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Intermolecular hydrogenation of a C=C bond during π-cyclopentadienyliron complexation of 1,8-dichloro-9,10-dihydro-9,10-ethenoanthracene

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Abstract

Reaction of 1,8-dichloro-9,10-dihydro-9,10-ethenoanthracene with ferrocene in the presence of Al and $AlCl_3$ in cyclohexane affords the mono-iron complex [*endo*-(η^6-(1,8-dichloro-9,10-dihydro-9,10-ethanoanthracene))FeCp](PF_6) as the only isolable iron-containing product. X-ray and NMR analysis of this product confirms that the etheno bridge in the arene ligand has been hydrogenated. The intramolecular mechanism previously proposed for this type of hydrogenation accompanying π complexation (i.e. involving an Fe–H intermediate) is impossible for steric reasons; thus, an intermolecular process must be considered. The same reaction was attempted in methylcyclohexane–cyclohexane mixtures, in order to improve the complexation yield and favor the formation of diiron complexes. However, this led instead to the formation of [(η^6-toluene)FeCp](PF_6), in which the coordinated toluene ligand arises from dehydrogenation of the methylcyclohexane solvent. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Iron; Arene; Anthracene; Ethenoanthracene; Intermolecular; Hydrogenation

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1. Introduction

We have been exploring synthetic routes toward cofacial binuclear metal complexes based on 1,8-anthracenediylbis(acetylacetone) ($ABAH_2$; see Scheme 1) and its bis(β-keto enamine) analog $ABIH_2$ [1,2]. The rigid structure of the anthracene bridging group allows the formation of a variety of bimetallic complexes such as (ABI)$[ML_2]_2$ with controllable coordination environments around the metal centers. These complexes may bind small guest molecules and serve as catalysts for multi-electron redox reactions.

We have recently studied the activation of 1,8-dichloroanthracene (ACl_2; see Scheme 2) toward attack by carbon nucleophiles [2], as a route toward the synthesis of $ABAH_2$. We found that π complexation of ACl_2 to $CpFe^+$ moieties was accompanied by reduction of the anthracene ring to form both mono- and bis(cyclopentadienyliron) complexes of 1,8-dichloro-9,10-dihydroanthracene ([η^6-(AH_2Cl_2)FeCp](PF_6) and [η^6:η^6-(AH_2Cl_2)$(FeCp)_2$]$(PF_6)_2$). However, upon reaction with enolate carbanions, such as 2,4-pentanedionate and the conjugate bases of dimethyl malonate and diethyl ethylmalonate [3], both iron complexes decomposed. Several investigators have studied the acid–base chemistry of (η^6-arene)$FeCp^+$ complexes such as (η^6-fluorene)$FeCp^+$ and (η^6-9,10-dihydroanthracene)-$FeCp^+$ ((η^6-AH_2)$FeCp^+$) [4–7] in which the arene ligand has an α-carbon substituent containing one or more H atoms. They found that these complexes can be deprotonated in the presence of a base to give zwitterionic species that can further react in situ as nucleo-

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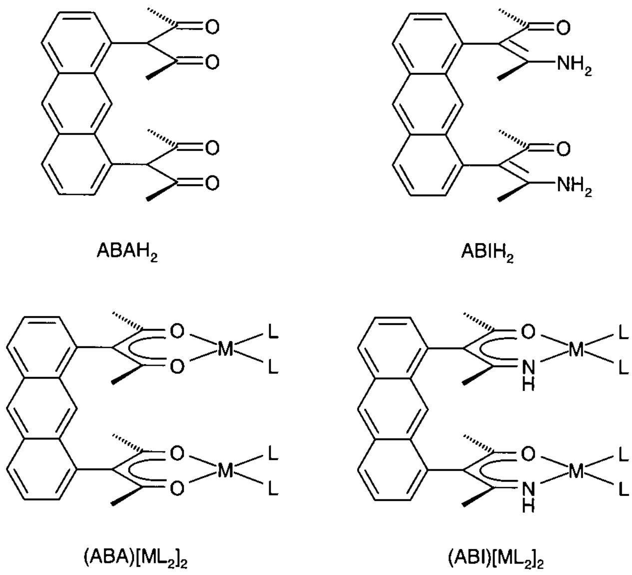
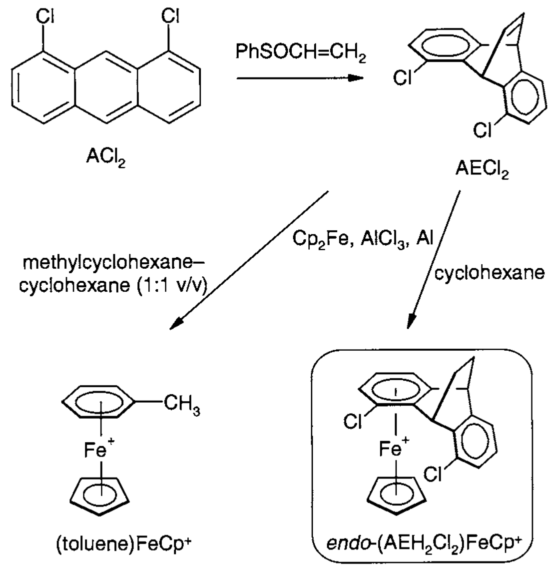


