Synthesis of an Anthracenebis(beta-Ketoenamine) Ligand and Its Cofacial Binuclear Metal Complexes.

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SYNTHESIS OF AN ANTHRACENE BIS(β-KETOENAMINE) LIGAND AND ITS COFACIAL BINUCLEAR METAL COMPLEXES

A Dissertation

Submitted to the Graduate Faculty of the Louisiana State University and Agricultural and Mechanical College in partial fulfillment of the requirement for the degree of Doctor of Philosophy in The Department of Chemistry

by
Maria del Rosario Benites
B.S., Pontificia Universidad Católica del Perú, 1990
December 1995
A mis padres
A mis hermanos Pilar, Lor y Nana
A Angelita y Martín
A José
Acknowledgments

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Abstract

Following our studies of cofacial binuclear transition metal complexes, such as Cu₂(XBA)₂ (see below), we became interested in the synthesis of a more rigid ligand, ABIH₂ which contains a 1,8-anthracene bridge. This new ligand, whose chelating moieties are 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.

\[ \text{Cu}_2(\text{XBA})_2, \quad \text{ABIH}_2, \quad 1 \]

Three routes have been pursued to synthesize the anthracene-based ligand. Using organometallic derivatives of 3,5-dimethylisoxazole as acetylacetone synthons, the bis(β-ketoenamine) ABIH₂ was successfully obtained. Two novel cofacial binuclear complexes 1, with MLₙ = (η⁴-1,5-cyclooctadiene)iridium and dicarbonylrhodium, have been synthesized. They are the first members of a new family of cofacial bimetallic complexes that may provide new models for redox-active enzymes, such as cytochrome oxidase.
Chapter 1

Cofacial Binuclear Metal Complexes Based on Bis(β-diketone) Ligands

1.1. Introduction

In recent years, our group has been investigating the chemistry of cofacial binuclear transition-metal complexes derived from bis(β-diketone) ligands, see example in Figure 1.1 [1.1-1.5]. The cofacial geometry is attractive in these systems because of the possibility of intramolecular binding of small redox-active substrates, which can be further activated by the metal atoms, as well as functional group substituents on the bridging groups. The use of bis(β-diketones) as ligands for these complexes offers two major advantages: first, β-diketones form planar complexes with a variety of metal ions, and second, their synthetic versatility provides an easy access to the modification of these chelating ligands by introduction of N and S atoms to the keto groups.

![Structure of cofacial binuclear complex derived from bis(β-diketone) ligand](image)

Figure 1.1 Structure of cofacial binuclear complex derived from bis(β-diketone) ligand
We have been interested in the use of these cofacial binuclear metal complexes as models for multi-metal redox-active enzymes. The study of the redox properties of these complexes will help us to understand the conditions that favor multielectron-transfer activity in enzymes, such as cytochrome oxidase, and also to develop new catalysts that promote electron transfer in a substrate molecule.

1.2. Cytochrome Oxidase

The terminal oxidase in respiration, cytochrome oxidase, occurs in all animals, plants, certain bacteria and yeasts. The enzyme spans the inner mitochondrial membrane. It is responsible for catalyzing the four-electron reduction of dioxygen to water, the terminal reaction in the mitochondrial electron transport chain [16-19]. This is accomplished by accepting four reducing equivalents from cytochrome $c$ and transferring them to the bound dioxygen, forming water:

$$4 \text{cyt} c^{2+} + \text{O}_2 + 4 \text{H}^+ \rightarrow 4 \text{cyt} c^{3+} + 2 \text{H}_2\text{O}$$

The physiological importance of this redox process is that free energy is released which can be stored by the conversion of two equivalents of ADP to ATP.

Each molecule of cytochrome oxidase contains two hemes ($a$, $a_1$) and two copper centers ($\text{Cu}_A$, $\text{Cu}_H$). The high resolution x-ray structure of the metal sites of the oxidized form of bovine heart cytochrome oxidase has been reported recently [110]. The $\text{O}_2$ binding site contains heme $a_1$ iron and copper atoms ($\text{Cu}_H$) with an interatomic distance of 4.5 Å and no bridging ligand. The electron transfer path within the enzyme has essentially been established as follows: cytochrome $c \rightarrow \text{Cu}_A \rightarrow$ heme $a \rightarrow$ the Fe$_{a_1}$-$\text{Cu}_H$ $\text{O}_2$ binding site [111] (The possibility for a direct electron transfer from $\text{Cu}_A$ to the Fe$_{a_1}$-$
(Cu site can not be excluded.) When the fully reduced (Fe$^{II}$-$\text{Cu}^{I}$-$\text{Fe}^{II}$-$\text{Cu}^{I}$) enzyme reacts with $O_2$, the following transformations are believed to occur in the Fe$_{\alpha_1}$-Cu$_{\beta_1}$ site [1.12]:

$$[\text{Fe}_{\alpha_1}^{II} \cdot \text{Cu}_{\beta_1}]^{3+} + O_2 \rightarrow [\text{Fe}_{\alpha_1}^{III} \cdot \text{O} \cdot \text{O} \cdot \text{Cu}_{\beta_1}]^{3+} \quad (1)$$

$$[\text{Fe}_{\alpha_3}^{III} \cdot \text{O} \cdot \text{O} \cdot \text{Cu}_{\beta}$]^{3+} + H^+ + e^- \rightarrow [\text{Fe}_{\alpha_3}^{IV} = \text{O} \cdot \text{HO} \cdot \text{Cu}_{\beta}]^{3+} \quad (2)$$

$$[\text{Fe}_{\alpha_3}^{IV} = \text{O} \cdot \text{HO} \cdot \text{Cu}_{\beta}]^{3+} + 3 H^+ + e^- \rightarrow [\text{Fe}_{\alpha_3}^{III} \cdot \text{Cu}_{\beta}]^{3+} + 2 H_2O \quad (3)$$

Despite this progress in understanding the reaction steps and coordination environments in the enzyme, the specific features of the heme $\mu_\gamma$-$\text{Cu}_{\beta_1}$ region that contribute to its high multielectron-transfer activity are not yet clear.

1.3. Synthetic Analogos of Cytochrome Oxidase

Among the synthetic inorganic complexes that have been studied as models of cytochrome oxidase are cofacial diporphyrin complexes 1-4 (Figure 1.2) and less symmetrical Fe-Cu complexes such as 5-7 (Figure 1.3). These complexes are based on specifically derivatized porphyrin molecules, which are difficult to synthesize and do not lend themselves readily to variations in metal coordination environment. Cobalt atoms have been extensively used for the metal centers of the porphyrin rings because they have the most positive M(II)/M(III) redox potential that still binds $O_2$ with measurable affinity [1.13].

The diporphyrin complexes 1-3 ($M = \text{Co}$) [1.13-1.17] are electrocatalysts for reduction of $O_2$ to $H_2O$, suggesting that a cofacial geometry of the two metal sites and a short M-M distance (3.4-4.6 Å) are necessary to stabilize intermediates and guide the reaction along the four-electron path [1.18-1.20]. However, this catalytic activity occurs
only when they are adsorbed on electrode surfaces in "multilayers" of 30 or more molecules [1.18]. The more rigid anthracene and biphenylene bridging ligands in complexes 2 and 3 are the most robust and chemically inert. Bridged oxo and superoxo complexes have also been assembled using the 4,5-xanthene bridged diporphyrin 4 (M = Co, Fe) [1.21].
The oxo-bridged heme-copper compounds 5 (Ar = C₆H₄-2,6-F₂) [1 22-1 24] and 6 [1 25], containing the [Fe³⁺-O-Cu²⁺] bridge unit, have been recently reported as models for the oxidized (spin-coupled) form of the enzyme. Compound 5 was obtained by coupling of the Cu(II)-OH complex with the Fe(III) porphyrin salt, while the bridged assembly 6 was generated directly from the reaction of O₂ with the reduced Cu(I) and
Fe(II) complexes at −80 °C. Alternatively, an O₂ adduct (presumably a μ-peroxo species) has been synthesized using a Cu binding site covalently linked to a porphyrin (complex 7) [1.26]. A preliminary characterization of its O₂ adduct, and demonstration of a stoichiometric cycle which reduces O₂ by four electrons have been reported.

1.4. Previous Work on Bis(β-diketone) Ligands

A variety of bis(β-diketone) ligands based on the m-xylylene bridging group (XBAH₂) have been synthesized by our group [1.2]. The binuclear complexes derived from these ligands, such as Cu₂(XBA)₂, undergo only irreversible electrochemical reactions under extreme potentials. However, conversion of the bis(β-diketones) to bis(β-ketoenamine) ligands, by treatment with NH₃, improves the redox properties of the binuclear complexes [1.3]. The resulting complexes, called M₂(BBI)₂ (M = Cu, Ni, Pd, see Figure 1.4) exhibit multi-electron redox activity that is not observed in analogous mononuclear systems M(acim)₂ (shown in Figure 1.4). First, whereas the mononuclear complexes decompose rapidly after oxidation, the Ni and Cu binuclear species undergo reversible two-electron oxidation. This suggests that the rigid structure improves the stability of the complexes when they are oxidized. In addition, oxidation is substantially easier for the binuclear palladium complex than for Pd(acim)₂. This latter observation indicates substantial stabilization of the singly oxidized complex, possibly through formation of a delocalized partial Pd-Pd bond.

Preliminary experiments suggested that Co⁰₂(BBI)₂ reacts with O₂ to produce a green diamagnetic product, possibly a μ-peroxo complex formed by intramolecular
Figure 1.4. Structures of metallic complexes derived from mono- and bis(β-ketoenamine) (BBIH$_2$) ligands

[Diagram of M$_2$(BBI)$_2$ and M(acim)$_2$]

coordination of O$_2$ to the binuclear complex [1,27]. However, attempts to isolate these species failed.

A larger bis(β-diketone) ligand, based on the 2,7-naphthalenediylbis(methylene) bridge (NBAH$_2$, Figure 1.5), has also been synthesized by our group [1,4,1,5]. Its copper complex Cu$_2$(NBA)$_2$ has shown to be capable of intramolecular coordination with a variety of Lewis bases as guest molecules, the product of its reaction with Dabco (1,4-diazabicyclo[2.2.2]octane) is shown in Figure 1.5.

[Diagram of Cu$_2$(NBA)$_2$(μ-Dabco)]
1.5. Synthesis of New Anthracene-based Bis(β-diketone) Ligand

Previous work on cofacial binuclear transition metal complexes derived from bis(β-diketone) ligands has demonstrated several types of behavior that are similar to those observed in the enzymes, e.g. distinct types of redox activity that are not present in the analogous mononuclear complexes and selective intramolecular complexation reactions with small guest molecules. However, the need for two bis(β-diketone) ligands, in order to enforce the desired cofacial geometry, restricts our area of research to M(diketonato)₂ and M(ketoenamine)₂ complexes. The use of a more conformationally rigid ligand, with its β-diketone moieties constrained to be cofacial, would eliminate the need for a second bridging group. Chang et al. have demonstrated this principle in their studies of diporphyrins containing 1,8-disubstituted anthracene and biphenylene [113-117] and 4,5-disubstituted xanthene [121] bridges. 1,8-Anthracenediylbis(acetylacetone) (ABAH₂, see Figure 16) and its bis(β-ketoenamine) ABIH₂ derivative are important synthetic goals. These ligands should make the synthesis of binuclear complexes easier, since their assembly will not depend on two moles each of metal and ligand reacting in the proper order, and also because the possibility of polymer formation will be ruled out. We will be able to obtain a wider variety of bimetallic complexes by employing a big selection of ligands along with the binucleating anthracene-based ligands. And finally, these ligands represent the simplest route to substantially different environments for the two metal atoms in a heterodinuclear complex. Examples of the complexes we plan to synthesize using these ligands are shown in Figure 17. The more
open structure of these complexes should provide for better access of substrate molecules to the intramolecular binding site.

Figure 1.6. Design of new binucleating ligands based on 1,8-disubstituted anthracenes

The Fe-Cu complex shown in Figure 1.7 could serve as a model for the O$_2$-binding site in cytochrome oxidase. The synthesis of the more rigid anthracene-based ligands should allow for flexibility in molecular and electronic structure, so as to approach as closely as possible to the chemical function of the enzyme active sites. In addition to the applications to cytochrome oxidase, the cavities in these complexes (M-

Figure 1.7. Cofacial binuclear complexes that could be synthesized using ABAH$_2$ or ABIH$_2$ ligands
M 4.5\textperiodcentered 5.0 \textAA) should also be well suited for binding and activating other guest molecules, such as NO$_2$, N$_2$H$_4$ and C$_2$H$_4$.

1.6. Approaches to the Synthesis of Anthracene-based Ligands

The preparation of previous bis(\beta-diketone) ligands has involved alkylation of the 2,4-pentanedioniate ion (acac) with organic dihalides [13,15]. However, this same strategy cannot be followed to prepare ABAH$_2$ because aryl halides are not ordinarily susceptible to attack by nucleophiles such as acac. Not even the highly electron-withdrawing NO$_2$ groups in 1,8-dichloro-4,5-dinitroanthraquinone activate the aromatic rings sufficiently towards acac [128].

Figure 1.8 outlines the three synthetic routes we have pursued for preparing ABAH$_2$ and ABIH$_2$, which are described extensively in the following chapters:

a) via $\pi$ complexation of 1,8-dichloroanthracene derivatives to CpFe' moieties, in order to enhance the substitution of chlorine atoms by carbon nucleophiles (Chapters 2 and 3),

b) via formation of the intermediate 1,8-diacetonylanthracene (Chapter 4), which could further undergo $\gamma$-acylation to give the bis(\beta-diketone) ABAH$_2$, and

c) via palladium-catalyzed cross coupling between 1,8-disubstituted anthracene derivatives and organometallic reagents of 3,5-dimethylisoxazole, used as an acac synthon (Chapter 5). Using this last strategy, we have successfully synthesized the bis(\beta-ketoenamine) ABIH$_2$. 
Finally, we present in Chapter 6 the preparation of the cofacial bis($\eta^4$-1,5-cyclooctadiene)iridium) and bis(dicarbonylrhodium) complexes of ABIH$_2$.
1.7. References


Chapter 2

Reduction During π-(Cyclopentadienyliiron) Complexation of 1,8-Dichloroanthracene

2.1. Introduction

We were interested in the preparation of ABAH$_2$ from 1,8-dichloroanthracene (ACI$_2$). 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 et al. [2.1.2.2] have reported the use of π complexation to CpFe$^+$ to convert chlorobenzene into 3-phenyl-2,4-pentanedione.

![Figure 2.1 Synthesis of 3-phenyl-2,4-pentanedione via π-(cyclopentadienyliiron) complexation of chlorobenzene](image)

Although these nucleophilic substitution reactions have been well studied for benzene compounds, there has been no attempt to reproduce them in condensed polycyclic arenes. Figure 2.2 contains our proposed strategy for extending this synthesis to ABAH$_2$ from ACI$_2$. 

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Following this approach, we report the preparation of the mono- and bis(cyclopentadienyliron) complexes of 1,8-dichloro-9,10-dihydroanthracene \([\eta^6-(\text{AH}_2\text{Cl}_2)(\text{CpFe})](\text{PF}_6)\) (I) and \([\eta^6:\eta^6-(\text{AH}_2\text{Cl}_2)(\text{CpFe})](\text{PF}_6)\) (II). In this reaction, \(\pi\) complexation of \(\text{ACl}_2\) is accompanied by reduction of its central ring in forming the two Fe complexes.

