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[8]Annulene Derivatives of Cerium

J.T. Rigsbee, Jr.
(Ph.D. Thesis)

August 1988

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LBL-28289

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J.T. Rigsbee, Jr.

Ph.D. Dissertation

August, 1988

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The Berkeley Work was supported in part by the Director,
Office of Energy Research, Office of Basic Energy Sciences,
Chemical Sciences Division of the U.S. Department of Energy,
under Contract No. DE-AC03-76SF00098

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[8]Annulene Derivatives of Cerium

John Taylor Rigsbee, Jr.

Abstract

A study has been performed on bis[8]annulene complexes of cerium, focussing primarily on tetravalent cerium. This unusual compound, cerocene, was originally prepared using a low yield, specific synthesis; a more general synthesis has now been found. It has been determined that treating a solution of the readily prepared $K[Ce(C_8H_8)_2]$ with an excess of silver iodide results in a high yield of the corresponding tetravalent cerium sandwich compound. This method has now been used to successfully prepare several substituted analogs in equally good yield.

The chemistry of this class of molecule has been explored using a variety of physical techniques. Variable temperature ^1H NMR shows an electron exchange on the NMR timescale, as has been observed for similar metallocenes. An examination of the visible spectrum of this molecule showed agreement with the previously calculated energy for this transition. The electrochemistry of these molecules has also been examined and the Ce(IV)/Ce(III) reduction potential was measured to be -1.3 V; this value is extremely low for a cerium species and suggests that a considerable amount of stability is being imparted by the COT rings.

The crystal structure of dimethylcerocene has now been solved. In general, the structure shows the features expected for this class of molecule, but there are several interesting features which are discussed.

Efforts have also been made to prepare another ligand, 1,3,5,7-tetramethylcyclooctatetraene are described as well. A new approach was tried to obtain this ligand based on the tetramerization of propargyl alcohol, but the results were inconclusive.

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CHAPTER I:

INTRODUCTION

General

In 1968, Streitwieser and Müller-Westerhoff prepared an unprecedented dark green, pyrophoric complex of uranium(IV) and cyclooctatetraene.[1] The molecule was subsequently characterized as bis[8]annuleneuranium(IV), and its structure proved to be the sandwich structure shown in Figure 1.1.[2,3] The molecule was dubbed uranocene, on the basis of its similarity to bis(cyclopentadienyl)iron(II), ferrocene. In the succeeding twenty years, much effort has been spent on examining the properties and characteristics of this molecule and its related derivatives, and they have proven to have many interesting properties.[4] As a result of this work, much has been learned about the

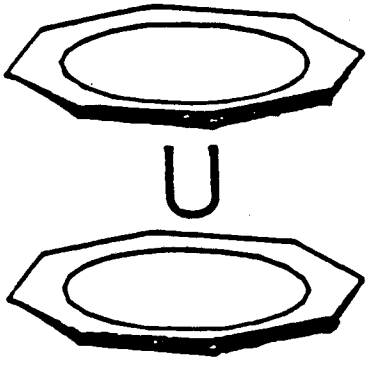


Figure 1.1 Uranocene

chemistry of the increasingly important class of f-block metals.

The historical connection of uranocene with ferrocene is actually closer than implied above. In fact, the original impetus towards the synthesis of uranocene developed as a result of an examination of the molecular orbital description of the bonding in ferrocene.[5] In the series of transition metal sandwich complexes, much of the stability associated with them is a result of the interaction of the highest occupied MO's of the two cyclopentadienyl ligands (e_{1g}) with 3d orbitals on the iron(II). (See Figure 1.2) The MO picture shows that these sets of orbitals have appropriate symmetry to overlap, and this covalent sharing of electrons results in remarkably robust molecules.

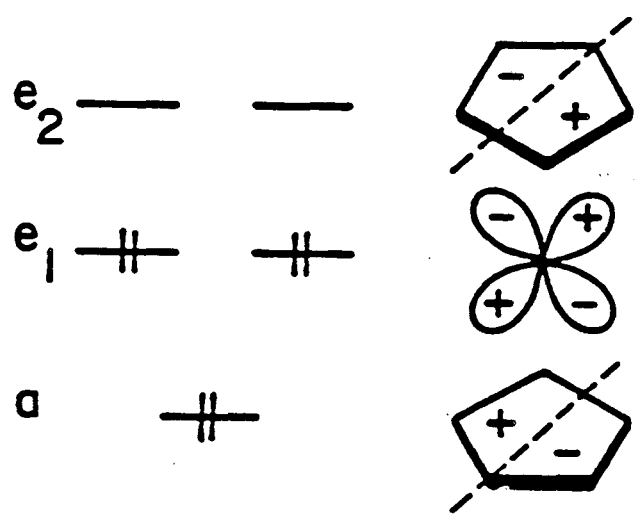


Figure 1.2: Ring - metal interaction in Ferrocene.

By analogy to the ferrocene case, Streitwieser predicted that there should be a symmetry allowed interaction between the highest occupied MO's of two [8]annulene dianions with the appropriate f-orbitals of an actinide or lanthanide. The analogous MO diagram for this situation is shown in Figure 1.3, showing the correct nodal properties to allow for interaction between the e_{2u} orbitals of the ligand rings and the e_{2u} f-orbitals ($l = \pm 2$). If there is in fact overlap between the orbitals, then a molecule such as bis[8]annuleneuranium(IV) should be reasonably stable. With this in mind, uranocene was successfully prepared, leading to the investigation of this new class of molecule.

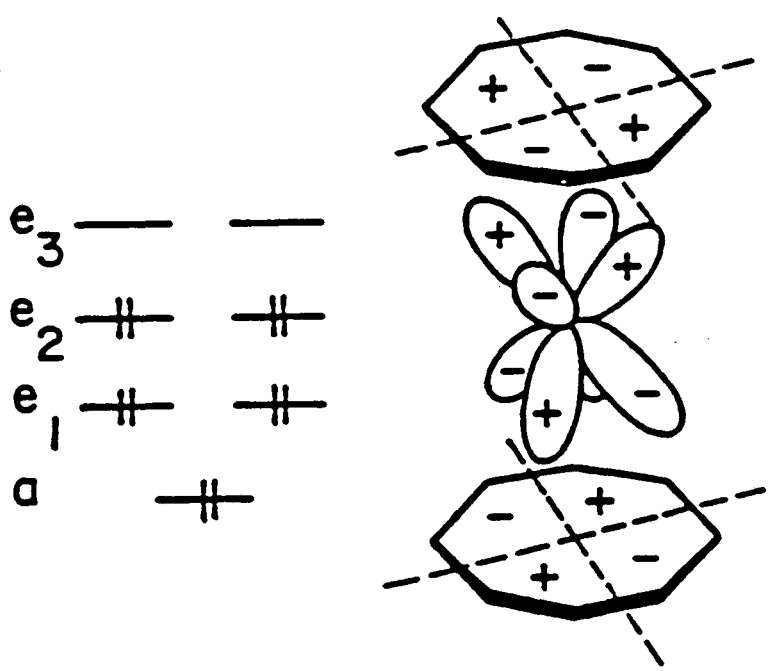


Figure 1.3: Ring - Metal ineraction in Uranocene.

Since the discovery of the parent compound, a large number of derivatives of uranocene have been prepared, varying the metal centers,[6-8] adding substituents to the cyclooctatetraene rings,[9] and to a lesser extent, exchanging one COT for some other ligand.[10] Physical studies on many of these compounds have been performed to try to obtain a better understanding of the nature of bonding in these metallocenes as well as their chemical and physical properties.[11] Some work has been done on examining their reactivity, which has been found to be quite limited. For instance, there has been some work published on the reactions of uranocene with nitro compounds[12] and with some organolithium reagents,[13, 9c] but few other types of reactions have been found. Reviews of both of these topics have been recently published, so in this work, only a brief summary of some germane properties will be discussed.[14]

The most obvious property shared by almost all of these compounds is their instability in air. As opposed to their ferrocene analog, these compounds are generally pyrophoric and must be carefully handled under inert atmosphere. In addition, all of the actinides are radioactive, which causes further difficulties in working with them. They are unstable towards water and alcohols, but the rate with which they react can vary a great deal; as a matter of fact, uranocene hydrolyzes so slowly that water was actually used in one step of the original workup. Their solubility is generally poor; ethereal solvents are usually the best, although many do show some limited solubility in non-polar solvents as well. This problem can often be avoided by making use of substituted cyclooctatetraenes, which can have dramatic effects on a compound's solubility.

The synthesis of uranocene is shown below ([1.1]). Cyclooctatetraene is allowed to react with two equivalents of metallic potassium in THF to yield the dianion.

This solution is then added slowly to a solution of UCl_4 in THF to produce the desired bis[8]annuleneuranium(IV). This method is only slightly modified from the original preparation of uranocene, and it is applicable in the synthesis of most of the actinide analogs prepared so far. An alternative technique which is useful in some cases is shown below in the case of plutonium ([1.2]).[7]

$$MCl_4 + 2\,K_2(C_8H_8)_2 \xrightarrow[\text{THF}]{} M(C_8H_8)_2 + 4\,KCl \qquad [1.1]$$

$$M = Th, Pa, U, Np$$

$$(C_5H_6N)_2PuCl_6 + 2\,K_2(C_8H_8) \xrightarrow[\text{THF}]{} Pu(C_8H_8)_2 + 4\,KCl + 2\,C_5H_6N^+\,Cl^- \qquad [1.2]$$

This same general procedure can also be used to prepare substituted metallocenes.[9] In this case, the substituted cyclooctatetraene is reacted with the potassium to form the dianion prior to reaction with the metal. The properties of many of the substituted sandwich compounds are fairly similar to their unsubstituted counterparts, as mentioned above, but their greatly increased solubility can make the work-up slightly different. This property, however, is the reason why, for many purposes, these substituted metallocenes are the most important members of the class. The major problem with preparing these substituted compounds often lies with obtaining the ligand itself; the synthetic chemistry of cyclooctatetraene is generally poor, giving product mixtures which are difficult to separate and which generally result in low yields.[15]

The vast majority of the work done with the actinide members of this class have been with metals in the +4 oxidation state. There are some reports of the preparations

of molecules of the type $K[An(C_8H_8)_2]$, prepared in the analogous fashion to the preparation of the tetravalent sandwich compounds, but with the actinide trihalide.[16, 17] Trace amounts of oxidizing agents generally oxidize the metal center back to their tetravalent state.

Organolanthanide Chemistry

Within the lanthanide series, by contrast, the most stable oxidation is the trivalent state.[18] This difference in oxidation state stability is responsible for many differences between the chemistry of the bis[8]annulene derivatives of the two series of f-elements.

The lanthanide series comprises the 14 elements following lanthanum in the periodic table. Because of the similarity in their properties, lanthanum, yttrium, and scandium are often included when discussing these elements, even though their 4f shells are not being filled. In general, the 4f-shells of these elements are thought to have insufficient energy and spatial extension to overcome the shielding effects of the filled $5s^2$ and $5p^6$ shells.[19] Many of the chemical and physical properties of the lanthanides reflect this lack of involvement by the f-orbitals; in fact, lanthanide compounds are generally thought to behave as essentially ionic.[20] Thus, their properties can be quite different from both the d-shell transition metals or the 5f-shell actinides.

The most stable oxidation state for all of the lanthanides is the trivalent, despite the fact that one would expect the divalent to be the most stable (from removing the two 5s electrons). The reason for this is not completely clear, but it is usually attributed more to factors such as solvation energies and ionization energies than to added stability due to half-filled or unfilled shells.[21] The divalent lanthanides are known in alkaline earth halide matrices, but only a few have been made in aqueous solutions, predominantly solutions of europium.[22] However, organometallic compounds of not only Eu, but also of samarium and ytterbium are now known with a variety of organic ligands. The tetravalent state is stable only for cerium, although several other lanthanides have now been reported as solid compounds in the +4 state; this topic will be discussed further below.

There is a fairly extensive body of literature now on the organometallics of lanthanides.[19, 23, 24] The work has predominantly been with the trivalent state as one would expect. One additional property of the lanthanides which is clear from this work is that the generally large ionic radii of the lanthanide ions result in complexes with fairly high coordination numbers. They range from 8 to 12, and the major driving force seems to be to sterically block the metal. This points out a principal difference between the organometallic chemistry of the lanthanides, and to some extent of the actinides, and that of the d-shell transition metals; there is no corresponding 18-electron rule for the f-elements as observed in general in d-transition metal complexes.

Most of the organometallic chemistry known for the lanthanides involves their complexes with the cyclopentadienyl ligand. The first lanthanide organometallic compounds, the triscyclopentadienides, were prepared by Wilkinson and co-workers in the mid-1950's,[25] and by Fischer and Fischer in a slightly modified procedure,[26] and

the first crystal structure (of $Sm(C_5H_5)_3$) was reported in 1969 [27](see Eq. [1.3] and [1.4]). Most of the work done with these compounds supported the conclusions that the lanthanide complexes are essentially ionic. For instance, they generally react rapidly with water and alcohols, and produce ferrocene when mixed with ferrous chloride.[28] Extensive reviews of this literature are available, and will not be attempted here.[19, 23, 24]

$$LnCl_3 + 3NaC_5H_5 \xrightarrow{THF} Ln(C_5H_5)_3 + 3\,NaCl \qquad [1.3]$$

Ln = La, Ce, Pr, Nd, Sm, Gd, Dy, Er, Yb

$$LnCl_3 + 3KC_5H_5 \xrightarrow[\text{or } Et_2O]{\text{benzene}} Ln(C_5H_5)_3 + 3\,KCl \qquad [1.4]$$

Ln = Tb, Ho, Tm, Lu

The number of reports of lanthanide complexes with cyclooctatetraene is much more limited. There have been reports of two divalent lanthanide complexes with a single COT, as illustrated in [1.5].[29] Europium or ytterbium metal is reacted with neutral cyclooctatetraene in liquid ammonia, resulting in the highly pyrophoric powders of the appropriate complex. The ytterbium complex has also been prepared by the reaction of ytterbium metal atoms and cyclooctatetraene vapor.[30] These compounds are insoluble in hydrocarbons and ethers, but will dissolve in coordinating solvents such as dimethylformamide and pyridine. Magnetic and EPR data are consistent with the lanthanides being +2 ions, but a crystal structure has not been reported.

$$Ln + C_8H_8 \xrightarrow{NH_3} Ln(C_8H_8) \qquad [1.5]$$

$$Ln = Eu, Yb$$

With the trivalent lanthanides, several types of mono-COT complexes have been prepared and studied. The first class is prepared by the addition of one equivalent of cyclooctatetraene dianion in THF to a suspension of one equivalent of the appropriate $LnCl_3$ in THF.[31, 32] The crystal structure of the cerium compound will be discussed in Chapter 3, but it showed the complex to be a dimer with the stoichiometry shown in [1.6].[33] The basic structure consists of two Ce-COT moieties bridged by two chlorides. The THF molecules serve to fill the coordination spheres of the metal centers. These complexes cannot be sublimed and show significant decomposition upon heating over 100 °C. The coordinated THF molecules are lost as the compounds are heated to about 80 °C under vacuum.

$$LnCl_3 + K_2C_8H_8 \xrightarrow{THF} 1/2[Ln(C_8H_8)Cl \cdot 2THF]_2 + 2KCl \qquad [1.6]$$

$$Ln = Ce, Pr, Nd, Sm$$

Wayda has recently shown that it is possible to isolate aryl monocyclooctatetraenyl lanthanide complexes by derivatizing these molecules with bulky, chelating ligands. For instance, she has recently prepared and solved the crystal structure of the mono-COT complex of an amine as shown in Eq. [1.7].[34, 35] This sort of derivatization should prove to be an important property of these compounds, as it will enable studies to be made of a series of closely related lanthanide organometallic compounds.

$$(C_8H_8)LuCl(THF) + Li[o\text{-}C_6H_4CH_2N(CH_3)_2] \longrightarrow$$

$$(C_8H_8)Lu[o\text{-}C_6H_4CH_2N(CH_3)_2](THF) + LiCl \quad [1.7]$$

Another related molecule has been synthesized by Greco, Bertolini and Cesca.[36] They treated cerium(IV) isopropoxide with triethylaluminum and cyclooctatetraene in toluene as shown in Eq. [1.8], obtaining the bimetallic product shown. Their physical data were consistent with a structure consisting of a COT-Ce moiety complexed to a diethylaluminum moiety by two bridging alkoxy groups.

$$Ce(O\text{-}i\text{-}Pr)_4 + Al(C_2H_5)_3 \xrightarrow[\text{toluene}]{C_8H_8} (C_8H_8)Ce(O\text{-}i\text{-}Pr)_2 \cdot Al(C_2H_5)_2 \quad [1.8]$$

The other class of mono-COT compounds known is the mixed cyclopentadienyl-cyclooctatetraene series.[10] They are prepared by either of two routes ([1.9] or [1.10]) with the coordinating THF easily removable under vacuum.

$$Ln(C_5H_5)Cl_2 \cdot 3THF + K_2C_8H_8 \xrightarrow{THF}$$

$$Ln(C_8H_8)(C_5H_5) \cdot THF + 2KCl \quad [1.9]$$

$$[Ln(C_8H_8)Cl \cdot 2THF]_2 + 2NaC_5H_5 \xrightarrow{THF}$$

$$2\ Ln(C_8H_8)(C_5H_5) \cdot THF + 2NaCl \quad [1.10]$$

The majority of the COT complexes with lanthanides have been of the bis[8]annulene class, and of these, the most common are with the trivalent metals. There are actually two types of compounds in this class, one in which there is a coordinating alkali metal cation, with the stoichiometry $K[Ln(C_8H_8)_2]$. This complex is prepared as shown in [1.11], by the reaction of a THF solution of two equivalents of [8]annulene dianion to a suspension of the appropriate lanthanide trichloride.[32,37] The crystal structure of this class of compound is discussed in Chapter 3, but it consists of the bis[8]annulenelanthanide(III) anion, in a structure closely resembling that of uranocene, coordinated by the potassium counterion.[38] These compounds are extremely pyrophoric and must be handled under inert atmosphere with great care to avoid decomposition. They do not sublime at 1×10^{-4} Torr, and do show significant decomposition when heated above 160 °C under vacuum. They are insoluble in solvents such as $CHCl_3$ and hexane, slightly soluble in benzene and toluene, and moderately soluble in THF.

$$LnCl_3 + 2K_2C_8H_8 \xrightarrow{THF} K[Ln(C_8H_8)_2] + 3KCl \qquad [1.11]$$

Ln = Y, La, Ce, Pr, Nd, Sm, Gd, Tb, Yb, Lu

Several substituted analogs to these compounds have been prepared, including the *t*-butyl[39] and the 1,3,5,7-tetramethylcyclooctatetraene sandwiches.[40] A few examples of the metallocenes with lanthanide(II) have also been reported; this topic will be discussed further in Chapter III.

The other class of bis[8]annulene derivatives of lanthanide(III) is of the type that contains the bis[8]annulene sandwich arrangement, but instead of a potassium ion,

it is coordinated by an [8]annulenelanthanide(III) cation. This class of compound is usually prepared by the reaction of the metal atom vapor with cyclooctatetraene vapor at -198°C (see Eq. [1.12]).[30] These complexes are generally poorly soluble, but they will dissolve in THF to give a bis-THF adduct, and the crystal structure of the neodymium member of this class has been solved (Figure 1.4).[42, 30] The structure shows the anion portion in a distorted sandwich arrangement, with the rings not quite parallel planar (they intersect at an angle of a little more than 7°). The bis-THF adduct of the [8]annuleneneodymium(III) cation then coordinates in a trihapto fashion to the $Nd(C_8H_8)_2$ anion.

$$2Ln^{o} + 3C_8H_8 \xrightarrow{-198^{o}} Ln_2(C_8H_8)_3 \qquad [1.12]$$

Tetravalent Lanthanide Background

As can be seen from the above discussion, much work has been done with lanthanides in the trivalent state. There is a smaller body of work done with the less common divalent oxidation state for those elements which have this as a stable state. The only other oxidation state accessible to any of the lanthanides is the tetravalent, but there is little work with this ionic state. The reason for this is clearly that the tetravalent is generally not the preferred state, so it is difficult to isolate compounds involving tetravalent lanthanides.

Nugent and co-workers have done a fair amount of work in examining many of the physical and spectroscopic properties of lanthanides and actinides.[41] As part of this work, they examined the standard oxidation potentials for these metals, both from experimentally based sources and from calculations. Table 1.1 presents some of their results with reference to the $E^{o}M(IV - III)$. Their calculated values are derived from a technique they have developed to correlate theoretical and atomic spectroscopic results, and are generally thought to be quite accurate.

Table 1.1 E^o Ln(IV/III) Reduction Potentials [41]

Ln	Meas'd	Calc'd	Ln	Meas'd	Calc'd
Ce	1.74	1.8	Tb	3.1 ± 0.2	3.3
Pr	3.2 ± 0.2	3.4	Dy	5.2 ± 0.4	5.0
Nd	5.0 ± 0.4	4.6	Ho		6.2
Pm		4.9	Er		6.1
Sm		5.2	Tm		6.1
Eu		6.4	Yb		7.1
Gd		7.9	Lu		8.5

As can be seen from this Table, the most stable of the Ln(IV) ions is cerium, and in fact, this is the only tetravalent lanthanide which shows enough stability to be isolated and worked with. The next two most stable ions are those of praseodymium and terbium , whose potential is measured as about 3 V. These have been shown to be stable as solid compounds of oxides and fluorides, but they are generally not stable in other media.[18] Finally, there have also been some reports of the existence of dysprosium(IV) and neodymium(IV), but these are only isolable as alkali metal fluorides, which is consistent with the values reported for their oxidation by Nugent et al.[42] The potentials calculated for all of the other lanthanides are higher than the values calculated for the observed Ln^{+4} species, so it is doubtful that these ions can exist. Thus, the chemistry of lanthanides in the tetravalent oxidation state is limited to five elements, and thus far the most is known about cerium.

