Chemical reduction of polycyclic aromatic ligands with heavy group 2 metals

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Chemical Reduction of Polycyclic Aromatic Ligands with Heavy Group 2 Metals

By

Andrew Uresk

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ABSTRACT

The chemistry of the alkaline earth metals has received a renewed interest in the last decades. The lighter Group 2 metal, magnesium, has gathered the most attention, as it is a key component of Grignard reagents, while the heavier metals have been less studied. The early alkaline earth metals are known to exhibit some similarity with both the alkali and lanthanide metals in $\pi$-complexation reactions with planar aromatic hydrocarbons (PAHs). However, the products of heavier Group 2 elements such as strontium and barium were found to be more difficult to synthesize and isolate, thus requiring the development of new synthetic approaches. The history of the Group 2 organometallic compounds, especially those of the heavy congeners calcium, strontium, and barium, is discussed in Chapter 1 with a few key applications.

The focus of this experimental work is the synthesis and X-ray structural analysis of complexes of the heavy Group 2 metals with planar polycyclic aromatic ligands. In Chapter 2, the activation methods used for the Group 2 metals are described. Unlike the alkali metals, the alkaline earth metals require either exposure of their surface as finely divided metal powders or chemical activation prior to use. As new and improved methods to activate the Group 2 metals are developed, the chemistry and applications of alkaline earth metals can be greatly expanded. The entrainment method utilizing diiodoethane (DIE) has been selected for this work, as it has been successful in activation reactions of magnesium and calcium. Chapter 3 reports the details on synthesis and crystallization of two new barium complexes with anthracene ($C_{14}H_{10}$) and fluoranthene ($C_{16}H_{10}$). This is the first study where the entrainment with DIE has been applied for activation of barium metal. The resulting products were found to be mixed-ligand in type, as confirmed by their X-ray structural characterization, namely \{[BaI(THF)$_3$]$^2^+$[C$_{14}$H$_{10}$]$^2^-$\}$\infty$ and
Nevertheless, they represent the first two examples of structurally characterized barium(II) complexes with the dianions of anthracene and fluoranthene. It is worth mentioning here that only a handful of such complexes with alkali and light alkaline earth metals have been reported prior to this work. The new barium products are the first examples of Group 2 π-complexes with planar PAHs forming the extended 1D polymeric structures in the solid state.

In summary, this work provides the first investigation of the synthesis and single crystal X-ray diffraction of two new complexes of barium(II) with anthracene and fluoranthene dianions. The difference in activation pathways utilizing DIE was revealed for barium metal compared with lighter Group 2 congeners. Further development and expansion of the heavy Group 2 metal organometallic chemistry is necessary as the complexes show applications in organic synthesis, materials design, and catalysis. This work provides an entry for future research into the coordination and organometallic chemistry of the heavy alkaline earth metals.
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Chapter 1

Introduction: Organometallic Chemistry of the Heavy Alkaline Earth Metals

Chemistry of the Group 2 metals has been progressing with a slow pace compared to alkali metals due to a number of difficulties. The challenges of the alkaline earth metals lie mainly with their low reactivity, high insolubility, and extreme air and moisture sensitivity. As interest increased in the organometallic chemistry of these elements, the available information on the reactions and structures of alkaline earth metal compounds has recently been expanded. However, the focus mainly remains on the early Group 2 metals, while the heavy congeners receive less attention. At the same time, the heavy alkaline earth organo metallics show a range of applications in both organic and materials synthesis,[1,2] as well as in catalysis,[3] thus requiring further development and expansion of their chemistry.

1.1 Grignard Reagents

The first organometallic compound of the Group 2 metals goes back to 1866 when James Alfred Wanklyn discovered diethylmagnesium.[4] However, it was not until François Auguste Victor Grignard developed the Grignard reagents in 1900 that organometallic chemistry utilizing the alkaline earth metals began to be explored. By 1912, when Grignard won the Nobel Prize for his achievement, these reagents were already commonly used in organic chemistry (1; Scheme 1.1). The most common application for Grignard reagents is their use as metalating reagents or as transfer reagents for alkyl and aryl groups.[5]
Scheme 1.1. Structure of phenylmagnesium bromide, a typical Grignard reagent.

The other early metals in Group 2, such as beryllium and calcium, proved to be much more difficult to engage in the synthesis of Grignard reagents, owing to their decreased reactivity. Organocalcium halide complexes are limited to primary alkyl iodides; their reactions proceed slowly and irregularly, and have unsatisfactory yields. The organoberyllium halides require heating at high temperatures for extended time periods. Additionally, due to the high toxicity of beryllium, its organometallic chemistry was not pursued. The heavy Group 2 analogues of the Grignard reagents remained virtually untouched by organometallic chemists until the mid-1900s. Beckman began the study of the dialkyls and alkyl halides of the Group 2 elements in 1905. Gilman and coworkers continued his work into the development of new Group 2 Grignard reagents from 1920 to 1940. However, it was found that many of these compounds are thermally unstable and have low solubility in organic solvents. The difficult synthesis of these compounds made them unsatisfactory for general use in organometallic chemistry, leaving the early Grignard reagents as the most useful agents for this type of chemistry.

1.2 Metallocene Chemistry

The discovery of the sandwich structure of ferrocene, Fe(C₅H₅)₂, (2; Scheme 1.2) in 1952 by Wilkinson and Woodward sparked a rapid interest and development into this field of chemistry.
organometallic chemistry. Ferrocene has an extended number of applications including its use in optical and redox devices, batteries, and catalysis, to name a few. From the discovery of ferrocene, many “sandwich” compounds have been investigated. Of these metallocenes, those of the heavy Group 2 metals (Ca, Sr, and Ba) are of particular interest.

Scheme 1.2. Structure of bis(η⁵-cyclopentadienyl)iron, ferrocene.

1.2.1 Light Group 2 Metallocenes

Beryllocene (3; Scheme 1.3), bis(cyclopentadiene)beryllium (Be(C₅H₅)₂), was first synthesized by Fischer and Hoffman in 1959 through the reaction of beryllium(II) chloride and sodium cyclopentadienyl (Scheme 1.4). The structure of the beryllium sandwich was shown to be different from that of ferrocene. Using electron diffraction, a slip sandwich structure was confirmed for beryllocene with beryllium disordered between the two nonequivalent cyclopentadienyl (Cp) rings. In the solid-state, beryllium is η⁵-bound to one Cp-ring and η¹-coordinated to the other. The ring to ring distance in beryllocene is 3.375(5) Å, which is marginally larger than that observed for ferrocene with a ring to ring distance of 3.286(6) Å. Additionally, beryllocene is much less stable in air than ferrocene and decomposes to beryllium hydroxide and Cp when exposed to water.
Scheme 1.3. Structures of bis(cyclopentadienyl) metallocenes of beryllium and magnesium.

\[
\begin{align*}
\text{BeCl}_2 + 2 \text{Na(C}_5\text{H}_5) & \rightarrow \text{Be(C}_5\text{H}_5)_2 + 2 \text{NaCl} \\
\text{MgBr}_2 + 2 \text{Na(C}_5\text{H}_5) & \rightarrow \text{Mg(C}_5\text{H}_5)_2 + 2 \text{NaBr}
\end{align*}
\]

Scheme 1.4. Syntheses of bis(cyclopentadienyl)beryllium (left) and bis(cyclopentadienyl)magnesium (right).

Magnesocene (4; Scheme 1.3), bis(cyclopentadienyl)magnesium (Mg(C₅H₅)₂), was first synthesized in 1954 by Cotton and Wilkinson, through addition of sodium cyclopentadienyl to magnesium(II) bromide (Scheme 1.4). Magnesocene adopts a sandwich structure isostructural to that found for ferrocene. In contrast to ferrocene, magnesocene shows slight dissociation and ion association in ethereal solvents, which gives solutions of magnesocene a small conductivity. Magnesium is 1.96 Å from each Cp-ring making the ring to ring distance to be 3.960(6) Å in magnesocene, which is significantly greater than that found in beryllocene. This increase in the ring to ring distance is likely due to the increased metal radius. The ionic radii of the alkali earth metals increase down the group with beryllium and magnesium having ionic radii of 0.31 Å and 0.65 Å, respectively (Scheme 1.5).
1.2.2 Heavy Group 2 Metallocenes

Zerger and Stucky\textsuperscript{[18]} were the first to isolate and structurally characterize the heavy Group 2 sandwich compound, bis(cyclopentadienyl)calcium or calcocene (Ca(C$_5$H$_5$)$_2$) in 1974, almost 20 years after it was first prepared by Ziegler and coworkers (5).\textsuperscript{[19]} The easiest way to prepare organocalcium compounds is with the use of liquid ammonia, where calcium metal is soluble. However, this reaction leads to insoluble products that are not easily characterized after the evaporation of the solvent.\textsuperscript{[20]} Ziegler and coworkers synthesized calcocene using calcium(II) carbide and cyclopentadiene in liquid ammonia (Scheme 1.6), but they were only able to analyze the structure in solution with infrared spectroscopy (IR). The IR spectrum of the compound suggested a weak coupling of the two Cp-rings through a covalent bonding component.\textsuperscript{[21]} Based on these findings, the structure of this compound was alleged to be held together by electrostatic forces as well as a significant attraction with calcium to the Cp-rings in the solid-state. To get more information on the structure of this compound, Zerger and Stucky used Fisher’s\textsuperscript{[22]} method (Scheme 1.6) to prepare the unsolvated calcocene complex. Utilizing this method, Zerger and Stucky were able to isolate crystals of the dicyclopentadienylcalcium complex and to solve its structure using X-ray diffraction.
Scheme 1.6. Synthesis of bis(cyclopentadienyl)calcium, calcocene.

The X-ray structure of calcocene is interesting because it exhibits a unique nonparallel polymeric arrangement in the solid-state with four inequivalent cyclopentadienyl rings coordinated to each calcium atom (5; Figure 1.1). The structure of calcocene shows a trigonal geometry with calcium coordinated to three bridging Cp-rings with a fourth perpendicular to a plane generated by the centroids of the other three Cp-rings. The C–C distances for the cyclopentadienyl rings are essentially all the same with an average of 1.385(23) Å and bond angles of 108.0(15)°. The average Ca–C distance is 2.791(2) Å for the two η⁵-bound rings, 2.838(2) Å for the η³-bound ring, and 3.100(2) Å for the terminal η¹-coordinated Cp-ring. The non-sandwich structure of calcocene is the first example of a cyclopentadienyl complex with this type of coordination.[168] As a result, the unique structure of calcocene cannot be directly compared to those of beryllocene and magnesocene.

Figure 1.1. Solid-state packing of 5 showing a 3D polymeric structure. Hydrogen atoms and disordered C₅H₅ rings have been omitted for clarity.
The strontium dicyclopentadienyl complex, Sr(C_5H_5)_2 (6), was successfully prepared by Fischer and Stölzle[22] in 1961, using strontium(II) hydride and cyclopentadiene in dimethylformamide (DMF) (Scheme 1.7). However, isolation of the compounds in solution for both the strontium and barium complexes is much more complicated than for the calcium analogue.[25] No structural analysis on bis(cyclopentadienyl)strontium has been completed to date, as isolation of the product has proven difficult due to its low solubility in ethereal solvents. However, it is suspected that it is a polymer in the solid-state due to its high sublimation temperature and a similar IR spectrum to that of the calcium analogue.[21,23]

$$\text{SrH}_2 + 2 \text{C}_5\text{H}_6 \overset{\text{DMF}}{\rightarrow} \text{Sr(C}_5\text{H}_5)_2 + 2 \text{H}_2$$

**Scheme 1.7.** Synthesis of bis(cyclopentadienyl)strontium.

Bis(cyclopentadienyl)barium, (Ba(C_5H_5)_2) (7), was first synthesized in 1976 by Gowenlock and coworkers using a cocondensation of cyclopentadiene and barium at −196 °C (Scheme 1.8).[24] A more efficient synthesis was developed by Hanusa and coworkers in 1988; however, this approach (Scheme 1.8) provided only crude material of Ba(C_5H_5)_2.[25] It was not until Behrens and coworkers[26] adapted a procedure from Hanusa that barocene was isolated and crystallographically characterized in 2004 (Scheme 1.8).

$$2 \text{(C}_5\text{H}_5) + \text{Ba} \overset{\text{cocond.}}{\rightarrow} \text{Ba(C}_5\text{H}_5)_2$$

$$2 \text{LiC}_5\text{H}_5 + \text{BaI}_2 \overset{\text{THF}}{\rightarrow} \text{Ba(C}_5\text{H}_5)_2 + \text{LiI}_2$$

$$\text{Ba[NSiMe}_3)_2]_2 + 2 \text{(C}_5\text{H}_5)^- \overset{\text{THF}}{\rightarrow} \text{Ba(C}_5\text{H}_5)_2 + [\text{NSiMe}_3)_2]^{2-}$$

**Scheme 1.8.** Syntheses of bis(cyclopentadienyl)barium. Gowenlock and coworkers (left), Hanusa and coworkers (right), and Behrens and coworkers (bottom).
The X-ray structure of barocene was solved by Behrens and a polymeric structure of Ba(C₅H₅)₂•(DMSO) was revealed (Figure 1.2). Barocene adopts a similar polymeric structure to that observed in calcocene (5). Barium is coordinated to four η⁵-bound cyclopentadienyl rings in a tetrahedral geometry, where each ring is coordinated to two barium ions building a threedimensional polymeric array. The product crystallizes with disordered DMSO molecules, which are found in the voids of the structure and have very long Ba–O subDMSO contacts averaged to 5.840(3) Å. The average Ba–C subcentroid bond distance is 2.924(4) Å with average Ba–C bond lengths ranging from 3.141(2) to 3.166(2) Å. The C subcentroid–Ba–C subcentroid bond angles range between 108.9(2)° and 110.1(2)°.[26]

![Figure 1.2](image-url)  
**Figure 1.2.** Solid-state packing of 7 showing a 3D polymeric structure. Hydrogen atoms, disordered C₅H₅ rings, and DMSO molecules have been removed for clarity.

The crystal structures of the alkali earth metallocenes exhibit different arrangements. The lighter Group 2 metals of beryllium and magnesium adopt similar structures to that of ferrocene. Beryllium has a slip sandwich geometry with one cyclopentadienyl ring coordinated in an η⁵-fashion and the other cyclopentadienyl ring η¹-coordinated to beryllium, whereas magnesium
adopts a sandwich geometry isostructural to that in ferrocene. While no structural information is available for strontocene, the heavier Group 2 metals seem to favor polymeric arrangements with multiple cyclopentadienyl rings coordinated to the metals as found for both calcium and barium.

1.3 Cyclopentadiene Derivatives

The insolubility of the heavy alkaline earth metallocenes due to their coordinative unsaturation of the metal ion centers has led researchers to develop more soluble options. It was found that steric crowdedness provided by bulky ligands sterically saturated the large ionic radii of the Group 2 metals (Scheme 1.5). This allowed the products solubility in organic solvents and led to the development of various cyclopentadienyl derivatives in Group 2 metallocene complexes. Hanusa and coworkers\cite{24} widely used the pentamethyl derivative of cyclopentadiene, pentamethylcyclopentadiene, due to the improved solubility of its complexes.\cite{27,28,29} What they found was a dramatic increase in the solubility of the heavy alkaline earth metal substituted metallocenes over that of the unsubstituted analogues in tetrahydrofuran (THF), aromatic solvents, and alkanes in calcium, strontium, and barium derivatives. The increased solubility of these compounds allowed one to easily purify the reaction mixtures by removing alkali-halide byproducts, thus making these metallocenes useful reagents in synthetic chemistry.