### 2.2. Results and Discussion

#### 2.2.1. Synthesis of \([\eta^6-(1,8\text{-dichloro}-9,10\text{-dihydroanthracene})(\text{FeCp})](\text{PF}_6)\) (I) and \([\eta^6:\eta^6-(1,8\text{-dichloro}-9,10\text{-dihydroanthracene})(\text{FeCp})_2](\text{PF}_6)_2\) (II)

One of the most extensively studied families of metal \(\pi\)-arene complexes for the formation of C-C bonds is \((\eta^6\text{-haloarene})\text{Cr(CO)}_3\) [2.3]. In the early stages of this investigation, we pursued the \(\pi\) complexation of 1,8-dichloroanthracene (ACl\(_2\)) to this Cr(CO)\(_3\) moiety, by reaction of Cr(CO)\(_6\) with ACl\(_2\) in n-butyl ether and THF. However, the reaction mixture decomposed after a few hours and no product could be isolated. We later found that although \((\eta^6\text{-anthracene})\text{Cr(CO)}_3\) has been reported [2.4], it is very
unstable. Also, no bis-coordinated \((\eta^6,\eta^6\text{-anthracene})(\text{Cr(CO)}_3)_2\) appears to have been prepared.

We then turned our attention to the \((\eta^6\text{-haloarene})(\text{FeCp})^+\) system, due to its ease of formation and due to the greater susceptibility of its coordinated arene to nucleophilic attack. Following the method of Nesmeyanov et al. [2.5], we prepared the cationic complexes \([\eta^6\text{-}(\text{AH}_2\text{Cl}_2)\text{CpFe}]^+\) and \([\eta^6\cdot\eta^6\text{-}(\text{AH}_2\text{Cl}_2)(\text{CpFe})_2]^+\) by \(\text{AlCl}_3\)-induced cleavage of ferrocene in the presence of \(\text{ACl}_2\) and \(\text{Al}\) in refluxing cyclohexane or methylcyclohexane. Further treatment with \(\text{NH}_4\text{PF}_6\) led to the precipitation of the hexafluorophosphate salts I and II (Figure 2.3).

![Figure 2.3. Synthesis of 1,8-dichloro-9,10-dihydroanthracene complexes I and II](image)

No dehalogenation of the arene occurred under our reaction conditions \((T = 81\) or \(101\) °C). However, when we increased the reaction temperature to 135-155 °C, using
decalin as the solvent, no product could be obtained; this may be due to decomposition of AC\textsubscript{12} under the more vigorous conditions.

Our initial experiments, using a 1:1 molar ratio of AC\textsubscript{12} and FeC\textsubscript{2}, led to compound I in 6\% yield. Better yields were obtained by using a large excess of FeC\textsubscript{2}, AlCl\textsubscript{3} and Al, leading to I and II in 13 and 26\% yield, respectively. Separation of these compounds was possible on the basis of their solubilities. Both of them are soluble in polar solvents, such as acetone, CH\textsubscript{3}CN and CH\textsubscript{3}OH, but only I is soluble in CHCl\textsubscript{3}. Thus, treating the crude product with CHCl\textsubscript{3}, 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 1,8-dichloro-9,10-dihydroanthracene (AH\textsubscript{2}Cl\textsubscript{2}) with small traces of AC\textsubscript{12}, as identified by \textsuperscript{1}H NMR, solid AH\textsubscript{2}Cl\textsubscript{2} and its solutions slowly oxidize in air to form AC\textsubscript{12}.

\textsuperscript{1}H and \textsuperscript{13}C NMR data for I and II and several reference compounds are presented in Tables 2.1 and 2.2. In general appearance, the spectra of I and II are similar to those of the analogous mono- and diiron complexes of 9,10-dihydroanthracene (AH\textsubscript{2}) [2,6]. For both complexes I and II the \textsuperscript{1}H and \textsuperscript{13}C resonances of the complexed ring(s) of AH\textsubscript{2}Cl\textsubscript{2} are shifted upfield compared to those of the parent AH\textsubscript{2}Cl\textsubscript{2}. There is also a downfield shift of the non-coordinated ring and methylene atoms of AH\textsubscript{2}Cl\textsubscript{2} in complex I compared to the free arene. Bis-coordination in complex II increases the downfield shift of the methylene and Cp ring protons and carbons.
# Table 2.1. $^1$H NMR data $^a$ of complexes I, II and other related compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>uncomplexed arene</th>
<th>complexed arene</th>
<th>Cp</th>
<th>CH$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>I</strong>$^b$</td>
<td>7.53 (m,3H)</td>
<td>6.92 (t,1H, 3.8)</td>
<td>4.91 (s,5H)</td>
<td>4.86 (d,1H, 19.6)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6.65 (d,2H, 3.9)</td>
<td>4.43 (d,1H, 18.5)</td>
<td>4.31 (dd,1H, 18.4,2.6)</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>4.07 (dd,1H, 19.6,2.5)</td>
<td></td>
</tr>
<tr>
<td><strong>II</strong></td>
<td>7.03 (t,2H, 3.6)</td>
<td>6.74 (d,4H, 3.6)</td>
<td>5.25 (s,10H)</td>
<td>4.97 (s,2H)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>4.94 (s,2H)</td>
<td></td>
</tr>
<tr>
<td><strong>AH$_2$Cl$_2$</strong></td>
<td>7.29 (m,6H)</td>
<td></td>
<td></td>
<td>4.12 (m,4H)</td>
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<tr>
<td><strong>ACl$_2$</strong></td>
<td>8.15 (d,2H, 8.5)</td>
<td></td>
<td></td>
<td>9.17 (s,1H)</td>
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<tr>
<td></td>
<td>7.77 (dd,2H, 0.9,7)</td>
<td></td>
<td>8.72 (s,1H)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>7.56 (dd,2H, 8,5,7)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(AH$_2$)[FeCp]$^c$</td>
<td>7.51 (m,4H)</td>
<td>6.51 (m,4H)</td>
<td>4.67 (s,5H)</td>
<td>4.12 (s,4H)</td>
</tr>
<tr>
<td>(AH$_2$)[FeCp]$_2$$^c$</td>
<td>6.60 (m,8H)</td>
<td>5.02 (s,10H)</td>
<td>4.55 (s,4H)</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ 200 MHz and in acetone-d$_6$, unless otherwise noted. $\delta$/ppm vs. TMS ($\delta$/Hz in parentheses). $^b$ 250 MHz. $^c$ In DMSO-d$_6$, from ref. [26].

Reduction of ACI$_2$ during $\pi$ complexation is evidenced by signals in both $^1$H NMR ($\delta$ 4-5 ppm) and $^{13}$C NMR (30-35 ppm), indicative of the methylene groups in the $\pi$-coordinated AH$_2$Cl$_2$. This was confirmed in both iron compounds by using the DEPT experiment.

The $^1$H 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. If the two CpFe groups were *cis*, then each of the two
### Table 2.2. $^{13}$C NMR data $^a$ of complexes I, II and other related compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>uncomplexed arene</th>
<th>complexed arene</th>
<th>Cp</th>
<th>CH$_2$</th>
</tr>
</thead>
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</tr>
<tr>
<td>I $^b$</td>
<td>136.9, 133.8, 131.6.</td>
<td>107.3, 101.0, 98.0.</td>
<td>79.7</td>
<td>34 9, 29 9</td>
</tr>
<tr>
<td></td>
<td>129.8(CH), 129.0(CH),</td>
<td>88.3(CH), 87.4(CH),</td>
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<tr>
<td></td>
<td>127.7(CH)</td>
<td>87.1(CH)</td>
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<tr>
<td>II $^b$</td>
<td></td>
<td>119.9, 107.4, 99.5.</td>
<td>81.2</td>
<td>33 2, 30 9</td>
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<tr>
<td></td>
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<td>89.0(CH), 88.2(CH),</td>
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</tr>
<tr>
<td></td>
<td></td>
<td>87.4(CH)</td>
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<tr>
<td>AH$_2$Cl$_2$ $^c$</td>
<td>127.2, 127.1, 125.9,</td>
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<td>36.1</td>
<td>30 0</td>
</tr>
<tr>
<td></td>
<td>125.0</td>
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</tr>
<tr>
<td>ACl$_2$ $^{b,d}$</td>
<td>133.8, 132.5, 130.3,</td>
<td>102.7, 86.3(CH),</td>
<td>75.8</td>
<td>33 5</td>
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<td>85.7(CH)</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>127.5(CH), 127.0(CH),</td>
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<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>120.8(CH)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(AH$_2$)[FeCp]$^+$ $^*$</td>
<td>134 1, 127.2(CH),</td>
<td>99.0, 86.5(CH),</td>
<td>77.1</td>
<td>31 9</td>
</tr>
<tr>
<td></td>
<td>126.7(CH)</td>
<td>86.3(CH)</td>
<td></td>
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</tbody>
</table>

$^a$ 200 MHz and in acetone-$d_6$, unless otherwise noted. $^b$ Assignments were made using DEPT experiment. $^c$ In CDC$_1$, $^d$ 250 MHz. $^*$ In DMSO-$d_6$, from ref. 2.6.

CH$_2$ groups would contain one exo and one endo proton, thus, two AB quartets should result.

In addition to the spectral data, hydrogenation of the arene ligand was established by the X-ray analysis of I (see Section 2.2.3). The reduction of ACl$_2$ during $\pi$ 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) [2.6-2.9]. In the case of anthracene, the mono- and diiron complexes of 9,10-dihydroanthracene (AH₂) have been prepared [2.6]. Reaction of Cp*Fe(CO)₂Br (Cp* = η⁵-C₅H₅) with anthracene in the presence of AlCl₃ [2.10] afforded a 6:4 mixture of (η⁶-1,2,3,4-tetrahydroanthracene)[FeCp*]⁺ and (η⁶-9,10-dihydroanthracene)[FeCp*]⁺. In this case, the more sterically hindered Cp* ligand may partially inhibit the hydrogenation of the 9 and 10 positions of anthracene, favoring reaction instead at the more remote 1-4 positions. Two radical mechanisms, involving Fe(III) or Fe(I) 17-electron intermediates, have been proposed [2.9-2.11], in which the formation of a Fe-H species leads to a stereospecific transfer (cis and endo) of the hydrogen atom to the arene.

2.2.2. Attempted Nucleophilic Substitution of I and II with acac

We explored the nucleophilic substitution reaction of π-complexed AC₁₂ in compounds I and II with acac. Based on the products described by Sutherland et al [2.1,2.2], a series of reactions were carried out under Ar treating either I or II with acac-H in the presence of a base (KF supported on celite or K₂CO₃), with different solvents (DMF, THF and CH₃CN) at room temperature or -20 °C (Fig. 2.4). However, in all cases the reaction mixture decomposed, turning blue immediately after the iron complex was added. The products obtained were FeCp₂, AC₁₂, AH₂Cl₂ and Fe(acac)₃, as shown by ¹H NMR and IR. Two other enolate carbanions were also tested: the conjugate bases of dimethyl malonate and diethyl ethylmalonate, with no net reaction.
Sutherland et al. have reported that ($\eta^6$-arene)[FeCp]$^+$ complexes such as ($\eta^6$-fluorene)[FeCp]$^+$ and ($\eta^6$-AH$_2$)[FeCp]$^+$ [212-214], in which the arene ligand has an $\alpha$-carbon substituent containing one or more hydrogens, can be deprotonated with base (e.g. t-BuOK, K$_2$CO$_3$, NaNH$_2$) to give zwitterionic species. These zwitterions can further react *in situ* as nucleophiles. However, the need for low reaction temperatures (\(-20^\circ\)C) during deprotonation of ($\eta^6$-AH$_2$)[FeCp]$^+$ [212] may suggest the unstability of its zwitterion. A possible explanation for the decomposition of I and II during our nucleophilic reaction conditions may come from the deprotonation of the AH$_2$Cl$_2$ ligand to give a less electrophilic and relatively unstable zwitterionic compound, which could then suffer attack by the strong chelating acac to the iron center to yield Fe(acac)$_2$ and the free arene. Further oxidation of these compounds in air during work-up may account for the isolation of Fe(acac)$_3$, AH$_2$Cl$_2$ and AC$_2$ as the final products.
2.2.3. Crystal Structures of Mono- and Diiron Complexes

Complex I was crystallized in two forms, with space groups Pbc a (Ia) and P 1 (Ib), by layering solutions of I in CHCl₃ with ether and hexane, respectively. The Ia form contains a poorly defined CHCl₃ molecule. This diffuse solvent molecule may be responsible for the somewhat poorer structural results (as judged by agreement indices R, goodness of fit, and esd values for atomic coordinates and displacement parameters) obtained for Ia than for Ib. A view of the cation in Ib with the atom labelling scheme is shown in Figure 2.5. Crystallographic data are summarized in Table 2.3. Selected bond distances and angles of the two forms are listed in Table 2.4.

Both crystal forms show an endo conformation for compound I, where the FeCp moiety is located inside the fold of the AH₂Cl₂ ligand. The most significant difference between the two crystal forms of I is the dihedral angle formed by the benzene rings of the AH₂Cl₂ ligand: the uncomplexed ring in AH₂Cl₂ 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 AH₂ (145°) [2 15,2 16]. Previous studies of CpFe⁺ compounds of bent heterocyclic systems related to AH₂, containing two heteroatoms at the 9,10-positions [2 17,2 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 AH₂Cl₂ ligand shows the same or even greater degree of folding in comparison to free AH₂. The difference in the dihedral angles of the
Figure 2.5 Ortep diagram of $\eta^5\cdot(1,8\text{-dichloro-9,19\text{-dihydroanthracene}})\text{FeCp}^+$ of complex I
Table 2.3 Crystal data and summary of intensity data collection and structure refinement

<table>
<thead>
<tr>
<th>Compound</th>
<th>[(AH_2Cl_2)(CpFe)]PF_6 · CHCl_3 (Ia)</th>
<th>[(AH_2Cl_2)(CpFe)]PF_6 (Ib)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>C_{20}H_{16}Cl_3FeF_6</td>
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$2\theta$ range (°)  
\[ 2 < 2\theta < 50 \quad 2 < 2\theta < 50 \]

Range of $h,k,l$  
\[ 12, 18, 35 \quad 9, \pm 11, \pm 15 \]

Unique reflections  
\[ 4272 \quad 3472 \]

Observed reflections  
\[ 2306 \quad 2660 \]

No of parameters varied  
\[ 298 \quad 263 \]

GOF $^b$  
\[ 3.454 \quad 2.297 \]

$R^c$  
\[ 0.074 \quad 0.043 \]

$R_w$ $^{d}$  
\[ 0.085 \quad 0.051 \]

Max. shift/esd  
\[ <0.01 \quad 0.01 \]

Largest feature final diff. map  
\[ 0.90 \text{ e}^{-}\text{Å}^{-1} \quad 0.52 \text{ e}^{-}\text{Å}^{-1} \]

\[ ^a \sigma(I) \quad ^b \text{GOF} = \left( \frac{\sum w(|F_o|^2 - |F_c|^2)^2/N_{\text{obs}} - N_{\text{param}}}{} \right)^{1/2} \quad ^c R = \frac{\sum w|F_o| - |F_c|/\sum |F_o|}{\sum w|F_o|^2}^{1/2} \quad ^d R_w = \left( \frac{\sum w|F_o|^2 - |F_c|^2/\sum wF_o^2}{} \right)^{1/2} \]

---

Table 2.4 Selected bond distances (Å) and angles (°)

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Bond angles

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complexed AH₂Cl₂ in la and lb may originate from crystal packing forces, and the energy difference between the two conformations may be small. Conformational studies of AH₂ [2.19] indicate that the variation of potential energy is small (ca. 4 kJ mol⁻¹) over the range of dihedral angles between −140° and 180°.