Cerium (IV) salts have been used in organic synthesis for many years. It behaves as a strong oxidizing agent towards functional groups such as ketones and alcohols, as well as in many inorganic systems. The exact potential of the couple, however, is highly dependent on the nature of the solution. In aqueous, acidic solutions, for instance, the potential will vary depending on type of acid present, as well as concentrations. Table 1.2 shows the potential in various acid solutions, and the magnitude of the changes is apparent.[43]

Table 1.2: Ce(IV)/Ce(III) Reduction Potential in Acidic Aqueous Solutions

Solution	Potential (V)
8M $HClO_4$	1.87
1M $HClO_4$	1.70
1M HNO_3	1.61
1M H_2SO_4	1.44
3M HCl	1.27

The effect of coordination on the cerium ion is even more dramatically apparent in a complex prepared by Raymond and coworkers.[44] In the course of studying the structural properties of actinide catecholates, they discovered that the corresponding Ce(IV) tetracatecholate was stable enough to be prepared and studied crystallography. Rather than oxidizing the normally strongly reducing catechol dianion, a discrete Ce(IV) compound is prepared, suggesting that the catechol ligands are very strongly

stabilizing forces. The potential was measured for this system in a solution 1M in catechol and was found to be a remarkably low -0.4 V, implying that the ligands are complexing the Ce(IV) much better than they are the Ce(III), and thus act as the driving force to make the Ce(IV) the preferred state in this system.

These workers related their cyclic voltammetric data with the relative equilibrium constants for the reaction of the metal in each oxidation state n with the appropriate ligands:

$$M^{n+} + 4cat^{2-} = [M(cat)_4]^{n-8}$$

The K_n for this reaction can be related to the electrochemical data for this system using the following equation

$$E_f - E_o = -59 \log (K_{IV} / K_{III}) \text{ mV}$$

where E_f is the observed potential for the Ce(IV) / Ce(III) catecholate couple, E_o is the Ce(IV) / Ce(III) standard potential (E_o = +1.70 V vs NHE), and K_{IV} and K_{III} are the formation constants of the tetrakis complexes in the tetravalent and trivalent states respectively. In their case the formation constants were determined to differ by a factor of 10^{36}, which emphasizes the tremendous importance of the complexation of these species.

Basic solutions have also been found to stabilize the other reasonably accessible tetravalent lanthanides, Pr and Tb. In a study by Hobart, solutions of Ce, Pr, and Tb were examined using a combination of electrochemistry and absorption spectroscopy.[45] Potentials were applied to solutions of $CeCl_3$ that were 5.5 M in K_2CO_3, and their absorption spectra was recorded. By plotting the potential applied

versus the ratio of the concentration of the tetravalent to the trivalent cerium species as measured spectroscopically, a formal potential for the Ce(IV)/Ce(III) couple in the solution was found to be +0.05 V, a drop of roughly 1.7 V from the potential in the absence of the coordinating carbonate. By assuming a similar amount of stabilization in the Pr and Tb cases, a potential sufficient to oxidize the trivalent lanthanides to their tetravalent states was applied and spectra were recorded which were consistent with what one would expect for the respective tetravalent species. It was found that adjustment of the hydroxide ion concentration to about 1 M produced relatively stable solutions of the tetravalent ions, but further electrochemical studies were thwarted by problems resulting from oxygen evolution at the potentials required to effect the oxidations.

So, cerium (IV) compounds have been found to be stable with strongly complexing ligands, often oxygen based, such as the commercially available tetrahydroxide or the catecholates mentioned above. Another example is the series of tetraalkoxides, prepared as far back as 1956.[46] These were prepared from the complex salt dipyridinium cerium hexachloride, which is also reasonably stable. What is unusual for tetravalent cerium are reports of organometallic complexes of this metal, there being until very recently really only two reports in the literature.

The first report was actually a series of papers by Kalsotra and coworkers.[47] In these papers, this group reported the synthesis of several compounds of Ce (IV), starting with the complex salt dipyridinium cerium hexachloride as shown in Eqs [1.13] to [1.16]. They also reported derivatizing several of these compounds to their tetrahydroborate, carboxylate, alkyl and aryl, and mercaptide analogs. However, the characteristics reported by this group for these compounds were frequently quite

unreasonable in comparison to other species of their respective classes. The bis[8]annulene derivative, for instance, was reported as stable towards water, acetic acid and sodium hydroxide, and soluble in hot concentrated acids, properties which are not common among the bis[8]annulene metallocenes. The reported stability of the strongly oxidizing Ce^{4+} towards strong reducing agents such as BH_4^- or $C_8H_8^{2-}$ was also quite surprising.

$$(pyH)_2CeCl_6 + 5NaC_5H_5 \xrightarrow{THF} Ce(C_5H_5)_3Cl + 2C_5H_6 + 2py \quad [1.13]$$

$$(pyH)_2CeCl_6 + 6NaC_5H_5 \xrightarrow{THF} Ce(C_5H_5)_4 + 2C_5H_6 + 2py \quad [1.14]$$

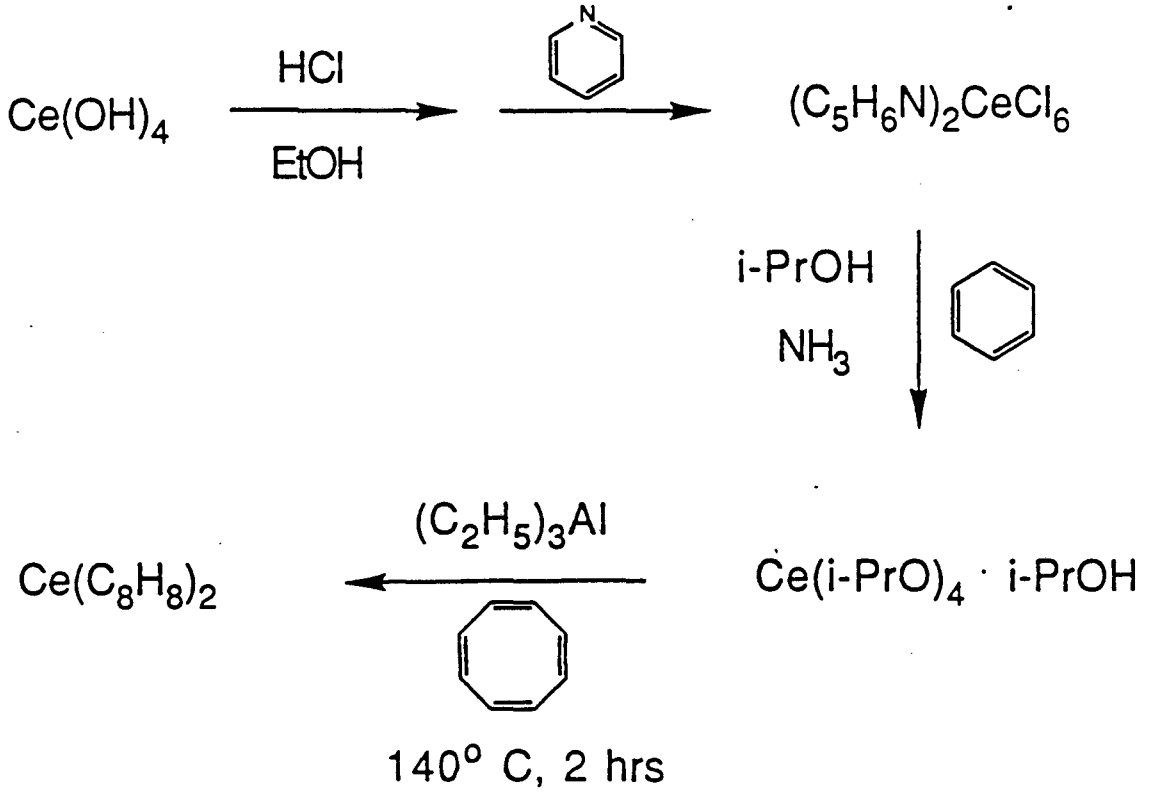
$$(pyH)_2CeCl_6 + 4NaC_9H_7 \xrightarrow{THF} Ce(C_9H_7)_2Cl_2 + 2C_9H_8 + 2py \quad [1.15]$$

$$(pyH)_2CeCl_6 + 6NaC_9H_7 \xrightarrow{THF} Ce(C_9H_7)_4 + 2C_9H_8 + 2py \quad [1.16]$$

Not surprisingly, reports have now appeared in the literature refuting the work of this group with Ce (IV).[48] Efforts to repeat their work on $CeCp_4$, the tetrafluorenide, and $Ce(C_7H_7)_2Cl_2$ were all unsuccessful. Recent work by Kinsley of this group resulted in the inability to repeat the work on the bis[8]annulene species as well, so it appears that these reports of Ce(IV) organometallics are not to be trusted.[43]

In 1976, however, the second report of a cerium (IV) organometallic species appeared.[49] In this case, the Italian group of Greco, Cesca and Bertolini reported the preparation of bis[8]annulenecerium(IV) using the same starting material as did the Indian group. Their complete reaction sequence is shown in Scheme 1.1. The preparation of the tetraisopropoxide of the Ce(IV) is based on the work of Bradley, Chatterjee and Wardlaw, and it is a fairly well characterized species.[50] The final step involves the reaction of the tetraalkoxide with triethylaluminum in the presence of cyclooctatetraene, based on Wilke's work with $(C_8H_8)_3Ti_2$.[51]

Initial Synthesis of Cerocene



(Scheme 1.1 Italian Prep)

The product of this reaction is reported to be black needles which are sparingly soluble in aromatic hydrocarbons, chlorinated aromatic hydrocarbons and ethers. It is reported to be pyrophoric in the presence of oxygen, and slowly decomposed by water. Their characterization consisted of IR , ^1H NMR, mass spectrum, and preliminary x-ray data, all of which are consistent with what one would expect for this formulation. Reaction of the material with one equivalent of potassium in monoglyme resulted in the formation of the monoglyme adduct of $K[Ce(C_8H_8)_2]$.

In this same paper, the Italian group also reported the preparation of several other tetravalent cerium compounds, including the cerium analog of the previously mentioned $(C_8H_8)_3Nd_2$ ([1.17]); again, the characterization is consistent with this class of molecule. The complex $(C_5H_5)_3CeO\text{-}i\text{-}C_3H_7$ was prepared by the reaction of the tetraisopropoxide with bis(cyclopentadienyl)magnesium(II) as shown in [1.18]. The reported yield was extremely low (<5%) after purification by sublimation. The complex was characterized by elemental analysis, mass spectrometry, IR and ^1H NMR, all of which were in agreement with the proposed structure. Attempted preparations of the tetrakiscyclopentadienyl analog by the same technique, however, were unsuccessful, in contrast to the previous report of this compound.

$$2Ce(O\text{-}i\text{-}Pr)_4 \cdot i\text{-}PrOH + 10(Et)_3Al + 3C_8H_8 \xrightarrow{CHT} (C_8H_8)_3Ce_2 + 10(Et)_2Al(O\text{-}i\text{-}Pr) + 2C_2H_6 + 8\,C_2H_5 \quad [1.17]$$

CHT = cycloheptatriene

$$3(C_5H_5)_2Mg + 2Ce(O\text{-}i\text{-}Pr)_4 \xrightarrow[20^\circ C]{benzene} 2(C_5H_5)_3CeO\text{-}i\text{-}Pr + 3Mg(O\text{-}i\text{-}Pr)_2 \quad [1.18]$$

Recently, Marks and coworkers have reexamined the complex $(C_5H_5)_3CeO\text{-}i\text{-}C_3H_7$, including an improved synthesis, electrochemical properties, PES, and calculational results.[52] Their synthesis involved the reaction of the isopropoxide with Me_3SnCp in toluene, and they obtained about 70 % yield (Eq. [1.19]). Their characterizations match well with the proposed compound and with the report by Greco. Further discussion of the other studies performed by this group on this molecule will be postponed until Chapter VI, so that comparisons with similar studies on cerocene can be more easily made.

$$Ce(O\text{-}i\text{-}Pr)_4 + 3R_3SnCp \xrightarrow[toluene]{65^\circ C} Cp_3Ce(O\text{-}i\text{-}Pr) + 3R_3Sn(O\text{-}i\text{-}Pr) \quad [1.19]$$

R = CH_3
n-Bu

Theoretical Modeling of Bis([8]annulene) Complexes

The bonding in these metallocenes has been examined several times by calculational methods. The fact that these compounds can be isolated is evidence that there is a significant stabilizing force present, but it does not in and of itself prove the existence of any sort of metal-ring bond. High level calculational methods, however, can provide some evidence as to the nature of the bonding, but it is necessary to establish the quality of the theoretical work before its results can be considered significant. One method that has proven useful in the case of this class of molecule is by comparing the photoelectron spectra with the calculational results; close agreement between the two should provide additional confidence in the results derived from the calculations.

Hayes and Edelstein performed early calculations on bis[8]annulene complexes of tetravalent actinides, considering only the ligand e_{2u} π orbitals and the metal 5f orbitals; it was assumed that the metal d-orbitals were of too high energy to interact significantly with the ligands.[53] These results were used to interpret the first set of PES spectra of uranocene and thorocene, with one of the results being an energy level ordering of $e_{2g} > e_{2u}$ as a result of the overlap between the ligand π orbitals and the metal 5f orbitals.[54,55]

This result, however, was called into question by the results of Clark and Greene upon further examination of these PES spectra.[56] These workers examined both the He-I and He-II spectra, and on the basis of changes in intensity upon changing the light source, they assigned the previously mentioned energy level ordering as $e_{2u} > e_{2g}$. If this assignment were true, it would imply that the d-orbital involvement is significant, and must be accounted for in any calculation.

The next theoretical examination of these two compounds was performed by Rösch and Streitwieser, using the SCF-Xα scattered wave methodology.[57] The agreement with Clark and Greene's PES work was much improved relative to the preceding calculations. This work confirmed the PES assignment of the $e_{2u} > e_{2g}$ energy ordering, and suggested that the d-orbital involvement is significant in these compounds, contributing at least as much as do the f-orbitals.

Pyykkö and Lohr subsequently performed relativistically parameterized extended Hückel MO (REX) calculations on bis[8]annuleneuranium(IV), and it agreed reasonably well with the Xα results.[58] Many of the differences between the two calculations could be related to different methods of parameterization, which tend to overemphasize different effects.

The first Xα calculations ignored the effects of relativity on these compounds, so it was thought that the inclusion of some relativistic effects should improve the comparisons with the experimental results. In 1983, Rösch and Streitwieser reported a quasirelativistic Xα study of not only uranocene and thorocene, but also of cerocene.[59,60] These are the highest quality calculations published on these compounds to date, and the insights they provide into the nature of these metal-ring bonds are important to the present work and warrant discussion. In addition, Fragalà has studied the PES spectra of cerocene,[61] so it is now possible to evaluate the quality of these calculations for all the compounds.

The energy level diagrams for the lowest unoccupied and the highest occupied molecular orbitals is shown in Figure 1.5. The gross similarity between the three compounds is apparent; the lower level σ-type orbitals in all three compounds are of similar energies, as is expected for these ligand based orbitals, whereas the π-type

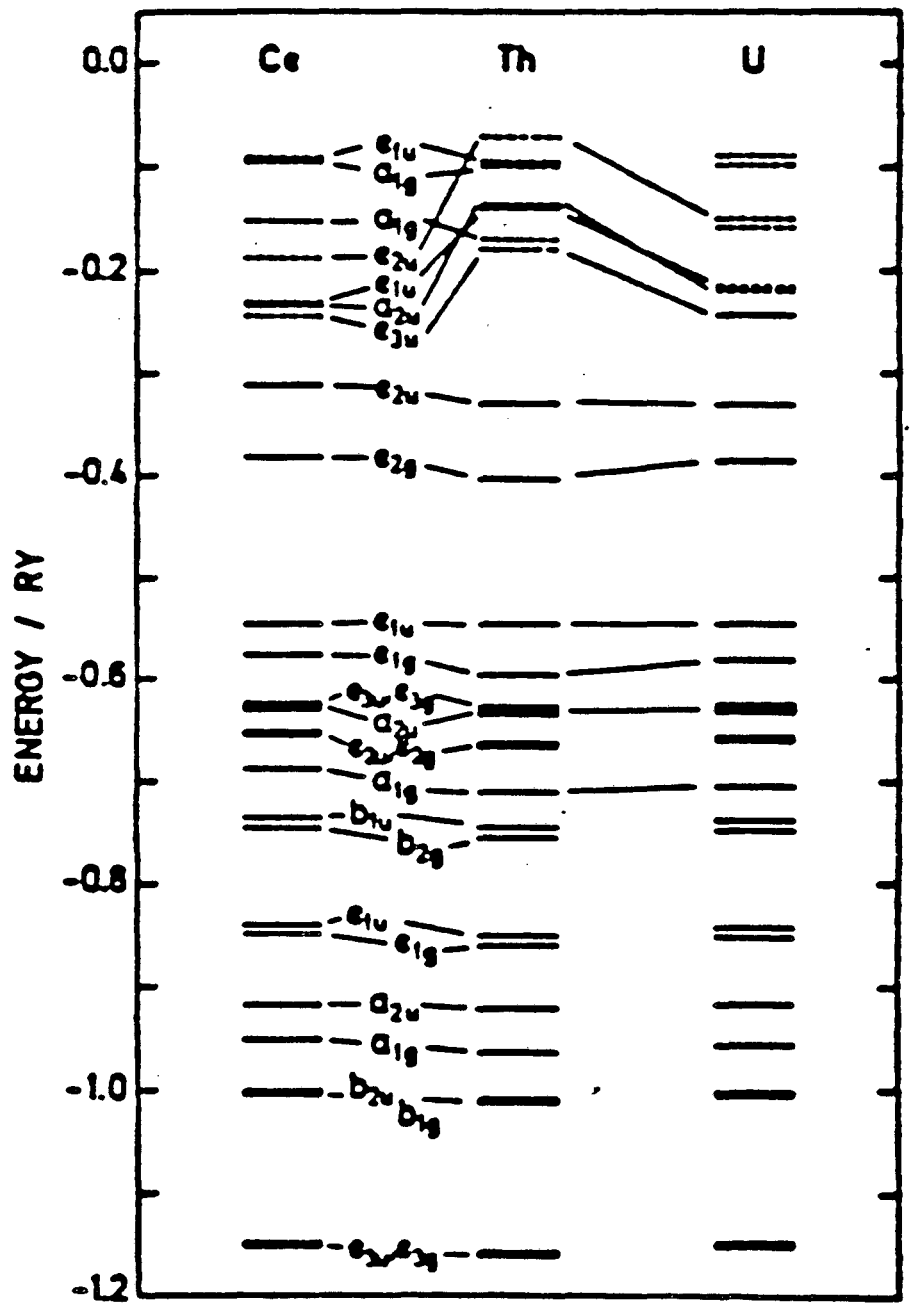


Figure 1.5: Orbital Energy Diagrams for Bis([8]annulene)M(IV).

orbitals show slight changes in energies resulting from interactions between the metal and ligand orbitals. Examination of the relative positions of these orbitals should provide some insight into the nature of the bonding in these compounds.

One major difference between these molecules in terms of their electronic structures is the fact the the HOMO for cerocene and thorocene is the $e_{2u}(\pi)$ orbital, whereas in uranocene it is the e_{3u} (f). If the strong absorption in the visible spectra of these compounds is attributed to the e_{2g} (π) - e_{3u} (f) charge transfer excitation, the agreement between the calculated value is quite close to the measured value. In the case of thorocene, the measured value is 2.75 eV versus a calculated value of 3.03 eV, while for uranocene , the values are 2.01 eV (measured) and 1.97 eV (experimental), so this supports the unusually high calculated value for the thorium e_{3u} (f) level. The visible spectrum of cerocene has also now been reported, and the agreement with its calculated value is also quite satisfactory; this topic will be discussed in more detail in the next chapter.

Table 1.3 shows the comparison between the calculated ionization energies of thorocene and uranocene, and those determined from Clark and Green's PES work.[60a] The agreement is generally good. The calculated energy level ordering of $e_{2u} > e_{2g}$ is now in accord with the ordering assigned in the experimental work, and the relative energy levels are quite consistent.

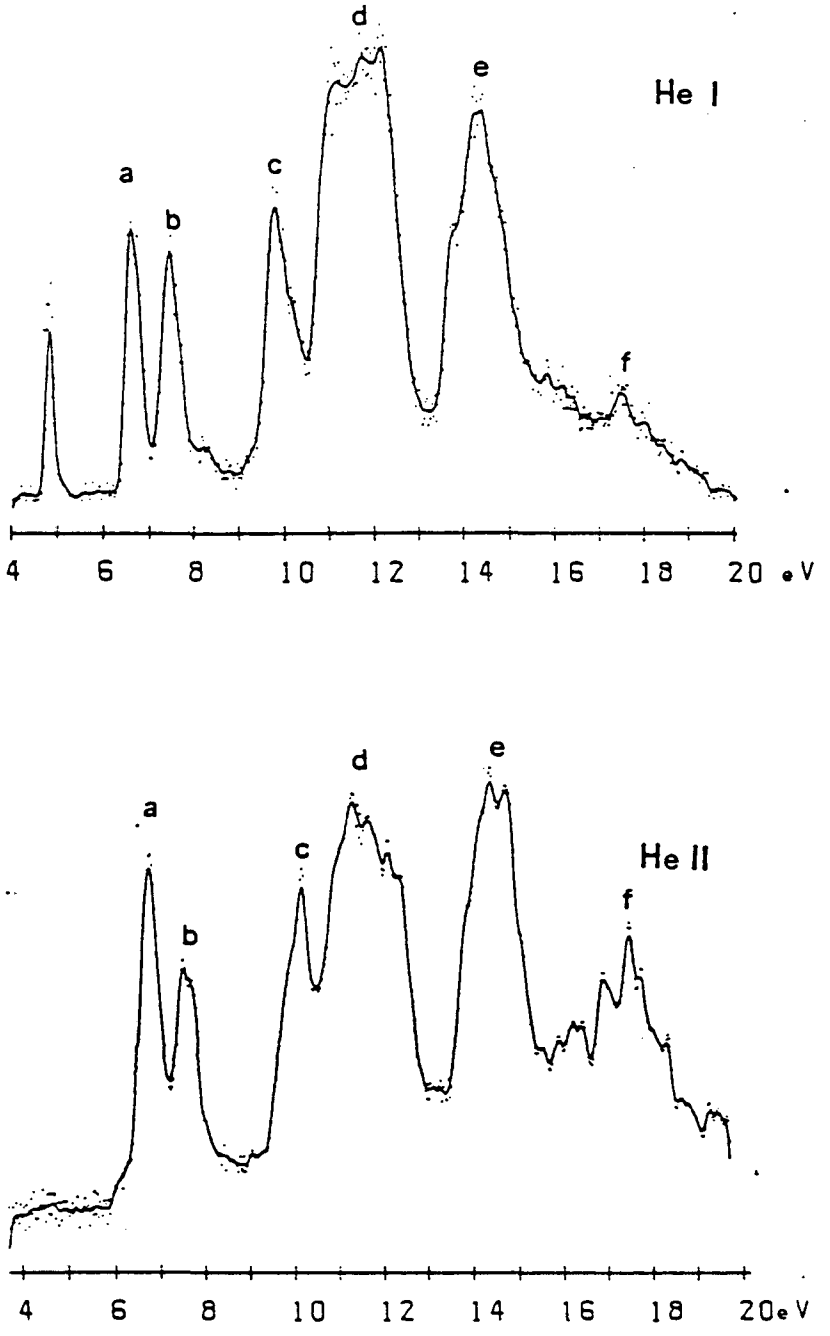
Table 1.3

Comparison of Xα Calculations with PES

(Energies in eV)

	Thorocene		Uranocene	
	Calcd	Exptl	Calcd	Exptl
$e_{3u}(f)$			5.75	6.20
$e_{2u}(\pi)$	6.53	6.79	6.57	6.90
$e_{2g}(\pi)$	7.51	7.91	7.29	7.85
$e_{1u}(\pi)$	9.44	9.90	9.43	9.95
		10.14		10.28
$e_{1g}(\pi)$	10.11	10.65	9.94	10.56

Since the PES spectrum of bis[8]annulenecerium(IV) is now available, comparisons between it and the calculated results will permit a better evaluation of the success of these calculations for this lanthanide derivative. The He-I and He-II spectra of cerocene as measured by Fragalà are shown in Figure 1.6. The band assignments are Fragalà's. The general appearance of the spectra is quite similar to that of thorocene. There are three fairly well resolved peaks which show some fine structure between 6 - 10 eV, followed by a series of overlapping peaks above about 11 eV. These high energy peaks are common to all of the complexes of this type which have been studied so far, and are thought to belong to the predominantly ligand-based inner π and σ MO's.