In the 1980s, Prof. F. A. Cotton published a textbook where he stated that “the organic compounds of calcium, strontium and barium are relatively obscure and of little utility.”\cite{30} Since then, new synthetic routes to create the heavy alkaline earth metal complexes have opened the door to considerable expansion into this type of chemistry. Using the substituted pentamethylocyclopentadiene ligand, the heavy alkaline earth metal complexes were synthesized.
in good yields using sodium or potassium pentamethylcyclopentadienyl and the metal diiodides
in THF or diethyl ether (Scheme 1.9).\cite{25}

\[
\text{MI}_2 + 2 \text{K(Me}_5\text{C}_5) \xrightarrow{\text{THF}} \text{M = Ca, Sr, Ba} \quad \text{(Me}_5\text{C}_5)_2\text{M(THF)}_2 + 2 \text{KI}
\]

**Scheme 1.9.** Synthesis of decamethylmetalloccenes.

Due to the added bulk and increased solubility of the pentamethylcyclopentadienyl
derivatives all three of the heavy Group 2 metal products have been structurally characterized by
either X-ray or gas phase electron diffraction.\cite{23,31,32} In 1988, Huffman and coworkers\cite{32}
synthesized the decamethylcyclopentadienyl calcium complex, \(\text{Ca(Me}_5\text{C}_5)_2\) (8, Scheme 1.10),
which was only the second structurally characterized heavy alkaline earth metal compound after
the calcocene complex reported in 1974.\cite{6} Bis(pentamethylcyclopentadienyl)calcium exhibits a
bent geometry in the solid-state with a \(\text{C}_{\text{centroid}}\text{–Ca–C}_{\text{centroid}}\) bond angle of 147.0(2)\(^{\circ}\). Unlike the
polymeric parent metalloccene, the decamethyl derivative consists of monomeric units in the
solid-state and crystallizes with two crystallographically independent but essentially identical
molecules in the unit cell. The coordination sphere of calcium is filled by two \(\eta^5\)-bound
pentamethylcyclopentadienyl rings in a bent geometry. The Ca–\(\text{C}_{\text{centroid}}\) distance is 2.64(2) Å,
which is comparable to that found in 5 (2.801(2) Å).
Scheme 1.10. Structures of bis(pentamethylcyclopentadienyl) metallocenes of calcium, strontium, and barium.

In 1987, Volden and coworkers\cite{23} utilized gas phase electron diffraction to study the base-free structure of bis(pentamethylcyclopentadienyl)strontium, Sr(Me$_5$C$_5$)$_2$ (9; Scheme 1.10). The coordination sphere of strontium is filled by two η$_5$-bound pentamethylcyclopentadienyl rings in a bent sandwich geometry. The C$_{centroid}$–Sr–C$_{centroid}$ bond angle of the strontium derivative is 149.5(5)$^\circ$ with a Sr–C$_{centroid}$ distance of 2.75(4) Å. It is important to remember that this is a thermal average structure in the solid-state without correction for shrinkage effects. The gas phase electron diffraction studies of the calcium and barium derivatives model similarly to what is found in the solid-state with slight deviations in the bend angles and metal-carbon bond distances.\cite{23} Unfortunately, no solid-state structural data has been reported for bis(pentamethylcyclopentadienyl)strontium, but based on the calcium and barium gas phase electron diffraction and solid-state data it is safe to assume that the structural model provided by the gas phase electron diffraction of bis(pentamethylcyclopentadienyl)strontium is valid.

The base-free structure of bis(pentamethylcyclopentadienyl)barium, Ba(Me$_5$C$_5$)$_2$ (10; Scheme 1.10), was solved by Hoffman and coworkers in 1988\cite{32} using X-ray diffraction studies,
which show a bent geometry and two crystallographically independent molecules in the unit cell, similar to that of the calcium derivative. The barium pentamethylcyclopentadiene derivative is interesting. Instead of the single monomeric units found for the calcium derivative, a quasi-polymeric chain is formed in the solid-state. The shortest intermolecular contacts forming these polymeric chains are the Ba–CMe interactions with distances of 3.349(5) Å and 3.395(5) Å. Considering the larger radius of the barium ion, the distances are similar to those found in the analogous samarium pentamethylcyclopentadienyl derivative[35] with a Sm–CMe bond distance of 3.22(1) Å. The structure of bis(pentamethylcyclopentadienyl)barium is bent following the rest of the heavy Group 2 derivatives and has a Ccentroid–Ba–Ccentroid bond angle of 130.3(3)°, which is the smallest angle observed in such systems. The average Ba–C bond distance is 2.98(1) Å and the Ba–Ccentroid distance is 2.99(1) Å.[31,32]

The structural studies of this class of compounds show that in the solid-state all of the heavy Group 2 compounds have a bent geometry. As metal radius increases, a decrease is observed in the Ccentroid–M–Ccentroid bond angles as well as an increase in the average M–C bond distances.[32] The bent nature of these compounds has not been rationalized since an arrangement with parallel rings should be favored to reduce intermolecular interactions. This geometry is also observed in the lanthanide derivatives, and an explanation has been proposed that the bending of these complexes is due to reverse polarization, where a dipole created in the cation favors a bent geometry.[33,34] Computational calculations have also been done using Hartree-Fock (HF) theoretical studies that based an explanation for the bent geometries on the sd hybrid orbitals of the compounds.[35]
1.4 Lewis Base Adducts of Decamethylmetallocenes

The ability of the decamethylmetallocenes to react with Lewis bases allows for a great number of different adducts to be formed with ethers, aromatic amines, phosphines, isonitriles, and unsaturated hydrocarbons. The organo-alkaline earth metal complexes form adducts with unsaturated hydrocarbons, which is unusual for complexes outside of the d and f block metals. (Me₅C₅)₂Ba, a colorless solid, is yellow when dissolved in aromatic solvents, suggesting there is some interaction happening. However, no adduct has been obtained, as when the solvent is removed only the colorless metallocene remains. When alkynes are used instead of alkenes, a stronger interaction is observed. Thus, when bis(pentamethylcyclopentadienyl)calcium is reacted with 2-butyne, a colorless adduct is formed and proved by NMR resonance spectroscopy. Bis(pentamethylcyclopentadienyl)calcium(1,4-bis(trimethylsilyl)butadiene), [(Me₅C₅)₂Ca(C₁₀H₁₈Si₂)] (11; Scheme 1.11), is the first successfully structurally characterized organo-alkaline earth metal alkyne compound, which was formed from the reaction of bis(pentamethylcyclopentadienyl)calcium and 1,4-bis(trimethylsilyl)butadiyne (BTMSBD) in toluene (Scheme 1.12) by Williams and Hanusa in 1990. This reaction was tested using the other heavy Group 2 metals, and works using the barium metallocene derivative and BTMSBD. However, evaporation of the solution yields only the decamethylcyclopentadienyl barium complex.

Scheme 1.11. First structurally characterized organo-alkaline earth metal alkyne complex.
Scheme 1.12. Reactions of bis(pentamethylcyclopentadienyl)metallocenes with alkynes.

Through X-ray diffraction study, the structure of 11 was found to contain two crystallographically independent molecules in the solid-state. The calcium atom is coordinated to two η₅-bound pentamethylcyclopentadienyl rings with a BTMSBD unit wedged between them. The major difference between the two conformers is the fashion in which butadiyne is coordinated to the metal center. In adduct “A”, butadiyne is coordinated symmetrically around the C_{centroid}–M–C_{centroid} plane, whereas in adduct “B” the diyne has slipped by 0.81(2) Å to one side of the plane. The C_{centroid}–Ca–C_{centroid} bond angles and average Ca–C_{centroid} distances for the two conformers are 143.4(3)° and 145.4(3)° and 2.64(2) Å and 2.66(2) Å, respectively. The average Ca–C_{centroid} distances are identical to those found in the parent decamethyl metallocene (8); however, the bond angles have decreased slightly (147(3)°).[6,40]

1.5 Alkyl Substituted Cyclopentadienyl Metallocenes

Metallocenes other than decamethylcyclopentadiene and its derivatives, such as alkyl-substituted cyclopentadienes, have also been used to access alkaline earth metal complexes. Bis(methylcyclopentadienyl) metallocenes have been prepared for calcium, strontium, and barium using metathesis reactions (Scheme 1.13).[25] It is also possible to produce the calcium compound using liquid ammonia and calcium metal (Scheme 1.13).[41] The solubility of this
class of compounds is similar to that of the parents, as they do show some solubility in aromatic hydrocarbons.

\[
\begin{align*}
&2 (\text{MeC}_5\text{H}_4)\text{K} + \text{MI}_2 & M = \text{Ca, Sr, Ba} \rightarrow \text{THF} \\
&2 (\text{MeC}_5\text{H}_4) + \text{Ca} & \text{NH}_3(\text{l}), \text{DME} \rightarrow (\text{MeC}_5\text{H}_4)_2\text{Ca(DME)} + \text{H}_2
\end{align*}
\]

**Scheme 1.13.** Metathesis reactions for the preparation of bis(methylcyclopentadienyl) metallocenes.

The X-ray structure of the dimethoxyethane (DME) adduct of bis(methylcyclopentadienyl)calcium, \((\text{MeC}_5\text{H}_4)_2\text{Ca(C}_4\text{H}_{10}\text{O)} \) (12; Scheme 1.14), was characterized by Weidlein and coworkers in 1989.\[41\] This compound is isostructural to the \(\text{Cp}_2\text{Yb(DME)}\) analogue, as shown by Taylor and coworkers.\[42\] Bis(methylcyclopentadienyl)calcium(DME) crystallizes in a bent sandwich geometry, where calcium is coordinated to two \(\eta^5\)-rings and the bidentate ligand DME in a distorted tetrahedral environment. The \(\text{C}_{\text{centroid}}–\text{Ca–C}_{\text{centroid}}\) bond angle is 134.8(2)°, with a \(\text{Ca–C}_{\text{centroid}}\) bond distance of 2.398(2) Å and \(\text{Ca–O}_{\text{DME}}\) bond distance of 2.405(1) Å. Interestingly, the above bond distances are nearly identical.

Tert-butyl and isopropyl substituted cyclopentadienes have also been synthesized and complexed with the heavy alkaline earth metals. The tert-butyl substituted derivative, Ca(t-Bu₃C₅H₂)₂ (13; Scheme 1.15), was structurally characterized by Sitzmann and coworkers in 2001. The compound was prepared in high yield by reacting sodium 1,2,4-tri-tert-butylcyclopentadiene and the metal iodide in THF (Scheme 1.16). This metalloocene with six tert-butyl groups is base-free and forms a spherical molecule in the unit cell, which is not constrained to give a well-ordered packing. As a result, only a low angle diffraction data set was collected; however, the geometry and arrangement of the rings are clear. The metalloocene crystallizes in a bent sandwich geometry with two η⁵-bound 1,2,4-tert-butylcyclopentadienyl rings in an eclipsed fashion, such that only one of the tert-butyl groups is located directly over the other on the adjacent ring. The Ca–C_centroid distance is 2.639(2) Å, and the C_centroid–Ca–C_centroid bond angle of 171.4(3)° is almost linear.
Scheme 1.15. Structures of 1,2,3-tri-\textit{t}ert-butylcyclopentadienyl metallocenes.

\[
\text{M} = \text{Ca, Sr, Ba}
\]

\[
\text{MI}_2 + 2 \text{Na}[\text{1,2,4-(Me}_3\text{C)}_3\text{C}_5\text{H}_2] \xrightarrow{\text{THF}} [\text{1,2,4-(Me}_3\text{C)}_3\text{C}_5\text{H}_2]_2\text{M} + 2 \text{NaI}
\]

Scheme 1.16. Syntheses of \([\text{1,2,4-(Me}_3\text{C)}_3\text{C}_5\text{H}_2]_2\) metallocenes of calcium, strontium, and barium.

The base-free strontium, \(\text{Sr}(\text{t-Bu}_3\text{C}_5\text{H}_2)_2\), (14; Scheme 1.15) and barium, \(\text{Ba}(\text{t-Bu}_3\text{C}_5\text{H}_2)_2\), (15; Scheme 1.15) analogues were crystallized by Hatanpää and coworkers in 2007\(^{[44]}\) using the same metathesis method (Scheme 1.16). The strontium analogue (14) is isostructural to that of the calcium derivative (13). The \(\text{Sr}–\text{C}_{\text{centroid}}\) bond distance and \(\text{C}_{\text{centroid}}–\text{Sr}–\text{C}_{\text{centroid}}\) bond angle are 2.519(3) Å and 165.7(2)^\circ, respectively.

The barium analogue (15) differs from the other Group 2 metallocenes in that it crystallizes in two distinct space groups, depending on which method of crystallization is used. One method utilizes sublimation and the other relies on slow evaporation from toluene. In the first crystal structure, “A”, the barium metallocene crystallizes in an orthorhombic space group,
where a polymeric chain structure is observed. These chains are formed through a methyl carbon stretching to an adjacent barium atom with a \( \text{Ba--C}_\text{Me} \) bond distance of 3.352(2) Å. The \( \text{Ba--C}_{\text{centroid}} \) distance is 2.749(2) Å and the \( \text{C}_{\text{centroid}}--\text{Ba--C}_{\text{centroid}} \) bond angle is 159.7(4)°. In the second conformer, “B”, there are no intermolecular interactions. The \( \text{Ba--C}_{\text{centroid}} \) bond distances vary from 2.923(4) Å to 2.997(4) Å and the \( \text{C}_{\text{centroid}}--\text{Ba--C}_{\text{centroid}} \) bond angles vary from 161.1(3)° to 165.5(3)°. The variation in the bond distances and angles is a result of four distinct individual \( \text{Ba}(t\text{-Bu}_3\text{C}_5\text{H}_2)_2 \) molecules in the asymmetric unit.\[^{[44]}\]

Bis(1,2,3,4-tetraisopropylcyclopentadienyl)calcium, \( \text{Ca}((t\text{-Pr})_4\text{C}_5\text{H})_2 \) (16; Scheme 1.17), was synthesized using a halide metathesis reaction of 1,2,3,4-tetraisopropylcyclopentadienyl potassium and calcium iodide in diethyl ether by Hanusa and Williams in 1991 (Scheme 1.18).\[^{[45]}\] The bulkiness of the isopropyl group gives tremendous kinetic stability to the resulting organo-alkaline earth metal complexes. The stability of the products is improved greatly. For example, the crystallized calcium compound can be handled in air for several minutes without decomposition, which is not the case for the decamethyl derivatives. The bulkiness of the isopropyl groups fully encompasses the metal center in the X-ray structure, resulting in the inability of the isopropyl derivatives to undergo various transformations that the decamethylmetallocenes are able to do with ethers, and aromatic amines.\[^{[6]}\]
Scheme 1.17. Structure of bis(1,2,3,4-tetraisopropylcyclopentadienyl)calcium and bis(1,2,3,4-tetraisopropylcyclopentadiene)barium.

\[
2 \text{K}[(i-\text{Pr})_4\text{C}_5\text{H}]_2 + \text{MI}_2 \xrightarrow{\text{M} = \text{Ca}, (\text{Ba}) \quad \text{Et}_2\text{O}, \text{(THF)}} [(i-\text{Pr})_4\text{C}_5\text{H}]_2\text{M} + 2 \text{KI}
\]

Scheme 1.18. Synthesis of tetraisopropylcyclopentadienyl metalloccenes.

In the solid-state, the tetraisopropyl calcium metalloccene (16) crystallizes with two \(\eta^5\)-bound rings around the calcium center in a bent geometry. The average Ca–C\text{centroid} distance is 2.64(1) Å, which is similar to that found in the decamethylcyclopentadienyl calcium derivative (8). The C\text{centroid}–Ca–C\text{centroid} bond angle in this metalloccene is 162.4(2)°, larger than in the decamethylcyclopentadienyl derivative (8) with a bond angle of 147.0(2)°. The added bulk of the isopropyl groups is what is believed to have opened up the rings to a more parallel alignment. The isopropyl groups on the ring are essentially perpendicular to the ring plane shielding the metal atom in a cage. This cage-like structure protects the metal ion, providing increased stability for the metalloccene in air.\textsuperscript{[45]}
Although the strontium analogue has been prepared by Hanusa and Burkey, there is no structural information available for it. The complex was synthesized using the metathesis reaction shown above (Scheme 1.18).\(^{[45]}\)

The tetraisopropylcyclopentadienyl barium derivative \(\text{Ba}(i\text{-Pr}_4\text{C}_5\text{H})_2\) (17; Scheme 1.17), was also synthesized by Hanusa and Williams using the reaction detailed above (Scheme 1.18). The solid-state structure of the barium derivative (17) is analogous to that found for the calcium metallocene (16), with two \(\eta^5\)-rings around the barium center in a bent geometry. The compound crystallizes in two crystallographically independent, but nearly identical molecules in the unit cell. The average \(\text{Ba}–\text{C}\) and \(\text{Ba}–\text{C}_{\text{centroid}}\) bond distances are 2.946(1) Å and 2.683(1) Å, respectively, and the metallocene has a \(\text{C}_{\text{centroid}}–\text{Ba}–\text{C}_{\text{centroid}}\) bond angle of 154.8(2)°. The bond distances correlate with those found in the decamethylcyclopentadienyl metallocene (10), while the bond angle is significantly larger than the value 130.3(3)° found in 10. Similarly to the calcium case (16), the isopropyl groups are found perpendicular to the ring plane forming a cage around the barium center. The increased separation of the tetraisopropyl rings, due to the larger radius of barium, lowers the stability of the metallocene compound in air compared to the calcium derivative (16).\(^{[45]}\)

In 1994, Hanusa and coworkers\(^{[46]}\) synthesized bis(triisopropylcyclopentadienyl)calcium (18; Scheme 1.19) in an attempt to determine the air stability compared to the bulkier tetraisopropyl metallocene derivatives. The compound, \(\text{Ca}(i\text{-Pr}_3\text{C}_5\text{H}_2)_2\), was prepared through the reaction of potassium triisopropylcyclopentadienyl and calcium diiodide in diethyl ether (Scheme 1.20). Due to the encapsulated nature of the tetraisopropylcyclopentadienyl derivatives it was believed that a similar protecting phenomenon would be found in the triisopropyl analogue; however, it seems that the orientation of the six isopropyl groups is more flexible. This
allows the isopropyl groups to rotate around causing a mixture of different orientations, which makes crystallization difficult and also decreases the stability of the compounds in air.\textsuperscript{[46]}

Scheme 1.19. Structures of triisopropylcyclopentadienyl metalloccenes of calcium and barium.

\[ \text{M} = \text{Ca}, \text{(Ba)} \]
\[ 2 \text{K(iPr}_3\text{C}_5\text{H}_2) + \text{MI}_2 \xrightarrow{\text{Et}_2\text{O}, \text{(THF)}} \text{M(iPr}_3\text{C}_5\text{H}_2)_2 + 2 \text{KI} \]

Scheme 1.20. Synthesis of triisopropylcyclopentadienyl metalloccenes.