The aromatic rings of the AH₂Cl₂ ligands are planar (no deviations larger than 0.018 Å in either structure) in both crystal forms. Longer average carbon-carbon distances are observed in lb for the complexed ring of AH₂Cl₂ (1.406(3) Å) in comparison to the uncomplexed ring (1.381(3) Å), and also in comparison to free AH₂ (1.386(1) Å) [2.15, 2.16]. This increase in bond length on π complexation to CpFe⁺ has been reported for other aromatic ligands [2.20, 2.21] 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 la 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) [2.15], while C-Cl distances remain close to those in ACL (1.745(4) and 1.756(4) Å) [2.22]. The coordinated arene and Cp ring planes form dihedral angles of 4.1° and 2.8° in la and lb, respectively. The distances between Fe and the coordinated arene ring planes (1.533(1) Å in la and 1.5361(5) Å in lb) are shorter than the distances between Fe and Cp ring planes (1.660(1) Å in la and 1.6624(5) Å in lb), 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
Cl, C2, C3, C4) and 2.103(3) Å (average, Fe to Cl1, Cl2). All of these values are within the range of distances observed in other (η⁶-arene)[FeCp]⁺ compounds [2.20,2.21].

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 [η⁶:η⁶-(ACl₂)(FeCp)₂](PF₆)₂, containing the non-hydrogenated 1,8-dichloroanthracene ligand. Attempts to prepare the mono- and diiron complex of 1,8-dichloroanthracene by oxidation of the AH₂Cl₂ ligand in I and II respectively, using DDQ in the presence of a base (Et₃N or K₂CO₃) in CH₃CN or benzene as solvent, were unsuccessful. Instead, decomposition of the starting materials occurred, and only AH₂Cl₂ and ACl₂ could be isolated.

2.3. Conclusions

The synthesis of complexes I and II shows the feasibility of π complexation of chloroanthracene derivatives to CpFe⁺ moieties under mild reaction temperatures in moderate yields. The reduction of ACl₂ during π complexation to CpFe⁺ agrees with the

---

1) The black crystal, grown from acetone/diethyl ether, appears to be [η⁶:η⁶-(1,8-dichloroanthracene)(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), V = 14.140(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) Å) are more similar to those in ACl₂ (1.385(6)-1.453(5) Å) than to those in 1a and 1b. The Fe dimer lies on a crystallographic twofold axis.
behavior previously reported for anthracene. Formation of \([\eta^6,\eta^6-(\text{ABA}H_2)(\text{FeCp})_2]^2\) was unsuccessful. Compound II decomposed instead during the reaction conditions to form FeCp$_2$ and Fe(acac)$_3$. Reactions of II with other nucleophiles derived from dimethyl malonate and diethyl ethylmalonate were also unsuccessful.

2.4. Experimental Part

1,8-Dichloroanthracene (ACl$_2$) was prepared by reduction of 1,8-dichloroanthraquinone in Zn/NH$_3$ (aq) following literature procedures [2.23, 2.24]. 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.

2.4.1. Synthesis of \([\eta^6-(\text{AH}_2\text{Cl}_2)\text{FeCp}](\text{PF}_6)(\text{I})

\[
\begin{align*}
\text{ACl}_2 & \quad \text{Cp}_2\text{Fe} \\
\text{AlCl}_3, \text{Al} & \quad \text{CH}_3\text{Cy} \\
\end{align*}
\]

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 (0.38 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$_2$O, 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 NH₄PF₆ dissolved in the minimum amount of H₂O. The yellow hexafluorophosphate salt I precipitated (0.4 g, 6%) and was crystallized from either CHCl₃/ether or CHCl₃/hexane as orange-yellow needles.

2.4.2. Synthesis of \([\eta^6:\eta^6-(\mathrm{AH}_2\mathrm{Cl}_2)(\mathrm{FeCp})_2((\mathrm{PF}_6)_2 (\text{II})]

A mixture of ACI₂ (2.5 g, 10 mmol), ferrocene (26.5 g, 142 mmol), AlCl₃ (37.7 g, 283 mmol) and Al powder (3.83 g, 142 mmol) in 200 mL of cyclohexane was heated at reflux under N₂ for 40 h. The resulting material was worked up as described above for I using 3.3 g (20 mmol) of NH₄PF₆. The crude product (2.2 g), containing a mixture of I and II, was treated first with CHCl₃, 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.
2.4.3. Synthesis of 1,8-Dichloro-9,10-dihydroanthracene (AH₂Cl₂)

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 AH₂Cl₂ with a small amount of ACI₂ (approx. 1% by ¹H NMR). EI-MS m/z (%): 252, 250, 248 (68, M'); 215, 213 (92, M' - Cl), 178 (100, M' - 2 Cl), 106 (26), 88 (41).

2.4.4. Attempted synthesis of [η⁶:η⁶-(ABA)FeCp](PF₆)

A mixture of II (0.50 mg, 0.64 mmol), acac-H (0.13 mL, 1.3 mmol) and 3.2 mmol of base (KF/Celite (1:1.5) [2.5] or K₂CO₃) in 5 mL of solvent (DMF, THF, CH₃CN or DMF/THF) was stirred under Ar at room temperature or -20 °C. The reaction mixture turned blue immediately after II came in contact with acac. After 4-5 hours, the resulting mixture was filtered into 10% aqueous HCl (5 mL) and a saturated aqueous solution of NH₄PF₆ (0.22 g, 1.35 mmol) was added to it. The final yellow
solution was then extracted with a 4:1 mixture of $\text{CH}_2\text{Cl}_2, \text{CH}_3\text{NO}_2$ and the organic phase was dried over $\text{MgSO}_4$, filtered and concentrated to dryness. $^1\text{H}$ NMR and IR spectra of the resulting reddish solid showed a mixture of $\text{FeCp}_2$, $\text{ACl}_2$, $\text{AH}_2\text{Cl}_2$ and $\text{Fe(acac)}_3$.

2.4.5. 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 MoKα 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 the intensities of standard reflections remained approximately constant, making a decay correction unnecessary. The structures were solved by direct methods and refined by full-matrix least squares, treating nonhydrogen atoms anisotropically, using the Enraf-Nonius MolEN programs [2.25]. Hydrogen atoms were placed in calculated positions.

2.5. References


Chapter 3

Synthesis of 1,8-Dichlorodibenzobarrelene and Remote Hydrogenation During its $\pi$-(Cyclopentadienyliiron) Complexation

3.1. Introduction

The synthesis of I and II (Chapter 2) stimulated our interest to study other 1,8-dichloroanthracene derivatives that may be more susceptible to attack by nucleophiles on the chlorine atoms, via $\pi$ complexation to CpFe$^+$ moieties. Since the presence of acidic protons in $\text{AH}_2\text{Cl}_2$ may be the reason for the failure of I and II to react cleanly with C-nucleophiles, we became interested in 1,8-dichloro-9,10-etheno-9,10-dihydroanthracene (1,8-dichlorodibenzobarrelene, $\text{AECI}_2$), whose rigid barrelene skeleton should protect the hydrogens of the central anthracene ring from deprotonation. Figure 3.1 shows our proposed strategy for preparing the barrelene derivative of ABAH$_2$, AEBAH$_2$, from $\text{AECI}_2$ via $\pi$-CpFe$^+$ complexation.

Using this approach we have synthesized the mono-cyclopentadienyliiron complex of 1,8-dichloro-9,10-ethano-9,10-dihydroanthracene $[(\eta^6-\text{AEH}_2\text{Cl}_2)\text{FeCp}] (\text{PF}_6)$ (III). In this reaction, $\pi$ complexation of $\text{AECI}_2$ was unexpectedly accompanied by reduction of its ethene bridge.

3.2. Results and Discussion

3.2.1. Synthesis of 1,8-Dichlorodibenzobarrelene ($\text{AECI}_2$)

Following the general procedure described by Paquette et al. [3.1], $\text{AECI}_2$ was synthesized by Diels-Alder cycloaddition of $\text{ACl}_2$ with the acetylene synthon phenyl vinyl sulfoxide in refluxing chlorobenzene for 8 days (Figure 3.2)
Figure 3.1. Strategy for the synthesis of the barrelene derivative of ABAH₂ via π-(cyclopentadienyliron) complexation of 1,8-dichlorodibenzobarrelene

Figure 3.2. Synthesis of 1,8-dichlorodibenzobarrelene (AECI₂)
Due to the large amount of tar present in the resulting solution, purification of AECI\textsubscript{2} was not possible by conventional chromatography. Instead, AECI\textsubscript{2} was isolated by crystallization from the reaction solution at -15 °C. Further recrystallization from CCl\textsubscript{4}/CH\textsubscript{2}Cl\textsubscript{2} by slow evaporation afforded pure AECI\textsubscript{2} in 30% yield. The use of a higher boiling point solvent, such as \(\alpha\)-dichlorobenzene (180 °C), did not accelerate the reaction. \(^{1}\text{H}\) and \(^{13}\text{C}\) NMR data (Tables 3.1 and 3.2) as well as its crystal structure determination (Figure 3.3) confirm the identity of AECI\textsubscript{2}.

3.2.2. Synthesis of \(\text{[endo-}(\eta^6-(1,8-dichloro-9,10-ethano-9,10-dihydroanthracene))\text{FeCp}](\text{PF}_6))\) (III)

We pursued \(\pi\) complexation of AECI\textsubscript{2} to CpFe\textsuperscript{+} by reaction of ferrocene with AECI\textsubscript{2} in the presence of AlCl\textsubscript{3} and Al, following the method reported by Nesmeyanov [32]. Our initial experiments, carried out in a 1:1 (v/v) mixture of...
methylcyclohexane/cyclohexane, using a 4:1 molar ratio of FeCp₂ and AECl₂, led unexpectedly to the formation of [(η⁶-toluene)FeCp](PF₆) as the major product (12% yield with respect to FeCp₂). ¹H NMR of the crude product in d₆-acetone showed peaks at 7.0-7.6 and 6.1-6.4 ppm in the aromatic region and a Cp signal at 4.3 ppm, as expected for a π complex of AECl₂, but in very low yield (<1%). Still higher yields of [(η⁶-toluene)FeCp](PF₆) (20%) were obtained by increasing the ratio of CH₃Cy/CyH to 3.5:1. The identity of [(η⁶-toluene)FeCp](PF₆) was confirmed by comparison of its ¹H NMR spectra with that reported in the literature [3.3].

It has been suggested that during ligand-substitution reactions involving condensed polycyclic arenes, the cycloaliphatic solvents, such as cyclohexane, methylcyclohexane and tetralin, serve as major sources of hydrogen for the reduction of the arene ligand [3.4-3.6]. In the process, the solvent is expected to be dehydrogenated to aromatic compounds. The behavior of methylcyclohexane as hydrogen donor in this reaction may explain the formation of toluene, which would further undergo a more favorable π complexation to CpFe⁺, to form (η⁶-toluene)[FeCp]⁺, than the less electron-rich AECl₂ system. If this mechanism is correct, we would expect to find a reduced product, presumably from AECl₂, corresponding to the dehydrogenation of CH₃Cy. No such product has been identified. More studies are necessary to confirm this mechanism.

* CH₃Cy is preferred as the reaction solvent because its higher boiling point generally leads to higher yields. However, when CH₃Cy is used along with a large excess of AlCl₃, AlCl₃ is lost by sublimation into the condenser. Using a mixture of CH₃Cy/CyH leads to a somewhat lower b.p. that prevents the loss of AlCl₃ from the reaction.
Treatment of a large excess of ferrocene with \( \text{AECl}_2 \), \( \text{AlCl}_3 \), and Al using cyclohexane as the only solvent afforded \([\text{η}^6-\text{AEH}_2\text{Cl}_2]\text{FeCp}]\text{(PF}_6\text{)} (\text{III})\) in 36% yield (Figure 3.4). No bis-coordination seemed to occur during these reaction conditions. Crystallization from CHCl\(_3\)/hexane gave \text{III} as yellow needles. Although \text{III} is stable in air in the solid state, it starts decomposing in aerated solution after several hours. In principle, two isomers can be produced for the mono-iron complex \text{III}: \text{endo} and \text{exo}, depending on the position of the \text{CpFe} moiety relative to the ethano bridge of the \text{AEH}_2\text{Cl}_2 ligand (Figure 3.5) [3.7] Crystal structure determination shows an \text{endo} conformation for compound \text{III} (Figure 3.6).

![Figure 3.4. Synthesis of 1,8-dichloro-9,10-ethano-9,10-dihydroanthracene complex III](image)

![Figure 3.5. Possible isomers of complex III](image)
Figure 3.6. Ortep diagram of [endo-(η⁶-(1,8-dichloro-9,10-ethano-9,10-dihydroanthracene))FeCp]⁺ in complex III.

¹H and ¹³C NMR data for III, AECl₂ and the reference compound 9,10-ethano-9,10-dihydroanthracene (AEH₂) [3,8] are presented in Tables 3.1 and 3.2. The spectral data support the formation of a single isomer for compound III, with a pattern similar to that previously displayed by the mono-iron complexes of AH₂Cl₂ and AH₂ (see Chapter 2). The resonances of the proton and carbon atoms of the complexed ring of 1,8-dichloro-9,10-ethano-9,10-dihydroanthracene (AEH₂Cl₂) are shifted upfield compared to those of the parent compound AECl₂ and AEH₂, while the non-coordinated ring atoms of AEH₂Cl₂ are shifted downfield. Reduction of the etheno bridge of AECl₂ into a saturated ethano bridge in compound III is supported by signals in the saturated region,
Table 3. $^1$H NMR data $^a$ of AECl$_2$, AEH$_2$ and complex III

<table>
<thead>
<tr>
<th>Compound</th>
<th>uncomplexed arene</th>
<th>complexed arene</th>
<th>H9, H10</th>
<th>Cp</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>AECl$_2$</td>
<td>7.19-6.85 (m)$^c$</td>
<td>6.14 (dd, 1H, 5.6, 1.8)</td>
<td>5.18 (dd, 1H, 5.4, 1.9)</td>
<td>7.1-6.9 (m, 2 CH)$^c$</td>
<td></td>
</tr>
<tr>
<td>AEH$_2$</td>
<td>7.01 (m, 8H)</td>
<td>4.13 (m, 2H)</td>
<td>1.68 (m, 4H, CH$_2$)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>III$^e$</td>
<td>7.58 (d, 1H, 7.2)</td>
<td>6.71 (d, 1H, 5.5)</td>
<td>5.33 (s, 1H)</td>
<td>4.35 (s, 5H)</td>
<td>1.87 (d, CH$_2$, 8.1)</td>
</tr>
<tr>
<td></td>
<td>7.42 (d, 1H, 7.7)</td>
<td>6.40 (d, 1H, 6.2)</td>
<td>4.66 (s, 1H)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>7.35 (t, 1H, 7.7)</td>
<td>6.34 (t, 1H, 5.8)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ In CDCl$_3$, $^/$ppm vs TMS ($^/$Hz in parenthesis). $^b$ 200 MHz. $^c$ Olefinic and aromatic protons (8H) appear overlapped in the same region. $^d$ From ref. [3.8]. $^e$ 400 MHz.
Table 3.2. $^{13}$C NMR data * of complex AECl₂, AEH₂ and complex III

<table>
<thead>
<tr>
<th>Compound</th>
<th>uncomplexed arene</th>
<th>complexed arene</th>
<th>C9, C10</th>
<th>Cp</th>
<th>Others</th>
</tr>
</thead>
</table>
| AECl₂    | 148.5, 142.7, 129.4, 125.8  
(CH), 125.3 (CH), 121.5  
(CH) | 51.7, 44.3  | 140.1 (CH), 138.5 (CH) |
| AEH₂ b   | 143.8, 125.5, 123.2  | 44.1  | 26.7 (CH₂) |
| III      | 144.5, 139.2, 129.3, 128.8  
(CH), 127.4 (CH), 123.3  
(CH) | 109.9, 106.5, 103.8, 85.0  
(CH) 84.8 (CH)  | 41.2, 35.5  | 78.4  | 24.6 (CH₂), 24.1 (CH₂) |

* 200 MHz, in CDCl₃, δ/ppm vs. TMS. Assignments were made using DEPT experiment. b From ref [3.8] c Higher intensity of this resonance suggests coincidental overlap of two CH signals.
in both $^1$H (δ 1.87 and 1.69 ppm) and $^{13}$C NMR (δ 24.6 and 24.1 ppm). The assignment of III to the endo isomer 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$_2$Cl$_2$ ligand, by comparison to those of the free AEH$_2$, whereas an exo conformation of the CpFe moiety would be expected to exert a strong shift on the methylenic protons immediately adjacent to the metal, resulting in two AB quartets.

