.7259(6)	0.6307(4)	0.118(4)
C18	0.670(1)	0.7276(8)	0.5972(3)	0.165(5)
C19	0.563(1)	0.7734(8)	0.6093(4)	0.203(5)
P	0.6268(3)	0.8359(2)	0.80629(9)	0.0761(8)
F1	0.7318(9)	0.8178(7)	0.7714(2)	0.206(4)
F2	0.5246(8)	0.8384(8)	0.7703(3)	0.244(5)
F3	0.5244(8)	0.8541(5)	0.8423(3)	0.185(3)
F4	0.7348(8)	0.8271(6)	0.8432(2)	0.162(3)
F5	0.6513(9)	0.9308(5)	0.8013(3)	0.192(4)
F6	0.6049(9)	0.7422(5)	0.8124(4)	0.211(5)
C1S	1.108(1)	0.8019(7)	0.5547(3)	0.108(4)
Cl(1S)	1.0979(7)	0.6967(3)	0.5558(2)	0.265(3)
Cl(2S)	0.9759(5)	0.8380(3)	0.5274(1)	0.202(2)
Cl(3S)	1.2465(5)	0.8316(4)	0.5294(1)	0.265(3)
Ib				
Fe	0.58806(6)	0.17187(6)	0.20529(4)	0.0408(1)
Cl(1)	0.2750(1)	-0.0199(1)	0.2181(1)	0.0732(4)
Cl(2)	0.0082(2)	0.1660(1)	0.5345(1)	0.0848(5)
C1	0.3882(5)	0.1252(4)	0.1629(3)	0.049(1)
C2	0.5424(5)	0.1100(4)	0.0827(3)	0.053(1)
C3	0.6404(5)	0.2228(5)	0.0393(3)	0.055(1)
C4	0.5851(5)	0.3488(4)	0.0760(3)	0.052(1)
C5	0.3327(5)	0.5197(4)	0.3894(4)	0.063(1)
C6	0.2673(6)	0.4774(5)	0.4994(4)	0.074(2)
C7	0.1671(6)	0.3691(5)	0.5440(3)	0.070(2)
C8	0.1341(5)	0.3035(4)	0.4764(3)	0.056(1)
C9	0.1703(5)	0.2697(4)	0.2897(3)	0.052(1)
C10	0.3712(5)	0.4927(4)	0.2022(3)	0.054(1)
C11	0.3304(4)	0.2502(4)	0.2008(3)	0.044(1)
C12	0.4313(5)	0.3632(4)	0.1565(3)	0.045(1)
C13	0.1997(5)	0.3420(4)	0.3660(3)	0.048(1)
C14	0.2999(5)	0.4524(4)	0.3226(3)	0.049(1)
C15	0.8010(6)	0.0340(6)	0.2373(4)	0.084(2)
C16	0.8176(6)	0.1691(6)	0.2353(4)	0.085(2)
C17	0.6861(6)	0.2152(5)	0.3122(3)	0.085(2)
C18	0.5802(6)	0.1101(8)	0.3644(4)	0.103(2)
C19	0.6557(6)	-0.0060(5)	0.3141(4)	0.091(2)
P	0.8519(1)	0.6815(1)	0.11141(9)	0.0550(3)
F1	0.8739(5)	0.8350(4)	0.0377(3)	0.135(2)
F2	0.6833(4)	0.7428(4)	0.1843(3)	0.144(2)

Table 4 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}^a
F3	0.8288(5)	0.5300(4)	0.1861(4)	0.149(2)
F4	1.0249(4)	0.6205(4)	0.0436(3)	0.139(1)
F5	0.9578(4)	0.7145(4)	0.1798(3)	0.127(1)
F6	0.7497(4)	0.6477(4)	0.0447(3)	0.133(1)

^a U_{eq} defined as one third of the trace of the orthogonalized U_{ij} tensor.

AH₂Cl₂ (1.406(3) Å) in comparison with the uncomplexed ring (1.381(3) Å), and also in comparison with free AH₂ (1.386(1) Å) [15,16]. This increase in bond length on π complexation to CpFe⁺ has been reported for other aromatic ligands [20,21] and is consistent with π backbonding from Fe into the antibonding orbitals on the arene ring. (We see no significant variation of corresponding C–C lengths in **Ia** within the level of precision obtained in its structure determination.) In both forms, bond lengths to the 9 and 10 carbon atoms in AH₂Cl₂ are very similar and close to the values found in AH₂ (1.512(6) Å) [15], while C–Cl distances remain close to those in AlCl₃ (1.745(4) and 1.756(4) Å) [22]. The coordinated arene and Cp ring planes form dihedral angles of 4.1° and 2.8° in **Ia** and **Ib** respectively. The distances between Fe and the coordinated arene ring planes (1.533(1) Å in **Ia** and 1.5361(5) Å in **Ib**) are shorter than the distances between Fe and Cp ring planes (1.660(1) Å in **Ia** and 1.6624(5) Å in **Ib**), despite longer Fe–C_{arene} than Fe–C_{Cp} distances, owing to the larger size of the arene ring. The Fe center is not equidistant from the six carbons of the complexed arene ring. Instead, it is displaced so that four short and two long Fe–C distances result: 2.071(2) (average distance from Fe to C1, C2, C3, C4) and 2.103(3) Å (average, Fe to C11, C12). All of these values are within the range of distances observed in other (η^6 -arene)[FeCp]⁺ compounds [20,21].