In the solid-state, the monomeric triisopropyl calcium derivative (18) is coordinated to two $\eta^5$-triisopropylcyclopentadienyl rings in a bent sandwich geometry. The cyclopentadienyl rings are essentially eclipsed and the average Ca–C\text{centroid} bond distance is 2.627(2) Å, which falls in line with other base-free calcium metalloccenes, such as the tetraisopropyl calcium derivative (16).\textsuperscript{[44]} The C\text{centroid}–Ca–C\text{centroid} bond angle is 169.1(3)$^\circ$, which is slightly larger than that found for the tetraisopropyl calcium derivative (16), (162.4(2)$^\circ$). This is surprising since the tetraisopropyl cyclopentadienyl ligand is bulkier than the triisopropyl analogue, indicating that
the C\textsubscript{centroid}–M–C\textsubscript{centroid} bond angles in the Group 2 metallocenes do not vary directly with ligand bulk.[46]

As a result of the difficulty in the crystallization of the base-free triisopropylcyclopentadienyl Group 2 metallocenes, only the calcium complex is known. The only other structurally characterized triisopropylcyclopentadienyl Group 2 compound is the solvated barium complex, \((i\text{-Pr}_3\text{C}_5\text{H}_2)_2\text{Ba(THF)}_2\) (19; Scheme 1.19).[47] The compound was synthesized using the procedure detailed above (Scheme 1.20).

In the solid-state, the bent sandwich metallocene shows barium coordinated to two \(\eta^5\)-bound triisopropylcyclopentadienyl ligands and two THF molecules forming a distorted tetrahedral geometry. The average Ba–C\textsubscript{centroid} distance is 3.031(4) Å, longer than that (2.946(1) Å) found in the tetraisopropyl derivative (17), but the increased distance is expected with the increase in coordination to the barium center. The C\textsubscript{centroid}–Ba–C\textsubscript{centroid} bond angle is 132.3(4)° and is only slightly larger than that (130.3(3)°) found in the decamethyl metallocene analogue (10). Because the isopropyl groups are free to rotate they can move out of the way to accommodate the two THF solvent molecules opening up the sandwich, which accounts for the smaller bond angle compared to that of the calcium analogue.[47]

1.6 Trimethylsilyl-Substituted Cyclopentadienyl Metallocenes

It is well known that the stability of cyclopentadienyl complexes with the heavy alkaline earth metal complexes is related to steric effects, metal size, ligand basicity, and solubility equilibria.[48] Trimethylsilyl-substituted cyclopentadienes (TMS) have been used to increase ligand bulk, thus increasing the stability of the products. The bulky tris(trimethylsilyl)cyclopentadienyl metallocenes of calcium (20; Scheme 1.21), strontium (21;
Scheme 1.21, and barium (22; Scheme 1.21) were synthesized by Hanusa and coworkers in 2003 and structurally characterized using X-ray diffraction. The compounds were synthesized using tris(trimethylsilyl)cyclopentadienyl potassium and the metal diiodides in diethyl ether (Scheme 1.22). Diethyl ether is used over THF to prevent the formation of the mono-ring complexes. However, once formed, the complexes can be recrystallized from THF as the base-free metallocenes. These compounds provided a test of how metal-carbon distances affect the degree of bending found in Group 2 metallocenes.

Scheme 1.21. Structures of tris(trimethylsilyl)cyclopentadienyl metallocenes.

\[
M = \text{Ca, Sr, Ba} \\
2 \text{K}[(\text{SiMe}_3)_3\text{C}_5\text{H}_2] + \text{MI}_2 \xrightarrow{\text{Et}_2\text{O}} [(\text{SiMe}_3)_3\text{C}_5\text{H}_2]_2\text{M} + 2 \text{KI}
\]

Scheme 1.22. Syntheses of tristrimethylsilylcyclopentadienyl metallocenes.

In the solid-state, bis[tris(trimethylsilyl)cyclopentadiene]calcium (20), \(\text{Ca}[(\text{SiMe}_3)_3\text{C}_5\text{H}_2]_2\), crystallizes as a monomeric unit with two eclipsed \(\eta^5\)-cyclopentadienyl...
rings in a bent geometry with a twist angle of 8°. The average Ca–C bond distance is 2.63(2) Å with a Ca–C\textsubscript{centroid} distance of 2.35(2) Å. These distances are similar to those observed for the other base-free calcium metallocenes, such as the tetraisopropylcyclopentadienyl complex 16. The C\textsubscript{centroid}–Ca–C\textsubscript{centroid} bond angle is 166.7(3)°, which is larger than those in both the tetraisopropyl (16) (162.4(2)°) and decamethyl (8) (147.0(2)°) metallocenes.\textsuperscript{[48]}

The strontium complex (21), Sr[(SiMe\textsubscript{3})\textsubscript{3}C\textsubscript{5}H\textsubscript{2}]\textsubscript{2}, exists as a monomeric unit with strontium coordinated to two staggered \(\eta^5\)-cyclopentadienyl rings in a bent geometry with a twist angle of 18°. The average Sr–C bond distance is 2.812(9) Å with a Sr–C\textsubscript{centroid} distance of 2.54(9) Å, which is essentially equivalent to that found in the tri-tert-butyl derivative (14) with a Sr–C\textsubscript{centroid} bond distance of 2.519(3) Å. The C\textsubscript{centroid}–Sr–C\textsubscript{centroid} bond angle is 159.4(4)°, which is smaller than that (165.7(2)°) found in the tert-butyl derivative.\textsuperscript{[48]}

The barium trimethylsilyl complex (22), Ba[(SiMe\textsubscript{3})\textsubscript{3}C\textsubscript{5}H\textsubscript{2}]\textsubscript{2}, differs from both the calcium and strontium analogues. It crystallizes as a coordination dimer where barium is surrounded by two eclipsed \(\eta^5\)-rings, with a twist angle of 2°, and a methyl group from an adjacent unit. The average Ba–C bond distance is 3.01(2) Å and the Ba–C\textsubscript{centroid} distance is 2.75(2) Å. Both are elongated compared to the tetraisopropyl metallocene (17) with average Ba–C bond and Ba–C\textsubscript{centroid} distances of 2.946(1) Å and 2.683(1) Å, respectively. The C\textsubscript{centroid}–Ba–C\textsubscript{centroid} bond angle is 162.2(4)°, which is greater than that found in both the tetraisopropyl (17) (154.8(2)°) and decamethyl (10) (130.3(3)°) analogues. The intermolecular contact for the Ba–C\textsubscript{Me} is measured at 3.275(2) Å, shorter than the van der Waals radius of a methyl group and the ionic radius of barium (1.35 Å).\textsuperscript{[17]} These intermolecular contacts fall in line with those found for the polymeric decamethyl metallocene analogue (10) ranging from 3.349(5) Å to 3.395(5) Å.\textsuperscript{[48]}
Despite the bulkiness of the trimethylsilyl groups in the calcium compound with a bend angle of 166.7(3)°, the bend angle is larger for the triisopropyl analogue at 169.1(3)°. This shows that bulk might not be the only reason affecting planarity in cyclopentadienyl systems of the heavy alkaline earth metals, but that packing may also play an important role.\[48\]

1.7 Monocyclopentadienyl Complexes

Monocyclopentadienyl complexes of the heavy Group 2 elements are of particular interest due to their potentially unique chemistry. The idea for these monocyclopentadienyl complexes, (CpMX), is that the cyclopentadienyl ring would provide solubility, while the X group can act as a functionalization site. The synthesis of these mixed-ligand complexes was initially difficult due to the Schlenk equilibria of the reactions (Scheme 1.23); however, by now there are several examples of this type of compound known.\[1,49,50,51,52,53,54\]

\[
2 \text{CpMX} \rightleftharpoons \text{Cp}_2\text{M} + \text{MX}_2
\]

**Scheme 1.23.** Schlenk equilibria for the synthesis of monocyclopentadienyl compounds.

The first monocyclopentadienyl complex (23; Scheme 1.24) was synthesized and structurally characterized in 1989 by Hanusa and coworkers.\[49\] The monopentamethylcyclopentadienyl complex with calcium, [(Me₅C₅)Ca(μ-I)(THF)]₂, was prepared using a metathesis reaction with potassium pentamethylcyclopentadienyl and calcium iodide (Scheme 1.25). The pentamethylcyclopentadienyl ligand was chosen to provide stability to the complex in the form of steric saturation, as well as to block oligomerization and
decomposition pathways. This compound is the first structurally characterized cyclopentadienyl halide complex of the heavy Group 2 metals.

![Scheme 1.24](image)

**Scheme 1.24.** Structure of \([(\text{Me}_5\text{C}_5)\text{Ca}(\mu\text{-I})(\text{THF})_2]\), the first cyclopentadienyl halide complex.

\[
2 \text{K(Me}_5\text{C}_5) + 2 \text{CaI}_2 \xrightarrow{\text{THF}} [(\text{Me}_5\text{C}_5)\text{Ca}(\mu\text{-I})(\text{THF})_2] + 2 \text{KI}
\]

**Scheme 1.25.** Synthesis of monopentamethylcyclopentadienyl calcium complex.

The solid-state structure of the calcium complex 23 shows a halide bridged dimer, with calcium coordinated to one Me$_5$C$_5$ ring in an \(\eta^5\)-fashion, two THF molecules, and two bridging iodides. The asymmetric unit contains two independent dimers, each with an inversion center. The average Ca–C bond distance is 2.67(1) Å in both conformers with a Ca–C$_\text{centroid}$ distance of 2.38(1) Å in “A” and 2.39(1) Å in “B”. The average C–O$_\text{THF}$ distances in the two dimers are 2.422(4) Å and 2.386(5) Å, respectively. The Ca–I bond distances are 3.1356(15) Å and 3.1980(16) Å in the dimer “A” and 3.1283(15) Å and 3.2743(16) Å in the dimer “B”.

26
Additionally, the Ca–I bond angles in both the “A” and “B” dimers are 94.59(4)° and 97.73(4)°, respectively. The Ca–C bond length of 2.67(1) Å correlates with the isostructural samarium compound (2.81(1) Å). The I–Ca–I bond angle in the monocyclopentadienyl calcium complex is 85.41° for “A” and 82.27° for “B”, which matches that found in the samarium analogue (82.04(4)°). The main difference between the isostructural compounds stems from the variation found in the Ca–I and Sm–I bonds. In the calcium complex, the Ca–I bond distances differ by 0.062 Å in the dimer “A” and 0.146 Å in the dimer “B”, whereas in the samarium analogue the Sm–I bond lengths differ by 0.103 Å.

Monocyclopentadienyl compounds of strontium and barium are increasingly more difficult to isolate due to their larger metal radii of 1.13 Å and 1.35 Å, respectively (Scheme 1.5). Using the encapsulation strategy, strontium and barium monocyclopentadienyl complexes have become accessible. The encapsulation strategy involves the use of bulky ligands that can fill the coordination sphere of the metal centers such as those shown for the triisopropyl, tetraisopropyl, and tris(trimethylsilyl)cyclopentadienyl metallocenes. The encapsulation method works against the Schlenk equilibrium of the reactions protecting the mono ring complexes from rearrangement. This method works better for smaller metals as shown by the tetraisopropyl mono-ring complexes of the heavy Group 2 metals. In 1994, Hanusa and Burkey were able to successfully synthesize mono(tetraisopropylcyclopentadienyl)calcium complexes using the encapsulation method. However, when strontium and barium were used it was found that the tetraisopropyl groups do not fully encapsulate these large metal ions leading to the bis(tetraisopropylcyclopentadienyl) metallocenes due to the Schlenk equilibrium.

Using 1,2,4-tris(trimethylsilyl)cyclopentadiene as a ligand, Hanusa and Harvey were able to successfully utilize the encapsulation method to produce the calcium (24; Scheme 1.26),
strontium (25; Scheme 1.26), and barium (26; Scheme 1.26) monocyclopentadienyl products.\[1\]

The compounds were synthesized using 1,2,4-tris(trimethylsilyl)cyclopentadienyl potassium and the metal diiodides in THF (Scheme 1.27). The yield of the reactions decreases with metal size, with calcium having the greatest yield of 75% followed by 50% and 30% for the strontium and barium analogues, respectively.

\[
2 \text{K}[(\text{SiMe}_3)_3\text{C}_5\text{H}_2] + 2 \text{MI}_2 \rightarrow [\{(\text{SiMe}_3)_3\text{C}_5\text{H}_2\}M(\mu-\text{I})(\text{THF})_n]_2 + 2 \text{KI}
\]

\(\text{M} = \text{Ca}, n = 1; \text{M} = \text{Sr}, \text{Ba}, n = 2\)


In the solid-state, the monocyclopentadienyl calcium complex 24, [\{(\text{SiMe}_3)_3\text{C}_5\text{H}_2\}\text{Ca}(\mu-\text{I})(\text{THF})]_2, exists as an iodide-bridged dimer with calcium coordinated to one \(\eta^5\)-
cyclopentadienyl ring, two iodides, and a terminal THF molecule. The average Ca–C bond distance is 2.65(2) Å and the Ca–C_{centroid} distance is 2.36(2) Å, which are identical to those found in the related mono(tetraisopropyl) derivative, [(i-Pr₄C₅H)(µ-I)(THF)]₂, with average Ca–C and Ca–C_{centroid} distances of 2.67(1) Å and 2.38(1) Å, respectively. The Ca–I bond distances are 3.06(6) Å and 3.10(2) Å, and the Ca–I–Ca bond angle is 92.27(9)°, forming an almost square arrangement. The Ca–O_{THF} distance is 2.31(2) Å.

The strontium analogue (25), [{(SiMe₃)₃C₅H₂}Sr(µ-I)(THF)]₂, crystallizes in a similar manner to that found in the calcium complex (24). In the solid-state, the compound crystallizes as an iodide-bridged dimer with strontium coordinated to one η⁵-cyclopentadienyl ring, two iodides, and two THF molecules. The average Sr–C bond distance is 2.868(7) Å and Sr–C_{centroid} distance is 2.604(7) Å. The bond distances in this compound correlate to those found in a decamethyl samarium derivative, [(MesC₅)Sm(µ-I)(THF)]₂, with a Sm–C bond distance of 2.81(2) Å. The average Sr–O_{THF} bond distance is 2.547(5) Å compared to that found for the samarium complex, which has a bond distance of 2.64(3) Å. The Sr–I bond distances are 3.278(3) Å and 3.355(3) Å and the Sr–I–Sr bond angle is 103.17(7)°.