Formation of III is in contrast with the corresponding π complexation of the Cr(CO)$_3$ moiety to 9,10-etheno-9,10-dihydroanthracene [3.7], where no reduction of the arene takes place under reaction conditions that do not require the presence of Al and AlCl$_3$. On the other hand, AlCl$_3$ has been claimed 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 [3.9]. Although it is not clear if reduction of AECl$_2$ occurs before or after π complexation to CpFe', or even in both cases, it does not seem probable that the reduction is a simple intramolecular process as has been demonstrated for 9,10-dimethylanthracene [3.10]. This is because the endo geometry of III places the FeCp moiety too far away for any hydrogen transfer from a Fe-H species [3.6,3.10] to the ethene bridge.

3.2.3. Attempted nucleophilic substitution of III with acac

Using the procedure described by Sutherland et al. [3.11], we explored the nucleophilic substitution of the chlorine atoms in the π-CpFe' complexed AEH$_2$Cl$_2$ with acac. Treatment of III with acac-H and K$_2$CO$_3$ in DMF (Figure 3.7) resulted in an orange reaction solution, which decomposed rapidly after work-up to give a mixture of
AECl₂ and AEH₂Cl₂. ¹H NMR and GC-MS analysis of this mixture showed no evidence of a nucleophilic substituted product.

Further studies of this substrate using other carbon nucleophiles and reaction conditions may be worthwhile. However, they will not lend to bis(β-diketones), because only one ring is complexed to CpFe⁺. Also, the low yield of the complexation, and the difficulty of preparing AECl₂ in pure form, make this route less convenient than those presented in Chapters 2, 4, and 5.

3.3 Conclusions

The ligand substitution reaction of ferrocene with AECl₂ afforded the mono-iron complex III as the only reaction product, in moderate yield. X-ray and spectral analysis confirm the endo conformation of complex III. More studies are recommended to establish the mechanism for the reduction of AECl₂ during π complexation.

Reaction of III with acac did not give any substitution product, and the free arenes AECl₂ and AEH₂Cl₂ were recovered on workup.
3.4. Experimental Part

NMR spectra were recorded by using Bruker AC 200 and AM 400 spectrometer. An HP 5971 instrument was used for GC-MS

3.3.1. Synthesis of 1,8-Dichlorodibenzobarrelene (AECl₂)

Following the general method described by Paquette et al [3.1], a solution of AECl₂ (3.7 g, 15 mmol) and phenyl vinyl sulfoxide (2.96 mL, 22.2 mmol) in chlorobenzene (25 mL) was refluxed under N₂ 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 CCl₄, dissolved in acetone, and the solution flooded with water, to precipitate AECl₂ as a white solid (1.2 g, 30% yield). Crystallization from CCl₄/CH₂Cl₂ by slow evaporation afforded AECl₂ as colorless needles, m.p. 178-179 °C. El-MS m/z (%) 276, 274, 272 (M⁺, 73), 239, 237 (M⁺- Cl, 100), 202 (M⁺- 2 Cl, 95); 200 (3), 176 (M⁺- 2 Cl - C₂H₂, 13); 118 (19); 101 (20); 100(22).

3.3.2. Synthesis of [endo-[(η⁴-1,8-dichlorodibenzobarrelene)FeCp]][PF₆] (III)

a) Attempted preparation using CH₂Cy/CyH

A mixture of AECl₂ (0.30 g, 1.1 mmol), ferrocene (0.83 g, 4.5 mmol), AlCl₃ (1.2 g, 8.8 mmol) and Al (0.12 g, 4.4 mmol) in methycyclohexane/cyclohexane (3:5:1 v/v, 70 mL) was heated at reflux under N₂ for 38 hours. The resulting material consisting of a
yellow solution and a dark precipitate in the sides of the flask, was allowed to cool to room temperature under N2 and then hydrolyzed with 5-10 mL of ice water. The organic layer was separated and extracted with H2O, and the aqueous layers were combined, washed several times with hexane and filtered into a saturated aqueous solution of NH4PF6 (0.41 g, 2.5 mmol). The yellow-green precipitate was filtered and dried over MgSO4 to yield [(η6-toluene)FeCp](PF6) (0.32 g, 20%) and some product from π-complexation to AECI2 (less than 1% by 1H NMR). [(η6-toluene)FeCp](PF6) was purified by crystallization from acetone/ether as yellow needles. In another experiment under the same reaction conditions but using a 1:1 solution of methylcyclohexane/cyclohexane as solvent, [(η6-toluene)FeCp](PF6) was obtained in 12% yield.

[(η6-toluene)FeCp](PF6): 1H NMR (CDCl3, 200 MHz) δ 6.40 (s, 5H), 5.17 (s, 5H), 2.55 (s, 3H), 13C NMR (CDCl3, 50 MHz) δ 104.8, 89.6 (CH), 88.6 (CH), 87.4 (CH), 77.8 (Cp), 20.8 (CH3).

b) Using CyH

A mixture of AECI2 (0.21 g, 0.73 mmol), FeCp2 (2.1 g, 11 mmol), AlCl3 (2.72 g, 20.4 mmol) and Al (0.28 g, 10 mmol) in cyclohexane (23 mL) was refluxed under N2 for 72 hours. The resulting material was worked up as described above to give III as a
greenish precipitate (0.14 g, 36%). Purification by crystallization from CHCl₃/hexane yielded III as yellow needles.

3.5. References


Chapter 4

Synthesis of 1,8-Diacetonylanthracene

4.1. Introduction

In our search for routes to ABAH$_2$ we became interested in the preparation of 1,8-diacetonylanthracene (AA$_2$) as a possible intermediate. The reported synthesis of 1,4-phenylenbis(acetylacetone) from 1,4-diacetonylbenzene (Figure 4.1), albeit in very low yield [4.1], suggests the potentiality of this approach.

![Figure 4.1 Acetylation of 1,4-diacetonylbenzene](image)

Although several methods for acetylation of aryl halides are reported in the literature, they are subject to limitations. Thus, attack of enolate anions on aryl halides activated by π complexation to a metallic moiety (FeCp') [4.2], use of acetylacetone as an acetyl precursor [4.3], and photochemical acetylation in liquid NH$_3$ [4.4,4.5], require a multi-step procedure or afford the corresponding acetylated products only in moderate or poor yields.

The recent development of the palladium-catalyzed coupling of organic electrophiles with functionalized organostannanes (Stille reaction) offers an efficient method for formation of carbon-carbon bonds [4.6-4.9]. This is due mainly to the
compatibility of the Stille chemistry with virtually any functional group, eliminating the need for protection/deprotection strategies which are necessary for most organometallic reactions. Based on this method, Kosugi et al. [4.10,4.11] have reported the acetylation of bromobenzene from the Pd-catalyzed reaction of acetyltributyltin (prepared in situ) and bromobenzene in high yield (Figure 4.2).

Our strategy for extending this synthesis to AA₂ from 1,8-dibromoanthracene (ABr₂), which could further undergo C'-acylation to give the bis(β-diketone) ABAH₂, is outlined in Figure 4.3.

Figure 4.2. Palladium-catalyzed acetylation of bromobenzene

Figure 4.3 Strategy for the synthesis of ABAH₂ via 1,8-diacetonylanthracene intermediate
4.2. Results and Discussion

4.2.1. Synthesis of 1,8-Dibromoanthracene (ABr₂)

House et al. have reported the preparation of 1,8-diiodo- [4.12] and 1,8-dibromoanthraquinone (AQBr₂) [4.13], via diazotization of the 1,8-diaminoanthraquinone, in multi-step procedures and low overall yields (41% for 1,8-diiodoanthraquinone and 8% for AQBr₂). A second method described in the literature for preparing AQBr₂ involves bromination of the dipotassium 1,8-anthraquinone-disulfonate with bromine in water under harsh conditions (260 °C, 70% yield) [4.14]. A more convenient and less expensive method has been reported by Brienne and Jacques for the preparation of 1,5-dibromoanthraquinone [4.15], using 1,5-dichloroanthraquinone, excess KBr and aqueous H₃PO₄ as starting materials in nitrobenzene. Using this method, we obtained AQBr₂ from 1,8-dichloroanthraquinone (Figure 4.4) first as an approximately 6:1 mixture of 1,8-dibromo and 1-bromo-8-chloro compounds, as shown by GC-MS. In order to improve the yield of AQBr₂, the reaction was repeated using this mixture as the starting material to give AQBr₂ and 1-bromo-8-chloroanthraquinone in a 10:1 ratio. Purification of the crude material by column chromatography afforded the 10:1 mixture of anthraquinones (AQBr₂ in 45% yield) as a yellow-orange solid. Following this same procedure, Holden [4.16] recently obtained pure AQBr₂ by employing a purified intermediate mixture of AQBr₂ and 1-bromo-8-chloroanthraquinone, by crystallization from hot nitrobenzene, in a second reaction with KBr.
Reduction of this mixture of AQBr₂ with aluminum cyclohexoxide (Al(OCy)₃) in refluxing cyclohexanol (CyOH) [4,14,4,17], followed by purification by column chromatography afforded 1,8-dibromoanthracene (ABr₂) in 75% yield, also as a 10:1 mixture (by GC-MS) of the 1,8-dibromo- (ABr₂) and 1-bromo-8-chloro- anthracenes (Figure 4.5). The similar Rf values and solubility properties of ABr₂ and 1-bromo-8-chloroanthracene, as well as of AQBr₂ and 1-bromo-8-chloroanthraquinone, did not permit their separation by either column chromatography or crystallization. 'H NMR and GC-MS data of ABr₂ agree with those reported in the literature [4,14].

Due to the difficulty of removing cyclohexanol (b.p. 161 °C) from the crude product, we explored the reduction of AQBr₂ using aluminum sec-butoxide in sec-
butanol (b.p. 99.5 °C) [4.17], and the more common reductant Zn/NH₃(aq). Unfortunately, only mixtures of products were obtained when aluminum sec-butoxide was used, while Zn/NH₃(aq) caused decomposition of AQBr₂ to anthracene.

4.2.2. Synthesis of 1,8-Diacetonylanthracene (AA₂)

Following the acetonylation method designed by Kosugi et al [4.10,4.11], reaction of AB₇ with acetonyltributyltin, prepared from its enol acetate (isopropenyl acetate) and tributyltin methoxide in situ, in the presence of Pd(II) catalyst afforded 1,8-diacetonylanthracene (AA₂), as shown in Figure 4.6. Purification by flash chromatography gave AA₂ as a pale yellow solid in 80% yield. ¹H and ¹³C NMR data, as well as GC-MS and exact mass analysis, confirmed the structure of AA₂.

\[
\text{Bu}_3\text{SnOCH}_3 + \text{CH}_3\text{CO}_2\text{C(CH}_3\text{)=CH}_2 \rightarrow \text{Bu}_3\text{SnCH}_2\text{COCH}_3 + \text{CH}_3\text{CO}_2\text{CH}_3
\]

![Chemical Reaction](image)

Figure 4.6. Synthesis of 1,8-diacetonylanthracene (AA₂)

As a consequence of the presence of some 1-bromo-8-chloroanthracene in the starting material, 1-acetonyl-8-chloroanthracene was also obtained during the reaction in ~ 10% yield. Identification of this compound was possible by ¹H NMR and GC-MS.
analysis. Both acetonylated compounds are stable in the solid state. However, in CHCl₃ solution, they start decomposing over a period of several days to give unidentified product(s).

The synthesis of AA₂ provides a potential precursor for the preparation of our target compound ABAH₂. Although acetylation of 1,4-diacetonylbenzene with acetic anhydride and BF₃ is reported to give 1,4-phenylenebis(acetylacetone) (Figure 4.1) [4.1], its poor yield (5%) argues against the utility of this reaction in our case. Silyl enol ethers, obtained by silylation of ketones [4.18-4.20], are known to undergo C-acylation to give the corresponding 1,3-diketones. Reaction of a trialkylsilyl enol ether of AA₂ with an acetyl electrophile, e.g. acetyl tetrafluoroborate [4.21] or acetyl chloride in the presence of a Lewis acid (ZnCl₂, SbCl₃, ZnBr₂ or TiCl₄) [4.22,4.23], may provide an useful alternative to the synthesis of ABAH₂ (Figure 4.7). Future work is necessary in this area.

![Proposed strategy for the acetylation of AA₂](image)

**Figure 4.7. Proposed strategy for the acetylation of AA₂**

### 4.3. Conclusions

We have successfully synthesized the new diacetyl compound AA₂ via Pd-catalyzed reaction of acetonyltributyltin, prepared *in situ*, with 1,8-dibromoanthracene in
good yields. This compound may serve as a potential precursor for the preparation of the
bis(β-diketone) ABAH$_2$. Future work in the acetylation of AA$_2$ is recommended.

4.4. Experimental Part

PdCl$_2$(PPh$_3$)$_2$ was prepared following the literature procedure [4.23]. $^1$H and $^{13}$C
NMR spectra were recorded by using Bruker AC200 and AC250 NMR spectrometers
An HP 5971 instrument was used for GC-MS. The high resolution mass spectrum for
AA$_2$ was recorded with a Finnigan MAT-900 double focusing mass spectrometer using
fast atom bombardment (FAB) ionization, with 3-Nitrobenzyl alcohol as a matrix

4.4.1. Synthesis of 1,8-Dibromoanthraquinone (AQBr$_2$)

Following the method described by Brienne and Jacques [4.15] for the 1,5-
isomer, 1,8-dichloroanthraquinone (2.0 g, 7 mmol) was treated with KBr (4.01 g, 33.6
mmol), CuCl$_2$ (0.1 g, 0.7 mmol) and 85% H$_3$PO$_4$ (4 mL) in nitrobenzene (15 mL). Water
was distilled from the reaction mixture until the temperature reached 200 °C, and then
the mixture was refluxed for 24 hours. The product was precipitated from the cooled
mixture with methanol and collected. The crude product was extracted with CH$_2$Cl$_2$,
isolated by evaporation of the solvent, and purified by column chromatography (silica,
CH$_2$Cl$_2$) to yield 2.0 g of a mixture of AQBr$_2$ and 1-bromo-8-chloroanthraquinone (6:1
as estimated by GC-MS). The same procedure was repeated using this product as starting material to give 1.3 g of a 10:1 mixture of AQBr₂ and 1-bromo-8-chloroantraquinone.