Scheme 1.



Scheme 3.

philes. However, the need for low reaction temperatures (– 20°C) as well as the formation of anthracene during deprotonation of (η^6-AH_2)FeCp$^+$ [6,7] suggests that the zwitterions may have limited stability. The presence of these acidic protons in coordinated AH_2Cl_2 may be responsible for the failure of [η^6-(AH_2Cl_2)FeCp]$^+$ and [η^6:η^6-(AH_2Cl_2)(FeCp)$_2$]$^{2+}$ to react cleanly with carbon nucleophiles, by creating a less electrophilic and possibly unstable zwitterionic compound.

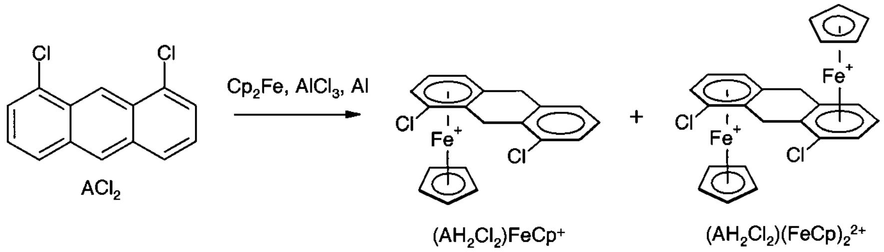
These difficulties led us to an interest in the more rigid ‘barrelene’ system 1,8-dichloro-9,10-dihydro-9,10-ethenoanthracene ($AECl_2$; see Scheme 3), whose central anthracene ring should no longer be subject to reduction. We now report the preparation of the mono(cyclopentadienyliron) complex of 1,8-dichloro-9,10-dihydro-9,10-ethanoanthracene, [(η^6-AEH_2Cl_2)FeCp]$^+$, by $AlCl_3$-induced cleavage of ferrocene in the presence of $AECl_2$. NMR and X-ray analysis show that the new compound is produced as the *endo* isomer. In this reaction, π complexation of $AECl_2$ is unexpectedly accompanied by reduction of its ethene bridge.

2. Results and discussion

2.1. Synthesis and NMR characterization

$AECl_2$ was synthesized by Diels–Alder cycloaddition of 1,8-dichloroanthracene with the acetylene synthon phenyl vinyl sulfoxide in chlorobenzene, following the method developed by Paquette et al. [8] (Scheme 3). Owing to the large amount of tar present in the resulting solution, purification of $AECl_2$ was not possible by conventional chromatography. Instead, it was isolated by crystallization from the reaction solution at – 15°C. Further recrystallization from CCl_4/CH_2Cl_2 afforded pure $AECl_2$ in 30% yield [9]. The use of a solvent with a higher boiling point, such as *o*-dichlorobenzene, for the cycloaddition did not improve the reaction yield.

Treatment of $AECl_2$ with a large excess of ferrocene, $AlCl_3$ and Al (after the general method developed by Nesmeyanov et al. [10]) using cyclohexane as the only solvent afforded [(η^6-AEH_2Cl_2)FeCp]$^+$, isolated as its PF_6^- salt in 36% yield (see Scheme 3). This orange–



Scheme 2.