The barium compound, [{(SiMe₃)₃C₅H₂}Ba(µ-I)(THF)]₂, crystallizes as a coordination polymer in the solid-state with each barium center coordinated to one η⁵-bound cyclopentadienyl ring, two iodides, and two THF molecules. The polymer forms through the barium iodide bridges forming a zigzag pattern. Solvent molecules of toluene are found to occupy the interstitial space formed between the barium iodide bonds. The Ba–C_{centroid} distance is 2.76(1) Å and the average Ba–C bond distance is 3.004(1) Å, which are close to those found for other seven-coordinate barium compounds. For example, [(C₅Me₃)₂Ba]₂(µ-C₅H₄N₂) has a bond length of 2.96(2) Å. The Ba–O_{THF} bond distance for both coordinated THF molecules is 2.74(1) Å and falls in line
with other \( \text{Ba}–\text{O}_{\text{THF}} \) distances, like that found in the THF adduct of bis(triisopropyl)cyclopentadienyl barium (19) (3.03(1) Å). The \( \text{Ba}–\text{I}–\text{Ba} \) bond angle is 180° due to one of the iodides location on an inversion center and the \( \text{I}–\text{Ba}–\text{I} \) bond angle is 177.78(9)°. The \( \text{Ba}–\text{I} \) bond distances measure at 3.390(1) Å and 3.475(2) Å. This is the first reported case with a polymeric structure built of the barium iodide zigzag bridges. \(^{[1]}\)

Cyclopentadiene chemistry with the heavy alkaline earth metals is a field that continues to be rapidly growing. Functionalization of these ligands allows for new structures with interesting chemical properties to be synthesized. \(^{[51,56]}\) In addition to the derivatization of these ligands, research has also been done with non-cyclopentadienyl ligands utilizing the techniques developed in this field. \(^{[57,58]}\)

1.8 Cyclooctatetraenyl Derivatives

As the organometallic chemistry of the heavy alkaline earth metals became more developed, other ligands were also investigated. From cyclopentadienyl ligands the research has moved to the cyclooctatetraenyl (COT) ligand. However, only few structures of the Group 2 metals with COT have been synthesized and even fewer have been structurally characterized.

Zalkin and coworkers successfully prepared the first heavy Group 2 metal COT sandwich compound in 1984. \(^{[59]}\) The bis(COT)calcium anion, \([\{\text{K(DME)}\}_2\text{Ca(COT)}_2]\) (27; Scheme 1.28), was formed from the reaction of COT with calcium and potassium in liquid ammonia, followed by slow cooling of the saturated solution in DME to produce the crystalline product (Scheme 1.29). While single crystal X-ray diffraction was not performed on the compound, structural analysis was done by powder X-ray diffraction. It showed that the calcium COT
complex is isostructural to that of the ytterbium analogue (28; Scheme 1.28), which was the first structure of a COT dianion with a divalent lanthanide.\[59\]

Scheme 1.28. Structures of bis(COT)calcium and bis(COT)ytterbium.

\[
2 \text{COT} + \text{Ca} + 2 \text{K} \xrightarrow{\text{NH}_3(\text{l}), \text{DME}} \{[\text{K(DME)}]_2[\text{Ca(COT)}_2]\}
\]

Scheme 1.29. Synthesis of bis(COT)calcium anion.

Through single crystal X-ray diffraction analysis, the solid-state structure of the ytterbium analogue (28) was found to have ytterbium coordinated to two \(\eta^8\)-bound COT rings, which have a potassium ion coordinated to DME bound to each COT ring. The ytterbium complex forms an ideal linear sandwich geometry with a \(\text{C}_{\text{centroid}}\text{–Yb–C}_{\text{centroid}}\) bond angle of 180°. Using the powder X-ray diffraction data and IR spectroscopy, the calcium and ytterbium structures were deemed isostructural. The powder pattern of the calcium analogue (27) has 2
weak lines out of 21 that are not observed when compared with that of the ytterbium compound. The IR spectrum of the two complexes are also identical in the 400-4000 cm\(^{-1}\) region, indicating that any metal absorbance must occur outside of this region.\(^{[59]}\)

Recently, the COT ligand has been used in nucleophilic substitution reactions with tetraisopropylcyclopentadienyl halides and the heavy alkaline earth metals to form triple-decker sandwiches (Scheme 1.30).\(^{[60]}\) The triple-decker sandwiches of calcium (29; Scheme 1.31), strontium (30; Scheme 1.31), and barium (31; Scheme 1.31) were synthesized by Sitzmann and coworkers in 2005. They attempted to access products with carbocycles possessing more than five-membered rings so that the ring plane encroaches on the metal, creating shorter inter-ring distances. The calcium and barium triple-decker sandwiches have been structurally characterized using X-ray diffraction.

\[
2\text{MX}_2 + 2\text{Na}[(i\text{Pr})_4\text{C}_5\text{H}] \xrightarrow{\text{Na}_2(\text{COT})/\text{THF}} [(i\text{Pr})_4\text{C}_5\text{H}]\text{M(COT)M}[(i\text{Pr})_4\text{C}_5\text{H}] + 4\text{NaX}
\]

\[
\text{M} = \text{Ca}, \text{X} = \text{Cl}; \text{M} = \text{Sr}, \text{X} = \text{I}
\]

\[
[(i\text{Pr})_4\text{C}_5\text{H}]\text{Ba(THF)}_2 + \text{Na}_2(\text{COT}) \xrightarrow{\text{THF}/\text{Hexane}} [(i\text{Pr})_4\text{C}_5\text{H}]\text{Ba(COT)Ba}[(i\text{Pr})_4\text{C}_5\text{H}] + 4\text{NaI}
\]

**Scheme 1.30.** Syntheses of triple-decker Group 2 metallocenes.

![Structures of metallocenes](image)

**Scheme 1.31.** Structures of triple-decker metallocenes of calcium, strontium, and barium.
The calcium triple-decker sandwich 29, \[\{\text{(i-Pr)}_4\text{C}_5\text{H}\}\text{Ca}(\text{C}_8\text{H}_8)\text{Ca}\{\text{(i-Pr)}_4\text{C}_5\text{H}\}\], consists of a bridging COT ligand coordinated to two calcium ions, each of which is coordinated to a tetraisopropylcyclopentadienyl ring. The average Ca–C\(_\text{Cp}\) bond distance is 2.62(2) Å which is comparable to that observed in the bis(tetraisopropylcyclopentadienyl) calcium complex 16, with a bond distance of 2.644(1) Å. The Ca–C\(_\text{COT}\) bond distances are longer and range from 2.660(3) Å to 2.703(3) Å with an average of 2.683(3) Å. Contrary to what the Ca–C\(_\text{COT}\) bond distances show, the metal actually lies closer to the COT plane, owing to the larger diameter of COT. This is supported by the Ca–C\(_\text{centroid}\) distances for the two rings. The Ca–C\(_\text{Cp}\) and Ca–C\(_\text{COT}\) centroid distances are 2.33(3) Å and 1.99(3) Å, respectively. The triple-decker sandwiches show little bending in their structures with a Cp–Ca–COT bond angle of 173.0(6)° for the calcium sandwich (29).[60]

The crystal structure of the barium triple-decker sandwich 31, \[\{\text{(i-Pr)}_4\text{C}_5\text{H}\}\text{Ba}(\text{C}_8\text{H}_8)\text{Ba}\{\text{(i-Pr)}_4\text{C}_5\text{H}\}\], is similar to that of the calcium analogue 29. The coordination is the same with a bridging COT ligand coordinated to two barium centers, each of which is coordinated to one tetraisopropylcyclopentadienyl ring. The average Ba–C\(_\text{Cp}\) distance is 2.96(2) Å and comparable to that of bis(tetraisopropylcyclopentadienyl) barium (17) with a bond distance of 2.946(1) Å. The Ba–C\(_\text{COT}\) bond distances range from 2.994(5) Å and 3.016(6) Å with an average of 3.006(6) Å. Once again, the metal is closer to the COT ligand than what the bond distances show, with Ba–C\(_\text{Cp}\) and Ba–C\(_\text{COT}\) centroid distances of 2.71(2) Å and 2.40(2) Å, respectively. The barium sandwich shows short Ba–C\(_\text{Me}\) contacts between two methyl groups and the central barium ion with distances of 3.56(4) Å and 3.57(4) Å, which indicate a bending of the isopropyl groups towards the barium atom. This is something that is not observed in the calcium analogue (29). The bending of the barium triple-decker sandwich is minimal with a Cp–Ba–COT
bond angle of 168.5(5)°, which is greater than that found for bis(tetraisopropylcyclopentadienyl) barium (17) with a bond angle of 154.8(2)°.\[60\]

The COT complexes of heavy Group 2 metals, M(COT) (32), have been developed by the co-condensation of the Group 2 metal vapors and excess COT in THF (Scheme 1.32). The mono(COT) metal complexes were synthesized by White and coworkers in 1989.\[61\] However, these compounds have not been structurally analyzed due to their low solubility, high air sensitivity, and their microcrystalline nature. White states that the compounds are likely to have structures analogous to that of the related ytterbium compound, [Yb(C₈H₈)(C₅H₅N)₃],\[62\] which has a symmetrically bound COT-dianion. These complexes, while highly unstable, can be useful in solutions of THF or pyridine as sources of soluble metal cations or as organic nucleophiles.\[6\]

\[
\text{M} + (\text{C}_8\text{H}_8) \xrightarrow{\text{cocond. at } -196^\circ} \text{M(COT)}
\]

**Scheme 1.32.** Synthesis of mono(COT) compounds.

### 1.9 Complexation of Planar Polycyclic Aromatic Hydrocarbons

The organometallic chemistry of the heavy alkaline earth metals has expanded considerably from the initial focus on cyclopentadienyl complexes and their bulky derivatives. These complexes have become useful due to their good solubility in organic solvents, a high thermal stability, and good volatility (with some exceptions).\[63\] This utility of the Cp-based complexes prompted organometallic chemists to investigate complexation of larger \( \pi \)-systems moving to polycyclic aromatic hydrocarbons (PAHs). However up to date, only very few of these complexes have been reported, leaving this field open to further investigation.
1.9.1 Fluorene Complexes

In 1992, Schleyer and coworkers\textsuperscript{[64]} were able to structurally characterize a heavy alkaline earth metal complex with fluorene. Bis(fluorenlyl)barium-tetrakis(ammonia), Ba[(C\textsubscript{13}H\textsubscript{9})\textsubscript{2}(NH\textsubscript{3})\textsubscript{4}] (33; Figure 1.3), was synthesized from barium metal and fluorene in liquid ammonia (Scheme 1.33) and is the first structurally characterized complex of fluorene with an alkaline earth metal. Bis(fluorenlyl)barium has been studied in solution through electronic, spectroscopic, and conductive methods, which suggested a tilted geometry of the fluorenyl units. In the solid-state, a bent geometry has been confirmed, supporting the results found from the solution studies.

\textbf{Figure 1.3.} X-ray structure of bis(fluorenlyl)barium-tetrakis(ammonia). Hydrogen atoms have been omitted for clarity.

\[2(\text{C}_{13}\text{H}_{10}) + \text{Ba} \xrightleftharpoons{\text{NH}_3(\text{l})}^{-80^\circ}\text{Ba}[(\text{C}_{13}\text{H}_{9})_2(\text{NH}_3)_4] + \text{H}_2\]

\textbf{Scheme 1.33.} Synthesis of bis(fluorenlyl)barium-tetrakis(ammonia).
In the solid-state, bis(fluorenyl)barium-tetrakis(ammonia) (33) crystallizes as two crystallographically independent but similar molecules in the unit cell. Each molecule crystallizes as a monomer with a bent geometry, where barium is coordinated to two fluorene ligands and four ammonia molecules. The main difference in the two conformers is the manner in which they are bound to the five-membered rings of the fluorene ligands. In conformer “A”, the metal is coordinated symmetrically having both five-membered rings of the fluorene ligands in an $\eta^5$-fashion. The average Ba–C bond distances for each of the two fluorenyl groups is 3.169(4) Å and the average Ba–C$_{\text{centroid}}$ distance is 2.936(4) Å. The average Ba–NH$_3$ distance is 2.886(3) Å and the C$_{\text{centroid}}$–Ba–C$_{\text{centroid}}$ bond angle is 112.27(8)$^\circ$.\[64\] In conformer “B”, the metal is coordinated to the five-membered rings of the fluorenyl ligands unsymmetrically with barium coordinated in an $\eta^5$-fashion to one, and in an $\eta^3$-fashion to the other. The average Ba–C distance for the $\eta^5$-fluorenyl ligand is 3.115(4) Å vs. 3.293(5) Å for the $\eta^3$-bound fluorenyl ligand. The average Ba–C$_{\text{centroid}}$ distance is 2.969(4) Å. The average Ba–NH$_3$ distance is 2.707(3) Å and the C$_{\text{centroid}}$–Ba–C$_{\text{centroid}}$ bond angle is 116.38(8)$^\circ$.\[64\] The preference of BaX$_2$L$_n$ compounds to crystallize in a bent arrangement is supported by computational measurements, which suggest that the nonlinear nature of these compounds is due to the presence and interaction of the d-orbitals on the metal as well as the polarization of the metal cation by the anions.\[65,66,67\]

In 2006, Behrens and coworkers\[68\] synthesized the tetrahydrofuran adduct of bis(fluorenyl)barium, Ba[(C$_{13}$H$_9$)$_2$(THF)$_3$] (34; Figure 1.4), by deprotonating fluorene with barium bis(hexamethyldisilazide) in THF (Scheme 1.34). The compound crystallizes in the same bent sandwich geometry as the previously characterized ammonia adduct (33).
Figure 1.4. X-ray structure of bis(fluorenyl)barium-tris(THF). Hydrogen atoms have been omitted for clarity.

\[
\text{Ba[N(SiMe_3)_2]_2 + 2 (C_{13}H_{10})}_{\text{THF}} \rightarrow \text{Ba[(C_{13}H_{9})_2(THF)_3] + [HN(SiMe_3)_2]_2}
\]

Scheme 1.34. Synthesis of bis(fluorenyl)barium-tris(THF).

In the solid-state, barium is \(\eta^5\)-coordinated to two fluorene ligands through the five-membered rings and to three THF molecules. This creates a distorted trigonal bipyramid where two fluorenyl ligands and one THF molecule are in the equatorial plane and the remaining THF molecules are located in the axial plane. The Ba–C bond distances range from 3.045(15) Å to 3.195(16) Å with an average of 3.127(16) Å and a Ba–C_{centroid} distance of 2.883(15) Å. The Ba–C_{centroid} distance is slightly shorter than that found in the ammonia adduct (33), which had a Ba–C_{centroid} distance of 2.936(4) Å. The average Ba–O_{THF} distance is 2.769(15) Å. The C_{centroid}–Ba–C_{centroid} bond angle of the THF adduct of bis(fluorenyl)barium is 135.26(4)°, greater than that of 112.27(8)° found in the ammonia adduct (33).[68]
The bis(fluorenlyl) calcium and strontium derivatives have yet to be structurally characterized. However, the hypersilyl-fluorenyl (hSi-Flu) calcium (35; Figure 1.5) and strontium (36; Figure 1.5) analogues have been synthesized and characterized using X-ray diffraction by Harder and Feil in 2003.\textsuperscript{[69]} The compounds were synthesized using hypersilyl fluorene and the metal diiodides in THF (Scheme 1.35). The high steric bulk of the hypersilyl fluorenyl ligand confines the coordination sphere around the metal. The hSi-Flu calcium and strontium complexes are also of interest and can be used as initiators in the stereoselective polymerization of styrene when mixed with a homoleptic dibenzyl calcium or strontium complex.\textsuperscript{[69]}

![Figure 1.5. X-ray Structures of hypersilyl-fluorenyl complexes of calcium and strontium. Hydrogen atoms have been omitted for clarity.](image)

\[
2 \text{K}[(\text{Me}_3\text{Si})_3\text{Si}\\{C_{13}H_8}]] + \text{MI}_2 \xrightarrow{\text{THF}} \text{M}[(\text{Me}_3\text{Si})_3\text{Si}\\{C_{13}H_8}]]_2 + 2 \text{KI}
\]

Scheme 1.35. Synthesis of hypersilyl-fluorene metal complexes.
In the solid-state, the calcium hSi-Flu complex 35, Ca[\{\text{Si}(\text{TMS})_3\}(\text{C}_{13}\text{H}_8)_2]\{\text{THF}\}_2], crystallizes as a monomer with the metal bound $\eta^5$ to the five-membered ring of one hSi-Flu ligand and $\eta^3$ to the six-membered ring of the other hSi-Flu ligand, as well as with two THF solvent molecules. The large bulk of the hypersilyl group on fluorene blocks the metal from binding $\eta^5$ to the six-membered ring of fluorene. The Ca–C bond distances to the five-membered ring range from 2.722(4) Å to 2.785(4) Å with an average distance of 2.751(4) Å and with a Ca–C_{centroid} distance of 2.462(4) Å. The Ca–C distances to the six-membered ring range from 2.663(4) Å to 2.993(4) Å with an average distance of 2.829(4) Å. The average Ca–O_{THF} bond distance is 2.335(3) Å and the C_{centroid}–Ca–C_{centroid} bond angle is 129.53(11)°.\[69]\]

The crystal structure of the strontium complex 36, Sr[\{\text{Si}(\text{TMS})_3\}(\text{C}_{13}\text{H}_8)_2]\{\text{THF}\}_2], is analogous to that found in the calcium derivative (35). Strontium is coordinated to two fluorene ligands, one of which bound $\eta^5$ to the five-membered ring and the other bound $\eta^5$ to the six-membered ring of fluorene, in addition to two THF solvent molecules. The steric bulk of the hypersilyl group again stops the metal ion from binding to the second five-membered ring. The average Sr–C distances for the five- and six-membered rings are 2.879(3) Å and 2.981(3) Å, respectively. The Sr–C_{centroid} distance to the five-membered ring is 2.606(3) Å and the average Sr–O_{THF} distance is 2.508(3) Å. The compound is bent in the solid-state and has a C_{centroid}–Sr–C_{centroid} bond angle of 133.73(9)°, similar to that found for bis(fluorenyl)barium-tris(THF) (34). The Sr–C bond distances are markedly smaller in 36 than those found in 34, as can be seen by an increase in the M–C_{centroid} bond, with a Ba–C_{centroid} distance of 2.88 Å in 34.\[69]\]

In both of the hypersilyl fluorenyl metal compounds 35 and 36, the geometries and bond lengths of the hypersilyl group remain unperturbed. However, the carbon to silicon bond length is elongated with C–Si bond distances ranging from 1.870(4) Å to 1.892(4) Å, when compared to
typical C\textsubscript{sp2}–Si bonds (1.84 Å). Additionally, the hypersilyl groups are bent out of the plane away from the metal, maximizing the metal’s Coulombic attraction to fluorene.\textsuperscript{[68]}

1.9.2 Indene Complexes

Indene chemistry with the heavy Group 2 metals was first reported in 1974 by Lindsell and coworkers.\textsuperscript{[70]} However, no structural characterization was completed on these compounds beyond the NMR analysis. It was not until 20 years later that an indene complex with a heavy alkaline earth metal was isolated and structurally characterized by Overby and Hanusa in 1995.\textsuperscript{[71]} Bis(indenyl)calcium, Ca(C\textsubscript{9}H\textsubscript{7})\textsubscript{2} (37; Figure 1.6), and bis(indenyl)strontium, Sr(C\textsubscript{9}H\textsubscript{7})\textsubscript{2} (38; Figure 1.6), were isolated from the reaction of potassium indenide and the metal diiodides in THF (Scheme 1.36).