AQBr₂: yield: ~45.0%, ¹H NMR (CDCl₃, 200 MHz) δ 8.25 (dd, 2H, J = 7.7, 1.2 Hz), 8.03 (dd, 2H, J = 7.9, 1.1 Hz), 7.55 (t, 2H, J = 7.9 Hz), ¹³C NMR (CDCl₃, 50 MHz) δ 181.7 (CO), 181.4 (CO), 141.1, 137.7, 135.0, 133.4 (CH), 126.7 (CH), 122.0 (CH); EI-MS m/z (%): 368, 366, 364 (100, M⁺), 340, 338, 336 (20, M⁺ - CO), 312, 310, 308 (28, M⁺ - 2 CO), 287, 285 (21, M⁺ - Br), 259, 257 (20, M⁺ - Br - CO), 231, 229 (31, M⁺ - Br - 2 CO), 150 (88), 75 (76), 74 (34);

1-Bromo-2-chloroanthraquinone: EI-MS m/z (%): 324, 322, 320 (100, M⁺), 296, 294, 292 (29, M⁺ - CO), 268, 266, 264 (38, M⁺ - 2 CO), 243, 241 (14, M⁺ - Br), 215, 213 (14.2, M⁺ - Br - CO), 185 (28), 150 (64), 75 (63), 74 (33)

4.4.2. Synthesis of 1,8-Dibromoanthracene (ABr₂)

Using the procedure reported by Haenel et al. [414,417], the above mixture of 1,8-dibromoanthraquinone and 1-bromo-2-chloroantraquinone (ca. 10.1, 1.3 g, ca. 3.2 mmol) in 10 mL of cyclohexanol and aluminum cyclohexoxide (18 mL, 2.2 M in cyclohexanol, 39 mmol), with a trace of HgCl₂ and CCl₄, was heated under N₂ at reflux.
for 72 hours. The final solution was poured into water, extracted with toluene and concentrated. Purification by column chromatography (silica, hexane) and crystallization from ethanol afforded 0.9 g of a mixture of ABr$_2$ and 1-bromo-8-chloroanthracene (ca. 10:1 by GC-MS).

ABr$_2$ yield: ~75%; $^1$H NMR (CDCl$_3$, 200 MHz) $\delta$ 9.22 (s, 1H), 8.45 (s, 1H), 8.0 (d, 2H, $J = 8.5$ Hz), 7.85 (d, 2H, $J = 7.2$ Hz), 7.35 (dd, 2H, $J = 7.3, 8.4$ Hz); El-MS $m/z$ (%) 338, 336, 334 (100, M$^+$); 257, 256 (11, M$^+$ - Br); 176 (49, M$^+$ - 2 Br), 88 (45), 75 (14).

1-Bromo-2-chloroanthracene El-MS $m/z$ (%) 294, 292, 290 (100, M$^+$), 211 (8, M$^+$ - Br), 176 (37, M$^+$ - Br - Cl), 146 (10), 88 (32), 87 (17).

4.4.3. Synthesis of 1,8-diacetonylanthracene (AA$_2$)

\[
\begin{array}{c}
\text{Br} & \text{Br} \\
\text{ABr}_2 & \text{Bu}_3\text{Sn-CH}_2\text{COCH}_3 & \downarrow \\
\text{Bu}_3\text{Sn-CH}_2\text{COCH}_3 & \text{PdCl}_2(\text{PPh}_3)_2 & \text{toluene} \\
100^\circ\text{C}, 8\text{h} & & \\
& & \text{AA}_2
\end{array}
\]

To a solution of a 10:1 mixture of ABr$_2$ (65 mg, 0.18 mmol) and 1-bromo-8-chloroanthracene, isopropenyl acetate (0.04 mL, 0.4 mmol) and tributyltin methoxide (0.12 mL, 0.41 mmol) in toluene (5 mL) was added PdCl$_2$(PPh$_3$)$_2$ (3 mg, 0.004 mmol), and heated to 100 °C with stirring under nitrogen for 8 hours. The cooled reaction mixture was then diluted with diethyl ether (20 mL) and washed subsequently with H$_2$O (5 mL), aqueous HCl (10%, 2x5 mL), and saturated solution of KF (2x5 mL). The organic phase was then filtered, dried over MgSO$_4$ and concentrated. The resulting
yellow solid was purified by column chromatography (silica, hexane/AcOEt 2:1) to give, in order of elution, 1-acetonyl-8-chloroanthracene and AA₂ as pale yellow solids after evaporation of the solvents.

AA₂: yield: 42 mg (80%), ¹H NMR (CDCl₃, 250 MHz) δ 8.48 (s, 1H), 8.42 (s, 1H), 7.96 (d, 2H, J = 8.15 Hz), 7.48-7.38 (m, 4H), 4.23 (s, 4H), 2.23 (s, 6H), ¹³C NMR (CDCl₃, 50 MHz) δ 207.0 (CO), 131.8, 131.6, 130.7, 128.1 (CH), 128.1 (CH), 128.0 (CH), 125.3 (CH), 119.3 (CH), 49.7 (CH₂), 29.0 (CH₃); El-MS m/z (%) 290 (50, M⁺), 247 (100, M' - COCH₃), 204 (47, M' - 2 COCH₃), 203 (46, M' - 2 COCH₃ - H), 202 (41, M' - 2 COCH₃ - 2 H), 43 (98, COCH₃). HRMS calcd for C₂₀H₁₈O₂ [M] 290.1307, found 290.1310.

1-acetonyl-8-chloroanthracene: yield: ~10%; ¹H NMR (CDCl₃, 250 MHz) δ 8.84 (s, 1H), 8.48 (s, 1H), 7.99 (d, 1H, J = 8.1 Hz), 7.94 (d, 1H, J = 8.4 Hz), 7.60 (d, 1H, J = 7.5 Hz), 7.52-7.35 (m, 3H), 4.30 (s, 2H), 2.24 (s, 3H); El-MS m/z (%) 270, 268 (30, M'), 227, 225 (100, M' - COCH₃), 189 (35, M' - COCH₃ - Cl), 43 (41, COCH₃).

4.5. References


Chapter 5

Synthesis of an Anthracenebis(β-ketoenamine) Ligand

5.1. Introduction

We were interested in the use of 3,5-dimethylisoxazole as a potential acac-H synthon for the preparation of ABAH₂. Although fairly stable, the isoxazole ring can be readily cleaved under reducing conditions to form a β-ketoenamine, which may then be hydrolyzed to give the corresponding β-diketone (Figure 5.1) [5.1].

![Figure 5.1. Deprotection of a 3,5-dimethylisoxazole to a 2,4-pentanedione](image)

Our proposed synthetic route for preparing ABAH₂ via formation of a bis(3,5-dimethylisoxazolyl) intermediate (A(DMI)₂) is outlined in Figure 5.2. Palladium-catalyzed cross coupling between a 1,8-disubstituted anthracene electrophile and an organometallic derivative of 3,5-dimethylisoxazole, followed by reduction of the A(DMI)₂ intermediate, successfully produced the bis(β-ketoenamine) ABIH₂. This compound may then be used as a cofacial binucleating ligand (Chapter 6), or further hydrolysis to give the bis(β-diketone) ABAH₂ may also be possible.
5.2. Results and Discussion

5.2.1. Synthesis of 1,8-disubstituted anthracene derivatives

We studied the synthesis of 1,8-ditriflatoanthraquinone (AQ(OTf)2) and 1,8-dibromoanthracene (ABr2) and -anthraquinone (AQBr2) as potential electrophiles for carbon-carbon bond formation. Following the general method described by Echevarren and Stille [5.2], we prepared AQ(OTf)2 by reaction of 1,8-dihydroxyanthraquinone with triflic anhydride in 95% yield (Figure 5.3). Crystallization from CHCl3/hexane afforded two crystal forms of AQ(OTf)2 (see Ortep diagram for one form in Figure 5.4).
We then attempted to prepare 1,8-ditrilatoanthracene by reduction of AQ(OTf)₂. Several reducing systems were studied: Al(cyclohexoxide)₃ in cyclohexanol [5.3,5.4], Zn/HOAc (aq) [5.5.5.6] and NaBH₄ in i-PrOH [5.7]. However, in all cases AQ(OTf)₂
was reduced to the anthrone, accompanied by a mixture of side products containing only one triflate group left in the molecule (as shown by GC-MS).

Using the procedure described in Section 4.4.1 and 4.4.2, AQBr₂ and ABr₂ were synthesized from 1,8-dichloroanthraquinone as ca. 10:1 mixtures of the 1,8-dibromo and 1-bromo-8-chloro compounds, and used as such for coupling reactions.

5.2.2. Synthesis of 3,5-dimethylisoxazole organometallic reagents

Although a Grignard reagent has been prepared from 4-iodo-3,5-dimethylisoxazole [58], its consistency, a syrup when prepared in diethyl ether or a suspension in diethyl ether/THF or pure THF, makes it difficult to handle. Attempts to prepare the organozinc reagent of 3,5-dimethylisoxazole from the Grignard [59], afforded an even more viscous material. In order to obtain a more manageable reagent, the organomercury, -boron, and -tin compounds of 3,5-dimethylisoxazole were prepared as shown in Figure 5.5.

Based on the procedure described by Kochetkov et al. for mercuration of isoxazoles [510], (3,5-dimethyl-4-isoxazolyl)mercuric acetate (DMI-HgOAc) was prepared by reaction of Hg(OAc)₂ with 3,5-dimethylisoxazole in EtOH, with a yield (76%) comparable to that previously reported by Cogoli and Grüninger (79%) [511]. Its structure was determined by X-ray analysis (Figure 5.6).

Using the general boronation method reported by Breuer and Thorpe [512,513], we prepared (3,5-dimethyl-4-isoxazolyl)boronic acid (DMI-B(OH)₂) by reaction of DMI-HgOAc with borane followed by hydrolysis (Figure 5.5). The ¹¹B NMR spectra of the crude product showed a mixture of boric acid (δ = 19.8 ppm) and DMI-B(OH)₂ (δ = 26.8
Figure 5.5. Synthesis of 3,5-dimethylisoxazole reagents: DMI-HgOAc, DMI-B(OH)$_2$, DMI-SnBu$_3$, and DMI-SnMe$_3$.

ppm), which were identified by comparison with standard solutions of boric acid and phenylboronic acid (δ -28.4 ppm). Our attempt to purify the product appeared to cause decomposition of the DMI-B(OH)$_2$. Therefore, the crude product was used as such in the coupling reaction.

Stannylation at the 4-position of 3,5-dimethylisoxazole was achieved by use of 4-iodo-3,5-dimethylisoxazole [5.14] as starting material. Preparation of the Grignard reagent in THF [5.8], followed by treatment with Bu$_3$SnCl or Me$_3$SnCl at room
temperature (Figure 5.5), afforded tributyl(3,5-dimethyl-4-isoxazolyl)tin (DMI-SnBu$_3$) and (3,5-dimethyl-4-isoxazolyl)trimethyltin (DMI-SnMe$_3$), respectively. Purification by distillation under reduced pressure gave DMI-SnBu$_3$ in 63% overall yield, while DMI-SnMe$_3$ was purified by flash chromatography in a 59% overall yield. $^1$H NMR of both compounds agree with those reported in the literature [5.15,5.16]. This method provides a good alternative to the literature procedure for the preparation of these compounds, which is via 3,5-dimethylisoxazole lithium intermediates, where DMI-SnBu$_3$ and DMI-SnMe$_3$ were obtained in 51 [5.15] and 69% [5.16] yield, respectively.

Figure 5.6. Ortep diagram of (3,5-dimethyl-4-isoxazolyl)mercuric acetate (DMI-HgOAc)
\(^1\)H and \(^{13}\)C NMR data for the organometallic compounds DMI-HgOAc, DMI-SnBu\(_3\) and DMI-SnMe\(_3\), and the reference compound dimethylisoxazole (DMI-H) \([5.17]\) are presented in Tables 5.1 and 5.2. Assignments of the signals were made by comparison to model compounds reported in the literature \([5.1]\) and by the use of DEPT experiments. Substitution by a MR\(_n\) group at the 4-position of DMI-H has little effect on the chemical shifts of the methyl group protons. A general downfield shift is observed in the isoxazole ring carbon atoms compared to the parent compound DMI-H. This deshielding effect has been explained \([5.16]\) by the dx-pr\(_\pi\) interactions between the isoxazole ring and the metal, in which the d orbitals of the metal act as \(\pi\) acceptors, prevailing over the inductive effect of the MR\(_n\) group. Mercury shows a larger deshielding effect (11 ppm) than tin (3.4-3.6 ppm), compared to DMI-H, on the C-4 carbon atom bound directly to the metal, which may originate from the energy match of the 6p orbitals of Hg than the 5d orbitals of Sn with the pr\(_\pi\) orbitals of the isoxazole.

5.2.3. Synthesis of 1,8-bis(3,5-dimethyl-4-isoxazolyl)anthracene derivatives

5.2.3.1. Via ditriflatoanthraquinone (AQ(OTf)\(_2\))

We examined first the reactivity of AQ(OTf)\(_2\) toward the Pd-catalyzed cross-coupling using a known aromatic substrate. Based on the reaction conditions reported by Shieh and Carlson \([5.17]\) for coupling of aryl triflates with arylboronic acids, 1,8-diphenylanthraquinone (AQPh\(_2\)) was synthesized (Figure 5.7) by reaction of AQ(OTf)\(_2\) with benzeneboronic acid under heterogeneous conditions: 3 mol % of Pd(PPh\(_3\))\(_4\) and anhydrous K\(_2\)CO\(_3\) in toluene. AQPh\(_2\) was purified by crystallization from \(t\)-PrOH in 80% yield, and its structure was elucidated by X-ray analysis (Figure 5.8).
### Table 5.1 \(^1\)H NMR data * for 3,5-dimethylisoxazole and its organometallic derivatives

<table>
<thead>
<tr>
<th>R</th>
<th>C-3-CH₃</th>
<th>C-5-CH₃</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>H (^b)</td>
<td>2.20</td>
<td>2.35</td>
<td></td>
</tr>
<tr>
<td>Hg(OAc)</td>
<td>2.27</td>
<td>2.45</td>
<td>2.11 (s. CH₃)</td>
</tr>
<tr>
<td>SnBu₁</td>
<td>2.23</td>
<td>2.35</td>
<td>1-1.55 (m, 6H, CH₂), 0.89 (s. CH₃)</td>
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<tr>
<td>SnMe₁</td>
<td>2.23</td>
<td>2.36</td>
<td>0.31 (s. CH₃)</td>
</tr>
</tbody>
</table>

* 250 MHz, in CDCl₃ vs. TMS. \(^b\) From ref [5.1].

### Table 5.2 \(^1\)C NMR data * for 3,5-dimethylisoxazole and its organometallic derivatives

<table>
<thead>
<tr>
<th>R</th>
<th>C-3</th>
<th>C-4</th>
<th>C-5</th>
<th>C-3-Me</th>
<th>C-5-Me</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>H (^b)</td>
<td>159.9</td>
<td>102.3</td>
<td>169.0</td>
<td>12.1</td>
<td>11.3</td>
<td></td>
</tr>
<tr>
<td>Hg(OAc)</td>
<td>162.6</td>
<td>113.6</td>
<td>172.9</td>
<td>13.1</td>
<td>13.5</td>
<td>177.9 (CO), 22.8 (CH₃)</td>
</tr>
<tr>
<td>SnBu₁</td>
<td>164.7</td>
<td>105.7</td>
<td>173.5</td>
<td>13.2</td>
<td>13.3</td>
<td>29.0, 27.2, 9.6 (CH₂), 13.6 (CH₃)</td>
</tr>
<tr>
<td>SnMe₁</td>
<td>164.4</td>
<td>105.9</td>
<td>173.4</td>
<td>13.0</td>
<td>13.2</td>
<td>-10.2 (CH₃)</td>
</tr>
</tbody>
</table>

* 63 MHz, in CDCl₃ vs. TMS. \(^b\) From ref [5.1].
Figure 5.7. Synthesis of 1,8-diphenylanthraquinone (AQPh₂)

Figure 5.8. Ortep diagram of 1,8-diphenylanthraquinone (AQPh₂)
House et al. have previously reported the synthesis of AQPh₂ by two routes: via cross-coupling of 1,8-diiodoanthraquinone and diphenylcuprate [5.18] in a multi-step procedure with an overall yield of 16%, and via oxidation of 1,8-diphenylanthracene [5.19,5.20] with a total yield of 50-71%. The mild reaction conditions, easy purification and high yields of our two-step procedure provide a more efficient route for the preparation of AQPh₂.