Table 1
^{1}H-NMR data[a]

Compound	Uncomplexed arene	Complexed arene	H10, H9	Cp	CH or CH_2
$AECl_2$[b]	6.90–7.10 (m)[c]		6.14 (dd, 5.6, 1.8) 5.18 (dd, 5.4, 1.9)		6.90–7.10 (m)[c]
AEH_2[d]	7.01 (m, 8H)		4.13 (m)		1.68 (m)
$[(\eta^6\text{-}AEH_2Cl_2)(FeCp)](PF_6)$[e]	7.58 (d, 1H, 7.2) 7.42 (d, 1H, 7.7) 7.35 (t, 1H, 7.7)	6.71 (d, 1H, 5.5) 6.40 (d, 1H, 6.2) 6.34 (t, 1H, 5.8)	5.33 (s) 4.66 (s)	4.35 (s)	1.87 (d, 8.1) 1.69 (d, 8.3)

[a] In $CDCl_3$, δ/ppm vs. TMS; J/Hz in parentheses.
[b] 200 MHz.
[c] Olefinic and aromatic protons (8H) overlap.
[d] Taken from Ref. [11].
[e] 400 MHz.

Table 2
^{13}C-NMR data[a]

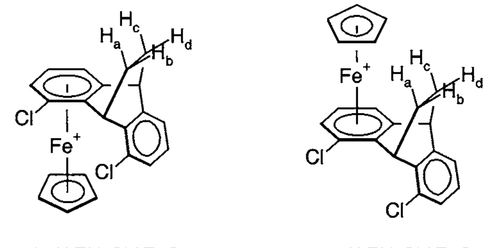
Compound	Uncomplexed arene	Complexed arene	C10, C9	Cp	CH or CH_2
$AECl_2$	148.5, 142.7, 129.4, 125.8 (CH), 125.3 (CH), 121.5 (CH)		51.7, 44.3		140.1, 138.5
AEH_2[b]	143.8, 125.5 (CH), 123.2 (CH)		44.1		26.7
$[(\eta^6\text{-}AEH_2Cl_2)FeCp](PF_6)$	144.5, 139.2, 129.3, 128.8 (CH), 127.4 (CH), 123.3 (CH)	109.9, 106.5, 103.8, 85.0 (CH)[c], 84.8 (CH)	41.2, 35.5	78.4	24.6, 24.1

[a] 50 MHz, in $CDCl_3$, δ/ppm vs. TMS; assignments were made using DEPT experiments.
[b] Taken from Ref. [11].
[c] Higher intensity of this resonance suggests coincidental overlap of two CH signals.

brown complex is stable in air in the solid state for weeks, but it starts decomposing in aerated solutions after several hours.

^{1}H- and ^{13}C-NMR data for $[(\eta^6\text{-}AEH_2Cl_2)FeCp](PF_6)$, $AECl_2$, and the reference compound 9,10-dihydro-9,10-ethanoanthracene (AEH_2) [11] are presented in Tables 1 and 2. The ^{1}H and ^{13}C resonances of the ring that is complexed to iron are shifted upfield compared to those of $AECl_2$ and AEH_2, while those for the non-coordinated ring atoms of AEH_2Cl_2 are shifted downfield. The etheno bridge of $AECl_2$ has been reduced to an ethano bridge, as evidenced by ^{1}H- (δ 1.87 and 1.69 ppm) and ^{13}C-NMR (δ 24.6 and 24.1 ppm) signals in the saturated region.