(Figure 1.6: PES of cerocene)

By analogy with the PES spectra of the other [8]annulene derivatives studied and by comparison to the calculated ionization energies, the bands can be assigned as shown in Table 1.4.[61] The values in parentheses are shoulders in the PES spectra. The lowest energy bands belong to the e_{2u} and e_{2g} MO's, with band c, which has a prominent shoulder, assigned to the ionizations from the e_{1g} and e_{1u} orbitals. It is clear that although the absolute values calculated for these ionizations are slightly different from the measured values, the differences calculated are in good agreement with the observed differences. In sum, then, these calculations seem to be doing a good job of representing the bonding in cerocene.

Table 1.4

Ionization Energies of Cerocene

	Experimental		Calculated	
Band label	Ionization Energy (IE), eV	Δ IE, eV	IE, eV	ΔIE, eV
a	6.75	0	6.31 (e_{2u})	0
a'	(6.92)			
b	7.68	0.93	7.20 (e_{2g})	0.89
b'	(7.81)			
c	9.98	3.23	9.42 (e_{1u})	3.11
c'	(10.32)	3.57	9.84 (e_{1g})	3.53

With the reliability of these calculations established, the nature of bonding predicted by them can now be discussed. What will be important for determining the amount of metal-orbital interaction will be the relative shifting of the MO energy levels resulting from this covalency. The problem is in deciding exactly which shifts should be examined. The orbitals which have the proper symmetry to interact are the $e_{2u}(f)$ orbitals based on the metal, and the $e_{2u}(\pi)$ orbitals based on the cerium. There can be involvement from the d-orbitals on the metal, but that will be discussed later.

One way to look at these results is to examine the splitting of the orbitals on the metal. For example, the e_{2u} and e_{3u} f-orbitals on the metals themselves, in the absence of any interaction with ligands would be degenerate. As interaction with a ligand e_{2u} π-ligand is increased, however, one ends up with a bonding -antibonding combination of e_{2u} orbitals. Using a simple MO scheme for this case, it is evident that the bonding combination should be lowered in energy relative to the unperturbed $e_{3u}(f)$ orbital. Thus, an examination of the size of this gap should give an indication of the relative importance of an interaction of this sort. If there is much interaction, the gap should be large; a smaller gap will be evident when there is little interaction.

The calculated results suggest that the amount of interaction increases in the order Ce < U < Th. The energy difference (in Ry) between the $e_{2u}(\pi)$ and the $e_{3u}(f)$, for instance, is 0.069 for Ce, 0.088 for U, and 0.149 for Th. This result, then, would indicate that there is the most overlap in the thorocene case and the least in cerocene.

However, if one examines another set of orbitals and their splitting, a different order is predicted. Consider the $e_{2u}(\pi)$ - $e_{2g}(\pi)$ splitting, for example. The e_{2g} orbitals on the ligands do have proper symmetry to interact with metal d-orbitals, but this covalency has been found to be approximately constant across the series. Thus, one

can look at the difference in these two levels as if it were arising solely from the interaction of the $e_{2u}(\pi)$ with the $e_{2u}(f)$ metal orbitals. In this case, a smaller splitting is indicative of increased covalency. The results for these energy differences are 0.069 for Ce, 0.057 for U, and 0.074 for Th. From this criterion, one would predict the order of increasing covalency to be Th < Ce < U.

As well as looking at the splitting of MO's, examinations of electron populations are also of use in an analysis like this. One can examine the sphere populations for the orbitals which have the proper symmetry to overlap, as shown in Table 1.5 in the case of the e_{2u} and e_{2g}. The e_{2u} orbital has suitable symmetry to overlap with the f-orbitals, whereas the e_{2g} can overlap with the metal d-orbitals. The important values in this Table are the fractions of electrons in the metal sphere; a higher fraction indicates there is more donation from the ligand orbitals into those of the metals. (The e2u orbital is filled for the dianion ligands, so electron fractions in the metal sphere are resulting from donation from the ligands.) From this table, one can see that the order of increasing sphere population, and thus increasing covalency is Th < Ce ≈ U, and further, since as noted above the contribution due to d-orbitals is constant for the series, this difference arises from different amounts of f-orbital interaction.

Table 1.5: Sphere Populations in $(COT)_2M$[a]

	Ce		Th		U	
	M[b]	L[c]	M	L	M	L
e_{2u}	0.321	0.437	0.203	0.512	0.328	0.430
e_{2g}	0.207	0.408	0.211	0.403	0.197	0.411

a) See Ref. 65.

b) electron in metal sphere

c) electron in ligand sphere

There are other features of these calculations which could be considered as well as those discussed above, but unfortunately, the results are not completely consistent with each other. It does appear, however, that when all these methods are examined, that although the exact ordering for the relative strength of the metal-ring interaction is somewhat uncertain, there is significant involvement for all the metals. This is particularly surprising in the case of the cerium, since conventional wisdom would have held that its f-orbitals especially should be much less significantly involved in bonding than its actinide counterparts, but this does not appear to be the case.

Recently, Chang and Pitzer have brought to our attention the results of new calculations on uranocene that disagree with the Xα results.[62] Using relativistically derived core potentials and spin-orbit operators, these workers have computed the wavefunctions and energy levels for uranocene at an *ab initio* level. One of their concerns was to assign the visible spectrum of uranocene with more accuracy, since the Xα formalism can give little detail about this property.

Their calculations suggest that the transitions seen in the visible spectrum of uranocene are f - d in nature, rather than π - d as previously assumed. Their calculated values are compared with the experimentally determined values in Table 1.6. For this study, the upper three transitions were considered (in the previous discussion, only the highest most intense transition was used). As can be seen, the calculated values are consistently about 0.9 eV higher than the measured. The polarizations of these transitions have been measured, and the calculational results predict the polarizations correctly.[63] The observed energy shifts associated with substituents on the rings,[64] which was part of the original basis for assigning the transition to π - d, is attributed to a moderate amount of mixing of π - d character.

Table 1.6:

Ab Initio Results on Uranocene

(energy in eV)

	Measured	Calculated	Δ
I	2.017	2.905	0.888
II	1.934	2.837	0.903
III	1.880	2.728	0.848

If these calculations are accurate, several questions arise. If the spectrum observed in uranocene is attributed to the f - d transition, the spectra of thorocene and cerocene would remain unexplained, since this transition is not available to them. As this is one of the criteria used to judge the quality of the previous calculations, it brings

into question the applicability of the Xα methodology to molecules of this sort; their correlation with the PES results, however, is still impressive.

In general, *ab initio* calculations are the highest quality available, but there is some discrepancy between the calculated and experimental values for the visible spectrum; the Xα calculations seem to be doing a better job of representing some of the properties of these molecules. It is clear that additional work must be done to determine the source of this discrepancy; as mentioned above, the Xα formalism has been used to predict properties of many systems, and if Pitzer's results are accurate, then some of these conclusions may have to be questioned.

Thus, it became increasingly important to examine this unusual molecule more closely, in order to determine whether the predicted stability is supported by its chemical properties.

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CHAPTER II:

SYNTHESIS AND CHARACTERIZATION OF CEROCENE

Introduction

As discussed in the last chapter, the impetus behind the synthesis of uranocene was to test whether there was any stabilization from metal-orbital overlap as suggested in the theoretical prediction.[1] The molecular orbital pictures do suggest that the orbitals have the appropriate symmetry to interact; the extent to which they do overlap, however, is more difficult to predict or to measure, and this has led to a great deal of controversy over the nature of the bonding in these compounds. The molecular orbital picture of this type of molecule would suggest the possibility of a covalent bond, since there is sharing of electrons between orbitals on the metal, and orbitals on the ligands. However, whether this interaction is significantly large enough to affect physical properties of the compound is the critical question in determining the covalent vs. the ionic character of these compounds.

One possible means of providing at least a qualitative measure of uranocene's covalency which had been considered was to compare it with analogous "ionic" systems. An obvious choice for this comparison is with the corresponding lanthanide systems. It has been pretty well accepted that, in general, the lanthanide orbitals are

less available for bonding interactions than are actinide orbitals and thus lanthanide compounds can be considered to be essentially ionic.[2] It was thought, then, that if one compared the properties of bis[8]annulene derivatives of the lanthanides with the properties of uranocene, observed differences could be attributed to differing amounts of covalency.

Some general properties of the lanthanides have been discussed in Chapter I. One feature of particular importance to the present discussion is that without exception, their most stable oxidation state is the +3 state. The trihalides of most of the lanthanides are commercially available and reasonably stable, whereas the availability of compounds with lanthanides in other oxidation states is quite limited.[2]

Hodgson and Streitwieser therefore prepared several members of the lanthanide series as the potassium salts of the bis[8]annulene analogs of uranocene.[3,4] The reaction used was analogous to that used to prepare bis([8]annulene)uranium(IV) and many of the other actinide sandwiches, the reaction of the metal trichloride with the dipotassium salt of cyclooctatetraene, as shown in Eq. [2.1]. Extraction with THF or, in some cases, recrystallization from cold THF, allowed the isolation of the pure sandwich compounds as powders.

$$LnCl_3 + 2K_2C_8H_8 \xrightarrow{THF} K[Ln(C_8H_8)_2] + 3KCl \qquad [2.1]$$

Ln = Y, La, Ce, Pr, Nd, Sm, Gd, Tb, Yb, Lu

The properties of these compounds have been closely examined by Hodgson and others.[3,4] They are all highly air-sensitive, inflaming violently on contact with air; moistening with solvent prior to exposure to air prevents the flaming, but

decomposition is still essentially instantaneous. The [8]annulene derivatives are very poorly soluble, with ethereal solvents being essentially the only solvents in which they can be used to any practical extent. This is in contrast to bis([8]annulene)uranium(IV), which is fairly soluble (~10^{-3} moles/liter) in a number of polar and non-polar solvents. They are non-volatile, but highly thermally stable; both uranocene and thorocene are sublimable at < 200^0C under vacuum, with significant decomposition.

Crystals of the diglyme adduct of potassium bis([8]annulene)cerate (III) were grown and the crystal structure was solved and its structure proved to be similar to that of bis([8]annulene)uranium(IV) (see Chapter III for structure).[5] The rings were reported to be coplanar with the cerium nearly centered between the rings. The potassium is coordinated by the diglyme, and is centered over one of the rings; the overall symmetry is C_s.

A number of studies were performed on these compounds to examine their stability relative to bis([8]annulene)uranium(IV). The physical properties mentioned above suggest some increased ionicity for the lanthanide case. For instance, the air-sensitivity of these compounds resembles that of the dianion itself, rather than the relatively more stable actinide sandwiches compounds.

Another indication of the stability of these compounds is their relationship to the dimer analog discussed in Chapter I, $K[Ln(C_8H_8)_2]$. If the bis([8]annulene) sandwich is treated with an excess of $LnCl_3$, the dimer is formed (Eq. [2.4]). This dimer, however, when treated with additional $K_2C_8H_8$, will itself revert to the bis([8]annulene) compound (Eq. [2.3]); there appears to be little preference for one of these compounds over the other.[3] In fact, it is thought that these equilibria are instrumental in the formation of these compounds, in combination with Eq [2.2],

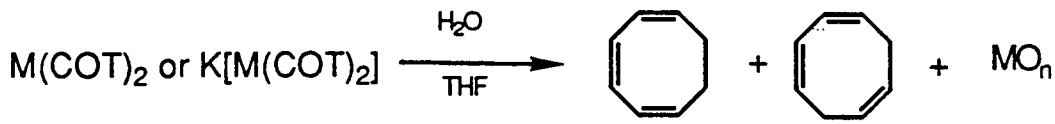
starting with the formation of the dimer by reaction of one equivalent of the dianion with one equivalent of the lanthanide trichloride, followed by its subsequent reaction with the second equivalent of dianion. This fast equilibrium between the two species would suggest that there is not much additional stability imparted by the second ring.

$$2K_2C_8H_8 + 2LnCl_3 \longrightarrow [(C_8H_8)LnCl \cdot 2THF]_2 + 4KCl \quad [2.2]$$

$$[(C_8H_8)LnCl \cdot 2THF]_2 + 2K_2C_8H_8 \longrightarrow 2K[Ln(C_8H_8)_2] + 2KCl \quad [2.3]$$

$$K[Ln(C_8H_8)_2] + LnCl_3 \longrightarrow [(C_8H_8)LnCl \cdot 2THF]_2 + KCl \quad [2.4]$$

The hydrolysis reaction of these metallocenes has been studied by Moore and Streitwieser, and the reaction is shown in Eq.[2.5].[6] The organic products of this reaction are a mixture of 1,3,5- and 1,3,6-cyclooctatrienes, with the relative ratios having been a topic of much study by Moore. It was thought that the rate of reaction should give some suggestion as to the stability of these complexes, and thus rates were measured for many members of this series. As mentioned previously, uranocene itself proved to be slowly decomposed by the water, with the half-life for this reaction being on the order of 20 hours. Since this was generally assumed to be the most stable of these complexes, it was postulated that the other analogs should hydrolyze more rapidly.



[2.5]

When the thorium(IV) derivative was allowed to react with a solution of water in THF under the same conditions, its half-life was found to be something under 60 seconds; as expected, the apparently less stable thorium analog hydrolyzes much more quickly. When the corresponding cerium(III) salt was treated in the analogous manner, it too reacted much more rapidly than the uranium(IV) compound; the rate was much more similar to that of the thorium species.

One important experiment performed to help determine the relative stabilities of these compounds is shown in Eq. [2.6]. This is the ligand exchange experiment between bis([8]annulene)cerium(III) and uranium tetrachloride.[3] It was found that the two do react, and they actually react quickly, suggesting that the bis([8]annulene)uranium complex is significantly more stable than the lanthanide complex. The corresponding experiment was performed with bis([8]annulene)thorium(IV) and uranium tetrachloride, and although this exchange was much slower, it did proceed to result in the formation of uranocene.[7]

$$K[Ln(COT)_2] + UCl_4 \xrightarrow{\text{rapid}} U(COT)_2 + LnCl_3 + KCl$$

[2.6]

Finally, comparisons between lanthanide sandwich compounds have been made with other bis([8]annulene) compounds which would appear to have even less

likelihood of forming anything but ionic molecules. Specifically, Kinsley has recently reported the syntheses and characterizations of the bis([8]annulene) complexes of ytterbium(II) and calcium(II).[8] These compounds show similar physical properties (^{1}H NMR, IR, and X-ray powder pattern), as well as similar thermal and air stabilities. And, along with the series of lanthanide (III) metallocenes prepared by Streitwieser and Hodgson, the yttrium analog, which lacks the accessible 4f orbitals of the true lanthanides, was prepared and showed similar properties to the other compounds.[3]

However, the problem with these properties and comparisons is that they are being made between a neutral species (uranocene) and a potassium salt of an anion. Many of the properties mentioned above, while indicative of less stability in these compounds, could be a result of this anionic nature. It is clearly desirable, when making comparisons of this sort, to examine molecules as closely related as possible, so the best lanthanide analogy of uranocene would be the corresponding bis[8]annulenecerium(IV) species, cerocene. Cerium, as stated in Chapter I, is the only reasonably stable tetravalent lanthanide, so it seems to be the most likely candidate for this study.

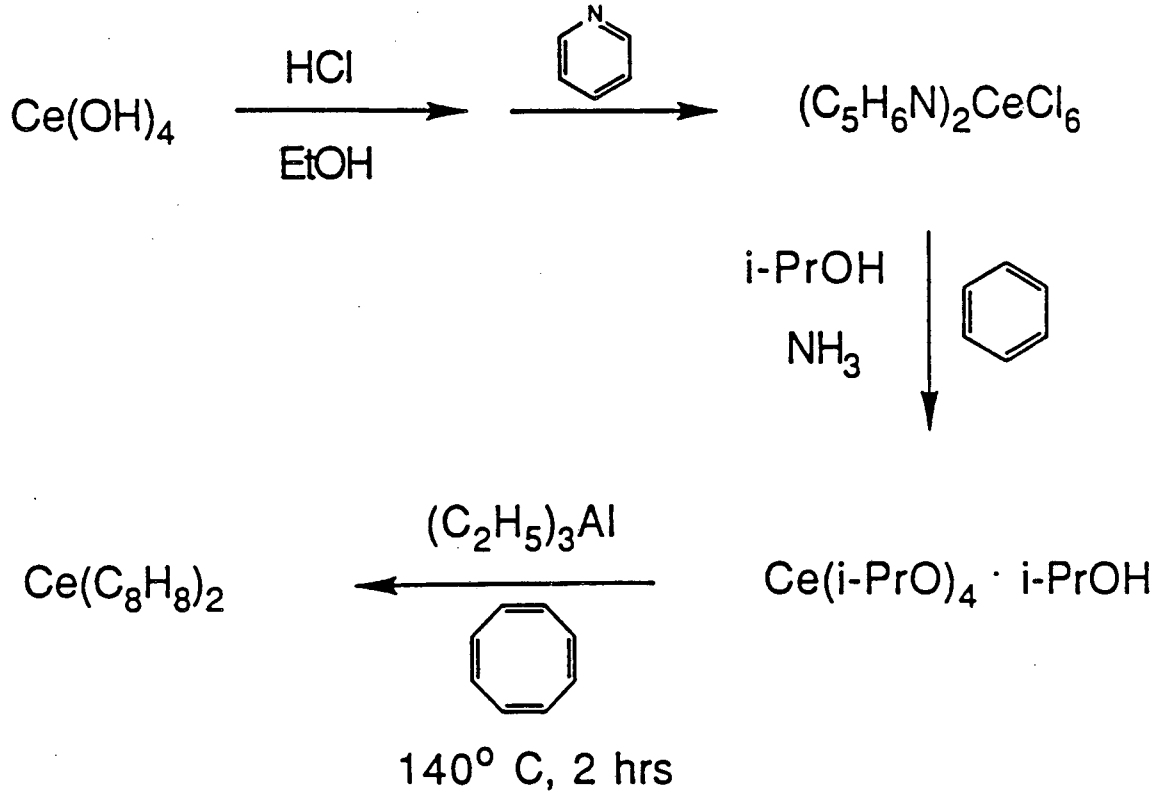
Previous Syntheses of Bis([8]annulene)cerium (IV)

Prior to this work, there were two syntheses of the cerium (IV) sandwich compound reported in the literature, as discussed in Chapter I. In light of the properties reported above, it is clear that the approach used by Kalsotra et al., is not suitable for the preparation of these compounds; the compound they identified as

bis([8]annulene)cerium(IV) had properties which were extremely inconsistent with what is known of this class of compound.[9] The preparation by the Italian group, however, appeared much more credible.[10] (See Scheme 2.1.) The properties as reported were consistent with what one would expect for this class of f-block element compound. They reported air-sensitivity and solubility properties in line with the other sandwich compounds, and the preliminary x-ray structure data are encouraging as well. They reported that the complex was decomposed by water and alcohols, and had one sharp signal in the NMR, as one would expect for a diamagnetic Ce(IV) species.

The report of the preparation of this compound was in and of itself somewhat surprising. It was generally accepted that if one tried to react the strong oxidizing agent Ce(IV) with the strongly reducing [8]annulene dianion, electron transfer would be the result, rather than the formation of a stable complex. However, the publication by Rösch and Streitwieser of their Xα results which predicted the stability of cerocene prompted renewed interest in this complex.[11] When Kinsley of this group followed the procedure of Greco et al., he obtained the reported dark brown microcrystalline material which was highly air- and water- sensitive.[12] The NMR of the material in toluene-d_8 shows one sharp singlet at δ 5.75 ppm and the sample decomposes to COT on exposure to air (the shift for COT is δ 5.61 ppm in toluene-d_8). The infrared spectrum of this complex is consistent with the report by the Italian group, and the similarity with the IR of bis([8]annulene)uranium(IV) is also apparent. Finally, he obtained the mass spectrum of this compound and it too matched with the reported MS of the Italians, which was consistent with the cerocene structure.