\textbf{Figure 1.6.} X-ray structures of bis(indenyl)calcium and bis(indenyl)strontium. Hydrogen atoms have been omitted for clarity.

\[ 2 \text{K(C} _9\text{H} _7\text{)} + \text{MI}_2 \xrightarrow{\text{THF}} \text{[M(C}_9\text{H} _7\text{)}\text{2(THF)}_n\text{]} + 2 \text{KI} \]

\[ M = \text{Sr, Ba; } n = 1; M = \text{Ca; } n = 2 \]

\textbf{Scheme 1.36.} Synthesis of calcium and strontium indenyl complexes.
Hanusa and Overby\textsuperscript{[71]} were also able to prepare functionalized diisopropylindene complexes of calcium, \( \text{Ca}[(i\text{-Pr}_2)\text{C}_9\text{H}_5](\text{THF})_2] \) (39; Figure 1.7), and barium, \( \text{Ba}[(i\text{-Pr}_2)\text{C}_9\text{H}_5](\text{THF})] \) (40; Figure 1.7), through the reaction of potassium diisopropylindene and the metal diiodides in THF (Scheme 1.37). These four compounds were the first structurally characterized heavy alkaline earth metal indenyl complexes.

![Figure 1.7. X-ray structures of bis(diisopropylindenyl)calcium and bis(diisopropylindenyl)barium. Hydrogen atoms have been omitted for clarity.](image)

\[
2 \text{K}[(i\text{Pr}_2)\text{C}_9\text{H}_5] + \text{MI}_2 \xrightarrow{\text{THF}} \text{M}[(i\text{Pr}_2)\text{C}_9\text{H}_5](\text{THF})_n], 2 \text{KI}
\]

\( \text{M} = \text{Sr, Ba; } n = 2; \text{ M} = \text{Ca; } n = 1 \)

**Scheme 1.37.** Synthesis of calcium and barium diisopropylindenyl complexes.

In the solid-state, bis(indenyl)calcium (37) crystallizes as a monomer with a bent geometry where calcium is coordinated \( \eta^5 \) to two indene ligands and two THF molecules forming a distorted tetrahedron. The average Ca–C bond distance is 2.73(3) Å which is the same
as that found in the THF adduct of bis(t-butylicyclopentadienyl)calcium, [{(t-Bu)C₅H₄}₂Ca(THF)₂]. The Ca–C centroid distance is 2.453(4) Å and the Ca–OₜH₅ bond distance is 2.360(3) Å. The indenyl rings are oriented in a staggered arrangement allowing them to open up and create a C centroid–Ca–C centroid bond angle of 128.27(6)°.

Unlike the calcium analogue 37, bis(indenyl)strontium (38) forms an infinite coordination polymer in the solid-state (Figure 1.8). Each strontium ion is coordinated to a terminal indene and THF ligand as well as to two bridging indene ligands, forming a tetrahedral geometry around the metal. The metal is bound to each of the indene ligands in an η⁵-fashion to their five-membered rings. The average Sr–C bond distance to the terminal indenyl ring is 2.94(3) Å and the Sr–C centroid bond distance is 2.69(3) Å. The average Sr–C distance to the bridging indenyl ligands is 3.07(2) Å with an average Sr–C centroid distance of 2.84(2) Å. The Sr–C bond distances for the bridging indene ligand have a variation of 0.25 Å, indicating a slippage of the ligand away from the metal. The average Sr–OₜH₅ bond distance is 2.560(9) Å. The C centroid–Sr–C centroid bond angle of 120.33(5)° is slightly smaller than that of the calcium analogue (37). The polymeric strontium product can be compared to the analogous samarium compound, [Sm(C₉H₇)₂(THF)₃], since strontium and samarium share essentially identical ionic radii. However, the samarium indene analogue exhibits a monomeric structure. Due to the similar ionic radii of the two metals (Sr: 1.13 Å Sm: 1.15 Å) it would be expected that the strontium analogue should crystallize in a similar manner to that found for samarium and not in the polymeric structure that has been obtained. This shows that other factors can have an effect on the overall structural types when comparing the main group metals with d- or f-elements.
Bis(diisopropylindenyl)calcium (39) crystallizes in a similar manner to the parent indenyl calcium complex (37). The diisopropylindenyl derivative crystallizes in a bent geometry with two $\eta^5$-bound diisopropylindene ligands and one THF molecule coordinated to the metal center forming a trigonal arrangement. The average Ca–C bond distance is 2.689(7) Å and average Ca–C$_{\text{centroid}}$ bond distance is 2.409(7) Å. The C$_{\text{centroid}}$–Ca–C$_{\text{centroid}}$ bond angle is 142.56(8)$^\circ$, which has opened up from the parent indene structure 37, due to the isopropyl substituents. The opening of the bond angle creates bulk around the metal center and allows only one THF molecule to coordinate to the metal center (Ca–O$_{\text{THF}}$, 2.323(5) Å).

The last structure crystallized by Overby and Hanusa\cite{71} is bis(diisopropylindenyl)barium (40) which crystallizes in a bent geometry with barium coordinated to two isopropyl indenyl ligands in an $\eta^5$-fashion and two THF molecules forming a distorted tetrahedral arrangement. The average Ba–C bond distance is 3.029(9) Å, identical to that of the THF adduct of bis(triisopropylcyclopentadienyl)barium, [(i-Pr)$_3$C$_5$H$_2$]$_2$Ba(THF)$_2$\cite{47}. The Ba–C$_{\text{centroid}}$ distance is 2.783(9) Å and the average Ba–O$_{\text{THF}}$ distance is 2.781(9) Å. The bulk of the isopropyl groups is
offset some by the larger radius of barium and as a result the $\text{C}_\text{centroid}$–$\text{Ba}$–$\text{C}_\text{centroid}$ angle opens up to $140.21(1)^\circ$, which is nearly the same as in the calcium diisopropyl indenyl derivative (39).[71]

1.9.3 Dibenzopentalene

Dibenzopentalene represents an interesting molecule due to its extended $\pi$-system but it has received little attention. In 2013, Xi and coworkers[76] were successful in their attempts to synthesize and structurally characterize barium dibenzopentalenide, Ba[C₁₆H₈(Me₃Si)₂] (42; Figure 1.9). This product is the first example of any pentalene or dibenzopentalene complex where a main group metal binds in an $\eta^8$-fashion. The team used barium bis(trimethylsilyl)amide and [2,3-diphenyl-1,4-bis(trimethylsilyl)-1,3-butadiene-1,4-diyl]dilithium in hexanes to yield the product (Scheme 1.38). Barium dibenzopentalenide has been used in subsequent reactions to afford dibenzopentalene derivatives, which attract considerable attention due to their planar structures and antiaromatic character.[77]

Figure 1.9. X-ray structure of barium dibenzopentalenide. Hydrogen atoms have been omitted for clarity.
Ba[N(SiMe$_3$)$_2$]$_2$ + Li$_2$[C$_{16}$H$_{10}$(Me$_3$Si)$_2$] $\rightarrow$ Ba(C$_{16}$H$_8$(Me$_3$Si)$_2$) + 2 Li[N(SiMe$_3$)$_2$] + H$_2$

**Scheme 1.38.** Synthesis of barium dibenzopentalenide.

In the solid-state, 42 crystallizes as a monomer with barium coordinated $\eta^8$ to dibenzopentalene, which again is the first known example of a main group element with this binding mode. The ligand $\pi$-framework is slightly distorted resulting in the pentalene bending about the bridgehead bond between the two cyclopentadienyl rings by 13.5°, likely caused by the large radius of the barium ion. This perturbation is smaller than those found for other pentalene structures with an $\eta^8$ coordination modes. The average Ba–C bond distance is 3.084(5) Å, the average Ba–C$_{\text{centroid}}$ distance is 2.773(5) Å, and the average Ba–O$_{\text{THF}}$ distance is 2.766(4) Å.$^{[76]}$

In summary, Group 2 organometallic complexes have steadily gained interest over the years due to an increased understanding of the special requirements of these metals. The heavy Group 2 metals possess unique properties that differentiate them from the alkali metals and the actinides and lanthanides, in addition to the lighter Group 2 metals of beryllium and magnesium, thus making the chemistry of these metals and their complexes special. Further expansion of chemistry of the Group 2 metals requires one to develop new synthetic approaches and to adapt those to new $\pi$-systems.
Chapter 2 Heavy Alkaline Earth Metal Activation

The metals of Group 1 require only the removal of the oxide layer to expose the metal surface for use in subsequent reduction reactions. In contrast, the metals of Group 2 require chemical activation in order to be used in the same types of reactions. Several methods have been reported in the literature to achieve the activation of the alkaline earth metals, as discussed below with a focus on heavy Group 2 metals.

2.1 Activated Metal Powders

One synthetic route to alkaline earth metal compounds is the creation of activated metal powders. The dark grey or black powders can be synthesized by stirring a mixture of an alkali metal and the anhydrous alkaline earth metal diiodide in dry THF or toluene under nitrogen and at ambient or reflux temperatures (Scheme 2.1). These powders are substantially more reactive than the bulk metal or metal amalgams. Barium powder, for example, reacts with decamethylcyclopentadiene in THF to produce bis(decamethylcyclopentadienyl)barium (10), whereas bulk barium metal does not react with decamethylcyclopentadiene. The metal iodides are much more readily reduced than the chloride salts, likely due to their increased solubility. Additionally, metal powders produced from toluene solutions tend to be unreactive and unsuitable for synthetic procedures.[78] One benefit of using metal powders is the increased surface area of the metal, thus increasing the rate of the reaction. The powders can be ground in a mortar and pestle or with glass beads that can be added into solution to further grind the metal powders, leading to further activation.[79]

\[
\text{M} = \text{Ca, Sr, Ba} \\
\text{M} \text{I}_2 + 2 \text{K} \xrightarrow{\text{Reflux}} \triangleleft \text{THF} \rightarrow \text{M} + 2 \text{KI}
\]

2.2 Entrainment Reagents

The entrainment method, or method of continuous activation, was developed by Grignard in 1934.[80] The method essentially works by treating excess bulk metal, in this case magnesium, with an ethereal solution of a mixture of halides, producing a clean, and reactive metal surface. The yields of reactions using this method of activation were not great with an average yield of 38%. However, in some cases yields over 60% have been achieved. Beckler and coworkers[81] took Grignard’s method and made a series of modifications to make it sufficient for general alkaline earth metal activation in 1958 (Scheme 2.2). These modifications included (i) addition of all inert halides at once in the beginning of the reaction so as to expose the metal surface to the highest concentration of these reagents, and (ii) change of the inert halide from ethyl bromide to ethylene bromide. With ethylene bromide, the only byproducts formed in the reaction are ethylene and the metal halide. No specific amount of the entrainment ligand is required since it works mechanically to activate the metal surface; however, it is reported that the best yields are obtained using one equivalent of the halide. These modifications to the entrainment method have made it a viable source of activated alkaline earth metals. The benefit of this method of activation is that the reaction is done all at once as a one-pot synthesis.[81]
2.3 Metal Vapor Methods

Metal vapor synthesis is another way of activation of the Group 2 metals. In 1987, Mochida and Yamanishi\[82] were able to successfully create a reactive calcium slurry through the co-condensation of calcium metal and THF. Calcium metal was evaporated at temperatures of approximately 900 °C using a tungsten filament under vacuum at a rate of approximately 20 mg per min. During this time, solvent is added through an inlet tube and it condenses on the walls of a quartz flask where the tungsten filament is housed. The latter remains immersed in liquid nitrogen at 77 K during the entire process (Scheme 2.3). The resulting calcium solvent slurry is then warmed to room temperature and could be used in reactions with organic halides. Additionally, the reactions can be done without the use of solvent and instead by co-condensing the metal vapor with an aryl halide, as shown by Mochida and Ogawa in 1983.\[83] Co-condensation reactions are useful as they can be done without the use of solvents. Furthermore, some products are only accessible through condensation reactions. For example, the reaction of chlorobenzene and calcium vapor only works in the absence of THF and can be produced using co-condensation with a yield of 42%.\[6]
2.4 Liquid Ammonia Method

Highly reactive metal powders can be created by dissolving the metal in liquid ammonia, followed immediately by the removal of the solvent to prevent the formation of metal amides (Scheme 2.4). This works well for calcium, but the formation of strontium and barium amides is much easier and trace amounts of the metal amides cannot be avoided.

To combat the formation of the heavier alkaline earth metal amides, a mixed ammonia ethereal solvent system can be used. In 1991, Drake and Otway\cite{84} reported the activation of the heavy alkaline earth metals in a dilute ammonia solution. Drake and Otway ran ammonia gas through an ethereal solvent, such as diethyl ether or THF, in order to get a solution containing more than 20% of ammonia. In the dilute ammonia solution, the solvated metal ions and electrons are formed, whereas the metal amides only form at higher concentrations. Using this method, the group was able to produce the THF adduct of bis(decamethylcyclopentadienyl)barium at room temperature in 84% yield.\cite{84}

The yield of these reactions can be increased even further by decreasing the temperature to –40 °C. By lowering the reaction temperature, the solubility of ammonia is increased in the solvent system until a 1:1 ratio is attained around –40 °C. The mixed ammonia-solvent systems are generally more reactive than other systems. Triphenylmethyl barium was readily synthesized using this method at low temperature in 80% yield.\cite{85}
2.5 Halide Metathesis

Halide metathesis reactions, also known as Rieke metal synthesis, involve activation of the alkaline earth metals through the reaction of the alkaline metal iodides and an alkali-based reagent, such as potassium or lithium biphenylide. This method is responsible for an array of different organoalkaline earth metal compounds. The synthesis is generally straightforward; however, the target alkaline earth compound is controlled by an equilibrium process that is affected by the choice of solvent, metal halide, alkali metal, as well as ligands. If these factors are not ideal, incomplete reactions may be observed and a mixture of products obtained. Additionally, the synthesis of more complex organometallics remains challenging using this synthetic procedure due to the need for highly reactive potassium organometallic reagents. The most common pairing of reagents includes the potassium salts and alkaline earth diiodides, given that removal of byproducts is the most straightforward with this combination (Scheme 2.5). These reactions can be done in THF and have become one of the most popular methods for utilization of the Group 2 elements in organometallic chemistry. The advantage to this method is its highly reproducible yields; however, soluble halide byproducts can present a serious problem for isolation.

\[
\begin{align*}
\text{NH}_3/\text{THF} & \quad \text{M}^2+ + 2e^- \\
\text{M} = \text{Ca, Sr, Ba}
\end{align*}
\]

Scheme 2.4. Activation of alkaline earth metals using ammonia solutions.
2.6 Transamination

A relatively new synthetic route of activation has been introduced with the recent characterization of bis(hexamethyldisilazide) alkaline earth metal compounds. The reaction works by reacting the bis(hexamethyldisilazide) alkaline earth metal compounds with an organic substrate, such as fluorene or cyclopentadiene (Scheme 2.6). This method is attractive due to the easy access and exceptional solubility of the metal amides in several different solvent systems. The alkaline metal amides have a relatively high pK\textsubscript{a}, which is important since the amide must have a larger pK\textsubscript{a} than the organic substrate for the reaction to proceed. Even with this restriction a variety of new complexes has successfully been prepared. Since the reaction is based on equilibrium, product yields can be increased by quick removal of the liberated amine, which can be done under vacuum. Side reactions are also possible, if reaction conditions are not controlled carefully. The deprotonation of ethereal solvents is observed, if the temperature of the reaction is not monitored. Furthermore, if excess acid is present in the reaction it can lead to protonation and cleavage of the amine, which can then quench the acid dramatically decreasing the yields.