In principle, two isomers can be produced for the mono-iron complex $[(\eta^6\text{-}AEH_2Cl_2)FeCp]^+$, *endo* and *exo*, depending on the position of the CpFe moiety relative to the ethano bridge of the AEH_2Cl_2 ligand (see Scheme 4). We find only the *endo* isomer. This assignment is consistent with the small effect the presence of the CpFe moiety has on the chemical shifts of the ethano bridge atoms of the AEH_2Cl_2 ligand, by comparison to those of free AEH_2. The methylene protons appear as two doublets, which indicate that the protons in each CH_2 group (H_a, H_b and H_c, H_d; see drawings of *endo* and *exo* isomers in Scheme 4) are nearly equivalent. Instead, if the CpFe moiety were *exo*, it would be expected to exert a strong influence on the methylene protons immediately adjacent to the metal (H_a, H_c), and H_{a-d} would be expected to appear as two doublets of AB quartets (see [12]; also, this pattern is observed for the *exo* isomer of a related Cr complex [13]). X-ray analysis also confirms the *endo* geometry for $[(\eta^6\text{-}AEH_2Cl_2)FeCp](PF_6)$.



endo-$(AEH_2Cl_2)FeCp^+$ *exo*-$(AEH_2Cl_2)FeCp^+$

Scheme 4.

2.2. Possible mechanisms for conversion of $AECl_2$ to AEH_2Cl_2 during complexation

The reduction of the etheno bridge during formation of $(\eta^6\text{-}AEH_2Cl_2)FeCp^+$ is similar to the hydrogenation reactions that occur during π complexation of other polycyclic arenes. For example, treatment of naphthalene with $CrCl_3$ in the presence of $AlCl_3$/Al yields mainly $[(\eta^6\text{-tetralin})_2Cr]$ [14]. $AlCl_3$ is believed to promote reduction of polycyclic arenes, e.g. naphthalene to tetralin and anthracene to AH_2 and 1,2,3,4-tetrahydroanthracene, in refluxing hexane [15]. Reduction of condensed polycyclic arenes, such as naphthalene, anthracene and pyrene [16–18], also occurs during π complexation to $CpFe^+$. Furthermore, reduction of 9,10-dimethylanthracene during π complexation produces a single product, *endo*-(η^6-*cis*-9,10-dihydro-9,10-dimethylanthracene)$FeCp^+$ [19]. The stereospecificity of this reaction (*cis* and *endo*) is postulated to result from an Fe–H intermediate, which then transfers its H atom to the coordinated arene in an intramolecular fashion.

The intramolecular H atom transfer mechanism suggested above for 9,10-dimethylanthracene cannot readily explain the hydrogenation of $AECl_2$ in our work. This is because the *endo* geometry of $[(\eta^6\text{-}AEH_2Cl_2)FeCp](PF_6)$ places the CpFe moiety too far away for any direct hydrogen transfer from a Fe–H species to the ethene bridge. Instead, an intermolecular mechanism for hydrogenation is more likely in our case.

Assuming that an iron hydride complex is the active reducing agent in this system, it can transfer its H atom to either an $AECl_2$ molecule or an Fe–$AECl_2$ complex. We believe both routes are possible; the following comparison of anthracene and $AECl_2$ hydrogenation may be useful.

When the central ring in anthracene is reduced, some aromatic stabilization is lost. For example, hydrogenation of anthracene is less exothermic (anthracene(g) + H_2(g) → 9,10-dihydroanthracene(g), $\Delta H = -71$ kJ mol^{-1}) than that of simple alkenes (e.g. *E*-2-butene(g) + H_2(g) → butane(g), $\Delta H = -116$ kJ mol^{-1}; both values calculated from NIST data [20]). Pi coordination of anthracene to a metal atom is also expected to interfere with the aromaticity of the anthracene system. This should make hydrogenation of coordinated anthracene more favorable than that of the free hydrocarbon. Thus, if the π system undergoing hydrogenation is the same one that is coordinated to the Fe atom (as in the previous work with anthracene and its derivatives), then hydrogenation is likely to occur after coordination, on both steric and energetic grounds.

In the present case, the aromaticity of the benzene rings in $AECl_2$ should not be affected by hydrogenation of the etheno bridge. This means that the thermodynamics of hydrogenation of the etheno bridge are probably approximately the same whether or not the $AECl_2$ is coordinated to iron. Thus, our intermolecular hydrogenation can occur either before or after π coordination of $AECl_2$.