Initial Synthesis of Cerocene



Scheme 2.1

So, all of the evidence supports the conclusion that this brown-black material is in fact bis([8]annulene)cerium(IV), and further, that the complex is isostructural with uranocene. Apparently the rings are stabilizing the Ce metal center enough to allow this unfavorable oxidation state to be stable; rather than being too unstable to be isolated, as had been expected, the compound appeared to be fairly stable, within the normal constraints of this type of organometallic complex.

However, the approach used by Greco and coworkers has several limitations. The synthesis has several steps which are fairly difficult to do on large scale and which introduce many opportunities for loss of product. For instance, the tetraisopropoxide of Ce(IV) must be handled with care, since it must be kept free of moisture. The final step involves working with triethylaluminum, which is not an ideal material to work with on large scale.

The major limitation to this procedure, however, results from the fact that the final step is run in cyclooctatetraene as a solvent. In order to study these complexes, it was discussed above that it is necessary to work with the substituted analogs. Solubility, NMR signals, and sometimes even air stability are enhanced by the addition of substituents on the rings. With the Greco synthesis, the final step is run in cyclooctatetraene as a solvent. Cyclooctatetraene itself is on the order of $1/gram so this gets expensive to do on a large scale. Preparing substituted cyclooctatetraenes is generally difficult, involving much purification and generally poor yields.[13] Obtaining enough of a substituted COT to use as a solvent is thus prohibitive, both in terms of cost and man-hours.

In order to study this interesting member of this class of compound, a good, general synthesis of cerocene and its substituted analogs was necessary, but the

approaches are limited. As discussed above, the availability of Ce(IV) starting materials is quite limited. A direct approach such as is employed with the Ln(III) and Ac(IV) sandwiches is thus ruled out. Any sort of ligand which would stabilize the metal enough to make the starting material stable would either be too difficult to displace, or would be unstable with respect to the COT dianion.

Thus, a different approach is necessary, and the one we chose to pursue is based on an observation made by Kinsley of this group.[12] Upon inadvertent oxidation of a small sample of $K[Ce(C_8H_8)_2]$ (lime-green in color), a brown material was observed. When a small sample of this material was dissolved in THF and examined with UV-Vis spectroscopy, the absorption characteristic of cerocene was observed. There was in addition to this, neutral COT as well as evidenced by UV tailing, but it was apparent that it was possible to oxidize the readily prepared Ce(III) sandwich compound to the desired Ce(IV), and this was the approach taken.

Results and Discussion

The preparation of the Ce(III) sandwich compound is well known, and yields of up to 60% are common. The complex can be isolated and purified to give a lime-green powder, which can be stored indefinitely in an argon glovebox. Little work had been done prior to this on substituted analogs, but what work had been done indicated that there should be little trouble in obtaining the desired substituted sandwiches.[14]

Kinsley's observation that the $K[Ce(C_8H_8)_2]$ could be oxidized by oxygen to the Ce(IV) complex gave a starting point for chemical oxidation of the material, but it had been accompanied by significant decomposition; the oxygen apparently oxidizes not only the Ce(III) complex, but also, not surprisingly, the Ce(IV) complex. It was thus necessary to find a reagent which could oxidize the Ce(III), but which would be stable with respect to cerocene. Since work with these compounds is basically limited to THF solutions and not many redox potentials are known in this solvent, the process began as basically a matter of trial and error. Since it is known that the acidic aqueous potential for the Ce(IV)/Ce(III) couple shows that the +3 state is strongly favored over the +4,[15] initial efforts were made with reagents which would be thought to be strong oxidizing agents in THF.

The attempted oxidations were performed by taking advantage of the difference in the visible spectrum of the two species; the $K[Ce(C_8H_8)_2]$ is a lime green solution in THF (λ_{max} = 690 nm), whereas the oxidized species is a deep chocolate brown (λ_{max} = 469 nm). Thus the color of the reaction mixture can give a quick indication of whether the oxidation is going or not. COT itself gives a pale yellow solution, due to tailing from the UV, so the visible spectrum can also give an indication of when the sandwich is decomposing. The experiments were therefore performed by dissolving a small amount of the cerate complex in THF in a UV-vis cell, adding a small amount of the appropriate oxidizing agent, and watching for formation of the cerocene by visible spectroscopy. Results are shown in Table 2.1. As can be seen, the only reagents which resulted in any cerocene at all were the original reagent, O_2, and nitrosyl tetrafluoroborate., which resulted in an isolated yield of < 5%. The other reagents resulted in the appearance of the COT UV tail, as well as the disappearance of the peak corresponding to the $K[Ce(C_8H_8)_2]$; apparently those reagents were too strong to be

stable with respect to the cerium (IV) complex, if it were formed, or reacted with the Ce(III) species via a pathway that did not involve a Ce(IV) species at all.

Table 2.1

Oxidation Attempts

$$K[Ce(COT)_2] \xrightarrow{[O]} Ce(COT)_2$$

Unsuccessful	Limited Success
$K_2S_2O_8$	O_2
PhC(O)OOC(O)Ph	$NOBF_4$ (< 5 % Yield)
Br_2	
$(NH_4)_2[Ce(NO_3)_6]$	

It became clear at this point that it was necessary to get a firmer grip on where the reduction potential for this couple lies, so electrochemical measurements of the system were undertaken. The details of this measurement are discussed in greater detail in the Chapter IV, but for the purposes of this discussion, suffice it to say that the value found for this $Ce(IV)_s/Ce(III)_s$ couple, where the subscript s refers to sandwich complex, is -1.3 ± 0.1 V vs NHE. This value is unprecedented for a Ce(IV) species and suggests that the complexing cyclooctatetraene rings are imparting a great deal of stabilization to the cerium center. It further suggests that the oxidizing agents used thus far are much stronger than are necessary to effect this oxidation; a gentle, one-electron oxidizing should suffice to yield the desired cerocene.

With this in mind, the next reagent tried was silver nitrate. A small amount of $AgNO_3$ was added to a cuvette filled with a solution of $K[Ce(C_8H_8)_2]$ in THF, and immediately the solution turned a deep brown color. Examination of this solution spectroscopically showed formation of cerocene, but some decomposition as well. A similar reagent which should be less soluble in THF and thus should be a slightly weaker oxidizing agent is silver iodide, and a cuvette scale reaction showed that this does go cleanly to cerocene.[16]

This reaction was scaled up to preparative scale with little problem. To a stirred solution of $K[Ce(C_8H_8)_2]$ in THF was added a ten fold excess of finely ground silver iodide, as in Eq. [2.7]. The solution turned dark immediately, with the formation of cerocene. The solution was filtered, which removes the excess AgI, as well as the by-products Ag(0) and KI. Removal of the solvent gives a ~80% yield of pure brown-black $Ce(C_8H_8)_2$ after rinsing with a small amount of hexane or toluene.

$$K[Ce(C_8H_8)_2] + \text{xs AgI} \xrightarrow{\text{THF}} Ce(C_8H_8)_2 + KI + Ag \qquad [2.7]$$

This, then, appears to be a good method for producing cerocene in good yield and relatively simply from readily prepared starting materials. The other desired property for a good synthesis of this molecule is that it be general enough to prepare substituted cerocenes, so this was the next thing attempted. n-Butylcyclooctatetraene, prepared according to literature methods,[17] can be reacted with K and subsequently with $CeCl_3$ to give the substituted Ce (III) sandwich compound. Not much work has been done with substituted lanthanide sandwich compounds, but in general the

properties are quite similar to the parent compounds. The most notable differences are in the solubility properties, which is the very property that makes these derivatives so useful.

A solution of $K[Ce(n\text{-}C_4H_9C_8H_7)_2]$ was treated with silver iodide in the same manner as above, and the solution again turned a deep brown-black. Filtration and subsequent evaporation of solvent resulted in the isolation of the substituted derivative, $Ce(n\text{-}C_4H_9C_8H_7)_2$. The reaction has also been performed on a number of differently substituted cerate complexes with equal success. Thus, it appears that this is a generally useful technique for preparing this class of f-block compound (see Eq. [2.8]).

$$K[Ce(R\text{-}C_8H_7)_2] + \text{xs AgI} \xrightarrow{\text{THF}} Ce(R\text{-}C_8H_7)_2 + KI + Ag \qquad [2.8]$$

R = H
n - butyl
t - butyl
t - butoxy
methyl

Now with a relatively easy method for the preparation of this class of molecule, it is possible to examine some of the properties and characteristics which may help to explain the stability of this unusual species.

Properties

The synthesis of the cerocene sandwich compounds results in a dark brown-black powder, which shows most of the physical properties expected from this class of molecule and whose properties match well with those reported by the Greco group.[10] It is extremely air-sensitive, has limited solubility in most solvents. The molecule can be sublimed to some extent, but it is accompanied by significant decomposition.

As well as examining the usual types of chemical properties, several experiments were performed to compare the chemistry of this compound with that of uranocene, in analogy to those performed on the Ce(III) sandwich. One important reaction was the ligand exchange experiment described above with the Ln(III) metallocene and uranium tetrachloride. In this case, a sample of bis([8]annulene)cerium(IV) was dissolved in an NMR tube with THF-d_8. To this tube was added UCl_4, and the mixture was examined by ^1H NMR. There was ligand exchange, as evidenced by the growing in of a peak corresponding to bis([8]annulene)uranium(IV) at -36 ppm (see Figure 2.1). However, this reaction proceeded much more slowly than did the reaction with either $K[Ce(C_8H_8)_2]$ or $Th(C_8H_8)_2$, requiring several days for the formation of uranocene. There is an additional complication with this reaction, and that is evident upon examination of the balanced Equation [2.9]. One of the initial products is $CeCl_4$, which, unlike its actinide analogs, is highly unstable and will rapidly be reduced.

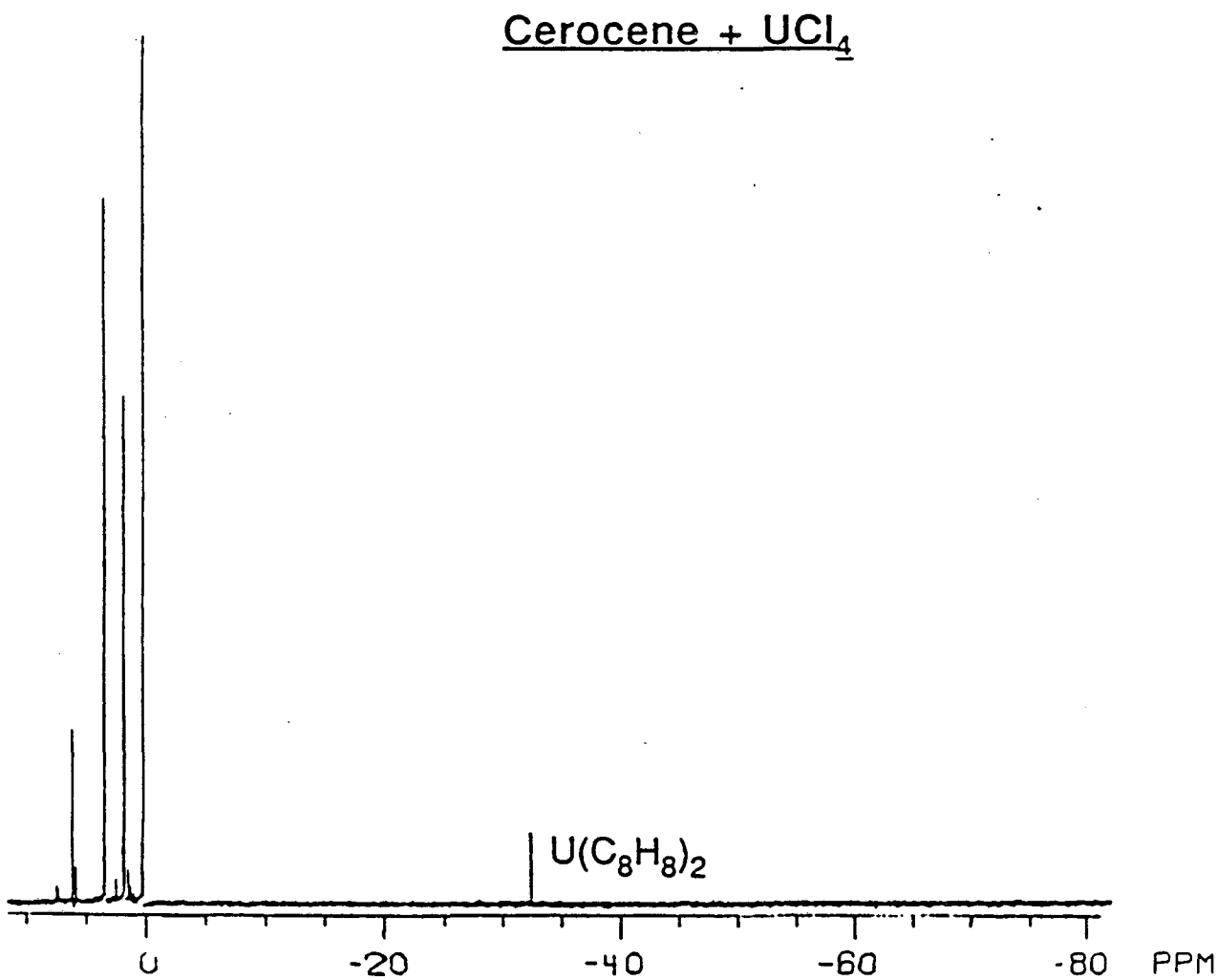


Figure 2.1: Reaction of $Ce(C_8H_8)_2$ with UCl_4.

It is thus possible that this subsequent reaction, rather than the stability of uranocene is the driving force for the reaction. However, the slowness of the reaction at least tentatively suggests that the cerocene is quite a stable molecule, since the presence of this further reaction would if anything probably cause the reaction to go faster than it would in its absence

$$Ce(COT)_2 + UCl_4 \xrightarrow[\text{THF-}d_8]{\text{days}} U(COT)_2 + \text{"}CeCl_4\text{"} \qquad [2.9]$$

The hydrolysis experiment on this molecule was performed by Moore, and he found that the rate at which this sandwich compound was hydrolyzed was nearly the same as the rate for thorocene, a half-life < 60 seconds.[18] This is in contrast, recall, to uranocene's half-life of 20 hours. This result thus agrees with the stability of cerocene being at least the same as that of thorocene.

NMR

It is known that [8]annulene derivatives of some of the lanthanides and actinides undergo electron transfer on the NMR time scale (Eq. [2.10]). Kinsley and Eisenberg of this group have examined the exchange in the system $K_2[Yb(RC_8H_7)_2]/K[Yb(RC_8H_7)_2]$ and found that it has a rate constant of about 10^7 sec^{-1}.[19] This is of the same order of magnitude as found for the ferrocene/ferricenium ion exchange studied in detail by Wahl and others.[20] Eisenberg has also examined the exchange between uranocene and its reduction product and found that it, too,

undergoes exchange on this time scale.[21] It was thus of interest to see if the corresponding lanthanide (IV)/(III) system would also undergo exchange.

$$M(COT)_2 \underset{-\,e^-}{\overset{+\,e^-}{\rightleftharpoons}} [M(COT)_2]^- \qquad [2.10]$$

In each of these cases, one is looking at the exchange between a paramagnetic and a diamagnetic species. It is possible to see the ring protons of the diamagnetic species clearly, but in the paramagnetic compounds, those peaks are usually too broad to be seen. It thus has been found best to use a substituted species, such as the t-butyl derivative. In addition to a more visible NMR signal, this also increases the solubility of the molecules, so it is generally much easier to work with.

To examine the electron exchange, a mixture of the complexes in the two different oxidation states is examined by NMR as the temperature is varied. For a system in which there is no exchange process, the peaks corresponding to the two individual compounds would be visible. However, for the case in which the compounds are undergoing exchange on the NMR timescale, one should see the individual peaks at temperatures low enough to slow the process to less than the NMR timescale, with a peak corresponding to a weighted average of the two at highly elevated temperatures.

The original experiments on this type of lanthanide system were performed by Steve Kinsley, with the bis([8]annulene)ytterbate (II) and the corresponding ytterbate(III) sandwich. [12, 19] The diamagnetic Yb(II) sandwich has a sharp NMR resonance at 5.47 ppm, whereas the paramagnetic Yb(III) analog has no visible

resonance. When these two compounds were mixed together in a THF-d_8 solution, the diamagnetic peak was not visible by room temperature NMR. However, cooling the solution to -50 °C resulted in the appearance of a singlet at 5.5 ppm which broadened and eventually disappeared on warming.

This sort of NMR behavior is indicative of an exchange process, but in this case, there was the possibility of it being ligand rather than electron exchange. Kinsley proved it was the electron exchange by comparing this behavior with that of a mixture of the similar calcium(II) analog with the ytterbium(III) metallocene. He reasoned that since the Ca had no accessible +3 oxidation state, the possibility of electron transfer in this case is ruled out; if any exchange were in evidence, it would be due to ligand exchange. The NMR of the mixture of these compounds showed no evidence of exchange at any temperature, implying the existence of an electron exchange process in this case, and, by analogy, in the Yb(II) - Yb(III) case as well.

This sort of exchange had been studied previously for the ferrocene system by Wahl and coworkers, who developed equations for determining the rate of exchange using NMR lineshape analysis.[20] Using these relationships, Kinsley and Eisenberg determined the rate of exchange in this system to be 1×10^7 M^{-1} s^{-1} at 19.3 °C, which turns out to be similar to that found for the ferrocene/ferricenium exchange.

The experiment with the cerocene was carried out in much the same manner. The ^1H NMR spectrum of the diamagnetic bis(t-butyl[8]annulene)cerium(IV) is shown in Figure 2.2. This spectrum was taken in THF-d_8, as will be all the spectra reported on in this section, and shows a clean singlet at δ 2.2, due to the nine t-butyl protons. The ring protons in this compound also show up as the multiplet at about δ 5.9; the fact that this is a diamagnetic compound results in these peaks being evident, but they

will not be useful in any of this work. The other peaks are due to the solvent (δ 1.73 and 3.58 ppm) and residual stopcock grease (δ 0.05 ppm). This shows the solubility limitations of these compounds; since this is a nearly saturated solution of the cerocene.

The room temperature (20 °C) ^{1}H NMR spectrum of the paramagnetic species potassium bis(t-butyl[8]annulene)cerate(III) is shown in Figure 2.3, and the difference between it and the corresponding tetravalent cerium spectrum is apparent. The ring protons which were visible in the diamagnetic sample are now too broad to be seen. The peak corresponding to the nine t-butyl protons is visible as a broad resonance at δ 4.4. The position of this peak is temperature dependent, as is usual with paramagnetic compounds of this sort.

An approximately 50:50 mixture of these two species was then prepared and examined in the NMR. The spectrum observed at room temperature is shown in Figure 2.4. The resonances corresponding to the solvent and grease as well as the same minor impurities which were seen in the spectrum of the cerium (IV) species alone are apparent, but the resonances attributable to the metallocene itself are gone. There is apparently an exchange process occurring, as otherwise there would be the two sets of peaks corresponding to the Ce (IV) and the one broad peak from the Ce(III).

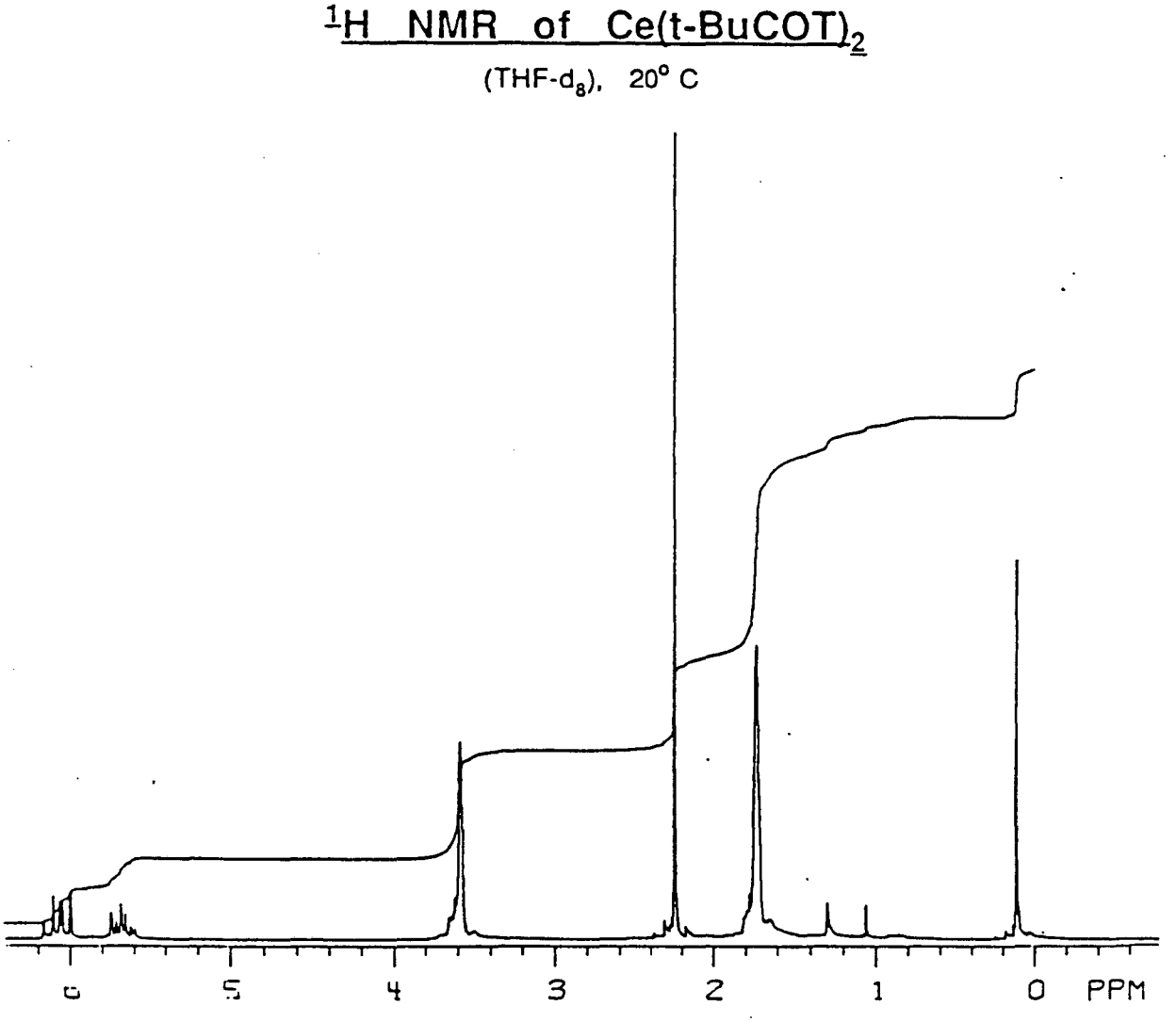


Figure 2.2: ^{1}H NMR of Ce(t-BuC$_8$H$_7$)$_2$ in THF-d$_8$.