Scheme 2.5. Halide metathesis method of alkaline earth metal activation.

\[
\begin{align*}
&\text{Ethereal solvents} \\
&2 \text{M[L]} + \text{AeX}_2 \overset{(\text{Et}_2\text{O/THF})}{\rightarrow} \text{AeL}_2(\text{THF})_2 + 2 \text{MX} \\
&M = \text{Li, Na, K}; \text{Ae} = \text{Ca, Sr, Ba}
\end{align*}
\]

Scheme 2.6. Transamination method for the synthesis of heavy alkaline earth metal compounds.

\[
\begin{align*}
&M[\text{N(SiMe}_3)_2]_2(\text{THF})_2 + 2 \text{RH} \overset{\text{THF}}{\leftrightarrow} \text{MR}_2(\text{THF})_2 + 2\text{HN(SiMe}_3)_2 \\
&M = \text{Ca, Sr, Ba}
\end{align*}
\]
The activation of the alkaline earth metals is a necessary step for their use in preparative organometallic chemistry. Multiple methods have been developed to accomplish this goal, as detailed above, each with their own benefits and drawbacks. These methods vary from approaches utilizing the elemental metals in the form of finely divided metal powders to those relying on the entrainment methods for surface activation and include the halide metathesis reactions.

Chapter 3 Results and Discussion

Since so few π-complexes of heavy Group 2 metals have been successfully isolated and structurally characterized, we sought out to develop new synthetic routes to synthesize these compounds. We have selected the entrainment method which utilizes an alkyl halide for activation of the alkaline earth metals.\(^{[80,81]}\) We opted to use diiodoethane (DIE) as an entrainment reagent for a couple reasons. DIE is a solid at room temperature and this makes it easy to measure for quantitative use in the subsequent reactions. The byproducts formed, ethane gas and the metal iodide, are innocuous and can be easily removed from the reaction mixture. The additional benefit to this synthetic method is that the solid DIE can be added directly to the reaction mixture in a one-pot synthesis. The development of one-pot reaction techniques allows one to minimize the number of steps and is favored in handling the resulting very air-sensitive and reactive products.

The entrainment method was successfully used in the activation of magnesium metal as first shown by Grignard in 1934.\(^{[79]}\) Advances for this method were later developed by Beckler and coworkers in 1958, which increased the yield and made the method viable as an activation
strategy to Group 2 metal compounds. The entrainment method still serves as an effective activation method; however, it seems to be limited to magnesium in the literature. It was recently shown by our group that the entrainment metal could be successful in the activation of calcium metal. Herein we report the first example of the entrainment method in the activation of barium metal.

The optimal conditions for these reactions were developed based on multiple successful and failed reactions that were performed in the pursuit of the products. Two planar polycyclic aromatic hydrocarbons (PAHs) have been selected, anthracene and fluoranthene (43 and 44; Scheme 3.1). It was found that the quantity of the PAH ligand is not very important; however, reactions performed on a scale of ≥ 10 mg seem to work better. Barium was selected for this work as the heaviest congener of Group 2. The metal was always added in excess in regards to the amount of PAH ligand used in the reaction. Typically, the metal was measured around five to seven equivalents, which facilitated the completion of reduction reactions within several (1–3) days. The amount of DIE was one of the main parameters, which was varied between reactions. At first, ca. 5% of an activator in regard to metal was used until it was ultimately increased to 10%. The color of the solution (characteristic of the reduction) became more intense in the reactions with 10% of DIE, thus indicating an increase in the reaction rate. It was expected that the amount of active metal that can react with the ligand should increase with an increase in the amount of DIE in the reaction.
Scheme 3.1. Anthracene (C\(_{14}\)H\(_{10}\)) 43 and fluoranthene (C\(_{16}\)H\(_{10}\)) 44.

The solvent amounts and reaction times were also manipulated over the course of developing the synthesis of the title products. The amount of THF is a key in order to prevent the product from precipitating too quickly and also to allow direct crystallization of the product from the reaction solution. We found that 2 to 3 mL of THF was optimal for these reactions to be completed within 12 to 24 hours at room temperatures. If the solution were to stir for any longer than that, the product would begin to precipitate out onto the walls of the reaction flask, and any shorter times increased the risk of reaction incompletion. The selected reaction conditions also allowed us to use the resulting reaction solutions for direct product crystallization, using slow diffusion of hexanes.

In the course of this work, two new products have been isolated in single-crystalline form and both were crystallographically characterized, as detailed below.

3.1 Synthesis and X-ray Crystallographic Characterization of \([\text{[BaI(THF)\(_3\)]\(_2\)}^{2+}[\text{C}_{14}\text{H}_{10}\text{]}^{2-}]\text{\(_\infty\)}\)

The barium anthracene complex, 45, was synthesized using anthracene, barium metal, and DIE in THF at room temperature (Scheme 3.2, see Experimental part for details). Upon layering the THF reaction solution with hexanes, brown block-shaped crystals of good quality
were obtained in moderate yield. The X-ray crystallographic study revealed that the product has the \([\{\text{Ba(I)(THF)}_3\}_2^{2+}[\text{C}_{14}\text{H}_{10}]^{2-}\}]\) composition.

\[
\text{C}_{14}\text{H}_{10} + \text{Ba}_{(ex)} + 2 \text{IC}_{2}\text{H}_4\text{I} \xrightarrow{24 \text{ hrs. THF}} \{[\text{Ba(µ-I)(THF)}_3]_2^{2+}[\text{C}_{14}\text{H}_{10}]^{2-}\}_∞ + 2 \text{C}_2\text{H}_4 + \text{BaI}_2
\]

**Scheme 3.2.** Synthesis of 45.

The X-ray diffraction analysis of the crystals showed that the product crystallizes in the \(P\)-1 space group. The asymmetric unit is shown in Figure 3.1.

**Figure 3.1.** ORTEP diagram of the asymmetric unit of 45 with thermal ellipsoids at the 35% probability level. Hydrogen atoms are shown as small spheres of arbitrary radii.

In the molecular structure of \([\{\text{Ba(I)(THF)}_3\}_2^{2+}[\text{C}_{14}\text{H}_{10}]^{2-}\}]\) (45), an anthracene dianion has two barium atoms bound symmetrically in an \(η^6\)-fashion to opposing six-membered rings (Figure 3.2). The Ba–C bond distances range from 3.041(6) Å to 3.174(6) Å with an average of 3.096(6) Å and a Ba–C

\(\text{centroid}\) distance of 2.754(6) Å. These Ba–π distances are similar to those
found in other complexes,[64,68,71,76] such as barium dibenzopentalene (42). For comparison, the average Ba–C bond length distance is 3.084 Å and Ba–C$_{\text{centroid}}$ distance is 2.773 Å in 42. Each barium has three THF molecules coordinated with the Ba–O$_{\text{THF}}$ distances ranging from 2.719(4) Å to 2.777(4) Å with an average of 2.742(4) Å.

**Figure 3.2.** Fragment of the structure of 45; hydrogen atoms have been removed for clarity (left). Space-filling model portraying the anthracene barium binding in 45, solvent and iodine atoms have been removed for clarity (right).

In the solid-state, 45 crystallizes as a coordination polymer, \{[\text{BaI(THF)$_3$}]$_2^2+\text{[C}_{14}\text{H}_{10}]^2^-$\}$_x$, propagating through the formation of iodide bridges between each pair of barium(II) ions (Figure 3.3). Each barium(II) ion is symmetrically bound to two iodide ligands with a Ba–I bond length of 3.513(6) Å. The Ba–I–Ba and I–Ba–I bond angles are 97.474(11)$^\circ$ and 82.525(11)$^\circ$, respectively.
In the $[\text{C}_{14}\text{H}_{10}]^{2-}$ dianion, the C–C bond length distances range from 1.374(9) Å to 1.453(8) Å and are within ± 0.055 Å from those found in the neutral ligand (Table 3.1).\cite{97} Notably, the planarity of the anthracene ligand is within 0.019 Å, which is calculated by measuring the deviation of each carbon atom from a plane created through the C1–C14 atoms of anthracene core. Thus, the reduction and binding of the barium(II) ions do not affect the planarity of the anthracene dianion.
Table 3.1. C–C bond lengths in neutral anthracene\(^ {197} \) and in \([C_{14}H_{10}]^{2–}\) of 45.

<table>
<thead>
<tr>
<th>C–C</th>
<th>(C_{14}H_{10}) Bond Distance (Å)</th>
<th>([C_{14}H_{10}]^{2–}) Bond Distance (Å)</th>
<th>(\Delta) (Å)</th>
<th>C–C</th>
<th>(C_{14}H_{10}) Bond Distance (Å)</th>
<th>([C_{14}H_{10}]^{2–}) Bond Distance (Å)</th>
<th>(\Delta) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1–C2</td>
<td>1.359(2)</td>
<td>1.414(9)</td>
<td>0.055</td>
<td>C9–C10</td>
<td>1.429(2)</td>
<td>1.426(8)</td>
<td>−0.003</td>
</tr>
<tr>
<td>C2–C3</td>
<td>1.429(2)</td>
<td>1.426(8)</td>
<td>0.003</td>
<td>C10–C11</td>
<td>1.398(2)</td>
<td>1.410(9)</td>
<td>0.012</td>
</tr>
<tr>
<td>C3–C4</td>
<td>1.398(2)</td>
<td>1.410(9)</td>
<td>0.012</td>
<td>C11–C12</td>
<td>1.398(2)</td>
<td>1.408(8)</td>
<td>0.010</td>
</tr>
<tr>
<td>C4–C5</td>
<td>1.398(2)</td>
<td>1.408(9)</td>
<td>0.010</td>
<td>C12–C13</td>
<td>1.432(2)</td>
<td>1.405(8)</td>
<td>−0.027</td>
</tr>
<tr>
<td>C5–C6</td>
<td>1.432(2)</td>
<td>1.405(8)</td>
<td>−0.027</td>
<td>C13–C14</td>
<td>1.363(2)</td>
<td>1.418(8)</td>
<td>0.055</td>
</tr>
<tr>
<td>C6–C7</td>
<td>1.363(2)</td>
<td>1.418(8)</td>
<td>0.055</td>
<td>C1–C14</td>
<td>1.424(2)</td>
<td>1.374(9)</td>
<td>−0.050</td>
</tr>
<tr>
<td>C7–C8</td>
<td>1.424(2)</td>
<td>1.374(9)</td>
<td>−0.050</td>
<td>C3–C12</td>
<td>1.436(2)</td>
<td>1.453(8)</td>
<td>0.017</td>
</tr>
<tr>
<td>C8–C9</td>
<td>1.359(2)</td>
<td>1.414(9)</td>
<td>0.055</td>
<td>C5–C10</td>
<td>1.436(2)</td>
<td>1.453(8)</td>
<td>0.017</td>
</tr>
</tbody>
</table>

*\(\Delta\) is calculated by subtracting the bond length of neutral anthracene from that for \([C_{14}H_{10}]^{2–}\).*

In searching the literature, it was found that the polymeric mono-tris(trimethylsilyl)cyclopentadienyl barium complex, \([\{(SiMe_3)_3C_5H_2\}Ba(I)(THF)_2]\), synthesized by Hanusa and Harvey in 2000 (26),\(^ {11} \) is the closest related compound and shows similar geometric parameters to those found in 45. Both complexes have very similar Ba–C\(_{\text{centroid}}\) bond distances, 2.76(1) Å and 2.754(6) Å. The average Ba–O\(_{\text{THF}}\) bond distances are identical (2.74(1) Å and 2.742(4) Å), while the average Ba–I distances are marginally longer in 45, 3.433(2) Å and 3.513(6) Å, respectively. The major difference in these two structures is found in the Ba–I–Ba and I–Ba–I bond angles. In the mono-cyclopentadienyl complex (26), the Ba–I–Ba bond angle is 180° and the I–Ba–I bond angle is 110.45(5)°. This is a drastic change from what is found in the anthracene barium complex 45, which has bond angles of 97.474(11)° and 82.525(11)°, respectively.
It can be mentioned here that no strong intermolecular interactions between the one-dimensional polymeric chains are found in the crystal structure of 45 (Figure 3.4). A space filling model of packing in 45 is also shown (Figure 3.5).

**Figure 3.4.** Solid-state packing of 45. Hydrogen atoms have been removed for clarity.

**Figure 3.5.** Space-filling model of packing in 45.
A careful literature search revealed that only a very few anthracene dianions with either the alkali or early alkaline earth metal magnesium have been reported (Table 3.2).\cite{98,99,100,101} The syntheses of these compounds can be found in Scheme 3.3 and their structures are shown in Scheme 3.4. Interestingly, all of the reported structures crystallize as monomers in the solid-state.

**Table 3.2.** Examples of structurally characterized products with \([\text{C}_{14}\text{H}_{10}]^{2–}\).

<table>
<thead>
<tr>
<th>#</th>
<th>Formula</th>
<th>Notes</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>46</td>
<td>{{[\text{Li(TMEDA)}]\text{2}^{2+}[\text{C}<em>{14}\text{H}</em>{10}]^{2–}}</td>
<td>CIP: One Li(^+) is coordinated (\eta^4) to the central ring while the second is (\eta^4)-bound to the adjacent ring.</td>
<td>[98]</td>
</tr>
<tr>
<td>47</td>
<td>{{[\text{K}<em>2(\text{THF})<em>3]\text{2}^{4+}[\text{C}</em>{14}\text{H}</em>{10}]^{2–}}</td>
<td>Triple-decker CIP sandwich is based on (\eta^6) binding of K(^+) ion</td>
<td>[99]</td>
</tr>
<tr>
<td>48</td>
<td>{{[\text{Mg}(\text{THF})<em>3]\text{2}^{2+}[\text{C}</em>{14}\text{H}_{10}]^{2–}}</td>
<td>Mg(^{2+}) ion is bound to the central two C-atoms of ([\text{C}<em>{14}\text{H}</em>{10}]^{2–}).</td>
<td>[100]</td>
</tr>
<tr>
<td>49</td>
<td>{{[\text{Mg}^{(\text{Mes}Nacnac)}]\text{2}^{2+}[\text{C}<em>{14}\text{H}</em>{10}]^{2–}}</td>
<td>One Mg(^{2+}) is bound by the central two C-atoms of ([\text{C}<em>{14}\text{H}</em>{10}]^{2–}) and the other is (\eta^3)-bound to the adjacent ring.</td>
<td>[101]</td>
</tr>
</tbody>
</table>

\[
\begin{align*}
\text{C}_{14}\text{H}_{12} + 2 \text{LiC}_{4}\text{H}_{9} &\xrightarrow{\text{Benzene/TMEDA}} \{\text{[Li(TMEDA)]}_2^{2+}[\text{C}_{14}\text{H}_{10}]^{2–}\} \\
2 \text{K} + 3 \text{C}_{14}\text{H}_{10} &\xrightarrow{\text{THF}} \{\text{[K}_2(\text{THF})_3]^{4+}[\text{C}_{14}\text{H}_{10}]^{2–}\} \\
\text{Mg} + \text{C}_{14}\text{H}_{10} + \text{BrC}_{2}\text{H}_{4}\text{Br} &\xrightarrow{\text{THF}} \{\text{[Mg(THF)]}_2^{2+}[\text{C}_{14}\text{H}_{10}]^{2–}\} + \text{MgBr}_2 + \text{C}_2\text{H}_4 \\
\{\text{[MesNacnac]}\text{MgMg[MesNacnac]}\} + \text{C}_{14}\text{H}_{10} &\xrightarrow{\text{Toluene}} \{\text{[Mg}^{(\text{Mes}Nacnac)}\text{]}_2^{2+}[\text{C}_{14}\text{H}_{10}]^{2–}\}
\end{align*}
\]

**Scheme 3.3.** Synthesis of 46, 47, 48, and 49, respectively from top to bottom.
Scheme 3.4. Schematic representations of structures of 46 (a), 47 (b), 48 (c), and 49 (d). Only metal-ligand interactions are shown; solvent and ancillary ligands have been removed for clarity.