2.3. Attempts to prepare diiron complexes from $AECl_2$

The NMR spectra of the products in the $CpFe^+$–$AECl_2$ reaction showed no evidence for formation of diiron complexes. In the analogous reaction of ACl_2, which we studied previously [2], the mono- and diiron products ($[\eta^6\text{-}(AH_2Cl_2)FeCp]^+$ and $[\eta^6{:}\eta^6\text{-}(AH_2Cl_2)(FeCp)_2]^{2+}$) were readily distinguishable on the basis of the chemical shift ranges of their ^{1}H-NMR spectra: In the mono-iron complex, one set of AH_2Cl_2 aromatic resonances is shifted upfield and the other downfield relative to free AH_2Cl_2 (this is very similar to what we observe here for $[(\eta^6\text{-}AEH_2Cl_2)FeCp]^+$. In $[\eta^6{:}\eta^6\text{-}(AH_2Cl_2)(FeCp)_2]^{2+}$, on the other hand, both sets of resonances are shifted slightly downfield, and the overall spectrum is simpler because of its higher symmetry. In the present $CpFe^+$–$AECl_2$ system, we observed no ^{1}H resonances in the chemical shift range appropriate for a diiron complex.

We were interested in preparing diiron complexes from $AECl_2$, as well as in increasing the overall yield of our $CpFe^+$ complexation reaction. We attempted to do this by increasing the reaction temperature, using a refluxing mixture of methylcyclohexane and cyclohexane as solvent. (We first tried pure methylcyclohexane as solvent, but we found that its use along with a large excess of $AlCl_3$ results in partial loss of $AlCl_3$ by sublimation into the condenser. Using the mixed solvent prevents loss of $AlCl_3$ by sublimation, though it does lead to a somewhat lower reaction temperature than pure methylcyclohexane.) Our initial experiments, carried out in 1:1 (v/v) methylcyclohexane–cyclohexane, using a 4:1 molar ratio of $FeCp_2$ and $AECl_2$, led unexpectedly to the formation of $[(\eta^6\text{-}toluene)FeCp](PF_6)$ (12% yield with respect to $FeCp_2$), as identified by its ^{1}H- (compared with that reported in the literature [21]) and ^{13}C-NMR spectra. This reaction is also illustrated in Scheme 3. The ^{1}H-NMR spectrum of the crude product in d_6-acetone showed peaks at 7.1–7.7 and 6.4–6.8 ppm in the aromatic region and Cp signals at 4.5 and 5.2 ppm, as expected for mono- and bis(π-complexation) of $AECl_2$, but in very low yield (< 1%). Still higher yields (20%) of $[(\eta^6\text{-}toluene)FeCp](PF_6)$ were obtained by increasing the proportion of methylcyclohexane in the solvent (3.5:1, v/v), but the desired $AECl_2$ complexes were never produced in isolable quantities.

As described above, π complexation of polycyclic aromatic compounds is often accompanied by reduction (hydrogenation) of uncomplexed rings. These reactions are frequently carried out in cycloaliphatic solvents (e.g. cyclohexane, methylcyclohexane, tetralin); the solvents are believed to be the sources of hydrogen for the reduction of the arene ligand [14,22]. In the process, the solvent is expected to be dehydrogenated; in the present system, methylcyclohexane is likely to be dehydrogenated to toluene. This process complicates the reaction because it makes a second aromatic compound available for π complexation. Since toluene is more electron-rich than $AECl_2$, it is expected to be a better π

Table 3
Crystal data and refinement parameters for $[(\eta^6\text{-}AEH_2Cl_2)FeCp](PF_6)$[a]

Formula	$C_{21}H_{17}Cl_2F_6FeP$
Color/shape	Yellow lath
Crystal dimensions (mm)	$0.50\times0.33\times0.10$
F_W	541.1
Space group	Monoclinic, $P2_1/n$
a (Å)	10.3092 (7)
b (Å)	19.073 (2)
c (Å)	10.5886 (8)
β (°)	90.554 (6)
V (Å^3)	2082.0 (5)
Z	4
T (°C)	25
λ (Å)	0.71073
$D_{calc.}$ (g cm^{-3})	1.726
μ (cm^{-1})	11.2
Transmission coefficient	0.809–0.998
2θ range (°)	$2<2\theta<55$
h, k, l range	0–12, −18–22, −12–12
Reflections collected	6037
Unique reflections	3703
Observed reflections[b]	2294
Parameters varied	281
R[c]	0.054
R_w[d]	0.062
Max residual (e Å^{-3})	0.71

[a] Values in parentheses are estimated S.D. of the last digits.