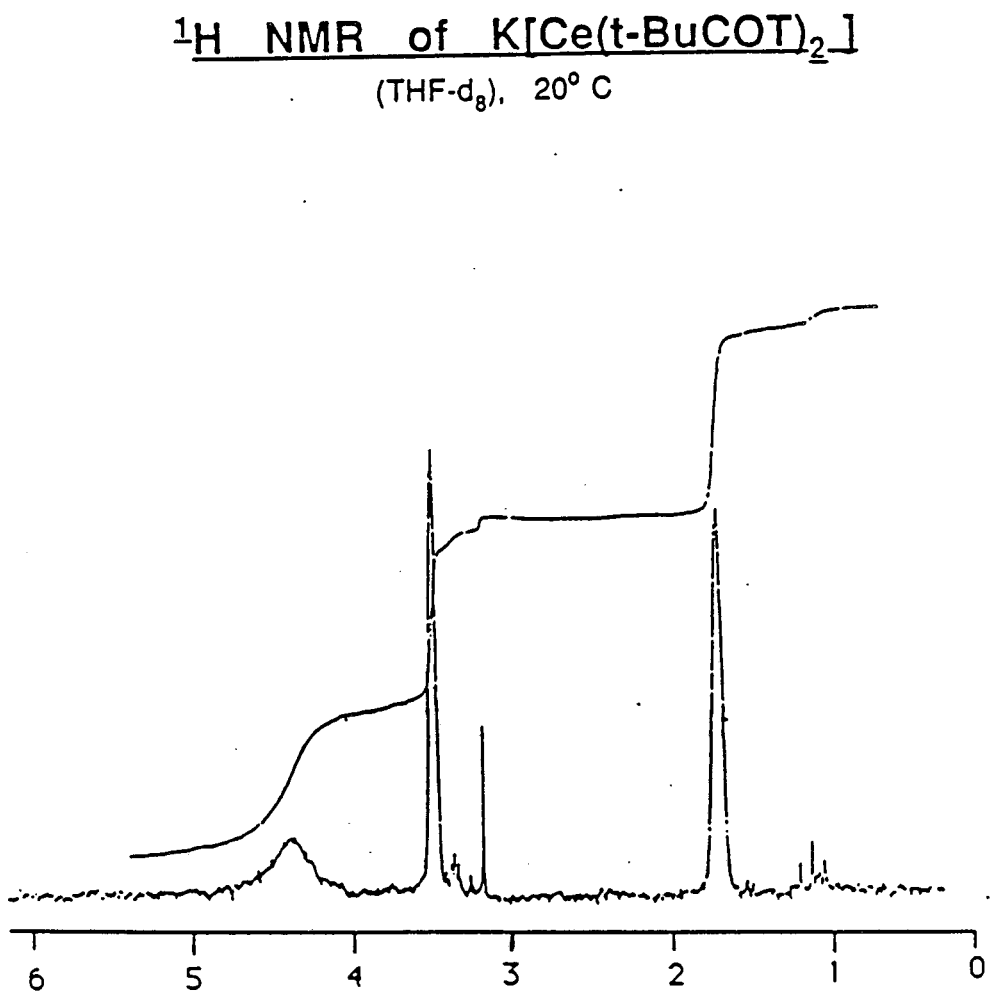


Figure 2.3: ^{1}H NMR of K[Ce(t-BuC$_8$H$_7$)$_2$] in THF-d$_8$ (20 °C).

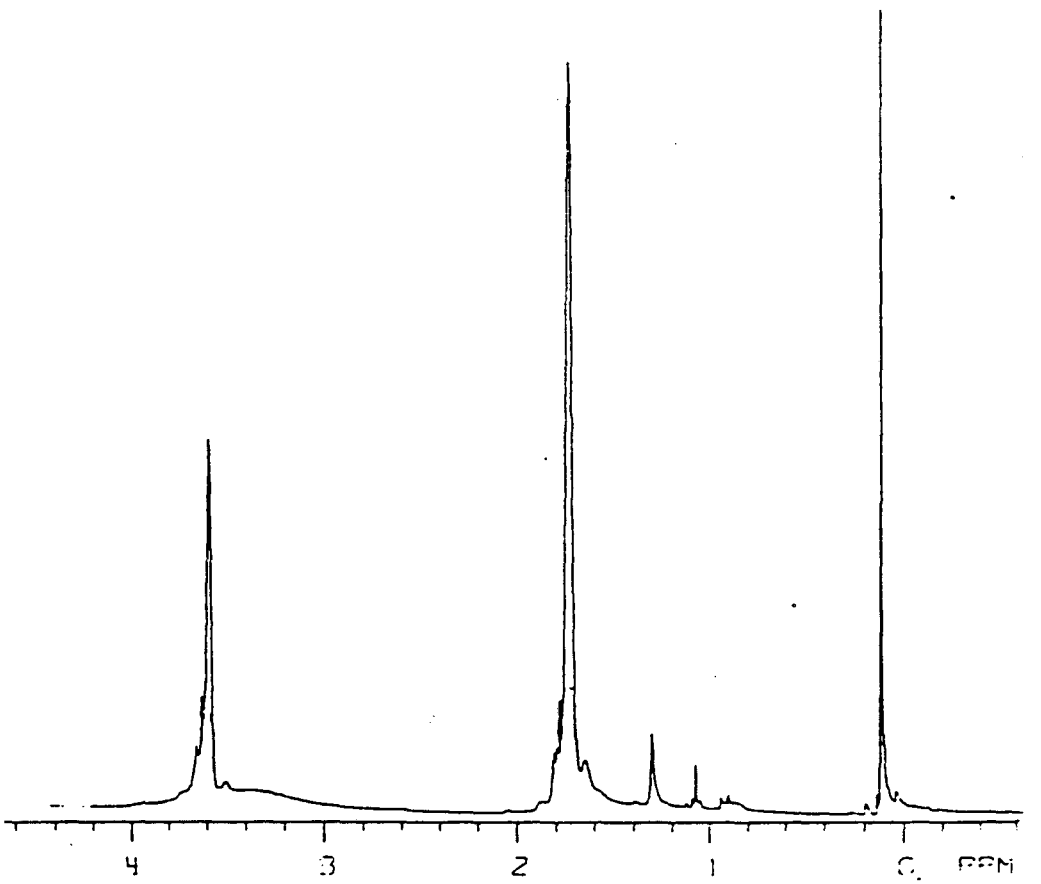


Figure 2.4: Room Temp. NMR of Mixture of Ce(III) and Ce(IV).

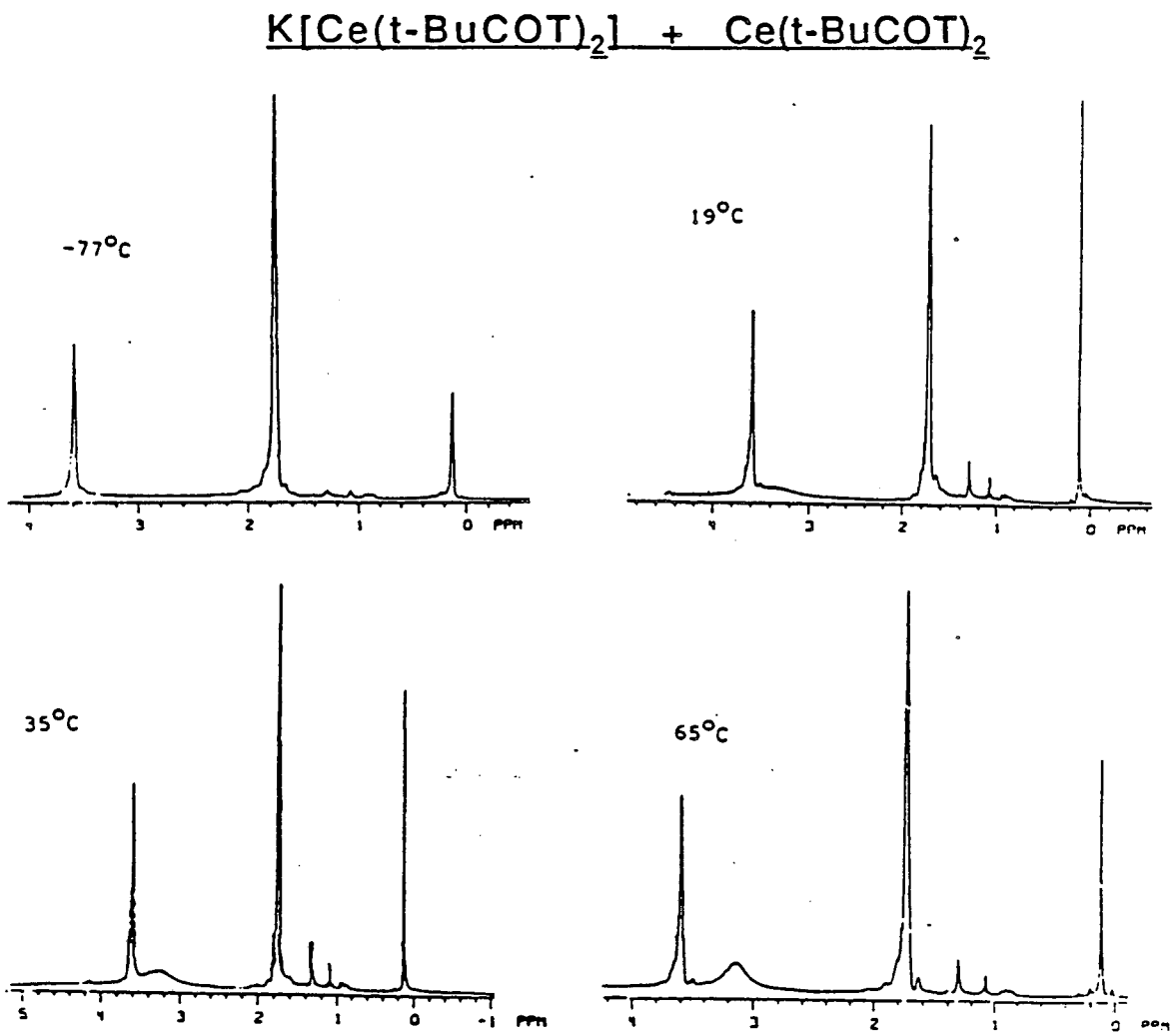


Figure 2.5: Variable Temperature NMR of Mixture.

On close examination, it can be seen that there is what appears to be a small lump in the baseline overlapping with the downfield solvent peak. If this is the exchanging peak, it should be affected by changes in the temperature, as the rate of the exchange changes. As the temperature is raised, this peak does clearly sharpen up, and the high temperature fast exchange limit is reached at about 65 °C (See Figure 2.5). At this temperature, the shift of the exchange peak is at slightly over 3 ppm, which is where one would expect the weighted average of an approximately 50:50 mixture of the two species.

Theoretically, in a system like this, as one cools the sample, the exchange peak should disappear into the baseline, and at temperatures low enough to prevent the exchange, the individual peaks should reappear. As this sample was cooled below 19 °C, the small hump did disappear; thus the first temperature we examined was about the coalescence temperature. However, as the temperature was lowered further, no sign of the individual resonances reappeared. The lowest temperature shown in Figure 2.5 is -77 °C, but the temperature was taken down to -105 °C on a 500-MHz instrument with no sign of the peaks. There are difficulties involving poor resolution of the instrument at these temperatures, as evidenced by broadening of the peaks corresponding to the solvent and grease, and there may be a problem with reduced solubility of the compounds, but it should still have been possible to observe the peaks if they had been present.

Since the difference in chemical shift between the two peaks is so small, it is not surprising that the exchange could not be frozen out. What made the Yb(III)/Yb(II) case so amenable to a study of this sort is that the difference in the chemical shift in that case was on the order of 20 ppm, so freezing out the process is possible at about -78

^{o}C. The corresponding Np(IV)/Np(III) case is also being studied; in this case, the resonances are separated by enough to enable this system to be frozen out at about -20 ^{o}C.[20]

Visible Spectra

In the Xα calculations performed by Rösch and Streitwieser, comparisons were made between the visible spectra of bis([8]annulene)uranium(IV) and thorium(IV) and the calculated e_{2g} (π) - e_{3u} (f) charge transfer excitation band.[21] If the strong absorption band in these compounds was attributed to this charge transfer, then there was found to be good agreement between the calculated energies and those derived from the visible spectra. For the uranium case, the measured value was 2.01 eV versus a calculated value of 1.97 eV; for the thorium, the values were 2.75 eV (measured) and 3.03 eV (calculated). The visible spectra for cerocene had not appeared at the time that work was published, but it has now been measured and the comparison can be made with the calculated values. The visible spectrum of bis([8]annulene)cerium(IV) in THF is shown in Figure 2.6. It shows a strong absorption at 469 nm, with a shoulder at slightly higher wavelength. The extinction coefficient of this peak was measured and was found to be $\varepsilon \approx 8000$. The energy associated with this transition corresponds to 2.63 eV.

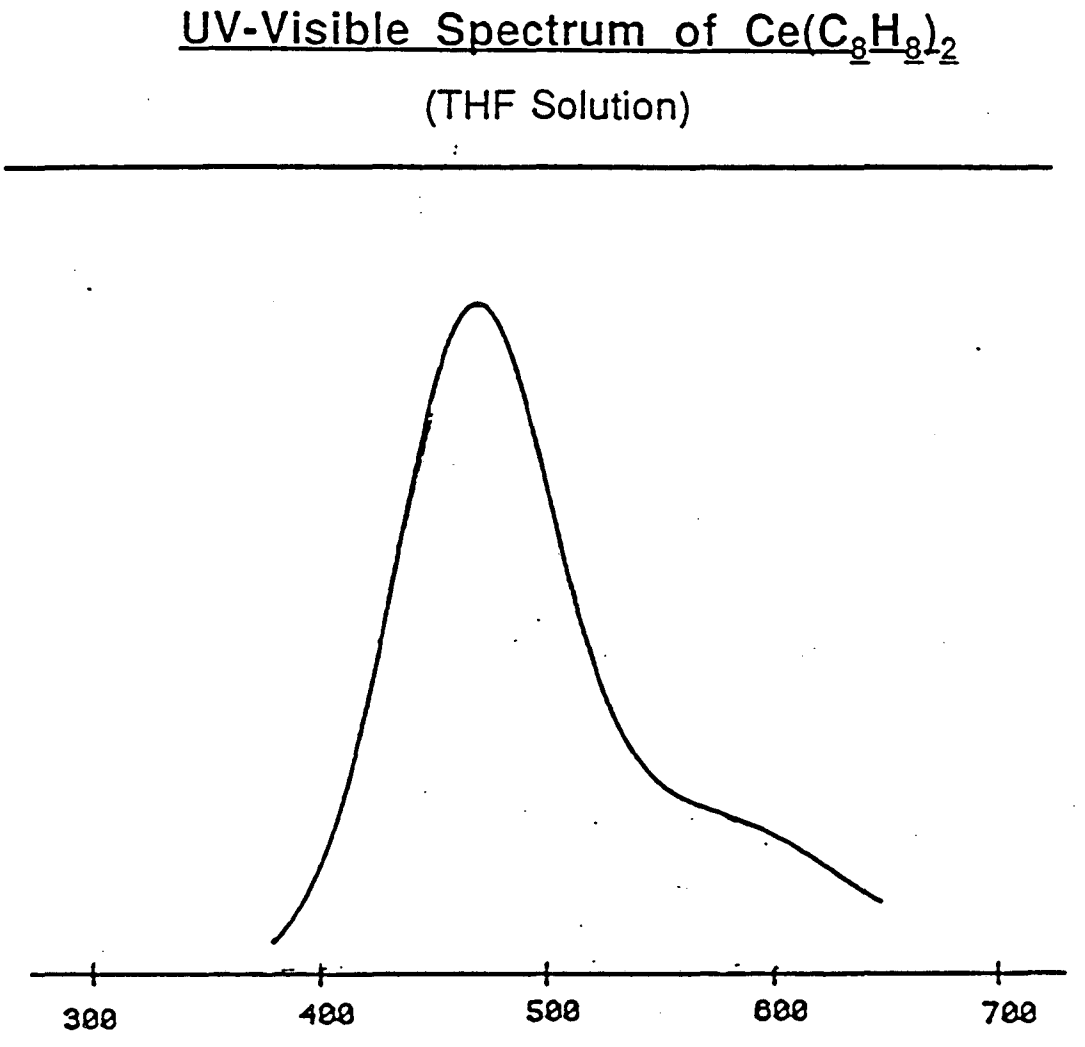


Figure 2.6: Visible Spectrum of Cerocene (THF Solution).

These values can now be compared with the experimental values for uranocene and thorocene, and with the predicted transition energy as calculated by Rösch and Streitwieser. The comparison with the uranocene spectrum is not very good. The observed extinction coefficient for bis([8]annulene)uranium(IV) is $\varepsilon \approx 1800$, and a similar intensity is observed for thorocene. If this is the same transition as the 469 nm band of cerocene, then the cerium transition is much more intense than would have been expected.

The comparison with the calculated transition energy is also less than satisfactory. The calculations predict a value of 1.92 eV for the $e_{2g}(\pi)$ - $e_{3u}(f)$ transition, as opposed to the 2.63 eV observed here. This agreement is clearly not good, and certainly not nearly as close as had been seen in the other two cases.

However, if one examines the visible spectrum more closely, it is apparent that the small shoulder previously mentioned does occur at a wavelength which would match the calculated value much more closely. In addition, the extinction coefficient appears to be much less than the main peak, and much closer to that expected on the basis of the uranocene analog.

We have found that it is possible to model this spectrum using a calculational deconvolution technique.[23] We have had good results with modeling it with a series of two Gaussian functions to represent the two absorbances, and a line to serve as a baseline correction. After fitting the equations to the spectrum using a least-squares method, the parameters of the equations can be related to both the position and relative intensity of each component peak.

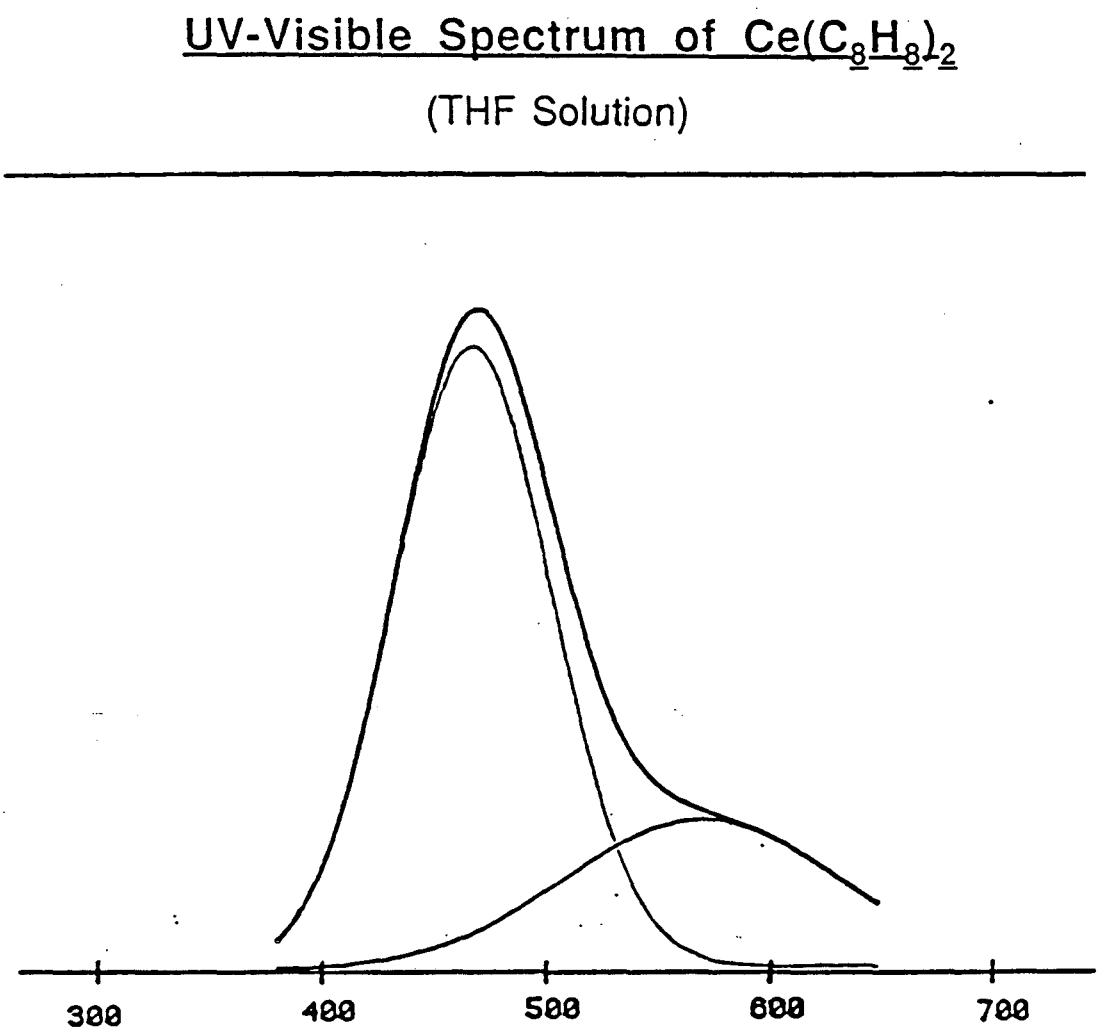


Figure 2.7: Deconvoluted Spectrum of Cerocene.

The graphical results are shown in Figure 2.7, which shows the measured spectrum as well as its two deconvoluted constituent peaks; the baseline correction has been omitted for clarity. The overall agreement between the modeled and the measured spectra is quite good and reproducible, so the modeling seems to be effective.