The monomeric lithium product with anthracene dianion, 46, has two lithium ions coordinated to the central and external rings of the anthracene core in an η⁴-fashion forming a contact-ion pair (CIP).[98] The coordination sphere of lithium is filled by the bidentate tetramethylethylenediamine (TMEDA) ligand. The Li–C bond distances range from 2.273(7) Å to 2.454(6) Å and the average Li–N_{TMEDA} distance is 2.099(6) Å. The planarity of the anthracene ligand is within 0.214 Å, which is calculated by measuring the deviation of each carbon atom from a plane created through the C1–C14 atoms of the anthracene dianion. In the [C_{14}H_{10}]^{2−} anion, the C–C bond length distances range from 1.353(6) Å to 1.451(4) Å and are within ±0.071 Å from those found in the neutral ligand. There is a moderate deviation in the lower bond range; however, the higher bond range is quite similar to that found in 45, which has C–C bond
length distances ranging over 1.374(9)–1.453(8) Å and within ± 0.055 Å from those found in the neutral ligand.\textsuperscript{[97]}

Product \textbf{47} is an interesting discrete triple-decker anthracene potassium sandwich.\textsuperscript{[99]} The triple-decker sandwich is comprised of two radical anthracene monoanions and one dianion in the center of the sandwich, which is separated by four potassium ions, forming a CIP. The structural formula of the product can be represented as following, \{[(C\textsubscript{14}H\textsubscript{10}\textsuperscript{+})][(K\textsubscript{2}(THF)\textsubscript{3})\textsuperscript{2+}]|(C\textsubscript{14}H\textsubscript{10}\textsuperscript{2−})]|[(K\textsubscript{2}(THF)\textsubscript{3})\textsuperscript{2+}]|(C\textsubscript{14}H\textsubscript{10}\textsuperscript{−})\}. The potassium ions coordinate through the exterior rings of the anthracene anions in an \(\eta^6\)-fashion. The K–C bond distances to the outer anthracene radical anions range from 3.12(3) Å to 3.22(3) Å with an average K–C\textsubscript{centroid} distance of 2.90(3) Å, while the K–C bond distances of the central anthracene dianion range from 2.90(3) Å to 3.35(3) Å with an average K–C\textsubscript{centroid} distance of 2.78(3) Å. The coordination sphere of potassium is completed by solvent THF molecules with an average K–O\textsubscript{THF} bond distance of 2.778(2) Å. The planar anthracene anions form a tilted triple-decker sandwich with interplanar angles of +54° and −54°. In the \(\text{[C}\textsubscript{14}\text{H}\textsubscript{10}\text{]}\textsuperscript{2−}\) dianion, the C–C bond length distances range over 1.372(4)–1.451(3) Å and are within ± 0.052 Å from those found in the neutral ligand. This is very similar to that found in \textbf{45}, which has C–C bond length distances ranging from 1.374(9) Å to 1.453(8) Å and within ± 0.055 Å from those found in the neutral ligand.\textsuperscript{[97]}

In \textbf{48}, one magnesium ion is coordinated to the anthracene dianion ligand through the two central carbon atoms in a polar covalent fashion.\textsuperscript{[100]} The polar covalent nature of the Mg–C bonds is reflected in the loss of the aromatic character in the dianion, folding of the ligand, and change in hybridization of the two carbon atoms from sp\textsuperscript{2} to sp\textsuperscript{3}. These data are supported by \(\text{^{13}C}\) NMR spectroscopy\textsuperscript{[102]} and contrast to the planar anthracene lithium dianion in \textbf{46},\textsuperscript{[98]} which exhibits essentially ionic bonding. Due to the metal binding to the central carbon site, the
anthracene dianion in 48 experiences an average folding of 28.6°. The rest of the coordination environment of the magnesium ion is filled by solvent THF molecules. The average Mg–C bond distance in 48 is 2.30(2) Å and the average Mg–O$_{\text{THF}}$ distance is 2.055(10) Å. In the [C$_{14}$H$_{10}$]$^{2-}$ dianion of 48, the C–C bond length distances range from 1.330(5) Å to 1.487(5) Å and are within ± 0.089 Å from those found in the neutral ligand. This is a significant deviation from that found in 45, which has C–C bond length distances within the 1.374(9)–1.453(8) Å range and within ± 0.055 Å from those found in the neutral ligand.$^{[65]}$ This deviation can be attributed to the polar covalent binding mode of the magnesium dication to the bridgehead carbon atoms of anthracene in 48.$^{[100]}$

In 49, two magnesium ions are coordinated through opposite sides of the anthracene ligand forming a monomeric structure.$^{[101]}$ One of the magnesium centers (Mg(1)) is coordinated to the central two carbon atoms of the central ring in a polar covalent fashion, almost identically to that found in 48.$^{[100]}$ The second magnesium ion (Mg(2)) is coordinated to the adjacent anthracene ring in an $\eta^4$-fashion. The magnesium ions are also coordinated to MesNacnac ligands (50; Scheme 3.5) to fill the coordination sphere through the Mg–N bonds. As a result of this coordination, the compound can be viewed as a contact ion pair (CIP) with the following formula: $\{[\text{Mg}^{\text{MesNacnac}}][\text{MesNacnac}\text{Mg}(\text{C}_{14}\text{H}_{10})]\}$. The average Mg(1)–C and Mg(2)–C bond distances are 2.358(7) Å and 2.406(7) Å, respectively. The Mg–N bond distances for both Mg(1) and Mg(2) are very similar with an average of 2.025(7) Å. Due to the polar covalent bonding of Mg(1), a folding of the anthracene dianion is found (17.3°) as in the case of 48. In the [C$_{14}$H$_{10}$]$^{2-}$ dianion, the C–C bond length distances range over 1.371(7)–1.474(7) Å and are within ± 0.076 Å from those found in the neutral ligand. These distances are similar to those found in 45, which has the C–C bond length distances from 1.374(9) Å to 1.453(8) Å and within
± 0.055 Å from those found in the neutral ligand.\[9^7\] The longest C–C bond distance of 1.474(7) Å in 49, can be attributed to the polar covalent bonding of Mg(1) to the central carbon atoms of the anthracene dianion.\[10^1\]

\[\text{Scheme 3.5. Structure of the MesNacnac ligand.}\]

The anthracene products 46, 47, 48, and 49 are the only reported structurally characterized dianions found in the literature. These products, containing either the Group 1 or 2 metals, exhibit different structures and show variations in metal ligand interactions. In the Group 1 metal complexes, the lithium anthracene dianion (46) forms a monomeric CIP product, while the potassium anthracene dianion (47) forms a triple-decker sandwich structure. In the Group 2 metal complexes, both 48 and 49 have magnesium ions with polar covalent interactions expressed by a loss of aromatic character, folding of the ligand about the central axis, and a change in hybridization of the corresponding carbon atoms from sp\(^2\) to sp\(^3\). Of these structures, 46 is the most similar to the anthracene barium complex 45, where two metals are coordinated to the anthracene dianion from opposing sides of the ligand.
3.2 Synthesis and X-ray Crystallographic Characterization of \{[\text{Ba}(\text{THF})_3]_2^{2+}[\text{C}_{16}\text{H}_{10}]^{2-}\}_\infty

The barium fluoranthene complex 51 was synthesized using fluoranthene, barium metal, and DIE in THF at room temperature (Scheme 3.6, see Experimental part for details). Upon layering the THF reaction solution with hexanes, brown block-shaped crystals of good quality were obtained in moderate yield. The X-ray crystallographic study revealed that the product has the \{[\text{Ba}(\text{I})(\text{THF})_3]_2^{2+}[\text{C}_{16}\text{H}_{10}]^{2-}\} composition.

\[
\text{C}_{16}\text{H}_{10} + \text{Ba}_{(ex)} + 2 \text{IC}_2\text{H}_4\text{I} \xrightarrow{24 \text{ hrs.}} \text{THF} \rightarrow \{[\text{Ba}(\mu\text{-I})(\text{THF})_3]_2^{2+}[\text{C}_{16}\text{H}_{10}]^{2-}\}_\infty + 2 \text{C}_2\text{H}_4 + \text{Ba}_2
\]

**Scheme 3.6.** Synthesis of 51.

The results of the X-ray diffraction analysis of the crystals show that the product crystallizes in the \emph{Pn}a2\emph{1} space group. The asymmetric unit contains one fluoranthene ligand with two nonequivalent barium and iodine atoms and six THF molecules (Figure 3.6).

**Figure 3.6.** ORTEP diagram of the asymmetric unit of 51 with thermal ellipsoids at the 35% probability level. Hydrogen atoms are shown as small spheres of arbitrary radii.
In the molecular structure of \{[\text{BaI}(\text{THF})_3]_2^{2+}[\text{C}_{16}\text{H}_{10}]^{2-}\} (51), one fluoranthene dianion has two barium atoms bound symmetrically in a $\eta^6$-fashion to opposing six-membered rings (Figure 3.7). All bond distances discussed below have been averaged due to the similar environments of Ba(1) and Ba(2). The Ba–C bond distances range from 2.983(14) Å to 3.257(14) Å with an average of 3.097(14) Å and a Ba–C$_{\text{centroid}}$ distance of 2.755(14) Å. These values are within the range of other Ba–π contacts$^{[71,76]}$, such as those found in bis(diisopropylindenyl)barium (40). For comparison, the average Ba–C bond distance is 3.029 Å and the Ba–C$_{\text{centroid}}$ distance is 2.783 Å in 40. In 51, each barium is coordinated to three THF molecules with the Ba–O$_{\text{THF}}$ distances ranging from 2.657(9) Å to 2.845(9) Å with an average of 2.749(11) Å.

![Figure 3.7. Fragment of the structure of 51; hydrogen atoms have been removed for clarity (left). Space-filling model portraying the fluoranthene barium binding in 51, solvent and iodine atoms have been removed for clarity (right).](image)

In the solid-state, 51 crystallizes as a coordination polymer, \{[\text{BaI}(\text{THF})_3]_2^{2+[\text{C}_{16}\text{H}_{10}]^{2-}}\}_x, propagating through the formation of iodide bridges between each pair of barium(II) ions (Figure 66).
Each barium(II) ion is bound to two iodide ligands with Ba–I(1) and Ba–I(2) bond lengths of 3.467(12) and 3.505(11) Å, respectively. The Ba(1)–I(1)–Ba(2) and Ba(1)–I(2)–Ba(2) bond angles are 98.92(3)° and 97.48(3)°, while the I(1)–Ba(1)–I(2) and I(1)–Ba(2)–I(2) bond angles are 81.75(3)° and 81.85(3)°, respectively.

**Figure 3.8.** Fragment of the polymeric structure of 51. Hydrogen atoms have been removed for clarity.

In the \([C_{16}H_{10}]^2−\) dianion, the C–C bond length distances range from 1.32(2) Å to 1.474(18) Å and are within ± 0.105 Å from neutral fluoranthene (Table 3.3). Additionally, the planarity of the fluoranthene ligand is within 0.076 Å, which is calculated by measuring the deviation of each carbon atom from a plane created through the C1–C16 atoms of fluoranthene. Thus, the reduction and binding of the barium(II) ions do not affect the planarity of the fluoranthene dianion.
Table 3.3. C–C bond lengths in neutral fluoranthene\textsuperscript{[103]} and in [C\textsubscript{16}H\textsubscript{10}]\textsuperscript{2} of 51.

<table>
<thead>
<tr>
<th>C–C</th>
<th>C\textsubscript{16}H\textsubscript{10} Bond Distance (Å)</th>
<th>[C\textsubscript{16}H\textsubscript{10}]\textsuperscript{2} Bond Distance (Å)</th>
<th>Δ (Å)</th>
<th>C–C</th>
<th>C\textsubscript{16}H\textsubscript{10} Bond Distance (Å)</th>
<th>[C\textsubscript{16}H\textsubscript{10}]\textsuperscript{2} Bond Distance (Å)</th>
<th>Δ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1–C2</td>
<td>1.395(3)</td>
<td>1.372(19)</td>
<td>−0.023</td>
<td>C11–C12</td>
<td>1.426(3)</td>
<td>1.454(19)</td>
<td>0.028</td>
</tr>
<tr>
<td>C2–C3</td>
<td>1.393(3)</td>
<td>1.38(2)</td>
<td>−0.013</td>
<td>C12–C13</td>
<td>1.377(3)</td>
<td>1.418(19)</td>
<td>0.041</td>
</tr>
<tr>
<td>C3–C4</td>
<td>1.395(3)</td>
<td>1.35(2)</td>
<td>−0.045</td>
<td>C13–C14</td>
<td>1.420(3)</td>
<td>1.32(2)</td>
<td>−0.100</td>
</tr>
<tr>
<td>C4–C5</td>
<td>1.388(3)</td>
<td>1.394(18)</td>
<td>0.006</td>
<td>C14–C15</td>
<td>1.370(3)</td>
<td>1.475(18)</td>
<td>0.105</td>
</tr>
<tr>
<td>C5–C6</td>
<td>1.420(3)</td>
<td>1.458(17)</td>
<td>0.038</td>
<td>C15–C16</td>
<td>1.417(3)</td>
<td>1.436(17)</td>
<td>0.019</td>
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<tr>
<td>C6–C7</td>
<td>1.481(3)</td>
<td>1.431(18)</td>
<td>−0.050</td>
<td>C1–C6</td>
<td>1.387(3)</td>
<td>1.423(18)</td>
<td>0.036</td>
</tr>
<tr>
<td>C7–C8</td>
<td>1.371(3)</td>
<td>1.434(18)</td>
<td>0.063</td>
<td>C5–C15</td>
<td>1.476(3)</td>
<td>1.405(18)</td>
<td>−0.071</td>
</tr>
<tr>
<td>C8–C9</td>
<td>1.417(3)</td>
<td>1.41(2)</td>
<td>−0.007</td>
<td>C7–C16</td>
<td>1.416(3)</td>
<td>1.398(18)</td>
<td>−0.018</td>
</tr>
<tr>
<td>C9–C10</td>
<td>1.387(3)</td>
<td>1.428(18)</td>
<td>0.041</td>
<td>C11–C16</td>
<td>1.394(3)</td>
<td>1.433(16)</td>
<td>0.039</td>
</tr>
<tr>
<td>C10–C11</td>
<td>1.424(3)</td>
<td>1.396(19)</td>
<td>−0.028</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Δ is calculated by subtracting the bond length of neutral anthracene from that for [C\textsubscript{16}H\textsubscript{10}]\textsuperscript{2}.

This new barium complex is a close analogue of the previously described 45. The average Ba–C bond distances are similar in both complexes, namely 3.096(6) Å in 45 and 3.097(14) Å in 51. The Ba–C\textsubscript{centroid} distance of 2.755(14) Å in 51 is also in close agreement with that found in 45 (2.754(6) Å). The average Ba–O\textsubscript{THF} bond distances are 2.742(4) Å in 45 and 2.749(11) Å in 51. The main difference between the two analogues is a small decrease in the Ba–I bond distances in 51 to 3.486(12) Å vs. 3.513(6) Å in 45. Despite this decrease in bond length, the Ba–I–Ba and I–Ba–I bond angles remain quite similar. The Ba–I–Ba bond angle is 97.474(11)° in 45 vs. 98.20(3)° in 51, while the I–Ba–I bond angles are 82.525(11)° and 81.80(3)°, respectively.
It can be mentioned here that there are no strong intermolecular interactions between the one-dimensional polymeric chains in the crystal structure of 51 (Figure 3.9). A space-filling model of packing in 51 is also shown (Figure 3.10).