[b] $I>3\sigma(I)$.

[c] $R=\Sigma[|F_o|-|F_c|]/\Sigma|F_o|$.

[d] $R_w=\{\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2\}^{1/2}$; $w=4F_o^2/(\sigma^2(I)+(0.02F_o^2)^2)$.

Table 4
Selected bond distances (Å) and angles (°) for $[(\eta^6\text{-}AEH_2Cl_2)FeCp](PF_6)$[a]

Bond length (Å)			
Fe–C1	2.066(6)	C3–C4	1.402(9)
Fe–C2	2.058(6)	C4–C12	1.386(8)
Fe–C3	2.056(6)	C9–C11	1.513(8)
Fe–C4	2.077(6)	C9–C13	1.497(8)
Fe–C11	2.118(5)	C9–C15	1.551(8)
Fe–C12	2.116(6)	C10–C12	1.525(8)
Fe–C17	2.046(7)	C10–C14	1.501(9)
Fe–C18	2.058(6)	C10–C16	1.565(9)
Fe–C19	2.046(6)	C11–C12	1.413(7)
Fe–C20	2.025(7)	C15–C16	1.510(9)
Fe–C21	2.031(6)	C17–C18	1.38(1)
Cl1–C1	1.735(6)	C17–C21	1.39(1)
Cl2–C8	1.728(6)	C18–C19	1.37(1)
C1–C2	1.399(8)	C19–C20	1.38(1)
C1–C11	1.399(8)	C20–C21	1.37(1)
C2–C3	1.396(9)		
Bond angle (°)			
Cl1–C1–C2	119.1(4)	C1–C11–C12	119.3(5)
Cl1–C1–C11	120.0(4)	C9–C11–C12	113.2(5)
C2–C1–C11	120.9(5)	C4–C12–C10	127.7(5)
C1–C2–C3	119.1(5)	C4–C12–C11	120.0(5)
C2–C3–C4	120.7(5)	C10–C12–C11	112.3(5)
C3–C4–C12	120.0(5)	C9–C15–C16	110.2(5)
C11–C9–C13	108.0(4)	C10–C16–C15	110.3(5)
C11–C9–C15	104.4(5)	C18–C17–C21	108.0(6)
C13–C9–C15	107.8(5)	C17–C18–C19	108.4(6)
C12–C10–C14	109.9(5)	C18–C19–C20	107.5(6)
C12–C10–C16	103.4(5)	C19–C20–C21	109.1(6)
C14–C10–C16	106.0(5)	C17–C21–C20	107.1(6)
C1–C11–C9	127.5(5)		

[a] Values in parentheses are estimated S.D. of the last digits.

ligand for $FeCp^+$. Thus, the formation of (η^6-toluene)$FeCp^+$ under our conditions is not surprising.

2.4. Crystal structure of $[(\eta^6\text{-}AEH_2Cl_2)FeCp](PF_6)$

$[(\eta^6\text{-}AEH_2Cl_2)FeCp](PF_6)$ was crystallized from $CHCl_3$/hexane as yellow needles. Crystallographic data and selected bond distances and angles are listed in Tables 3 and 4; full details have been deposited in the Cambridge Crystallographic Database [23]. The $[(\eta^6\text{-}AEH_2Cl_2)FeCp]^+$ cation has the *endo* geometry (see ORTEP [24] drawing in Fig. 1), i.e. with the CpFe moiety located inside the fold of the AEH_2Cl_2 ligand. The formation of the *endo* isomer agrees with the geometry shown by other monometalated complexes of bent diarenes, in which, in the absence of other directing groups (e.g. exocyclic double bonds), the concave face of the arene is favored [12]. The angles about the methine carbons C9 (C11–C9–C15, C13–C9–C15) and C10 (C12–C10–C16, C14–C10–C16) show a bending of 3.0 (4)° of the methylene bridge towards the complexed ring of AEH_2Cl_2, similar to that observed in the *endo* $Cr(CO)_3$ complex of the parent AEH_2 (1.5°) [25]. The bond length in the ethano bridge (C15–C16) is close to that expected for a C–C single bond and close to the values reported for the equivalent C–C bonds in *endo*- and *exo*-(η^6-AEH_2)$Cr(CO)_3$ [25]. The average carbon–carbon distance for the complexed ring of AEH_2Cl_2 (1.399 Å) is slightly longer than those for the uncomplexed ring (1.382 Å) and the parent $AECl_2$ (1.384 Å) [9] but close to the value exhibited by the