The results from this technique place the shoulder at about 570 nm, with an extinction coefficient of about $\varepsilon \approx 1000$. The extinction coefficient is definitely more in line with the other sandwich complexes of this sort. The energy value for this shoulder corresponds to 2.18 eV, and the comparison with the calculated value of 1.92 eV is clearly much more satisfactory, and lends additional credence to these calculations.

It should be reemphasized at this point that the results of Chang and Pitzer, discussed in Chapter I, cast significant doubt on the identification of these peaks as the ligand - metal charge transfer band.[24] The close agreement with the $X\alpha$ results may just be a coincidence, but it is curious that they predict the transition so well for the three compounds examined.

The substituted cerocenes have also been examined by visible spectroscopy, and Table 2.2 shows some of the results of this examination. The strong absorptions shift as the substituent is changed, actually in the Ce(III) case as well as in the Ce(IV). The value in parenthesis after the peak for the tetravalent compound is the value determined by the computer deconvolution for the location of the absorbance. This peak appears to be shifting as well, but a word of caution is necessary here. As the two peaks move together, the success of the computer deconvolution can be reduced. The reproducibility of the calculation is greatly diminished, and in the case of the t-BuO

substituted cerocene, the peaks were overlapping too much to identify the location with any accuracy.

Table 2.2

Visible Spectra of $(R\text{-}C_8H_7)_2Ce$

(THF solutions, λ_{max} in nm)

R	Ce^{+3}	Ce^{+4}
-H	692	472 (570)[a]
-Me	706	477 (570)
-n-Bu	708	478 (~585)
-t-Bu	707	483 (567)
-t-BuO	724	492

[a] The values shown in parentheses are the results of the deconvolution, when the shoulder was defined well enough.

It had been hoped that by examining the shifts in the absorbance of the differently substituted cerocenes in different solvents, some information might be learned about the nature of the transition. The assignment as a charge transfer transition were based on analogy with other types of compounds, but information of this type might have been helpful in this regard. However, the same problem mentioned above proved to occur in this study as well; in solvents such as toluene or

DMF, the shoulder peaks were generally too obscured to get a meaningful deconvolution of the spectra.

There were several other properties of this compound that were reported by Greco, et al., which we thought were interesting and worth repeating.[10] The related tris-Cp Ce(IV) alkoxide they reported has recently been confirmed by Marks and coworkers.[25] More will be mentioned with respect to this compound in Chapter VI.

The Italian group reported that the reaction of bis([8]annulene)cerium(IV) with metallic potassium in diglyme resulted in reduction. With one equivalent of the alkali metal, they reported conversion to the potassium salt of the bis([8]annulene)cerate(III), as in Eq. [2.11]. Reaction with an excess of potassium, however, resulted in the reputed preparation of the unprecedented complex of Ce(II) shown in Eq. [2.12]. The characterization of this unusual compound, however, was far from complete; it consisted of an elemental analysis which did not meet standards, and the IR spectrum. We thought this was an experiment that warranted repeating, so, following their procedure, we attempted to obtain this compound but were unsuccessful. We saw some disappearance of the Ce(IV) species (by its visible spectrum), but no sign of either the cerium(III) sandwich or a new peak which could be identified as a Ce(II) species. There was evidence of the UV-tailing of COT. The experiment was repeated with $K[Ce(C_8H_8)_2]$ as the starting material, but again what reaction there was seemed to be decomposition.

$$Ce(C_8H_8)_2 + K \xrightarrow[\text{glyme}]{30^\circ} [K(\text{glyme})]^+[Ce(C_8H_8)_2]^- \qquad [2.11]$$

$$Ce(C_8H_8)_2 + 2K \xrightarrow[\text{glyme}]{30^\circ} ([K(glyme)]^+)_2[Ce(C_8H_8)_2]^{2-} \qquad [2.12]$$

As part of their characterizations of their complexes, they reported that both the cerium(III) and cerium(IV) sandwich compounds yield a mixture of 1,3,5- and 1,3,6-cyclooctatriene when reacted with isopropanol, as well as about 20 % COT. This is quite a strange result in light of the other work done on reactions of this sort, which result in the cyclooctatriene mixtures, but with no COT. If the tetraene is being formed, that would imply that there is some unusual redox reaction going on as well as the alcoholysis. However, Moore repeated this work and found that the Greco group was in error; only the appropriate cyclooctatriene mixture was obtained.[26]

Experimental

General

All air-sensitive materials were handled under argon either in a Vacuum Atmospheres Model HE-243 glovebox with a Model HE-93A MOD drytrain or using standard Schlenk line techniques. Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. ^{1}H NMR spectra were obtained on UC Berkeley 200 and 250 MHz superconducting FT spectrometers equipped with Cryomagnets Inc., magnets and Nicolet model 1280 data collection systems, a Bruker 500 MHz AM 500 superconducting FT spectrometer with Aspect 3000 computer system, and a 90 MHz JEOL FX90Q FT spectrometer. Temperatures

were measured with a thermocouple mounted next to the NMR tube. Chemical shifts are reported in ppm with positive shifts reported for peaks downfield of TMS, and with peaks referenced to the upfield residual THF proton resonance at 3.58 ppm. Visible spectra were recorded on either a Cary model 118 or an IBM Model 9430 spectrophotometer; deconvolutions calculations were performed on an IBM Model 9000 computer. Tetrahydrofuran (THF) was distilled from either sodium / benzophenone or potassium / benzophenone and degassed using a freeze - thaw method (3 cycles) prior to use with air-sensitive materials, and stored over 4 Å sieves. Toluene and hexane were distilled from sodium / benzophenone or $LiAlH_4$, freeze - thawed, and stored over 4 Å sieves. Cyclooctatetraene (COT) (obtained from BASF) was vacuum distilled or vacuum transferred prior to use and stored over 3 Å molecular sieves.

Preparation of $Ce(C_8H_8)_2$

Into a 100 mL round bottomed flask in an argon atmosphere glovebox was added 0.200 g (0.52 mmol) of $K[Ce(C_8H_8)_2]$. To this was added 30 mL of THF, and the solution was stirred until the sample had all dissolved. At this point, a red light was turned on and the room lights were extinguished. To this pale green solution was then added 1.21 g (5.2 mmol) of AgI, which had been freshly ground in a mortar. The solution immediately turned a deep brown, and was left to stir for 2 minutes. The solution was then filtered with very fine filter paper, resulting in a clear dark brown solution. The filter paper was then rinsed several times with small portions of THF, leaving a fine black material in the filter paper. The solvent was removed from the filtrate *in vacuo*, resulting in a brown-black powder. This powder was rinsed several

times with small portions of hexane to yield 0.142 g (0.41 mmol, 78%) of $Ce(C_8H_8)_2$. ^{1}H-NMR (THF-d_8): δ 5.91 (s); (toluene-d_8): δ 5.75 (s).

Spectroscopic Examination of Oxidizing Agents

All spectra were recorded as THF solutions on either a Cary Model 118 or an IBM Instruments Model 9430 UV-Visible spectrophotometer. The peak for the $K[Ce(C_8H_8)_2]$ occurs at 692 nm, whereas the peak for $Ce(C_8H_8)_2$ is at 469 nm. Cyclooctatetraene appears as a strong UV tail into the visible region.

In an argon atmosphere glovebox, enough $K[Ce(C_8H_8)_2]$ was dissolved in THF in an airtight UV-Vis cuvette to show a pale green solution. In the case of the solid oxidizing agents a small amount of the reagent was then added to the cuvette, which was capped, removed from the glovebox and examined in the spectrometer. For the bromine, the sample was capped with an appropriately sized rubber septum, then removed from the box. The bromine was added via syringe after degassing by bubbling argon through the syringe. The sample was then examined as usual.

Ligand Exchange Reaction

A sample of $Ce(C_8H_8)_2$ was placed in an NMR tube equipped with a stopcock joint. THF-d_8 was added, and the cerocene was allowed to dissolve into a brown solution. To this tube was added an unmeasured amount of UCl_4, the tube was removed from the box and sealed under vacuum. After several days, a small peak in the ^{1}H NMR appeared at -36 ppm corresponding to uranocene.

Attempted Preparation of $K_2[Ce(C_8H_8)_2]$

To a solution of either $Ce(C_8H_8)_2$ or $K[Ce(C_8H_8)_2]$ stirring in glyme in a glovebox was added an excess of freshly shaved potassium. The solutions were allowed to stir until there was no apparent reduction in the size of the potassium (generally several hours). The solutions had turned light brown color. Examination of the reaction mixture by visible spectroscopy showed no peaks in the visible, but significant UV tailing, often indicative of the presence of COT. In addition, when the reaction was repeated in on NMR scale with THF-d_8, the predominant peak after reaction was at δ 5.7, indicative of COT.

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CHAPTER III:

CRYSTAL STRUCTURE OF DIMETHYLCEROCENE

One of the most important factors controlling the structure and properties of an organometallic compound is the oxidation state of the central metal. In order to accurately assess the effect of a change in oxidation state on the characteristics of a compound, it is necessary to compare compounds in which there is little or no change in the coordinating ligands. However, the number of systems of this type available is quite limited, the principal examples thus far having been the metallocenes. The ferrocene/ferricenium system has been particularly well studied and a number of interesting properties have been observed.[1]

[8]Annulene derivatives of the lanthanides and the actinides comprise another type of metallocene which would be useful for this purpose. The variety of oxidation states for the metals, as well as the stability of their compounds make them well suited to studies of this type.[2] In addition, it is possible to replace one of the cyclooctatetraene ligands with other types of ligands, which allow for probing of the structural effects even more closely. For instance, $(COT)ThCl_2$ is a known compound, and its structure has been solved.[3] Lanthanide complexes with one cyclooctatetraene ring and one cyclopentadienyl ring have also been studied, and make for an interesting comparison with the biscyclooctatetraene complexes.[4]

One major problem with examining the structural characteristics of these molecules lies with the difficulty in obtaining X-ray quality crystals. Once again, their poor solubility makes many of the common crystallization techniques difficult to employ here, and in most cases, sublimations are unsuccessful. Frequently, this problem is solved by using substituted COT's as ligands, which then permits use of temperature differential or solubility differential techniques to obtain high quality single crystals.

The first structure of this class of molecule was of the parent compound of this series, bis([8]annulene)uranium(IV), or uranocene.[5,6] The structure showed the central uranium atom coordinated by two parallel planar cyclooctatetraene rings (Figure 3.1). The molecule has D_{8h} symmetry, with the carbon atoms on the two [8]annulene rings being eclipsed. The metal to ring centroid distance is 1.92 Å, and the rings are truly planar systems with C-C bond lengths equivalent and equal to 1.39 Å.

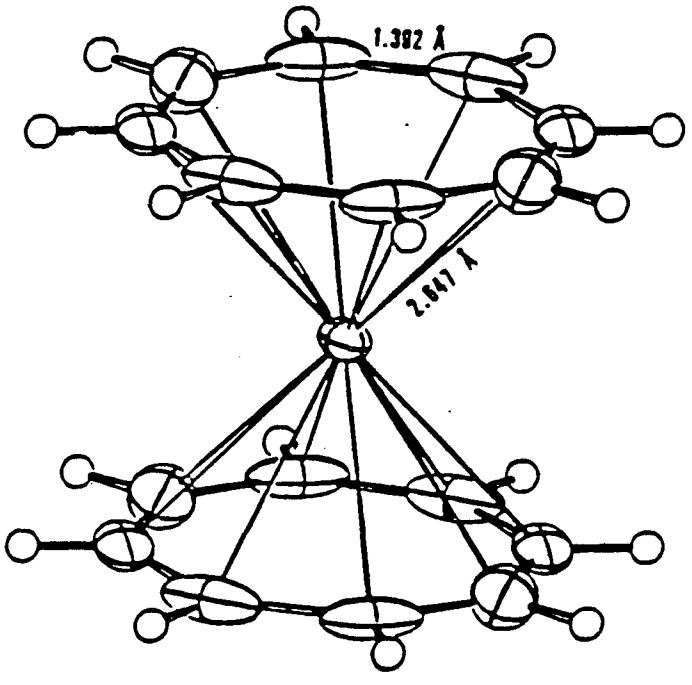


Figure 3.1: Structure of Uranocene.

The structure of bis([8]annulene)thorium(IV) has been solved as well, and it is also a D_{8h} system.[6] The most notable difference between this structure and that of bis([8]annulene)uranium(IV) is the difference in the metal-carbon or metal-ring centroid length. This difference can be attributed to the difference in the ionic radii between ten-coordinate thorium(IV) and ten-coordinate uranium(IV) (1.13 Å for Th, 1.08 Å for U).[7] Bis([8]annulene)neptunium(IV) and -plutonium(IV) have also been prepared, and infrared spectra and x-ray data indicate that these molecules are both isostructural with uranocene, although full structures for these complexes have not been solved.[8]

The two common [8]annulene derivatives of the Ln(III) discussed in Chapter I have also been examined by x-ray diffraction. The mono-COT derivative of cerium was crystallized as its THF adduct, and the crystal structure of this molecule, shown in Figure 3.2, shows it to be a dimer, $[(C_8H_8)CeCl \cdot 2\ THF]_2$.[9] The molecule consists of two mono-COT Ce (III) moieties bridged by the chlorides, with the THF's filling in the coordination spheres of the metals.

The more nearly analogous Ln(III) structure, $K[Ln(C_8H_8)_2]$ has also been studied, and the structure of the diglyme adduct of the cerium complex has been solved and is shown in Figure 3.3.[10] Its structure consists of two planar [8]annulene rings sandwiching the central metal, with the potassium solvated by the diglyme. The symmetry of the bis([8]annulene)cerium(III) anion is approximately D_{8d}; the carbons on the rings of this molecule are approximately staggered, rather than eclipsed as in uranocene. When this structure was originally published, Hodgson and Raymond reported that although it might be expected that the cerium atom might be shifted due to the inequivalence of the two ligating rings, within the experimental error the Ce - C distances were equal. Recently, structures of this sort with one coordinating

potassium have been solved which show this deviation (see below), which may suggest that there is a small effect from this. If one examines the structure closely, it can be seen that the metal-ring carbon length to the ring coordinated by the potassium is greater by 0.013 Å than to the uncoordinated ring, and the ring centroid difference is 0.068 Å.[11] Again, it must be reemphasized that these values are within the experimental errors of being equal, but it is interesting to note the trend; based solely on the crystallographic results one is not justified in saying this is a significant effect, but when it is compared with the related compounds, it does seem to fit the trend.

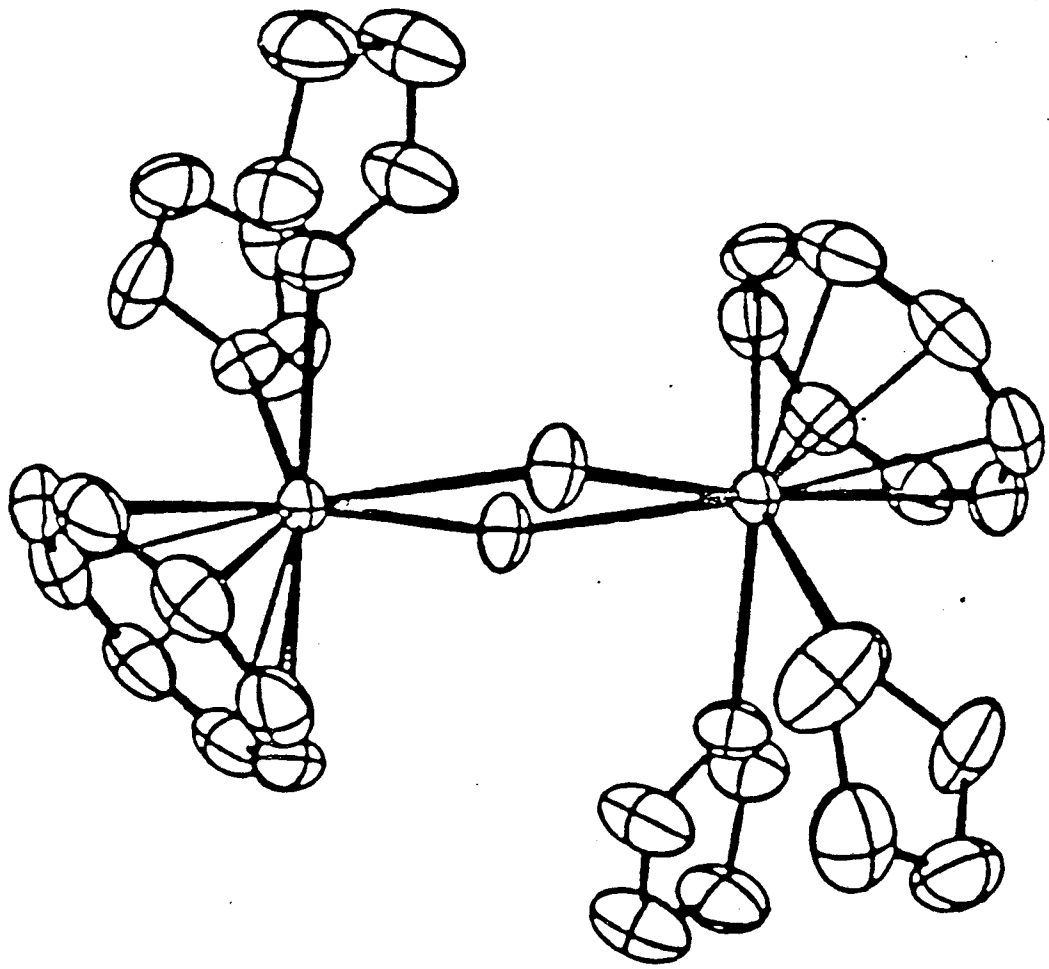


Figure 3.2: Structure of $[(C_8H_8)CeCl \cdot 2\ THF]_2$.

One possible explanation for this deviation could be that the ring coordinated by the potassium is essentially being drawn away from the cerium metal center. The opposite ring, with no other coordinating charges, is attracted only to the cerium, and thus might be expected to approach it more closely.

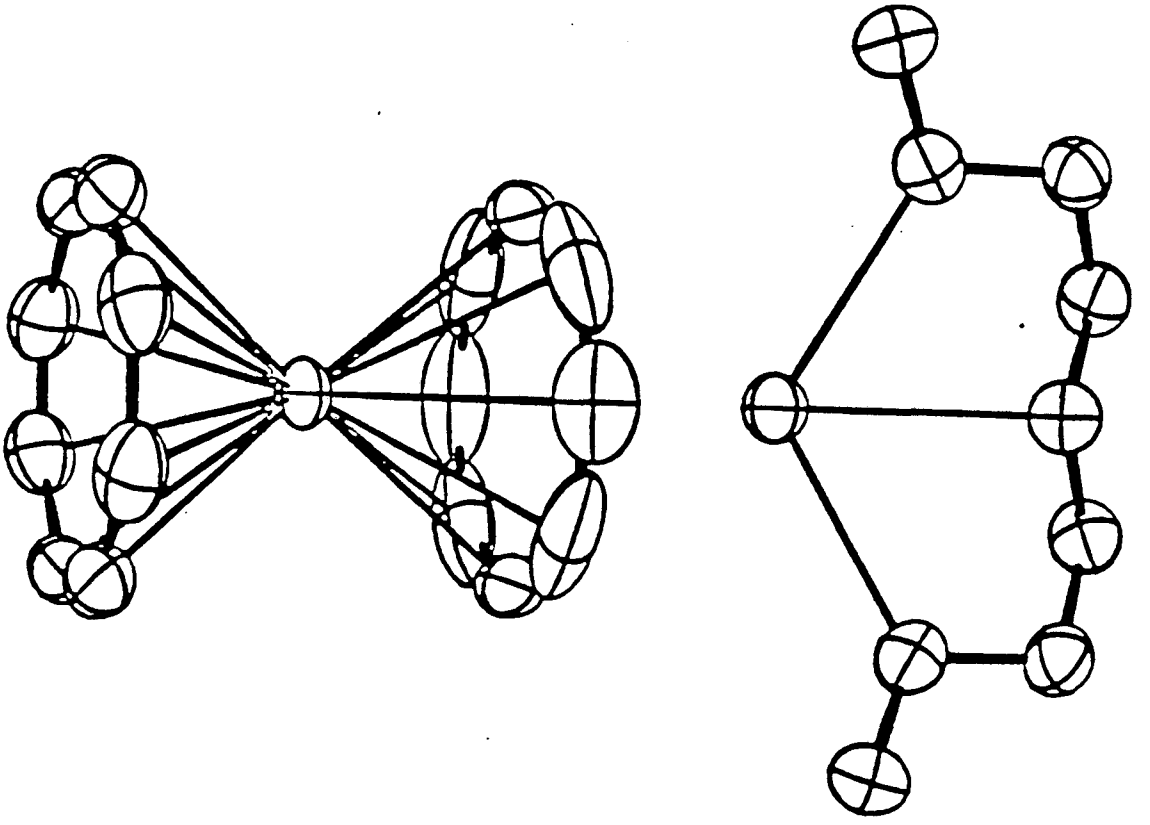


Figure 3.3: Structure of $[K(C_6H_{14}O_3)][Ce(C_8H_8)_2]$.

Recently, the structures of $K[Yb(C_8H_8)_2]$[12] and $K_2[Yb(C_8H_8)_2]$[13] have been solved and they show essentially the same structural features as their cerium counterpart (see Figure 3.4). The Yb(III) complex shows the difference in metal-ring distances seen in the cerium(III) case, whereas the Yb(II) is, of course, symmetric.

The symmetry of the $[Yb(C_8H_8)_2]$ dianion is D_{8h}; the carbons of the [8]annulene rings are eclipsed in this molecule.