Based on our new procedure for preparing AQPh₂, we proceeded to investigate the coupling reaction of AQ(OTf)₂ with the mercuric acetate (DMI-HgOAc) and boronic acid (DMI-B(OH)₂) derivatives of 3,5-dimethylisoxazole, using toluene or THF as solvents. No coupling occurred, and unreacted AQ(OTf)₂ was recovered. We also attempted this reaction using DMI-SnBu₃ as the coupling reagent in the presence of a Pd(0) (Pd(PPh₃)₄) or Pd(II) catalyst (PdCl₂(PPh₃)₂ or PdCl₂(AsPh₃)₂), in toluene or dioxane, also unsuccessfully.

### 5.2.3.2. Via 1,8-dibromoanthracene and -anthraquinone

We then turned our attention to the dibromo compound ABr₂ as potential electrophile for the desired coupling reaction. Although it is difficult to synthesize, ABr₂ has been shown to undergo efficient Pd-catalyzed coupling with an organotin reagent (see Chapter 4). Using the reaction conditions studied for the preparation of AA₂, treatment of ABr₂ with DMI-SnBu₃ and 3 mol % of PdCl₂(PPh₃)₂ in toluene, followed by purification using column chromatography, afforded 1,8-bis(3,5-dimethyl-4-isoxazolyl)anthracene (A(DMI)₂) in 30% yield (Figure 5.9). Slow evaporation of a hexane/AcOEt (3:1) solution gave A(DMI)₂ as light yellow needles.
Because of incomplete reaction and because some 1-bromo-8-chloroanthracene was present in the starting material, a small amount of the mono-coupled compounds: 1-bromo- and 1-chloro-8-(3,5-dimethyl-4-isoxazolyl)anthracenes, were also formed in the reaction and detected by GC-MS analysis ([M'] 351-353 and 307-309, respectively). However, because of their similar Rf values no attempt was made to separate them.

In order to improve the overall yield of the bis(3,5-dimethylisoxazolyl) product, we explored the reaction of the anthraquinone AQBr2 with the less sterically hindered tin reagent DMI-SnMe3. Under the same reaction conditions reported above for A(DMI)2, 1,8-bis(3,5-dimethylisoxazolyl)anthraquinone (AQ(DMI)2) was obtained in 47% yield (Figure 5.10) after purification by flash chromatography. Crystallization from toluene and i-PrOH/CH₂Cl₂ afforded two crystal forms of AQ(DMI)2; the X-ray structure of one of these is shown in Figure 5.11. Methyl coupling also occurred during the reaction to form 1-(3,5-dimethyl-4-isoxazolyl)-8-methylanthraquinone (AQMe(DMI)) in 12% yield. Slow evaporation of a hexane/EtOAc (2:1) solution gave AQMe(DMI) as yellow-orange needles, see X-ray structure in Figure 5.12. Poor yields of AQ(DMI)2 were obtained.
when DMI-SnMe$_3$ was stored in the refrigerator previous to its use, this may be caused by partial hydrolysis of the tin reagent.

![Chemical structures and reaction equation]

Figure 5.10. Synthesis of 1,8-bis(3,5-dimethylisoxazolyl)anthraquinone (AQ(DMI)$_2$)

Although trimethyltin compounds are known to afford faster rates of aryl transfer than their bulkier tributyltin counterparts [5.20], methyl transfer is also faster than butyl transfer. The use of the more hindered AQBr$_2$ may also explain the formation of some alkyl transfer product AQMe(DMI), while in the ABr$_2$ system, butyl coupling went undetected.

In addition to being formed in higher yields, the anthraquinone AQ(DMI)$_2$ is easier to isolate than the anthracene A(DMI)$_2$ by column chromatography due to its
Figure 5.11 Ortep diagram of 1,8-bis(3,5-dimethyl-4-isoxazolyl)anthraquinone (AQ(DMI)₂)

Figure 5.12 Ortep diagram of 1-(3,5-dimethyl-4-isoxazolyl)-8-methylanthraquinone (AQMe(DMI))
higher polarity in relation to the other side reaction products, while A(DMI)$_2$ usually elutes as a mixture with the side product 3,5,3',5'-tetramethyl-4,4'-biisoazole.

Following the literature procedure for reduction of 1,8-dichloroanthraquinone [5.21], treatment of AQ(DMI)$_2$ in aqueous Zn/NH$_3$ (Figure 5.13), afforded A(DMI)$_2$ in good yield (82%). The crystal structure of a second form of A(DMI)$_2$, obtained by crystallization from hot $i$-PrOH, was determined by X-ray analysis (Figure 5.14).

![Chemical structure](image)

**Figure 5.13.** Synthesis of A(DMI)$_2$ from AQ(DMI)$_2$

$^1$H and $^{13}$C NMR data, as well as the numbering scheme, for AQ(DMI)$_2$ and A(DMI)$_2$ are presented in Tables 5.3 and 5.4. The $^1$H NMR spectra are consistent with both compounds being formed as ca. 1:1 mixtures of atropisomers, with the isoxazole rings either facing each other (meso) or in opposite orientations (racemic). Two sets of methyl group protons (H-11 and H-12), corresponding to the two conformations of the bis(3,5-dimethyl-4-isoxazolyi) compound, are present in the same ratio. The $^{13}$C NMR spectrum of A(DMI)$_2$ also shows two signals each for C-13 and C-15 in approximately the same ratio.
5.2.4. Synthesis of 3,3'-[1,8-anthracenediyl]bis(4-amino-3-penten-2-one) (ABIH$_2$)

Hydrogenolysis of A(DMI)$_2$ with Raney nickel gave 3,3'-[1,8-anthracenediyl]bis(4-amino-3-penten-2-one) (ABIH$_2$), shown in Figure 5.15, in good yield (80%).
NMR spectra (Tables 5.3 and 5.4) reveal the formation of both meso and racemic atropisomers for ABIH₂, as shown by the two sets of resonances for several proton and carbon atoms. Integration of the methyl group protons indicate that the atropisomers are present in a 2.3:1 ratio.

We attempted to selectively cleave the N-O bond in AQ(DMI)₂, using RaNi [5 1] or Mo(CO)₆ [5.22] as reducing agents. However, these reactions gave unidentified mixtures of products (as shown by ¹H NMR). Reduction of the anthraquinone moiety in AQ(DMI)₂ is also possible under these conditions, which may account for the lack of selectivity and cleanliness of this reaction.

Compound ABIH₂ has shown considerable stability towards hydrolysis. Unlike most ketoenamines [5.1], ABIH₂ did not convert to its corresponding β-diketone (ABAH₂) when treated with acid (aqueous HCl or H₂SO₄) at room temperature or in refluxing EtOH (Figure 5.16). This unusual stability may be caused by steric factors and/or a strong H-bonding between the β-ketoenamine moieties.

Figure 5.16: Attempted synthesis of ABAH₂ from ABIH₂
<table>
<thead>
<tr>
<th>Compound</th>
<th>H-2</th>
<th>H-3</th>
<th>H-4</th>
<th>H-9</th>
<th>H-10</th>
<th>H-11</th>
<th>H-12</th>
<th>OH</th>
<th>NH</th>
</tr>
</thead>
<tbody>
<tr>
<td>AQ(DMI)$_2$</td>
<td>8.40</td>
<td>7.80</td>
<td>7.48</td>
<td>-</td>
<td>-</td>
<td>1.99</td>
<td>2.21</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(d, 7.8)</td>
<td>(l, 7.7)</td>
<td>(d, 7.8)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A(DMI)$_2$</td>
<td>8.10</td>
<td>7.55</td>
<td>7.32</td>
<td>8.16</td>
<td>7.87</td>
<td>2.03</td>
<td>2.20</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>(d, 8.4)</td>
<td>(dd, 8.6, 6.8)</td>
<td>(d, 6.6)</td>
<td>(d, 8.4)</td>
<td>(d, 8.6, 6.8)</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>ABIH$_2$</td>
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<td>7.48</td>
<td>8.00</td>
<td>8.50</td>
<td>8.40</td>
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<td>1.68</td>
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<td>(d, 8.5)</td>
<td>(d, 6.6)</td>
<td>(dd, 8.5, 6.7)</td>
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* 200 MHz, $\delta$/ppm vs. TMS ($J$/Hz in parentheses). $^b$ Possible dd. with overlapping peaks at 7.48 ppm.
Table 5.4. $^{13}$C NMR data * of AQ(DMI)$_2$, A(DMI)$_2$ and ABIH$_2$

<table>
<thead>
<tr>
<th>Compound</th>
<th>C-1</th>
<th>C-2</th>
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<th>C-4a</th>
<th>C-9a</th>
<th>C-9</th>
<th>C-10</th>
<th>C-11</th>
<th>C-12</th>
<th>C-13</th>
<th>C-14</th>
<th>C-15</th>
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<tbody>
<tr>
<td>AQ(DMI)$_2$</td>
<td>134.4</td>
<td>138.9</td>
<td>133.1</td>
<td>127.7</td>
<td>133.5</td>
<td>131.2</td>
<td>183.3</td>
<td>164.4</td>
<td>10.6</td>
<td>11.5</td>
<td>158.8</td>
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<td>A(DMI)$_2$</td>
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<td>128.6</td>
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<td>128.1</td>
<td>128.0</td>
<td>121.6</td>
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<td>11.4</td>
<td>159.5</td>
<td>114.5</td>
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<td>ABIH$_2$</td>
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<td>129.3</td>
<td>127.6</td>
<td>125.6</td>
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<td>28.5</td>
<td>161.0</td>
<td>106.4</td>
<td>196.8</td>
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</table>

* 63 MHz, unless otherwise noted; in CDCl$_3$, δ/ppm vs. TMS; assignments were made using DEPT experiments. $^b$ 50 MHz.
5.3. Conclusions

We have successfully obtained the bis(β-ketoenamine) ABIH$_2$ via Pd-catalyzed cross-coupling between 1,8-dibromoanthracene derivatives and trialkyltin reagents of 3,5-dimethylisoxazole, used as an acetylacetone synthon.

The synthesis of ABIH$_2$ will enable us to prepare a new family of cofacial bimetallic complexes either by direct complexation of ABIH$_2$ to metal atoms or by derivatization of the β-ketoenamine moieties to other chelating groups and subsequent reaction with metal centers.

In addition, we have synthesized the new compound AQ(OTf)$_2$, which is a valuable precursor for carbon-carbon bond formation, as evidenced by its use in our improved route for the preparation of AQPh$_2$.

5.4. Experimental Part

3,5-Dimethyl-4-iodoisoxazole was synthesized following the procedure described by Kochetkov et al. [5,14]. 1,8-Dibromoanthracene (ABr$_2$) and 1,8-dibromoanthraquinone (AQBr$_2$) were prepared as ca. 10:1 mixtures of 1,8-dibromo and 1-bromo-8-chloro compounds as reported in Section 4.4.1 and 4.4.2. PdCl$_2$(PPh$_3$)$_2$ was prepared following the literature procedure [5,23]. $^1$H and $^{13}$C NMR spectra were recorded by using Bruker AC200 and AC250 NMR spectrometers. An HP 5971 instrument was used for GC-MS. The mass spectrum of ABIH$_2$ was recorded with a Finnigan TSQ-70 triple quadrupole mass spectrometer using fast atom bombardment (FAB) ionization, with 3-nitrobenzyl alcohol as a matrix.
5.4.1. Synthesis of 1,8-ditriflatoanthraquinone (AQ(OTf)2)

Following the general method reported by Echavarren and Stille [5.2], to a solution of 1,8-dihydroxyanthraquinone (3.87 g, 16.1 mmol), in pyridine (20 mL) was added dropwise trifluoromethanesulfonic anhydride (5.96 mL, 35.4 mmol) at 0 °C under N2. The resulting red suspension was allowed to warm to room temperature and stirred for 23 h. The final mixture was quenched with H2O and the yellow precipitate formed was collected and washed with H2O to give 7.67 g (94.5%) of AQ(OTf)2. An additional amount of product left in the filtrate was recovered by extraction with diethyl ether. The organic layer was then washed with 10% HCl and H2O, dried over MgSO4, filtered and concentrated to yield 0.08 g (1%) more of AQ(OTf)2. Total yield 7.8 g (96%).

Crystallization from CHCl3/hexane afforded AQ(OTf)2 as yellow needles and chunks. 1H NMR (CDCl3, 200 MHz): 8.39 (dd, 2H, J = 7.9, 1.1), 7.91 (t, 2H, J = 7.9), 7.69 (dd, 2H, J = 8.3, 1.0), 13C NMR (CDCl3, 63 MHz): 180.1 (CO), 178.9 (CO), 147.5, 135.4 (CH), 134.6, 129.4 (CH), 127.7 (CH), 126.2, 118.8 (q, JCF = 127.4), EI-MS m/z (%): 504 (11, M′), 435 (2, M′- CF3), 348 (12), 307 (18), 279 (23), 251 (22), 223 (38), 182 (16), 157 (19), 126 (35), 91 (14, C8H6O′), 69 (100, CF3′).
5.4.2. Synthesis of 1,8-diphenylantraquinone (AQPh₂)

\[ \text{CF}_3\text{O}_2\text{SO} \quad \text{OSO}_2\text{CF}_3 \quad \text{B(OH)}_2 \quad \text{Pd}^{0}/\text{K}_2\text{CO}_3 \quad \text{toluene} \quad 70-90 \, ^\circ\text{C} \]

N₂ was passed through a suspension of AQ(OTf)₂ (0.33 g, 0.65 mmol), benzeneboronic acid (0.43 g, 3.5 mmol) and anhydrous K₂CO₃ (0.29 g, 1.8 mmol) in toluene (18 mL) for 15 minutes. Pd(PPh₃)₄ (0.05 g, 0.04 mmol) was added and the orange brown mixture was heated at 70-90 °C for 3 h. The final yellow reaction mixture was allowed to cool to room temperature and the yellow precipitate formed was collected. The remaining product left in the filtrate was recovered by extraction with diethyl ether. The organic layer was then washed with H₂O and 10% HCl, dried over MgSO₄, filtered and concentrated. The combined solids were crystallized from i-PrOH as yellow needles. Yield: 0.19 g (81%); ¹H NMR (CDCl₃, 200 MHz): 8 30 (dd, 2H, J = 7.6, 1.5), 7.72 (t, 2H, J = 7.6), 7.62 (dd, 2H, J = 7.6, 1.5), 7.37-7.27 (m, 10H); ¹³C NMR (CDCl₃, 63 MHz): 186.6 (CO), 183.6 (CO), 143.1, 140.4, 137.1 (CH), 134.9, 134.2, 132.1 (CH), 128.7 (CH), 128.1 (CH), 127.3 (CH), 126.3 (CH); EI-MS m/z (%)

- 360 (73, M⁺), 359 (100, M⁺ - H), 300 (10), 283 (9, M⁺ - C₆H₅), 180 (7), 171 (10), 164 (128), 150 (18.6), 77 (10, C₆H₅⁺).
5.4.3. Synthesis of (3,5-dimethyl-4-isoxazolyl)mercuric acetate (DMI-HgOAc)

Following the general method described by Kochetkov et al. [5.10], a solution of 3,5-dimethylisoxazole (2.78 mL, 28.6 mmol) and Hg(OAc)$_2$ (8.28 g, 26.0 mmol) in 20 mL of EtOH was refluxed on a steam bath for 20 minutes. The resulting colorless solution was allowed to cool to room temperature and the colorless crystals formed were collected and washed with H$_2$O. Yield: 3.5 g (76%).