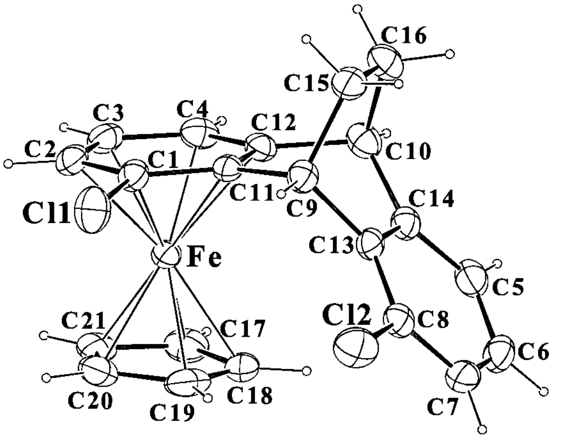


Fig. 1. ORTEP [24] diagram of [*endo*-(η^6-(1,8-dichloro-9,10-dihydro-9,10-ethanoanthracene))FeCp]$^+$, with ellipsoids at the 20% probability level.

complexed ring of *endo*-(η^6-AEH_2)$Cr(CO)_3$ (1.406 Å). The aromatic rings of the AEH_2Cl_2 ligand are essentially planar (no deviation larger than 0.013 Å). The Cl atoms lie out of these planes, with Cl1 showing a noticeable deviation (0.138 (2) Å) on the same side as the Fe atom, and Cl2 displaced very slightly away from the Fe center (0.023 (2) Å). The C–Cl distances in [(η^6-AEH_2Cl_2)FeCp](PF_6) are close to those in $AECl_2$ (1.741 (2) and 1.744 (2) Å) [9] and [(η^6-AH_2Cl_2)FeCp](PF_6) (1.734 (4) and 1.739 (5) Å) [2]. Other bond distances and angles for the complexed arene ligand in [(η^6-AEH_2Cl_2)FeCp](PF_6) are similar to those found in [(η^6-AEH_2)$Cr(CO)_3$]. The Fe–C_{arene} bond distances are normal (average 2.091 Å). The distances between the Fe atom and the Cp ring plane (1.6699 (8) Å) and between the Fe and the coordinated arene ring plane (1.5408 (8) Å) are within the range observed in other (η^6-arene)$FeCp^+$ complexes [2,26–29]. The coordinated arene and Cp ring planes form a dihedral angle of 5.1 (15)°, similar to values observed in the other (η^6-arene)$FeCp^+$ complexes (1.3–4.1°).

3. Conclusions

The ligand substitution reaction of ferrocene with $AECl_2$ in the presence of $AlCl_3$ affords the mono-iron complex [(η^6-AEH_2Cl_2)FeCp](PF_6), in which reduction of the C=C bridge of the arene ligand takes place. X-ray and spectral analysis confirm the *endo* geometry for the iron complex. Diiron complexes could not be isolated under our reaction conditions. This new complex may react more cleanly with carbon nucleophiles. However, such a reaction will not lead to the desired substitution of both Cl atoms, as was originally intended, because only one ring of the AEH_2Cl_2 ligand is complexed to $CpFe^+$. Therefore, we are also pursuing alternate strategies toward 1,8-difunctionalization of anthracene [1].

4. Experimental

1,8-Dichloroanthracene (ACl_2) was prepared by reduction of 1,8-dichloroanthraquinone in Zn/NH_3 (aq), followed by treatment with HCl, according to literature procedures [30,31]. Other chemicals and solvents were reagent grade and were used as received. NMR spectra were recorded by using Bruker AC 200 and AM 400 spectrometers. An HP 5971 instrument was used for GC–MS.