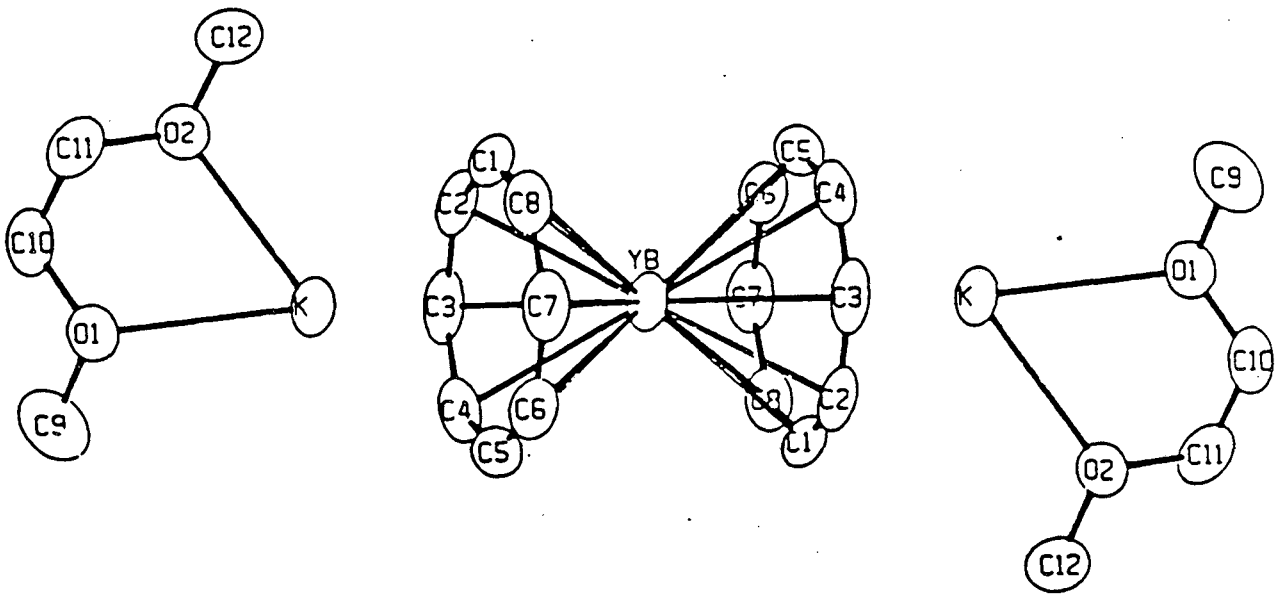


Figure 3.4: Structure of $[K(C_4H_{10}O_2)]_2[Yb(C_8H_8)_2]$.

Quite a number of substituted derivatives of these complexes have been prepared and studied crystallographically, and some of these are of particular interest to this discussion. In the structure of $K_2[Yb(t\text{-}BuC_8H_7)_2]$, shown in Figure 3.5, the two t-butyl groups seem to have at most a minimal effect on the metal-ring distance, with the distance being 2.03 Å in the unsubstituted case versus 2.05 Å for the t-butyl derivative.[14] The central carbon of each tertiary butyl group is nearly in the plane of the COT ring, with the pendant methyl groups arranged as shown in the diagram. The

top view of this molecule, which was the first of the bis(alkyl[8]annulene) sandwich compounds to be examined by X-ray diffraction, shows an interesting arrangement of the substituents. The relative orientation of the annulene rings is such that the t-butyl groups are close to each other, with the nearest approach of two carbons being the two in-plane methyl carbons, C12 and C24, which are 4.21 Å apart. No explanation for this effect was immediately obvious; crystal packing effects or some sort of van der Waals attraction are possible considerations.

Recently, Dave Eisenberg of this group prepared the elusive uranium(III) analog to $K[Ln(C_8H_8)_2]$ and obtained crystals of its dimethyl derivative.[12] The structure of this molecule was solved and is shown in Figure 3.6 and it shows several of the interesting features which have been seen in other structures. First of all, the compound shows the now familiar difference in metal-carbon bond lengths for the two rings. Secondly, the methyl groups seem to prefer the pseudo-cis arrangement as in the Yb case just mentioned. Finally, the methyl groups are bent in towards the metal center. This feature had been seen once before in one of the first alkyl-substituted structures solved, that of 1,1',3,3',5,5',7,7'-octamethyluranocene.

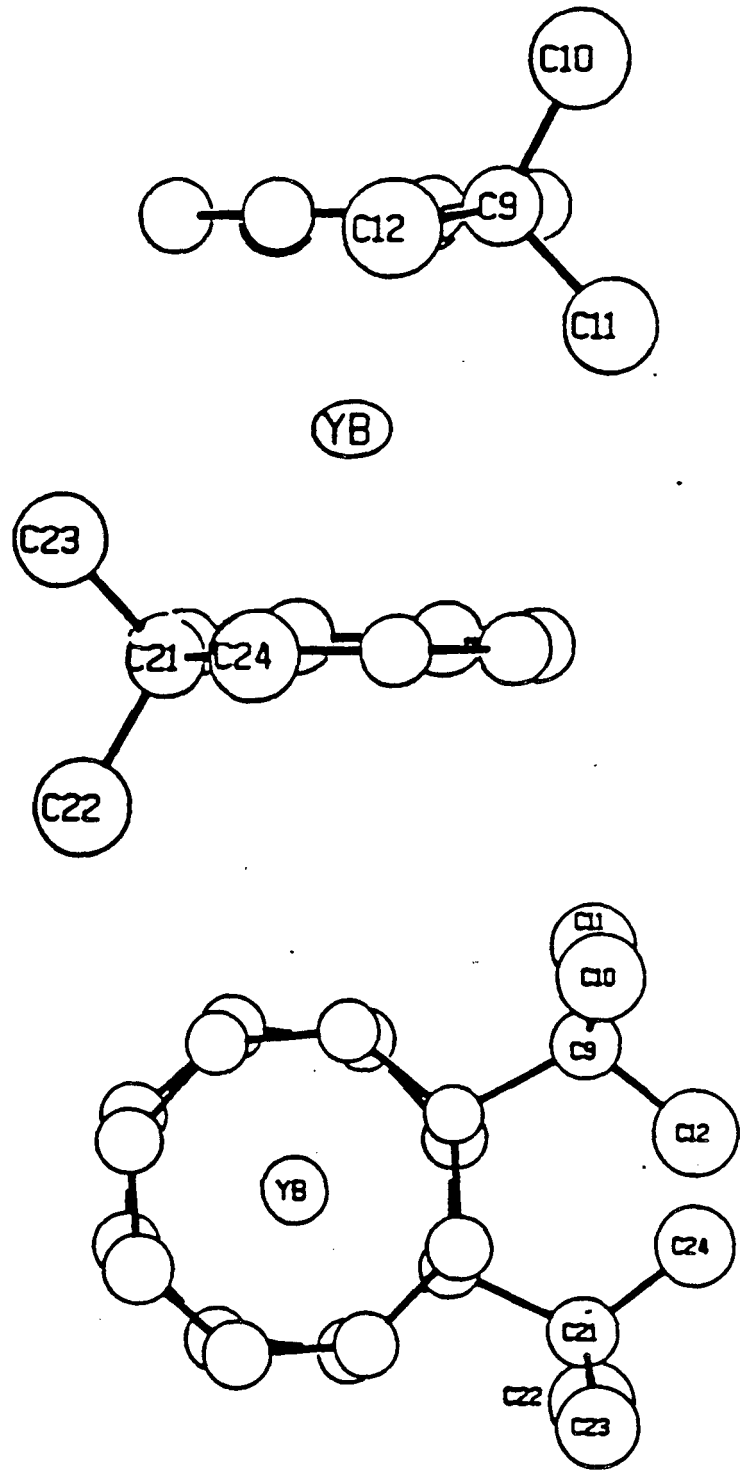


Figure 3.5: Side and Top View of [Yb(t-BuC_8H_7)$_2$] Dianion.

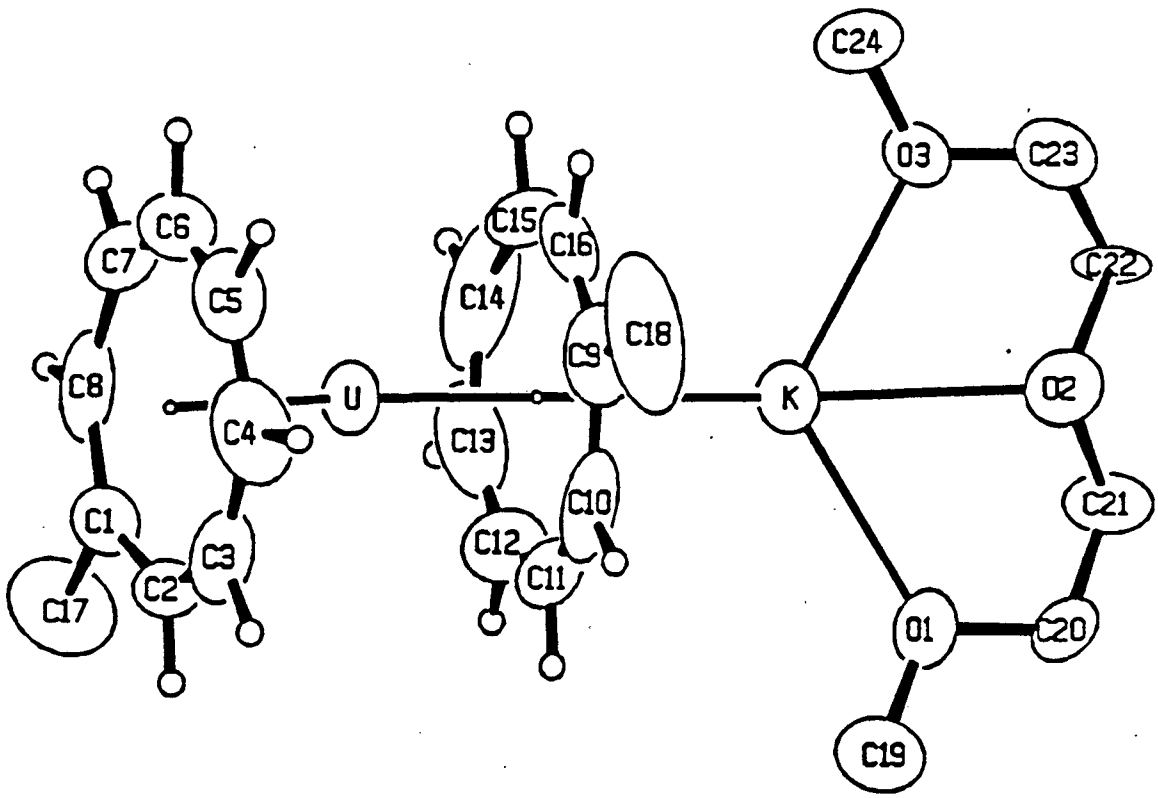


Figure 3.6: Structure of $[K(C_6H_{14}O_3)][U(MeC_8H_7)_2]$.

The crystal structure of bis(1,3,5,7-tetramethylcyclooctatetraene) uranium (IV) is shown in Figure 3.7, and it shows a number of interesting features.[15] The compound crystallized as a single crystal containing two rotomeric forms of the molecule, one in which the methyl groups (as well as the ring carbons) are nearly eclipsed, and one in which they are nearly staggered. This is consistent with the range of configurations observed thus far; there really appears to be little favoritism of one configuration over the other.

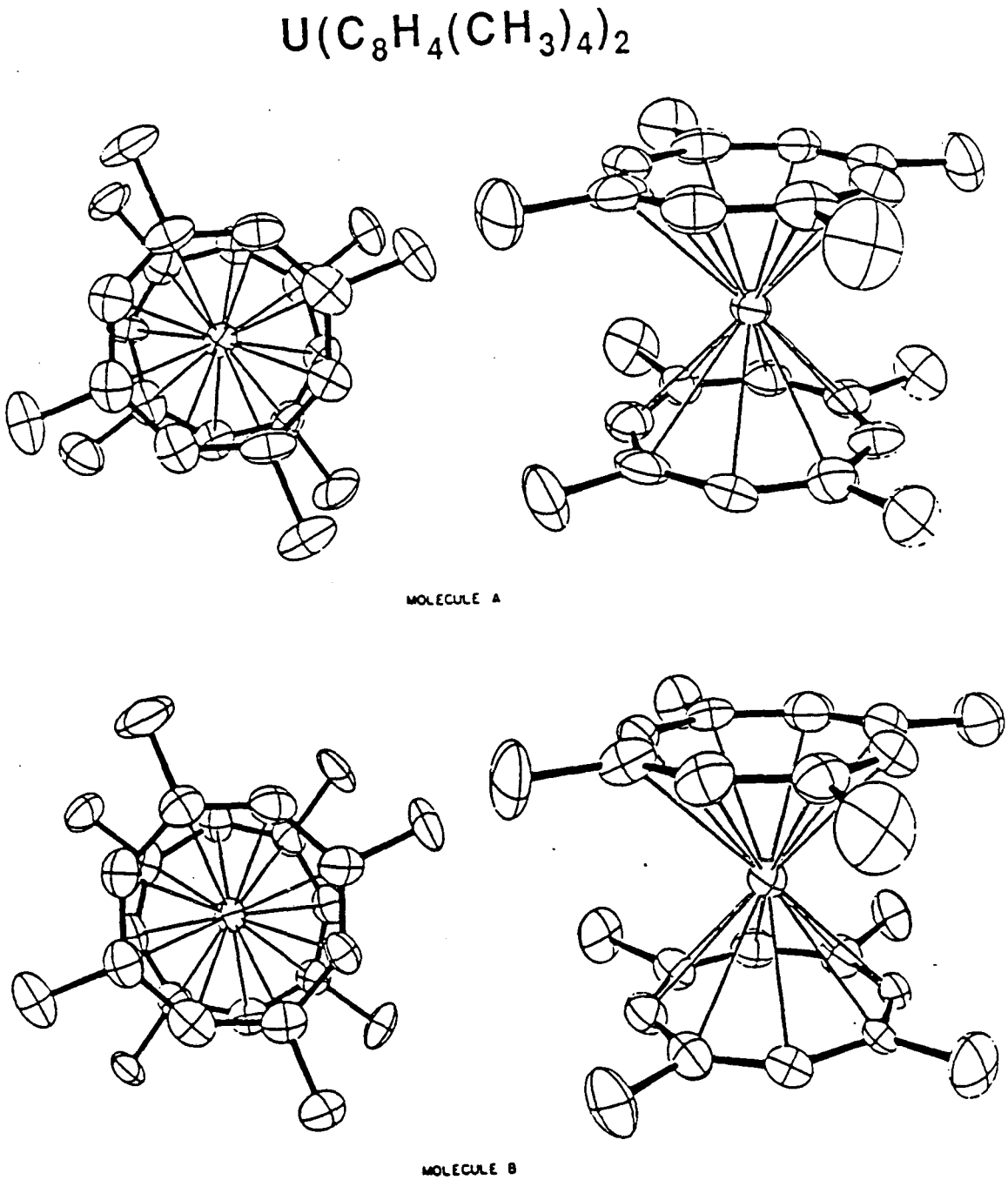
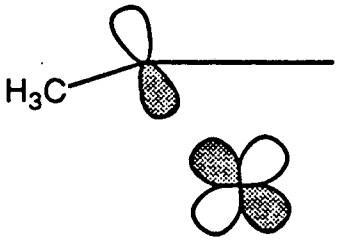


Figure 3.7: Structure of $U(Me_4C_8H_4)_2$.

Another curious feature of this structure is that all eight methyl groups on each of the two rotomeric molecules are bent in from the plane of the ring, towards the metal center. The bending angle varies from methyl group to methyl group, but averages about 4°. The x-ray diffraction powder patterns of the other actinide sandwich compounds prepared and studied to this point (Pa, Np, and Pu) have been obtained, and comparison with the calculated powder pattern of $U(TMCOT)_2$ suggests that these compounds are isostructural.[16] This is in contrast to the cyclopentadienyl compounds of such metals, which tend to show a bending of substituent groups away from the center of the molecules.[17]

A number of different explanations have been proposed to explain this bending phenomenon, which actually causes the methyl groups to approach within their Van der Waals contact distance.[18] Among these possibilities is the argument that the p-orbitals of the rings are rehybridizing to achieve better overlap with the metal orbitals (see diagram below, in one dimension). One can think up alternative explanations for this bending, but the fact that it has now been seen in two different compounds , as well as in the two forms of another compound suggest that this may be due to more than simple crystal packing effects.



There is currently a substantial range of crystal structures for this class of compounds in various different oxidation states and with varying ligands. The one

notable exception is the structure of a bis[8]annulene lanthanide (IV) sandwich, which should be the closest analogy to uranocene of any of the lanthanides. Now with the development of a good synthesis of bis[8]annulenecerium(IV) and its substituted derivatives, it is possible to add in this final needed structure.

RESULTS AND DISCUSSION

Greco, Cesca and Bertolini, in their original report of the synthesis of cerocene,[19] reported preliminary crystal data for this compound, but a full structure has never appeared in the literature. Their x-ray data suggested that bis[8]annulenecerium(IV) is isostructural with its uranium(IV) analog, as one would expect on the basis of the other work done in this field. However, it was important to obtain a fully solved structure of this complex, as cerium(IV) organometallic structures are unprecedented in the literature, and if there were significant differences between the lanthanides and the actinides in this system, it could show up in structural features.

Obtaining single crystals suitable for x-ray diffraction studies, however, proved to be quite difficult. Due to the typical poor solubility encountered with many of these compounds, solution methods of recrystallization were unsuitable. Sublimation was tried, but also proved unsuitable, resulting in only a small amount of poor crystalline material with significant amounts of decomposition. Although we thought that the unsubstituted structure would be preferable, it seemed that attempting to crystallize a substituted derivative might prove to be more successful. In the other substituted structures performed, the substituents seemed to have little effect on the

gross, overall structure; their major effects were mostly confined to properties involving the substituents themselves.

Initially, attempts were made to obtain crystals of di-t-butylcerocene, since in its preparation, the powder obtained appeared to be microcrystalline. In addition, the comparison with the t-butyl substituted ytterbium species was desirable, since the structure of the methyl substituted uranium (III) complex had not been obtained at that time. However, repeated attempts to crystallize this material resulted in plates that were too thin to be of use for a crystal structure.

The next ligand tried was methylcyclooctatetraene, prepared by literature methods.[20] Several attempts at the slow cooling of solutions of this sandwich compound resulted in crystals of near x-ray quality, and finally, good crystals were grown out of the slow cooling of a concentrated solution of the dimethylcerocene in hexane with a trace of toluene, and the structure of one of these crystals was solved by A. Zalkin.

The ORTEP drawing and the atomic numbering scheme for $(CH_3C_8H_7)_2Ce(IV)$ is given in Figure 3.8.[12] The crystallographic summary and data processing are included in the Experimental Section as Table 3.1, and selected interatomic distances and angles are given in Tables 3.2 and 3.3. The positional parameters are listed in Table 3.4.

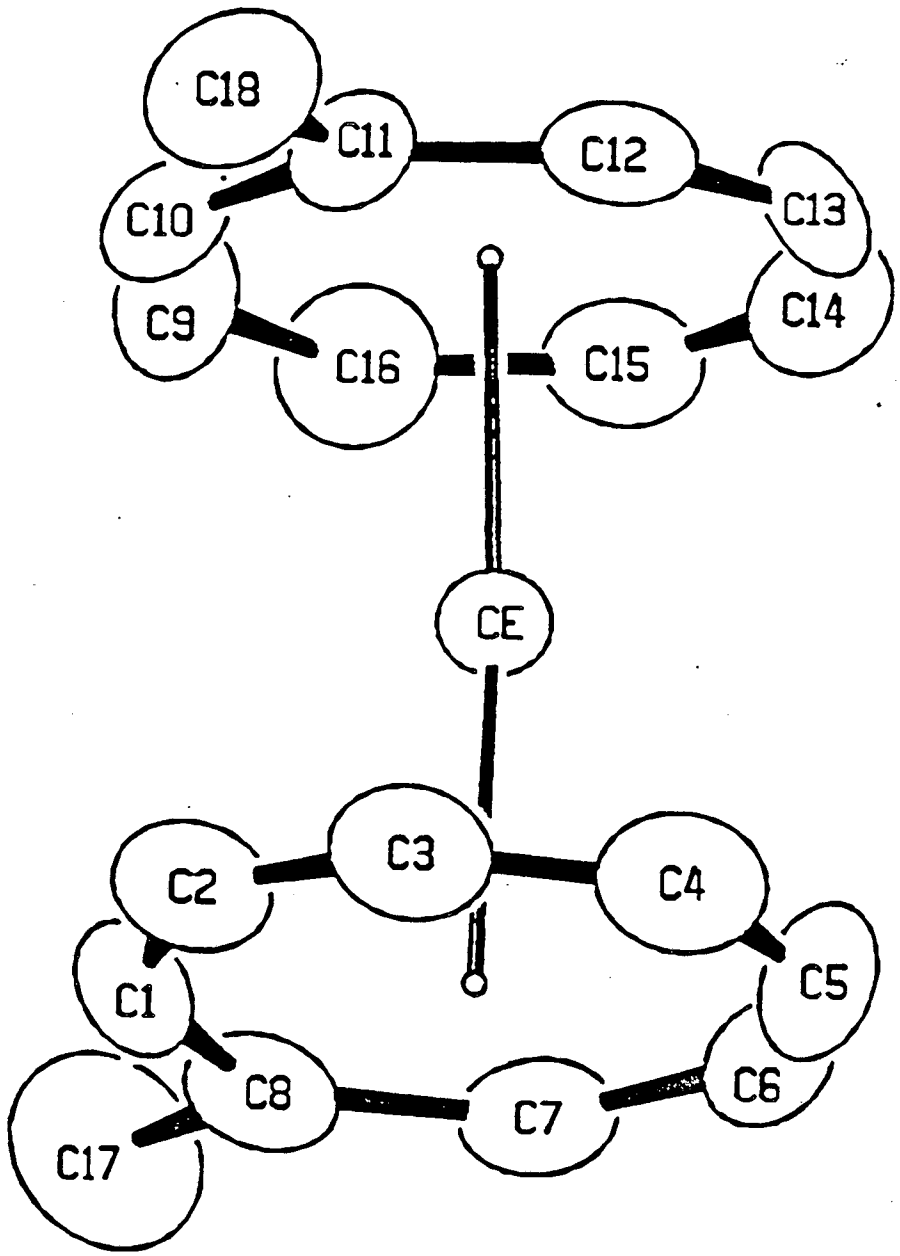


Figure 3.8: ORTEP and Numbering Scheme for $Ce(MeC_8H_7)_2$.