5.4.4. Synthesis of (3,5-dimethyl-4-isoxazolyl)boronic acid (DMI-B(OH)$_2$)

Based on the general procedure reported by Breuer and Thorpe [5.12, 5.13], a solution of DMI-HgOAc (1.24 g, 3.5 mmol) in THF (30 mL) was treated dropwise with 1 M BH$_3$.THF (14 mL, 14 mmol) at room temperature under Ar. The resulting black-gray suspension was stirred for 3 hours, at which point 2 mL more of 1 M BH$_3$.THF was added. After 0.5 h the reaction mixture turned colorless and Hg deposited at the bottom of the flask. The solution was then quenched with H$_2$O (6 mL), and filtered through
 Celite to remove Hg. After evaporation of the solvents, the resulting white solid containing a mixture of B(OH)$_3$ and DMI-B(OH)$_2$ was allowed to dry under vacuum overnight. $^1$B NMR (THF, 128 MHz) $\delta$ -26.8 (DMI-B(OH)$_2$), -19.8 (B(OH)$_3$).

5.4.5. Synthesis of tributyl(3,5-dimethyl-4-isoxazolyl)tin (DMI-SnBu$_3$)

A mixture of Mg turnings (1.3 g, 52 mmol) and 3,5-dimethyl-4-iodoisoxazole (3.64 g, 16.3 mmol) in THF (60 mL) was heated to reflux under N$_2$ [5.8]. A solution of BrCH$_2$CH$_2$Br (2.81 mL, 32.6 mmol) in THF (10 mL) was added dropwise to the reaction mixture for 2 h, at a rate that prevented extreme bubbling, and then the mixture was refluxed for an additional 2.5 h. The orange-brown suspension was allowed to cool to room temperature and after dropwise addition of Bu$_3$SnCl (3.85 mL, 13.6 mmol) the resulting yellow suspension was stirred at room temperature overnight. The final reaction mixture was quenched with H$_2$O (100 mL) and the product extracted with diethyl ether (3x20 mL). The organic phase was then dried over MgSO$_4$, filtered and concentrated to give a brown crude oil, which was purified by distillation under reduced pressure to give DMI-SnBu$_3$ as a light yellow liquid (b.p. 135-141 °C/0.6 mmHg; lit. 140-150 °C/0.6 mmHg [5.15]). Yield: 4.0 g (63%); EI-MS m/z (%): 386 (18, M$^+$), 330 (13, M$^+$-C$_4$H$_4$), 274 (78, M$^+$-2 C$_4$H$_4$), 218 (94, M$^+$-3 C$_4$H$_4$), 216 (100), 121 (36), 80 (54), 41 (40).
5.4.6. Synthesis of (3,5-dimethyl-4-isoxazolyl)trimethyltin (DMI-SnMe₃)

Following the same procedure reported above for DMI-SnBu₃, a mixture of Mg turnings (1.23 g, 50.8 mmol) and 3,5-dimethyl-4-iodoisoxazole (3.78 g, 16.9 mmol) in THF (60 mL) was allowed to react with a solution of BrCH₂CH₂Br (2.92 mL, 33.9 mmol) in THF (10 mL). The orange-brown suspension was allowed to cool to room temperature and 1 M Me₃SnCl in THF (17 mL, 17 mmol) was added dropwise. The resulting pale yellow suspension was stirred at room temperature overnight. The resulting material was worked up as described above for DMI-SnBu₃ to give a brown crude oil, which was purified by flash chromatography (silica gel, hexane/AcOEt 4:1, Rf = 0.52) to afford DMI-SnMe₃ as a light yellow liquid. Yield: 2.58 g (59%), EI-MS m/z (%): 261 (2, [M+H]+), 260 (1, M'), 246 (100, M'+ H - CH₃), 244 (76), 216 (52), 165 (31), 135 (44), 120 (25), 80 (26).

5.4.7. Synthesis of 1,8-bis(3,5-dimethyl-4-isoxazolyl)anthracene (A(DMI)₂)

ABr₂ + DMI-SnBu₃ \xrightarrow{PdCl₂(PPh₃)₂/ toluene reflux} A(DMI)₂
N₂ was passed through a solution of ABr₂ (0.36 g, 1.1 mmol) and DMI-SnBu₃ (1.8 g, 4.7 mmol) in toluene (25 mL) for 3 h. PdCl₂(PPh₃)₂ (0.03 g, 0.04 mmol) was added and the orange solution was heated to reflux for 62 h. The resulting dark brown solution was allowed to cool to room temperature, diluted with diethyl ether (30 mL) and extracted with H₂O (3×15 mL) and saturated aqueous KF solution (4×15 mL). The organic phase was filtered, dried over MgSO₄, filtered and concentrated to give a yellow solid. The crude product was purified by flash chromatography (silica gel, hexane/AcOEt (3:1), Rf = 0.39) to give A(DMI)₂ as a pale yellow solid. Slow evaporation of a hexane/AcOEt (3:1) solution afforded A(DMI)₂ as light yellow needles. Yield: 0.12 g (31%); EI-MS m/z (%) 368 (100, M⁺), 311 (12), 284 (25), 283 (25), 268 (23), 242 (38), 241 (50), 240 (35), 213 (43), 202 (20).

5.4.8. Synthesis of 1,8-bis(3,5-dimethylisoxazolyl)anthraquinone (AQ(DMI)₂)

\[
\text{AQBr₂} + \text{DMI-SnBu₃} \xrightarrow{\text{PdCl₂(PPh₃)₂, toluene reflux}} \text{AQ(DMI)₂} + \text{AQMe(CDMI)}
\]
$N_2$ was passed through a solution of $\text{AQBr}_2$ (0.68 g, 1.9 mmol) and $\text{DMI-SnMe}_3$ (1.7 g, 6.6 mmol) in toluene (45 mL) for 1-2 h. $\text{PdCl}_2(\text{PPh}_3)_2$ (0.03 g, 0.04 mmol) was added to the reaction mixture and the temperature was increased to reflux. After 72 h, the resulting brown mixture was allowed to cool to room temperature, diluted with diethyl ether (30 mL) and extracted with $\text{H}_2\text{O}$ (2×15 mL). The organic phase was then dried over $\text{MgSO}_4$ and concentrated to give a crude orange solid, which was purified by flash chromatography. $\text{AQMe(DMI)}$ (silica gel, hexane/EtOAc (2:1), $R_f$ = 0.51) was obtained as an orange-yellow solid. Slow evaporation of a hexane/EtOAc (2:1) solution afforded $\text{AQMe(DMI)}$ as yellow-orange needles, yield 0.07 g (12%). $\text{AQ(DMI)}_2$ (silica gel, hexane/EtOAc (1:1), $R_f$ = 0.23) was obtained as an orange-yellow solid. Two crystal forms of $\text{AQ(DMI)}_2$ were obtained: orange-yellow fragments from the crude toluene mixture, and brown needles from $i-$PrOH/CH$_2$Cl$_2$, yield 0.35 g (47%).

$\text{AQ(DMI)}_2$: EI-MS $m/z$ (%): 398 (47, $M^+$), 357 (86), 338 (14), 324 (36), 296 (41), 286 (40), 272 (53), 214 (40), 200 (26), 189 (100), 174 (36), 75 (24)

$\text{AQMe(DMI)}$: $^1\text{H NMR}$ (CDCl$_3$, 250 MHz): 8.37 (dd, 1H, $J = 7.8$, 1.6), 8.20 (dd, 1H, $J = 7.8$, 1.3), 7.77 (t, 1H, $J = 7.6$), 7.66-7.55 (m, 2H), 7.49 (dd, 1H, $J = 7.6$, 1.6), 2.68 (s, 3H), 2.28 (s, 3H), 2.06 (s, 3H), $^{13}\text{C NMR}$ (CDCl$_3$, 63 MHz): 185.8 (CO), 183.7 (CO), 164.2, 159.0, 141.3, 138.4 (CH), 138.2 (CH), 134.5, 134.3, 134.1, 132.8 (CH), 132.7, 130.9, 127.5 (CH), 125.6, 116.6, 22.7 (CH$_3$), 11.4 (CH$_3$), 10.6 (CH$_3$), EI-MS $m/z$ (%): 317 (9, $M^+$), 276 (100, $M^-$ - C$_3$H$_7$N), 261 (62, $M^-$ - C$_3$H$_7$N - CH$_3$), 205 (23), 176 (46), 151 (18), 88 (9), 75 (7), 63 (8).
5.4.9. Synthesis of $A(DMI)_2$ via reduction of $AQ(DMI)_2$

A mixture of $AQ(DMI)_2$ (0.27 g, 0.67 mmol) and Zn dust (2.0 g) in 28% aqueous NH$_3$ (30 mL) was heated at 50-55 °C for 7 h. The resulting red mixture was allowed to cool, filtered and the residue and filtrate were each extracted with CH$_2$Cl$_2$ and EtOAc. The combined organic extracts were evaporated to dryness. The pale yellow residue was then dissolved in hot $i$-PrOH (35-40 mL) and 12 M HCl (1-2 mL) and refluxed for 4 h. The final yellow solution was concentrated to give $A(DMI)_2$ as a yellow solid. Yield: 0.20 g (82%). Crystallization from hot $i$-PrOH afforded $A(DMI)_2$ as yellow-orange fragments.

5.4.10. Synthesis of 3,3'-(1,8-anthracenediyl)bis(4-amino-3-pent-2-one) ($ABIH_2$)

A mixture of $A(DMI)_2$ (0.20 g, 0.54 mmol) and RaNi (0.1-0.2 g) in EtOH (150 mL) was heated at reflux for 8 h. The final reaction mixture was allowed to cool, filtered
through Celite and the residue washed with EtOAc. The combined filtrates were concentrated to dryness to give AB1H₂ as an orange-brown solid. Yield: 0.16 g (80%); FAB-MS m/z 373.4 [M+H]+.

5.5. References


Chapter 6

Synthesis of Cofacial Iridium and Rhodium Complexes of an Anthracenebis(β-ketoenamine) Ligand

6.1. Introduction

The synthesis of the new binucleating ligand ABIH₂ (Chapter 5) allows the preparation of a new family of cofacial bimetallic complexes, such as M₂(ABI)₂ and (ABI)[ML₂]₂ (Figure 6.1), with controllable environments around the metal centers, and the more rigid M₂(ABI)₂, which may serve as catalysts for multi-electron redox reactions.

![Figure 6.1 General structure of cofacial bimetallic complexes derived from ABIH₂](image)

We report here the synthesis of the bis(η⁴-1,5-cyclooctadienyl)iridium) and bis(dicarbonylrhodium) derivatives of ABIH₂, (ABI)[Ir(COD)]₂ and (ABI)[Rh(CO)₂]₂ respectively (Figure 6.2), by direct complexation of [(μ-Cl)Ir(COD)]₂ or [(μ-Cl)Rh(CO)₂]₂ respectively, with ABIH₂ in the presence of aqueous K₂CO₃.
6.2. Results and Discussion

A variety of cofacial transition-metal complexes based on the bis(β-ketoenamine) ligands BBIH$_2$ [6.1] and α,α'-bis(salicylimino)-m-xylene, SIXH$_2$ [6.2] (see Figure 6.3), have been studied by our group in the past years. They are readily synthesized in good yields by treatment of the corresponding M(II) salt with the bis(β-ketoenamine) ligand in the presence of triethylamine or aqueous Cu(NH$_3$)$_4^{2-}$ with BBIH$_2$. Our attempts to prepare similar cofacial binuclear complexes using the anthracene-based ligand ABIH$_2$ by these same methods gave only insoluble powders. (Even if the desired M$_2$(ABI)$_2$ formed, it would be expected to have low solubility)

In order to obtain more soluble and versatile bimetallic complexes, we turned our attention to the synthesis of the less symmetric systems (ABI)[ML$_2$]$_2$ (Figure 6.1) Several mononuclear Rh(I) and Ir(I) carbonyl complexes of α-ketoenamine ligands [6.3] have been synthesized by reaction of the corresponding [(μ-Cl)M(CO)$_2$]$_2$ in benzene or
methanol with the ligand in the presence of BaCO$_3$. Kumar et al. have reported the formation of the bis(cyclooctadiene) Rh(I) and Ir(I) complexes containing the bridging bis(β-ketoenamine) ligand SIXH$_2$ [6,4], by treatment of an ethereal solution of the corresponding [((μ-Cl)M(COD))]$_2$ and SIXH$_2$ with aqueous NaOH (Figure 6.4).

Based on the method developed by Kumar et al., we prepared the bimetallic complexes (ABI)[Ir(COD)]$_2$ and (ABI)[Rh(CO)$_2$]$_2$ by the reaction of [((μ-Cl)Ir(COD))]$_2$,
or [(μ-Cl)Rh(CO)₂]₂ respectively, with ABIH₂ and aqueous K₂CO₃ in ether at room temperature (Figure 6.5). Conversion of the free ligand into its binuclear complexes was followed by ¹H NMR. No reaction occurred with the use of other bases, such as aqueous KOH or solid K₂CO₃, probably because deprotonation of the ligand did not take place.

Both complexes were isolated as yellow, air-stable solids, and they are soluble in organic solvents. (ABI)[Ir(COD)]₂ decomposes in aerated solutions after a few hours, unlike (ABI)[Rh(CO)₂]₂ which remains stable in solution for weeks.

Figure 6.5. Synthesis of binuclear iridium and rhodium complexes of ABIH₂ (meso atropisomer shown)
'H and 13C NMR data, Tables 6.1 and 6.2, are consistent with the proposed structures of (ABI)[Ir(COD)]2 and (ABI)[Rh(CO)2]2. Complexation of ABIH2 causes a general downfield shift of the proton and carbon atoms of the β-ketoenamine moiety, with the exception of C-9 and C-10, which show upfield shifts. In general appearance, the aromatic regions of both bimetallic complexes are similar to that of the parent ABIH2. The spectral data support the formation of both meso and racemic atropisomers for (ABI)[Rh(CO)2]2 (see Figure 6.6), as shown by the two sets of resonances for H-9 and the amino and methyl (H-11 and H-12) group protons, as well as for the carbons at the 2, 7, 10, 11 and 13-positions. Furthermore, the four doublets shown by the carbonyl ligands in (ABI)[Rh(CO)2]2, JRh = 46.8-53.1 Hz, are consistent with the presence of the two geometries for the rhodium complex.