**Figure 3.9.** Solid-state packing of 51. Hydrogen atoms have been removed for clarity.

**Figure 3.10.** Space-filling model of packing in 51.
Only three examples of fluoranthene dianions isolated with the Groups 1 and 2 metals have been reported in the literature. Bock was able to synthesize these fluoranthene dianions using lithium and sodium metals (Scheme 3.7).[104] However, the X-ray crystallographic data have not been reported for these complexes, making 51 the first fluoranthene dianion structurally characterized with either the alkali or alkaline earth metals. Since this is the only reported dianion of fluoranthene, comparison of the C–C bond distances was only possible with the neutral ligand.

\[
\begin{align*}
2 \text{C}_6\text{H}_{10} + 2 \text{Na} & \xrightarrow{\text{DME}} \left\{\text{Na(DME)}_2\right\}^2^+\left[\text{C}_6\text{H}_{10}\right]^2^- \\
2 \text{C}_6\text{H}_{10} + 2 \text{Na} & \xrightarrow{\text{Diglyme}} \left\{\text{Na(Diglyme)}_2\right\}^2^+\left[\text{C}_6\text{H}_{10}\right]^2^- \\
2 \text{C}_6\text{H}_{10} + 2 \text{Li} & \xrightarrow{\text{DME}} \left\{\text{Li}_2(\text{DME})_{2.5}\right\}^2^+\left[\text{C}_6\text{H}_{10}\right]^2^- \\
\end{align*}
\]

**Scheme 3.7.** Synthesis of fluoranthene dianions with sodium and lithium.

Of all the known structures of anthracene and fluoranthene dianions, the monomeric lithium product with anthracene dianion, 46, is the closest related to that of 45 and 51. Compound 46 is the only previously reported structure without polar covalent bonds coordinating the metal to the ligand, which is characterized by a change in the carbon hybridization and subsequent loss in aromaticity and folding of the ligand.[99,101] However, the two new barium products 45 and 51 exhibit 1D polymeric structures in the solid-state in contrast to all previously reported cases. Noteworthy, 45 and 51 are the first structurally characterized products of the reduced anthracene and fluoranthene isolated with a heavy Group 2 metal. The large ionic radius of Ba$^{2+}$ (1.35 A)$^{171}$ is likely responsible for the formation of iodide bridges propagating the polymeric 1D structures of 45 and 51.
3.3 Experimental Details

3.3.1 Materials and Methods. All manipulations were carried out using break-and-seal and glove-box techniques under an atmosphere of argon.\textsuperscript{[105]} Solvents (THF and hexanes) were dried over sodium/benzophenone and distilled prior to use. Barium metal was purchased from Sigma Aldrich and the oxide layer was removed before use. Fluoranthene and anthracene were purchased from Sigma Aldrich and sublimed prior to use at 100 °C and 170 °C, respectively. Diiodoethane (DIE) was purchased from Sigma Aldrich and used as received without any further purification. NMR spectra were measured on a Bruker Advance III spectrometer at 400 MHz for $^1$H and referenced to the residual resonances of THF-\textit{d}_8 (δ 3.62 and 1.79).\textsuperscript{[106]} The UV-vis spectra were recorded on a PerkinElmer Lambda 35 spectrometer.

3.3.2 Synthesis and Crystallization of $\{[\text{BaI(THF)}_3]_{2^2}[\text{C}_{14}\text{H}_{10}]_{2^-}\}_x$

In the glovebox, a custom-built glass system was loaded with anthracene (10.0 mg, 0.056 mmol), Ba metal (48.0 mg, 0.349 mmol), and DIE (12.0 mg, 0.043 mmol). Then anhydrous THF (2.0 mL) was added to the system via syringe. The solution turned yellow immediately and further reduced to a light blue color after stirring at room temperature for 1 hour. Over the next 24 hours, the solution slowly darkened to a dark blue-purple color. After filtration, the dark blue-purple solution was layered with hexanes (2.0 mL). The tube was sealed under vacuum and placed in the refrigerator at 10 °C. Dark brown block-shaped crystals were observed after 2 weeks. Yield (20.4 mg, 32 %).
3.3.3 NMR Probe Preparation of Ba/C\textsubscript{14}H\textsubscript{10} in THF-\textit{d}\textsubscript{8}

Crystals of 45 were washed with hexanes and added to an NMR tube with excess Ba metal. We found that the addition of barium metal is essential for the collection of \textsuperscript{1}H NMR data, most probably due to the extreme air and moisture sensitivity of the crystalline product. Crystals were dissolved in THF-\textit{d}\textsubscript{8}. The tube was sealed under argon and the \textsuperscript{1}H NMR spectrum (Figure 3.11) was recorded at room temperature (25 °C).

![Figure 3.11. \textsuperscript{1}H NMR spectrum of C\textsubscript{14}H\textsubscript{10}\textsuperscript{2-} in 45 recorded at 25 °C in THF-\textit{d}\textsubscript{8}.](image)

The \textsuperscript{1}H NMR spectrum of the anthracene dianion (45; Figure 3.11) shows peaks for aromatic protons at 6.87 (4H), 6.71 (4H), and 4.54 (2H) ppm. The signals of free THF appear at 3.62 and 1.77 ppm and those of the coordinated THF molecules are seen at 3.90 and 1.72 ppm. The first two signals of the anthracene dianion in 45 in the aromatic region are notably shifted upfield from their respective positions (8.46 and 8.00 ppm) in neutral anthracene (Figure, 3.12),
while the third signal is significantly upfield shifted (from 7.44 to 4.54 ppm). The $^1$H NMR spectra of other reported anthracene dianions support the significant shifting of the aromatic protons upon reduction.$^{[100,101,107]}$ For example, the anthracene dianion in magnesium(II) product (49) shows $^1$H NMR signals at 5.79 (4H), 5.12 (4H), and 3.49 (2H) ppm. While the $^1$H NMR signals are not quite as shifted in 45, the integration and the significant upfield shift of the two central aromatic protons of anthracene is consistent with what is found in the literature. The variation in the chemical shifts of the anthracene dianions may be reflective of their different binding with magnesium(II) centers in 49 and barium(II) ions in 45. The proton integration in the anthracene dianion of 2:4:4 in the title product is consistent with both the parent ligand and the reported example.

The $^1$H NMR of the neutral anthracene ligand (Figure 3.12) shows three signals in the aromatic region related to the anthracene protons and two peaks corresponding to THF. The anthracene signals appear at 8.46 (2H), 8.00 (4H), 7.44 (4H) ppm.

![Figure 3.12. $^1$H NMR spectrum of neutral anthracene recorded at 25 °C in THF-d$_8$.](image)

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3.3.4 UV-Vis Probe Preparation of Ba/$C_{14}H_{10}$ in THF

THF (3 mL) was added to a glass ampule containing excess Ba metal (~4 eq.), DIE (0.06 mg, $2.1 \times 10^{-4}$), and $C_{14}H_{10}$ (0.1 mg, $5.6 \times 10^{-4}$ mmol). The ampule was sealed and UV-Vis spectra were monitored at different reaction times (total 1 week) at room temperature (Figure 3.13).

![UV-Vis spectra of Ba/$C_{14}H_{10}$ in THF.](image)

<table>
<thead>
<tr>
<th>Label</th>
<th>Time (min.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5</td>
</tr>
<tr>
<td>2</td>
<td>60</td>
</tr>
<tr>
<td>3</td>
<td>120</td>
</tr>
<tr>
<td>4</td>
<td>1200 (20 h.)</td>
</tr>
<tr>
<td>5</td>
<td>10080 (7 d.)</td>
</tr>
</tbody>
</table>

**Figure 3.13.** UV-Vis spectra of Ba/$C_{14}H_{10}$ in THF.

The UV-Vis spectra of 45 (Figure 3.13) show absorbance in the ultraviolet region and a broad peak around 600 nm in the visible region. The only change observed in the spectrum is an intensity increase of the peak around 600 nm, associated with the formation of anthracene dianion.

The UV-Vis spectrum of the dissolved crystals shows that the product in solution matches the in situ generated one (Figure 3.14). Similar absorbance peaks are found in both spectra with no erroneous peaks observed in the dissolved crystal spectrum.
3.3.5 Synthesis and Crystallization of $\left\{ \text{BaI(THF)}_3 \right\}_{2^2}[\text{C}_{14}\text{H}_{10}]^{2^-}_\infty$ 10 $\text{C}_6\text{H}_{14}$

In the glovebox, a custom-built glass system was loaded with fluoranthene (10.0 mg, 0.049 mmol), Ba metal (45.0 mg, 0.327 mmol), DIE (10.8 mg, 0.038 mmol). Then anhydrous THF (2.2 mL) was added to the system via syringe. The solution turned yellow immediately and further reduced to a light brown color after stirring at room temperature for 1 hour. Over the next 24 hours, the solution slowly darkened to a dark brown color. After filtration, the dark brown solution was layered with hexanes (2.0 mL). The tube was sealed under vacuum and placed in the refrigerator at 10 °C. Dark brown block-shaped crystals were observed after 2 weeks. Yield (20.0 mg, 35 %).
3.3.6 NMR Probe Preparation of Ba/C$_{16}$H$_{10}$ in THF-$d_8$

Crystals of 51 were washed with hexanes and added to an NMR tube with excess Ba metal. We found that the addition of barium metal is essential for the collection of $^1$H NMR data, most probably due to the extreme air and moisture sensitivity of the crystalline product. Crystals were dissolved in THF-$d_8$. The tube was sealed under argon and the $^1$H NMR spectrum (Figure 3.15) was recorded at room temperature (25 °C).

![Figure 3.15. $^1$H NMR spectrum of C$_{16}$H$_{10}^{2−}$ in 51 recorded at 25 °C in THF-$d_8$.](image)

The $^1$H NMR spectrum of the fluoranthene dianion (51; Figure 3.15) shows peaks for the fluoranthene protons at 6.99 (2H) and 6.38 (2H), 5.04 (2H), 3.42 (2H), and 3.29 (2H) ppm. The signals of free THF appear at 3.62 and 1.76 ppm and those of the coordinated THF molecules are seen at 3.78 and 1.92 ppm. The former two signals of the fluoranthene dianion (51) that remain in the aromatic region (6.99 and 6.38 ppm) are shifted upfield from their respective positions in
the neutral fluoranthene (7.88 and 7.39 ppm; Figure 3.16). The three other fluoranthene proton
signals are significantly shifted upfield compared to the neutral ligand (Figure 3.16). While no
fluoranthene dianions of the alkali or alkaline earth metals have been structurally characterized,
the $^1$H NMR spectrum of the dianion of fluoranthene with sodium counterions has been reported
and supports the significant shifting of the aromatic protons upon reduction.$^{[107]}$ The $^1$H NMR
signals of the sodium salt of fluoranthene dianion appear at 6.89 (2H), 6.06 (2H), 5.04 (2H), 4.81
(2H), and 3.27 (2H) ppm. These data reinforce the assignment of the signals found in the $^1$H
NMR spectrum of barium product (51). The proton integration in the fluoranthene dianion of
2:2:2:2:2 is consistent with both the parent ligand and the literature reported example.

![Figure 3.16. $^1$H NMR spectrum of neutral fluoranthene recorded in THF-$d_8$ at 25 °C.](image)

The $^1$H NMR of the neutral fluoranthene ligand (Figure 3.16) shows five signals in the
aromatic region related to the fluoranthene protons and two peaks corresponding to THF. The
fluoranthene signals appear at 8.03 (2H), 7.98 (2H), 7.88 (2H), 7.66 (2H), and 7.39 (2H) ppm.
3.3.7 UV-Vis Probe Preparation of Ba/C_{16}H_{10} in THF

THF (3 mL) was added to a glass ampule containing excess Ba metal (~4 eq.), DIE (0.05 mg, 1.7×10^{-4}), and C_{16}H_{10} (0.1 mg, 4.9×10^{-4} mmol). The ampule was sealed and UV-Vis spectra were monitored at different reaction times (total 1 week) at room temperature (Figure 3.17).

![UV-Vis spectra of Ba/C_{16}H_{10} in THF.](image)

**Figure 3.17.** UV-Vis spectra of Ba/C_{16}H_{10} in THF.

The UV-Vis spectra of 51 (Figure 3.17) exhibit absorbance in the ultraviolet region and a peak around 450 nm in the visible region. The only change observed in the spectrum is an intensity increase of the 450 nm peak, associated with the formation of fluoranthene dianion.

The UV-Vis spectrum of the dissolved crystals shows that the product in solution matches the in situ generated one (Figure 3.18). Similar absorbance peaks are found in both spectra with no erroneous peaks observed in the dissolved crystal spectrum.
Figure 3.18. UV-Vis spectra of *in situ* generated product and dissolved crystals of \{[\text{BaI(THF)}_3]^2^+[\text{C}_{16}\text{H}_{10}]^{2^-}\}_\infty.

3.4 Crystal Structure Determination and Refinement

\{[\text{BaI(THF)}_3]^2^+[\text{C}_{16}\text{H}_{10}]^{2^-}\}_\infty

Data collection was performed on a Bruker D8 VENTURE X-ray diffractometer with PHOTON 100 CMOS shutterless mode detector equipped with a Mo-target X-ray tube (\(\lambda = 0.71073 \, \text{Å}\)) at \(T = 100(2) \, \text{K}\). Data reduction and integration were performed with the Bruker software package SAINT (version 8.38A).\textsuperscript{108} Data were corrected for absorption effects using the empirical methods as implemented in SADABS (version 2016/2).\textsuperscript{109} The structure was solved by SHELXT\textsuperscript{110} and refined by full-matrix least-squares procedures using the Bruker SHELXTL (version 2017/1)\textsuperscript{111} software package. All non-hydrogen atoms were refined anisotropically. The H-atoms were also included at calculated positions and refined as riders, with \(U_{iso}(\text{H}) = 1.2 \, U_{eq}(\text{C})\). The structure was refined as a two-component non-merohedral twin with the BASF value refined to 0.4980. Selected crystallographic data for 45 are shown in Table 3.4.
\{[\text{BaI(THF)}_3]^{2+}[\text{C}_{16}\text{H}_{10}]^{2-}\}_\infty 10 \text{C}_6\text{H}_{14}

Data collection was performed on a Bruker D8 VENTURE X-ray diffractometer with PHOTON 100 CMOS detector equipped with a Mo-target fine-focus sealed X-ray tube ($\lambda = 0.71073$ Å) at $T = 100(2)$ K. Data reduction and integration were performed with the Bruker software package SAINT (version 8.38A).\cite{108} Data were corrected for absorption effects using the empirical methods as implemented in SADABS (version 2016/2).\cite{109} The structure was solved by SHELXT (version 2018/2)\cite{110} and refined by full-matrix least-squares procedures using the Bruker SHELXTL (version 2018/3)\cite{111} software package. All non-hydrogen atoms were refined anisotropically. All H-atoms were included at calculated positions and refined as riders, with $U_{\text{iso}}(\text{H}) = 1.2 \ U_{\text{eq}}(\text{C})$ and $U_{\text{iso}}(\text{H}) = 1.5 \ U_{\text{eq}}(\text{C})$ for methyl groups. In each unit cell, there are ten \text{n-hexane} molecules that were found to be severely disordered and removed by the SQUEEZE subroutine in PLATON (version 230418).\cite{112} The total void volume was 1209 Å$^3$ indicated by PLATON, equivalent to 23.27 % of the unit cell’s total volume. Selected crystallographic data for \textbf{51} are shown in Table 3.4.
3.5 Crystallographic Data

Table 3.4. Crystal data and structure refinement parameters for \{[\text{BaI(THF)}_3\text{]}^{2+}[\text{C}_{14}\text{H}_{10}^{2-}]\}_{\infty} (45) and \{[\text{BaI(THF)}_3\text{]}^{2+}[\text{C}_{16}\text{H}_{10}^{2-}]\}_{\infty} 10 \text{C}_6\text{H}_{14} (51).

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<th>Parameter</th>
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<th>51</th>
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<tbody>
<tr>
<td>Empirical formula</td>
<td>C_{19}H_{20}BaIO_{3}</td>
<td>C_{55}H_{91}Ba_{2}I_{2}O_{6}</td>
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<tr>
<td>M_r</td>
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</tr>
<tr>
<td>T (K)</td>
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<td>100</td>
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<tr>
<td>b (Å)</td>
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<td>31.4725 (11)</td>
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<tr>
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<td>γ (°)</td>
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<tr>
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<td>μ [mm^{-1}]</td>
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<td>2.744</td>
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<td>9209/454/286</td>
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<tr>
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<td>1.608</td>
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<td>2.49/-1.36</td>
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^a_{R_1} = \Sigma |F_o| - |F_c|/|F_o|; ^b wR_2 = [\Sigma w(F_o^2-F_c^2)^2]/[\Sigma w(F_o^2)^2]^{1/2}; ^c Quality-of-fit = [\Sigma w(F_o^2-F_c^2)^2/(N_{obs}-N_{params})]^{1/2}, based on all data.
References


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