4.1. 1,8-Dichloro-9,10-ethenoanthracene ($AECl_2$)

Following the method described by Paquette et al. [8], a solution of ACl_2 (3.7 g, 15 mmol) and phenyl vinyl sulfoxide (2.96 ml, 22.2 mmol) in chlorobenzene (25 ml) was refluxed under N_2 for 8 days. The resulting brown solution was concentrated to two thirds of its volume and stored at −15°C for 2 days. Light brown crystals were collected, washed with cold methanol and CCl_4, dissolved in acetone, and the solution flooded with water, to precipitate $AECl_2$ as a white solid (1.2 g, 30% yield). Crystallization from CCl_4/CH_2Cl_2 by slow evaporation afforded $AECl_2$ as colorless needles. M.p. 178–179°C. EI-MS *m*/*z* (%): 276, 274, 272 (M^+, 73); 239, 237 ($M^+ - Cl$, 100); 202 ($M^+ - 2Cl$, 95); 176 ($M^+ - 2Cl - C_2H_2$, 13); 118 (19); 101 (20); 100 (22).

4.2. Attempted preparation of [η^6-(AEH_2Cl_2)FeCp](PF_6) in methylcyclohexane–cyclohexane

A mixture of $AECl_2$ (0.30 g, 1.1 mmol), ferrocene (0.83 g, 4.5 mmol), $AlCl_3$ (1.2 g, 9.0 mmol) and Al (0.12 g, 4.4 mmol) in methylcyclohexane–cyclohexane (3.5:1, v/v, 70 ml) was heated at reflux under N_2 for 38 h. The resulting material, consisting of a yellow solution and a dark precipitate, was allowed to cool to room temperature under N_2 and then hydrolyzed with 5–10 ml of ice water. The organic layer was separated and extracted with H_2O, and the aqueous layers were combined, washed several times with hexane and filtered into a saturated aqueous solution of NH_4PF_6 (0.41 g, 2.5 mmol) to yield a yellow–green precipitate. This material contained [(η^6-toluene)FeCp](PF_6) and a small amount of Fe–$AECl_2$ complex ($<1\%$ by ^{1}H-NMR). Crystallization of this solid from acetone/diethyl ether afforded pure [(η^6-toluene)FeCp](PF_6) (0.32 g, 20% with respect to $FeCp_2$) as yellow needles. In another experiment under the same reaction conditions but using methylcyclohexane–cyclohexane (1:1, v/v) as solvent, [(η^6-toluene)FeCp](PF_6) was obtained in 12% yield; again, no other Fe complexes could be isolated. ^{1}H-NMR ($CDCl_3$, 200 MHz): δ 6.40 (s, 5 H), 5.17 (s, 5H), 2,55 (s, 3H). ^{13}C-NMR ($CDCl_3$, 50 MHz) δ 104.8, 89.6 (CH), 88.6 (CH), 87.4 (CH), 77.8 (Cp), 20.8 (CH_3).

4.3. Successful preparation of [η^6-(AEH_2Cl_2)FeCp](PF_6) in cyclohexane

A mixture of $AECl_2$ (0.21 g, 0.73 mmol), ferrocene (2.1 g, 11 mmol), $AlCl_3$ (2.72 g, 20.4 mmol) and Al (0.28 g, 10 mmol) in cyclohexane (23 ml) was refluxed under N_2 for 72 h. The resulting material was worked up as described above to give [(η^6-AEH_2Cl_2)FeCp](PF_6) as a greenish precipitate (0.14 g, 36%). Purification by crystallization from $CHCl_3$/hexane yielded the iron complex as yellow needles.

4.4. Crystal structure determination of [(η^6-AEH_2Cl_2)FeCp](PF_6)

Intensity data were collected on an Enraf-Nonius CAD4 diffractometer equipped with Mo–K_α radiation and a graphite monochromator, by $\omega - 2\theta$ scans of variable rate. Data reduction included corrections for background, Lorentz, polarization, decay, and absorption effects. Absorption corrections were based on ψ scans, and linear decay corrections amounted to 3.1% of intensity. The structure was solved by heavy-atom methods and refined by full-matrix least-squares, treating non-hydrogen atoms anisotropically, using the Enraf-Nonius MolEN programs [32]. Hydrogen atoms were placed in calculated positions. Details of data collection and refinement are given in Table 3.

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