Figure 6.6. Structures of the atropisomers of (ABI)[ML2]2 complexes

The 'H and 13C NMR data for (ABI)[Ir(COD)]2 do not exhibit the same degree of splitting for the proton and carbon resonances for the two isomeric forms as (ABI)[Rh(CO)2]2. However, the presence of two sets of amino and methyl (H-11 and
Table 6.1. $^1$H NMR data * of ABIH₂ and its binuclear metal complexes

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* 200 MHz, unless otherwise noted. in CDCl₃, δ/ppm vs TMS (J/Hz in parentheses)  b Possible dd. with overlapping peaks at 7.48 ppm  c 250 MHz.
Table 6.2. $^{13}$C NMR data of ABIH$_2$ and its binuclear metal complexes

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$^a$ In CDCl$_3$, $\delta$/ppm vs. TMS, assignments were made using DEPT experiment. $^b$ 50 MHz. $^c$ 75 MHz. $^d$ $J$($^{13}$C,$^{103}$Rh). $^e$ 63 MHz.
H-12) protons and methyl carbon C-12 resonances reveals the formation of both atropisomers for (ABI)[Ir(COD)]$_2$. The proton resonances of the COD ligand in (ABI)[Ir(COD)]$_2$ show similar broadness and chemical shifts as the COD protons in (SIX)[Rh(CO)$_2$]$_2$ [6.4]. Both COD olefinic (3.4-4.4 ppm) and aliphatic (1.8-2.4 ppm) protons are shifted upfield compared to those of the free COD (5.60 and 2.39 ppm, respectively). Mass spectroscopy confirms the structure of (ABI)[Ir(COD)]$_2$, showing the parent ion at $m/e$ 968-973 with an ion distribution in agreement with that expected for $^{191}$Ir, $^{193}$Ir and $^{13}$C isotopes.

The atropisomers of (ABI)[Ir(COD)]$_2$ are present in a 2.3:1 ratio, as calculated from the integration of the imino group protons, identical to the value observed for the atropisomers of the free ligand AB1H$_2$ (see Section 5.2.4). The proximity of other signals to the amino and methyl group proton resonances of (ABI)[Rh(CO)$_2$]$_2$ prevent an accurate measurement of the ratio of its atropisomers.

Table 6.3: IR data of AB1H$_2$ and its bimetallic complexes

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<td>1608 (vs, CO)</td>
<td></td>
<td>3381 (vs br. NH), 2929 (w. CH), 1265 (m, CN)</td>
</tr>
<tr>
<td>(ABI)[Ir(COD)]$_2$</td>
<td>1614 (sh), 1559 (s, CO)</td>
<td>3421 (br. NH), 2934 (w, CH), 2873 (w, CH), 2828 (w, CH), 1472 (m), 1386 (m)</td>
<td></td>
</tr>
<tr>
<td>(ABI)[Rh(CO)$_2$]$_2$</td>
<td>2073 (vs), 2005 (vs)</td>
<td>1572 (m, CO)</td>
<td>3371 (w, NH)</td>
</tr>
</tbody>
</table>

* In KBr, unless otherwise noted. b In CHCl$_3$ solution.
Infrared data for \( \text{ABIH}_2, (\text{ABI})[\text{Ir(COD)}]_2 \) and \( (\text{ABI})[\text{Rh(CO)}]_2 \) are reported in Table 6.3. \( (\text{ABI})[\text{Rh(CO)}]_2 \) shows two strong absorptions at 2073 and 2005 \( \text{cm}^{-1} \) attributable to \( \nu_{\text{CO}} \) for the CO ligands. The carbonyl stretching for the \( \beta \)-ketoenamine moiety shifts to lower values on coordination of the \( \text{ABIH}_2 \) ligand, with \( (\text{ABI})[\text{Ir(COD)}]_2 \) showing a red shift that is 13 \( \text{cm}^{-1} \) greater than that for \( (\text{ABI})[\text{Rh(CO)}]_2 \).

6.3. Conclusions

We have successfully synthesized two new cofacial iridium and rhodium complexes from the anthracenebis(\( \beta \)-ketoenamine) ligand \( \text{ABIH}_2 \). Spectral data support the formation of both meso and racemic isomers for \( (\text{ABI})[\text{Ir(COD)}]_2 \) and \( (\text{ABI})[\text{Rh(CO)}]_2 \). These compounds represent the first members of a new family of cofacial bimetallic complexes that should provide for greater flexibility in their molecular and electronic structure and better access of substrate molecules to the intramolecular binding site than previous cofacial bis(\( \beta \)-diketonate) binuclear metal complexes.

6.4. Experimental Part

\( \text{^1H} \) and \( \text{^{13}C} \) NMR spectra were recorded by using Bruker AC200, AC250 and ARX300 NMR spectrometers. Infrared spectra were obtained with a Perkin Elmer 1760X instrument. The mass spectrum of \( (\text{ABI})[\text{Ir(COD)}]_2 \) was recorded with a Finnigan TSQ-70 triple quadrupole mass spectrometer using fast atom bombardment (FAB) ionization, with 3-nitrobenzyl alcohol as a matrix.
6.4.1. Synthesis of (ABI)[Ir(COD)]$_2$

To a solution containing $[(\mu$-Cl)Ir(COD)]$_2$ (30 mg, 0.042 mmol) and ABIH$_2$ (15 mg, 0.042 mmol) in ether (15 mL) was added dropwise aqueous K$_2$CO$_3$ solution (1.5 mL, 0.33 M) under N$_2$, the mixture was stirred vigorously for 0.5 h at room temperature. The resulting reaction mixture was then evaporated to dryness using a N$_2$ flow. The greenish yellow crude solid was washed with hexane under Ar to afford a yellow solid containing KCl, KHCO$_3$, and (ABI)[Ir(COD)]$_2$ as a yellow solid.

6.4.2. Synthesis of (ABI)[Rh(CO)$_2$)$_2$

To a solution containing $[(\mu$-Cl)Rh(CO)$_2$)$_2$ (12 mg, 0.03 mmol) and ABIH$_2$ (10 mg, 0.03 mmol) in ether (10 mL) was added dropwise aqueous K$_2$CO$_3$ solution (0.6 mL,
0.2 M) under N₂; the mixture was and stirred vigorously for 0.5 h at room temperature. The resulting reaction mixture was evaporated to dryness using a N₂ flow. The dark crude solid was then treated with CHCl₃, and the solution was filtered and concentrated to afford pure (ABI)[Rh(CO)₂]₂ as a yellow solid.

6.5. References


Chapter 7

Conclusions

The synthesis of complexes I and II shows the feasibility of π complexation of chloroanthracene derivatives to CpFe' moieties under mild reaction temperatures in moderate yields. The reduction of AC12 during π complexation to CpFe' agrees with the behavior previously reported for anthracene. Formation of \([\eta^6-\eta^6-(ABAH_2)(FeCp)_2]^2^+\) was unsuccessful. Compound II decomposed instead during the reaction conditions to form FeCp_2 and Fe(acac)_3. Reactions of II with other nucleophiles derived from dimethyl malonate and diethyl ethylmalonate were also unsuccessful.

The ligand substitution reaction of ferrocene with AEC12 afforded the mono-iron complex III as the only reaction product, in moderate yield. X-ray and spectral analysis confirm the endo conformation of complex III. More studies are recommended to establish the mechanism for the reduction of AEC12 during π complexation. Reaction of III with acac did not give any substitution product, and the free arenes AEC12 and AEH2Cl2 were recovered on workup.

We have successfully synthesized the new diacetonyl compound AA2 via Pd-catalyzed reaction of acetonyltributyltin, prepared in situ, with 1,8-dibromoanthracene in good yields. This compound may serve as a potential precursor for the preparation of the bis(β-diketone) ABAH2. Future work in the acetylation of AA2 is recommended.
We have successfully obtained the bis(β-ketoenamine) ABIH₂ via Pd-catalyzed cross-coupling between 1,8-dibromoanthracene derivatives and trialkyltin reagents of 3,5-dimethylisoxazole, used as an acetylacetone synthon. The synthesis of ABIH₂ will enable us to prepare a new family of cofacial bimetallic complexes either by direct complexation of ABIH₂ to metal atoms or by derivatization of the β-ketoenamine moieties to other chelating groups and subsequent reaction with metal centers. In addition, we have synthesized the new compound AQ(OTf)₂, which is a valuable precursor for carbon-carbon bond formation, as evidenced by its use in our improved route for the preparation of AQPh₂.

We have successfully synthesized two new cofacial iridium and rhodium complexes from the anthracenebis(β-ketoenamine) ligand ABIH₂. Spectral data support the formation of both meso and racemic isomers for (ABI)[Ir(COD)]₂ and (ABI)[Rh(CO)₂]₂. These compounds represent the first members of a new family of cofacial bimetallic complexes that should provide for greater flexibility in their molecular and electronic structure and better access of substrate molecules to the intramolecular binding site than previous cofacial bis(β-diketonate) binuclear metal complexes.
Appendixes
Appendix 1. $^1$H NMR spectrum of $[\eta^6-(1,8\text{-dichloro-9,10-dihydroanthracene})\text{FeCp}]\text{(PF}_6\text{)}$ (I) at 250 MHz in CD$_3$COCD$_3$.

Appendix 2. $^{13}$C NMR spectrum of $[\eta^6-(1,8\text{-dichloro-9,10-dihydroanthracene})\text{FeCp}]\text{(PF}_6\text{)}$ (I) at 50 MHz in CD$_3$COCD$_3$. 
Appendix 3. $^1$H NMR spectrum of $[\eta^6,\eta^6-(1,8\text{-dichloro-9,10-dihydroanthracene})\text{FeCp}_2]\text{(PF}_6)_2$ (II) at 200 MHz in CD$_3$COCD$_3$.

Appendix 4. $^{13}$C NMR spectrum of $[\eta^6,\eta^6-(1,8\text{-dichloro-9,10-dihydroanthracene})\text{FeCp}_2]\text{(PF}_6)_2$ (II) at 50 MHz in CD$_3$COCD$_3$. 
Appendix 5: \( ^1 \)H NMR spectrum of 1,8-dichloro-9,10-dihydroanthracene (AH;Cl\(_2\)) at 200 MHz in CD\(_3\)COCD\(_3\).

Appendix 6: \( ^{13} \)C NMR spectrum of 1,8-dichloro-9,10-dihydroanthracene (AH;Cl\(_2\)) at 50 MHz in CDCl\(_3\).
Appendix 7. $^1$H NMR spectrum of 1,8-dichlorodibenzobarrelene ($\text{AECI}_2$) at 200 MHz in CDCl$_3$.

Appendix 8. $^{13}$C NMR spectrum of 1,8-dichlorodibenzobarrelene ($\text{AECI}_2$) at 50 MHz in CDCl$_3$. 
Appendix 9  $^1$H NMR spectrum of [endo-(1,8-dichloro-9,10-ethano-9,10-
dihydroanthracene)FeCp](PF$_6$) (III) at 400 MHz in CDCl$_3$

Appendix 10  $^{13}$C NMR spectrum of [endo-(1,8-dichloro-9,10-ethano-9,10-
dihydroanthracene)FeCp](PF$_6$) (III) at 50 MHz in CDCl$_3$
Appendix 11 $^1$H NMR spectrum of 1,8-diacetonylanthracene (AA$_2$) at 250 MHz in CDCl$_3$

Appendix 12 $^{13}$C NMR spectrum of 1,8-diacetonylanthracene (AA$_2$) at 63 MHz in CDCl$_3$
Appendix 13 $^1$H NMR spectrum of 1,8-ditriflatoanthraquinone (AQ(OTf)$_2$) at 200 MHz in CDCl$_3$.

Appendix 14 $^{13}$C NMR spectrum of 1,8-ditriflatoanthraquinone (AQ(OTf)$_2$) at 63 MHz in CDCl$_3$. 
Appendix 15. $^1H$ NMR spectrum of 1,8-diphenylanthraquinone (AQPh$_2$) at 200 MHz in CDCl$_3$.

Appendix 16. $^{13}C$ NMR spectrum of 1,8-diphenylanthraquinone (AQPh$_2$) at 50 MHz in CDCl$_3$. 
Appendix 17 $^1$H NMR spectrum of (3,5-dimethyl-4-isoxazolyl)mercuric acetate (DML-HgOAc) at 250 MHz in CDCl$_3$.

Appendix 18 $^{13}$C NMR spectrum of (3,5-dimethyl-4-isoxazolyl)mercuric acetate (DML-HgOAc) at 63 MHz in CDCl$_3$. 
Appendix 19: $^1$H NMR spectrum of tributyltin(3,5-dimethyl-4-isoxazolyl)tin (DMI-SnBu$_3$) at 250 MHz in CDCl$_3$.

Appendix 20: $^1$C NMR spectrum of tributyltin(3,5-dimethyl-4-isoxazolyl)tin (DMI-SnBu$_3$) at 63 MHz in CDCl$_3$. 
Appendix 21 $^1$H NMR spectrum of (3,5-dimethyl-4-isoxazolyl)trimethyltin (DMI-SnMe$_3$) at 250 MHz in CDCl$_3$.

Appendix 22 $^{13}$C NMR spectrum of (3,5-dimethyl-4-isoxazolyl)trimethyltin (DMI-SnMe$_3$) at 63 MHz in CDCl$_3$. 
Appendix 23. $^1$H NMR spectrum of 1,8-bis(3,5-dimethyl-4-isoxazolyl)anthracene (A(DMI)$_2$) at 200 MHz in CDCl$_3$.

Appendix 24. $^{13}$C NMR spectrum of 1,8-bis(3,5-dimethyl-4-isoxazolyl)anthracene (A(DMI)$_2$) at 63 MHz in CDCl$_3$.
Appendix 25. $^1$H NMR spectrum of 1,8-bis(3,5-dimethyl-4-isoxazolyl)anthraquinone (AQ(DMI)$_2$) at 200 MHz in CDCl$_3$.

Appendix 26. $^{13}$C NMR spectrum of 1,8-bis(3,5-dimethyl-4-isoxazolyl)anthraquinone (AQ(DMI)$_2$) at 63 MHz in CDCl$_3$. 
Appendix 27 $^1$H NMR spectrum of 1-(3,5-dimethyl-4-isoxazolyl)-8-methylanthraquinone (AQMe(DMI)) at 250 MHz in CDCl$_3$.

Appendix 28 $^{13}$C NMR spectrum of 1-(3,5-dimethyl-4-isoxazolyl)-8-methylanthraquinone (AQMe(DMI)) at 63 MHz in CDCl$_3$. 
Appendix 29 $^1$H NMR spectrum of 3,3'-[1,8-anthracenediy]bis(4-amino-3-penten-2-one) (ABIH$_2$) at 200 MHz in CDCl$_3$

Appendix 30 $^{13}$C NMR spectrum of 3,3'-[1,8-anthracenediy]bis(4-amino-3-penten-2-one) (ABIH$_2$) at 50 MHz in CDCl$_3$
Appendix 31. $^1$H NMR spectrum of (ABI)[Ir(COD)]$_2$ at 250 MHz in CDCl$_3$

Appendix 32. $^{13}$C NMR spectrum of (ABI)[Ir(COD)]$_2$ at 63 MHz in CDCl$_3$
Appendix 33 $^1$H NMR spectrum of $(AB1)[Rh(CO)_2]_2$ at 200 MHz in CDCl$_3$.

Appendix 34 $^{13}$C NMR spectrum of $(AB1)[Rh(CO)_2]_2$ at 75 MHz in CDCl$_3$. 
Vita

Maria del Rosario Benites (Charo) was born on November 27, 1965 in Lima, Perú. She received her B.S. degree in Chemistry from the Pontificia Universidad Católica del Perú in 1990, and continued her education with Dr. Andrew W. Maverick at Louisiana State University from 1990 to the present. She is currently a candidate for the degree of Doctor of Philosophy in the department of Chemistry.
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Date of Examination: October 23, 1995