Crystals of **II** were not suitable for X-ray analysis. However, during one attempt to grow crystals of **II**, a small quantity of black crystals formed. A low-resolution X-ray analysis of these crystals showed what appears to be (AlCl₂)[FeCp]₂(PF₆)₂ containing the non-hydrogenated AlCl₂ ligand. (The black crystal, grown in acetone–diethyl ether, appears to be [η^6 : η^6 -(AlCl₂)[FeCp]₂](PF₆)₂ · solvent(s)). The structure is orthorhombic, space group *Fddd*, *a* = 18.050(3), *b* = 26.180(5), *c* = 29.922(3) Å, *V* = 14140(6) Å³, *Z* = 16. The crystal underwent severe anisotropic decay during data collection, amounting to about 60% intensity loss, apparently as a result of solvent loss. Refinement based upon 1157 observed data yields *R* = 0.186. The model is not fully chemically reasonable, and the disordered solvent region has not been modeled. It is clear, however, that the compound is dimeric with trans Fe atoms and C–C distances in the central ring (1.38(3)–1.49(3)

Table 5

Selected bond distances (Å) and angles (deg)

Bond distances	Ia	Ib
Fe–C1	2.076(8)	2.074(5)
Fe–C2	2.075(9)	2.077(5)
Fe–C3	2.046(9)	2.068(4)
Fe–C4	2.071(8)	2.074(3)
Fe–C11	2.099(7)	2.106(3)
Fe–C12	2.111(8)	2.095(3)
Fe–C15	2.016(9)	2.046(5)
Fe–C16	2.03(1)	2.042(5)
Fe–C17	2.05(1)	2.032(6)
Fe–C18	2.02(1)	2.031(5)
Fe–C19	2.00(1)	2.025(5)
C1–C2	1.41(1)	1.405(5)
C1–C11	1.41(1)	1.406(6)
C1–C1(1)	1.723(9)	1.734(4)
C2–C3	1.40(1)	1.398(6)
C3–C4	1.38(1)	1.406(6)
C4–C12	1.42(1)	1.404(5)
C5–C6	1.35(2)	1.380(6)
C5–C14	1.40(1)	1.379(7)
C6–C7	1.37(2)	1.374(7)
C7–C8	1.41(1)	1.377(8)
C8–C13	1.40(1)	1.383(5)
C8–C1(2)	1.71(1)	1.739(5)
C9–C11	1.50(1)	1.505(5)
C9–C13	1.50(1)	1.511(7)
C10–C12	1.51(1)	1.503(6)
C10–C14	1.51(1)	1.507(5)
C11–C12	1.40(1)	1.416(5)
C13–C14	1.40(1)	1.391(6)
C15–C16	1.33(2)	1.362(9)
C15–C19	1.36(2)	1.366(6)
C16–C17	1.37(1)	1.353(6)
C17–C18	1.35(2)	1.387(8)
C18–C19	1.37(2)	1.431(9)
<i>Bond angles</i>		
Cl(1)–C1–C2	118.3(7)	117.4(3)
Cl(1)–C1–C11	120.4(6)	120.7(2)
C2–C1–C11	121.2(8)	121.9(4)
C1–C2–C3	118.8(8)	118.9(4)
C2–C3–C4	121.1(8)	120.3(4)
C3–C4–C12	120.1(8)	120.6(4)
C6–C5–C14	120(1)	120.3(4)
C5–C6–C7	122(1)	120.7(5)
C6–C7–C8	119(1)	118.5(4)
Cl(2)–C8–C7	118.5(8)	117.8(3)
Cl(2)–C8–C13	120.5(7)	120.0(4)
C7–C8–C13	120.9(9)	122.2(4)
C11–C9–C13	112.5(7)	111.6(3)
C12–C10–C14	113.3(7)	111.8(3)
C1–C11–C9	121.4(7)	124.1(3)
C1–C11–C12	118.5(7)	118.6(3)
C9–C11–C12	120.1(7)	117.3(4)
C4–C12–C10	121.5(7)	122.6(4)
C4–C12–C11	120.1(8)	119.7(4)
C10–C12–C11	118.4(7)	117.6(3)
C8–C13–C9	121.3(7)	123.7(4)
C8–C13–C14	117.5(8)	118.3(4)
C9–C13–C14	121.2(7)	118.0(3)
C5–C14–C10	121.5(9)	122.3(4)
C5–C14–C13	120.9(9)	120.0(3)
C10–C14–C13	117.5(8)	117.7(4)

Table 5 (continued)

C16–C15–C19	110(1)	109.4(5)
C15–C16–C17	110(1)	108.5(4)
C16–C17–C18	105(1)	109.5(5)
C17–C18–C19	111(1)	105.7(4)
C15–C19–C18	105(1)	107.0(5)

Å) are more similar to those in ACl_2 (1.385(6)–1.453(5) Å) than to those of **Ia** and **Ib**. The Fe dimer lies on a crystallographic twofold axis.) Attempts to prepare the mono- and diiron complexes of ACl_2 by oxidation of the AH_2Cl_2 ligand in **I** and **II** respectively, using DDQ in the presence of a base (Et_3N or K_2CO_3) in CH_3CN or benzene as solvent, were unsuccessful. Instead, decomposition of the starting materials occurred, and only AH_2Cl_2 and ACl_2 could be isolated.

3. Conclusions

The synthesis of complexes **I** and **II** shows the feasibility of π complexation of chloroanthracene derivatives to CpFe^+ moieties under mild reaction conditions in moderate yields. These compounds may serve as intermediates for the activation of ACl_2 to nucleophilic attack. Although nucleophilic substitution reactions have been well studied for benzene compounds, there has been no attempt to reproduce them in condensed polycyclic arenes. We are now exploring the reactivities of these complexes with carbon nucleophiles.

4. Experimental part

ACl_2 was prepared by reduction of 1,8-dichloroanthraquinone by Zn in NH_3 (aq) following literature procedures [23,24]. Other chemicals and solvents were reagent grade and were used as-received. NMR spectra were recorded by using Bruker AC 200, AC 250 and AM 400 spectrometers. An HP5971 instrument was used for GC-MS.

4.1. $[\eta^6\text{-(AH}_2\text{Cl}_2)\text{FeCp}](\text{PF}_6)$ (**I**)

A mixture of ACl_2 (3.3 g, 14 mmol), ferrocene (2.5 g, 14 mmol), AlCl_3 (3.6 g, 27 mmol) and Al powder (0.4 g, 14 mmol) in methylcyclohexane (50 ml) was refluxed for 20 h under N_2 . The resulting solution was allowed to cool to room temperature under N_2 and with continuous stirring the mixture was hydrolyzed with 25 ml of ice water. The organic layer was separated and extracted with H_2O , and the aqueous layers were combined, washed with hexane several times to remove unreacted ferrocene, and then filtered into a solution of

2.2 g (14 mmol) of NH_4PF_6 dissolved in the minimum amount of H_2O . The yellow hexafluorophosphate salt **I** precipitated (0.4 g, 6%) and was crystallized from either CHCl_3 -ether or CHCl_3 -hexane as orange-yellow needles.

4.2. $[\eta^6:\eta^6\text{-(AH}_2\text{Cl}_2)(\text{FeCp})_2](\text{PF}_6)_2$ (**II**)

A mixture of ACl_2 (2.5 g, 10 mmol), ferrocene (26.5 g, 142 mmol), AlCl_3 (37.7 g, 283 mmol) and Al powder (3.8 g, 142 mmol) in 200 ml of cyclohexane was heated at reflux under N_2 for 40 h. The resulting material was worked up as described above for **I** using 3.3 g (20 mmol) of NH_4PF_6 . The crude product (2.2 g), containing a mixture of **I** and **II**, was treated first with CHCl_3 , and the mixture filtered. The filtrate was concentrated and flooded with hexane, precipitating pure **I** in 13% yield. The remaining crude solid was then treated with acetone, and the solution was filtered, concentrated and flooded with ether, giving **II** in 26% yield. Compound **II** was then crystallized from acetone-ether as yellow needles.

4.3. AH_2Cl_2

A methanolic solution of complex **I** or **II** was allowed to evaporate in a sublimator in order to form a thin film of the compound on the glass. After evacuation to ca. 10^{-2} Torr, heat was applied with an oil bath to 140–160 °C for 0.5 h. A yellowish-white solid (yield 50–60%) was collected from the cold finger, and identified as AH_2Cl_2 with a small amount of ACl_2 (approx. 1% by ^1H NMR). The ^{13}C NMR spectrum of AH_2Cl_2 (Table 2) shows only one quaternary carbon instead of the expected three; this may be caused by coincidental overlap with other arene signals or low signal to noise ratio. EI-MS m/z (%) 252, 250, 248 (68, M^+); 215, 213 (92, $\text{M}^+ - \text{Cl}$); 178 (100, $\text{M}^+ - 2\text{Cl}$); 106 (26); 88 (41).

4.4. Crystal structure determination of $[\eta^6\text{-(AH}_2\text{Cl}_2)\text{FeCp}](\text{PF}_6)$ (**I**)

Intensity data for **Ia** and **Ib** were collected on an Enraf–Nonius CAD4 diffractometer equipped with Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073$ Å), and a graphite monochromator, by ω - 2θ scans of variable rate. The crystals used for data collection were sealed in capillaries. Data reduction included corrections for background, Lorentz, polarization, and absorption effects. Absorption corrections were based on ψ scans, and no corrections were made for decay. The structures were solved by direct methods and refined by full-matrix least squares, treating non-hydrogen atoms anisotropically, using the Enraf–Nonius MolEN programs [25]. Hydro-

gen atoms were placed in calculated positions. Tables of displacement parameters and observed and calculated structure factors are available from the authors; all other structural data have been deposited at the Cambridge Crystallographic Data Centre.

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