The cerium atom is located between the two [8]annulene rings at distances of 1.975 and 1.971 Å from the two ring centroids. Within the statistical error, it can be said that the metal atom lies midway between the two ligand rings. This is what is expected for the more symmetric M(IV) structure, as opposed to the M(III) structures with a coordinating potassium on one of the rings. The two rings are both nearly planes; a list of the distances of selected atoms from the least squares planes is included in Table 3.5. It can be seen that only four of the atoms lie off the planes by more than their statistical limits. The C-C bond lengths are nearly equivalent, averaging 1.399 Å in ring 1 and 1.405 Å in ring 2. The C-C-C angles are also quite similar, as shown in Table 3.3, although there appears to be some distortion in the angles involving ring carbons bonded to the methyl substituents.

Table 3.2

Selected Interatomic Distances

Ce - Ct1[a]	1.975
Ce - Ct2	1.971
Ce - C1	2.671(5)
Ce - C2	2.671(6)
Ce - C3	2.699(6)
Ce - C4	2.695(6)
Ce - C5	2.699(7)
Ce - C6	2.692(6)
Ce - C7	2.697(6)
Ce - C8	2.705(7)
Ce - C9	2.703(6)
Ce - C10	2.688(5)
Ce - C11	2.711(6)
Ce - C12	2.682(7)
Ce - C13	2.676(6)
Ce - C14	2.681(6)
Ce - C15	2.700(7)
Ce - C16	2.707(7)

[a] Ct represents the centroid of the atoms in the cyclooctatetraene rings.

Table 3.3

Selected Angles

Ct1	-Ce	-Ct2	176.03
C2	-C1	-C8	135.93
C1	-C2	-C3	135.21
C2	-C3	-C4	135.04
C3	-C4	-C5	134.47
C4	-C5	-C6	136.20
C5	-C6	-C7	134.06
C6	-C7	-C8	136.54
C1	-C8	-C7	132.41
C1	-C8	-C17	113.24
C7	-C8	-C17	114.32
C10	-C9	-C16	135.55
C9	-C10	-C11	138.00
C10	-C11	-C12	130.71
C11	-C12	-C13	135.90
C12	-C13	-C14	135.89
C13	-C14	-C15	134.01
C14	-C15	-C16	135.90
C9	-C16	-C15	133.94
C10	-C11	-C18	114.54
C12	-C11	-C18	114.71

Table 3.4

Positional Parameters with Estimated Standard Deviations[a]

Atom	x	y	z
Ce	0.00726 (2)	0.02994 (2)	0.12506 (3)
C1	0.0138 (8)	0.0539 (4)	-0.1699 (5)
C2	0.0212 (7)	-0.0430 (4)	-0.1481 (7)
C3	0.0892 (6)	-0.1019 (5)	-0.0615 (8)
C4	0.1752 (6)	-0.0887 (5)	0.0444 (8)
C5	0.2318 (5)	-0.0114 (7)	0.1007 (10)
C6	0.2249 (5)	0.0854 (6)	0.0824 (9)
C7	0.1596 (6)	0.1440 (5)	-0.0086 (7)
C8	0.0702 (5)	0.1330 (4)	-0.1138 (9)
C9	-0.2106 (5)	0.0917 (6)	0.1468 (10)
C10	-0.2182 (4)	-0.0057 (6)	0.1391 (10)
C11	-0.1662 (5)	-0.0847 (5)	0.2075 (7)
C12	-0.0836 (5)	-0.0903 (6)	0.3211 (7)
C13	-0.0198 (5)	-0.0255 (8)	0.4075 (6)
C14	-0.0102 (8)	0.0725 (7)	0.4150 (6)
C15	-0.0649 (6)	0.1463 (7)	0.3424 (10)
C16	-0.1472 (6)	0.1550 (5)	0.2286 (9)
C17	0.0232 (10)	0.2247 (6)	-0.1754 (10)
C18	-0.2026 (6)	-0.1773 (6)	0.1438 (13)

[a] Estimated standard deviations are indicated in parentheses.

Table 3.5

Distance to the Least-Square Plane of the Rings

Ring 1		Ring 2	
Atom	Dist.(Å)	Atom	Dist.(Å)
C1	-0.010(11)	C9	0.006(11)
C2	-0.008(10)	C10	0.010(11)
C3	0.015(9)	C11	-0.010(9)
C4	-0.008(9)	C12	0.002(10)
C5	0.004(12)	C13	0.012(13)
C6	-0.016(11)	C14	-0.009(12)
C7	0.011(8)	C15	0.008(11)
C8	0.001(10)	C16	-0.009(10)

The top view of the molecule (Figure 3.9) shows that the relative orientation of the two rings is between eclipsed and staggered; once again, this property does not seem to be controlled by any overriding forces. It is also apparent that, much as in the case of the $K_2[Yb(t\text{-}BuC_8H_7)_2]$ and $K[U(MeC_8H_7)_2]$, the rings are not oriented such as to place the methyl groups on opposite sides of the molecule, in a "trans" type of arrangement. The angle between the two substituents is more on the order of 120°, as opposed to the 180° in the case of this trans arrangement. The methyl groups do not approach each other as closely as in the Yb case (4.21 Å); their nearest approach is greater than 6.0 Å. The closest approach of the methyl carbon to a ring carbon on the other ring is 4.025 Å (C18-C3), so it seems unlikely that there is much interaction

between a methyl group and the opposite ring. However, Lyttle of this group did observe some ^{1}H NMR evidence which suggested that in bis(mesityl[8]annulene)uranium(IV), there was a preference for the two mesityl groups to approach each other in solution.[21] The much larger size of the mesityl groups relative to the methyl groups in this case would, of course, make it easier for these groups to get within their Van der Waals distance and thus feel some attraction. But if this is a real phenomenon, the long-distance attraction felt by these methyl groups may be enough to give a slight preference for this configuration.

The structure shows several other interesting features. Although it does not show up well in the ORTEP drawing, the methyl groups on bis(methyl[8]annulene)cerium(IV) are bent in towards the metal center. In the case of Ring 1, the carbon atom (C17) lies 0.05 Å off the plane, and in the other ring,the carbon (C18) is about 0.11 Å displaced. This would correspond to bending angles of roughly 1.9 and 4.2 degrees, respectively (see Figure 3.10, not drawn to scale).Of course, calculations of this sort are difficult to make precisely due to the effect of problems such as polarization, but they should suffice for this discussion. One possible explanation for this bending was presented above, but there are clearly alternative explanations which could be proposed. For instance, the C18-Ce distance is 3.854 Å, so it might be possible that there is some long-range attraction between the two. Perhaps some of the negative charge of the dianion ring is polarized into the methyl group, and this slight buildup of electron density is enough to make for a slight coulombic attraction between the two atoms. Also, although statistically it is impossible to draw any firm conclusions from the data, if one examines the positions of the hydrogens on the rings, it can be seen that they are also displaced towards the metal.(Table 3.6). Again, they are all within their standard deviation of being coplanar

with the ring so not too much can be read into this, but it is curious that they show the same effect, and it makes it of

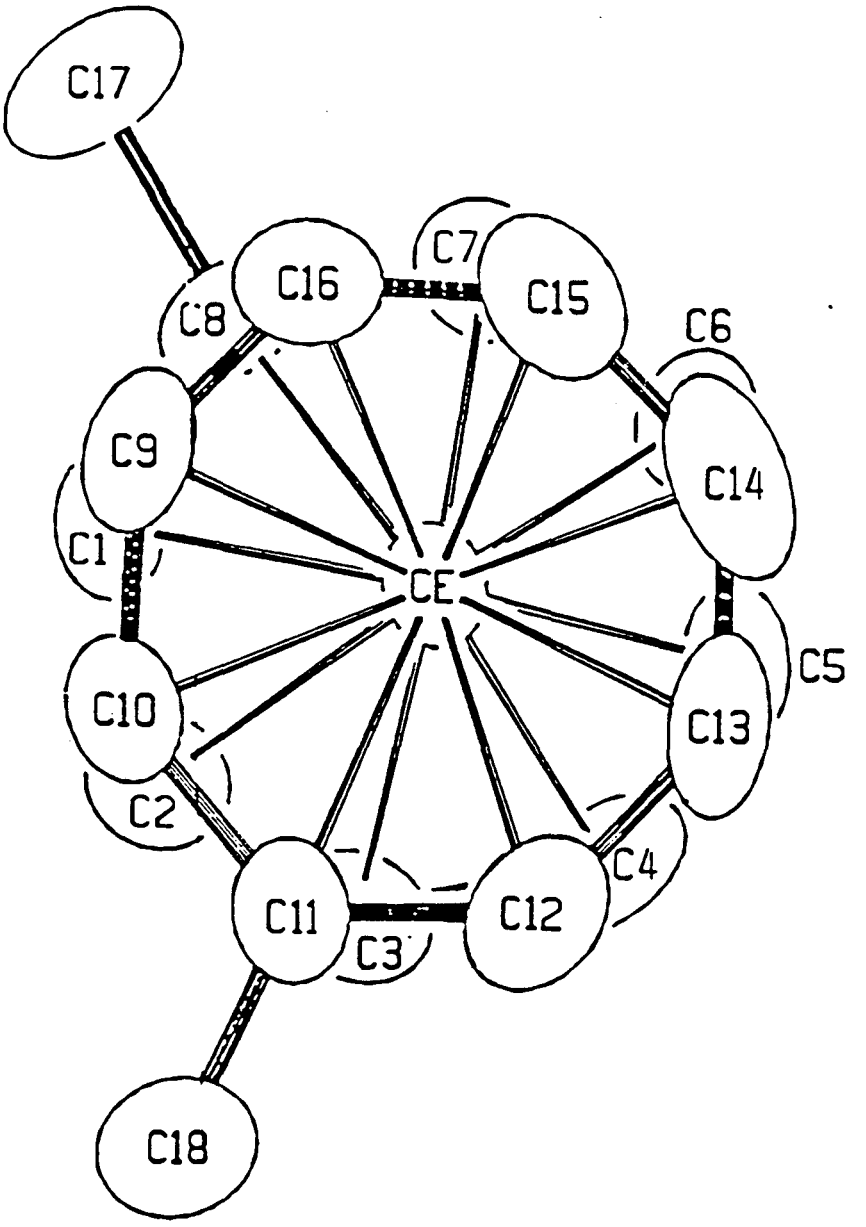


Figure 3.9: Top View of $Ce(MeC_8H_7)_2$.

great interest to solve a structure of one of these compounds of high enough quality to locate the hydrogens accurately.

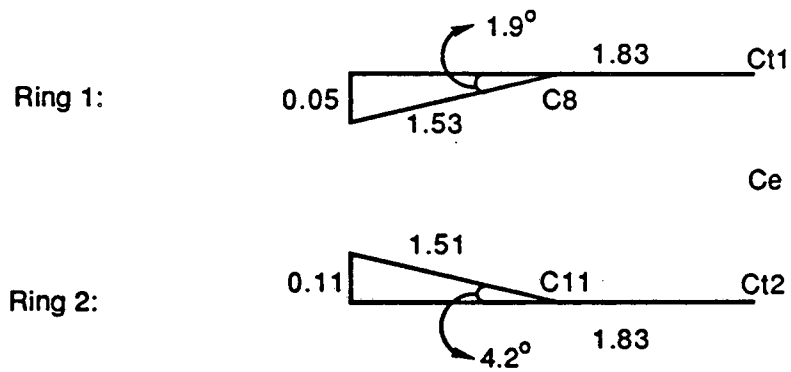


Figure 3.10

Table 3.6

Distance of Hydrogens to the Least-Square Plane of the Rings

Ring 1		Ring 2	
Atom	Dist.(Å)	Atom	Dist.(Å)
H1	-0.097(65)	H8	-0.056(69)
H2	-0.005(59)	H9	0.080(84)
H3	-0.185(65)	H10	0.044(72)
H4	-0.051(70)	H11	-0.066(63)
H5	-0.031(83)	H12	-0.106(70)
H6	-0.046(62)	H13	-0.216(70)
H7	-0.18(66)	H14	-0.068(67)

Another feature of interest is the Ct1-Ce-Ct2 angle of 176.03°. This bending of the molecule is quite unusual and unexpected for this class of molecule. Generally, only a slight deviation from parallel planar rings has been seen before for compounds of this type, although Kinsley did see a deviation of 2.7° in his structure of $K_2[Yb(t\text{-}BuC_8H_7)_2]$.[14] Recently, a bending on the order of 4° was observed in the structure of $K[U(MeC_8H_7)_2]$.[12]

What makes this tilting of the rings especially intriguing is its direction. On first inspection, one might expect that the bending would serve to reduce any sort of unfavorable steric interactions between one methyl group and the other, or with the other ring. However, the long distances between the groups as mentioned above would suggest that this is not necessary, and in fact if one looks at the data closely, it is clear that the bending is actually in a direction which would bring the two groups closer together. The closest approaches of ring carbons are shown in Table 3.7. It is clear that the closest approach by the rings is at C2-C10 (3.84 Å) and C3-C11 (3.85 Å), rather than at about C5-C13 or C6-C14, if it were increasing the separation of the methyl groups.

Table 3.7
Distances between ring carbons

C1 -C9	3.905
C2 -C10	3.843
C3 -C11	3.849
C4 -C12	3.915
C5 -C13	4.034
C6 -C14	4.063
C7 -C15	4.101
C8 -C16	4.001

If this is not being caused by some steric interaction within the molecule, it is possible that there is some unfavorable interaction between different molecules which is forcing the compound into this configuration. Examination of the packing diagrams for this crystal; however, are inconclusive. It has been impossible to obtain a view of the crystal packing which can show any sort of clear influence by neighboring molecules. An obvious possibility would be that the methyl groups from an adjacent molecule are oriented such that the rings will be spread apart. However, although we were unable to prepare packing diagrams which could show this sort of interaction clearly, this does not appear to be the case from examination of the poor quality packing diagrams obtained.

If one examines a listing of the long-range interactions (up to 6.0 Å for C-C) there again does not appear to be any significant interactions between molecules which could explain this bending. For example, C5 is 3.67 Å from a C1 on a neighboring molecule and 3.75 Å from that molecule's C2. However, C5's counterpart on the other ring, C13, does not show this closeness, with the distance being over 6.0 Å. This would suggest that the second molecule is not in between the rings, but rather on top of one, and if there were some sort of steric interaction, it would probably serve to push the two rings closer together at these carbons. There are other examples of this sort, as well as a few which do suggest the bending observed, but there really is no conclusive evidence from this source.

Part of the problem may derive from the definition of the centroid. For instance, if the ring is slightly skewed in one direction, the centroid of one ring could be shifted and thus the Ct-Ce-Ct angle would not be 180°. This sort of explanation is supported to some extent if one examines the trends in C-Ce bond lengths. There should be a tendency for the bond lengths for the part of the ring that is squeezed

together to be somewhat shorter than those on the other side. However, if one examines a diagram of the bond length for each position, as shown in Figure 3.11, the trends are not there. The average C-Ce bond length is 2.69 ± 0.01, and it can be seen that 11 of the 16 ring carbons fall within this range. The pattern of the 5 lengths which fall out of this range (shown in boldface), however, show no trend which can be rationalized as a result of this bending. Further, if one performs a rough calculation of what the C-Ce bond length should be, allowing for the 4° bending, one obtains a value of about 2.74 Å, which is clearly much more than the deviations observed. Thus, although there is the possibility that steric interactions are playing at least a minor role in the bending, the inconsistency with the C-Ce bond lengths would suggest that this phenomenon may for the most part an artifact of the calculations, with no real structural implications.

Basically, the structure of the dimethylcerocene proves to be what is expected for this class of molecule. The average M - C bond length here is 0.045 Å longer than in $U(C_8H_8)_2$, and 0.034 Å longer than in $U(MeC_8H_7)_2$, although there the ionic radius for Ce(IV) in a 10-coordinate species is expected to be .01 Å shorter than that of U(IV).[12] However, the bond length is identical with that of thorocene, within the standard deviation, even though the thorium ionic radius is 0.06 Å larger. We believe this discrepancy may be due to a problem with defining the ionic radii of these metals in the various coordination numbers. In the trivalent metals, the cerium radius is 0.03 Å larger than the uranium; if a similar trend in size held for the tetravalent radii, then all the M - C distances mentioned above would be basically within their standard deviations. Part of this problem may be due to the problems with trying to compare data obtained from crystal structures of organometallic species with data obtained primarily from oxides and fluorides;[7b] coordination number corrections derived from

the latter data may not be completely applicable to structures of the former. A more detailed discussion of this can be found in reference 12.

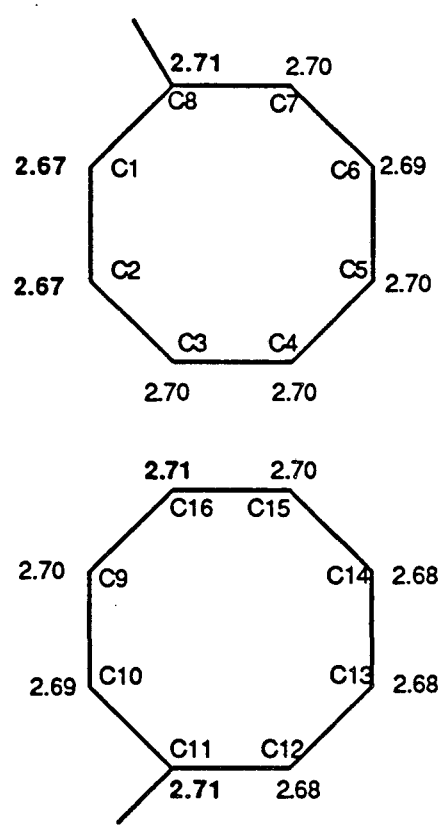


Figure 3.11

EXPERIMENTAL

X - RAY DIFFRACTION

The crystal structure of $Ce(CH_3C_8H_7)_2$ was solved by Dr. Allan Zalkin of the Lawrence Berkeley Laboratory. With the exception of ORTEP,[22] all computer programs were written by A. Zalkin; scattering factors and anomalous dispersion terms were taken from International Tables.[23]

The black, air-sensitive crystals of $Ce(CH_3C_8H_7)_2$ were sealed inside quartz capillaries in an argon glovebox. A modified Picker FACS-I automated diffractometer equipped with a graphite monochromator and a Mo x-ray tube (l ($K\alpha_1$) 0.70930 Å) was used to collect sets of θ - 2θ scanned x-ray diffraction intensities; the experimental details are given in Table X. The metal atom positions were deduced from three dimensional Patterson functions, and after least-squares refinement of the metal atom, the carbon atoms were located from subsequent Fourier maps. The positional and anisotropic thermal parameters of all of the non-hydrogen atoms were adjusted with the use of a full-matrix least squares refinement procedure. Hydrogen atom parameters were included with isotropic thermal parameters, but not all of them could be refined. The positional parameters of the hydrogen atoms were refined with

imposed distance restraints (C-H 0.95 $\pm$ 0.02; methyl H-H 1.51 $\pm$ 0.05);[24] isotropic thermal parameters were assigned to the hydrogen atoms globally for each ring and methyl group. The results of the least-squares refinements are given in Table 1. The least squares refinement to a conventional R factor of 0.029 gave a = 11.690(3), b = 14.315(3), c = 8.977(2)Å , at 23°C. For Z = 4 the calculated density if 1.664 g/cm^3.The crystals were orthorhombic, $P2_12_12_1$.

Table 3.1

Crystallographic Summary and Data Processing

	$(MeCOT)_2Ce$
a, Å [a]	1.690(3)
b, Å	4.315(3)
c, Å	8.977(2)
cryst syst	orthorhombic
space group	$P2_12_12_1$
volume, $Å^3$	1502.2
d(calcd), g/cm^{-3}	1.664
Z	4
temp (°C)	23
empirical formula	$C_{18}H_{20}Ce$
f(000)	744
fw	376.48
color	black
crystal size	0.21 x 0.20 x 0.14
abs coeff, cm^{-1}	30.63
abs corr range	1.68 - 1.95
sin θ/λ, min, max	0.06, 0.65
hkl limits, $\pm h \pm k \pm l$	0,15; 0,18; ± 11
scan width, °2θ	$1.50 + 0.693\tan\theta$
no. of standards	3
no. reflections between stds	250
standards corr range	0.97 - 1.02

no. scan data	3755
no. unique reflections	3468
no. non-zero wtd data	2794 ($F^2>2\sigma$)
p[b]	0.035
extinction k[c]	1.73×10^{-7}
max % extinction corr	19.5%
no. parameters	263
R (non-zero wtd data)[d]	0.029
R_w[e]	0.030
R (all data)	0.047
Goodness of fit[f]	1.01
max shift/esd	0.006
max/min, diff map (e/Å^3)	1.66, -0.55

(a) Unit cell parameters were derived by a least-squares fit to the setting angles of the unresolved Mo Kα components of 19 reflections ($25<2\theta<37$).

(b) In the least-squares, the assigned weight $w = 4F^2[\sigma^2(F^2) + (pF^2)^2]^{-1}$. F^2 is the observed structure amplitude and p is an assigned value that adjusts the weighted residuals of the strong reflections to be comparable to the weak ones.

(c) Simple extinction correction has the form $(Fobs)corr = (1 + kI)Fobs$, where I is the uncorrected intensity and Fobs is the observed scattering amplitude.

(d) $R = \Sigma|(Fobs - Fcal)| / \Sigma|Fobs|$

(e) $R_w = \sqrt{\{\Sigma[w(|Fobs| - |Fcal|)]^2 / \Sigma(w\, Fobs^2)\}}$

(f) σ_1 = error in observation of unit weight = $\sqrt{\{\Sigma w[|Fobs| - |Fcal|]^2 / (no - nv)\}}$, where no is the number of observations and nv is the number of variables.

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CHAPTER IV:

ELECTROCHEMISTRY OF CEROCENE

Introduction

Organometallic chemists have borrowed many different tools from the various fields of chemistry, and modified them to yield quite useful information about sometimes quite unusual systems. The improvement of NMR techniques over the years has not only greatly aided organic chemists, but has allowed a much deeper understanding of many facets of organometallic chemistry as well. Physical chemical techniques such as photoelectron spectroscopy have allowed organometallic chemists to gain a better understanding of the modes of bonding in these complexes, especially when combined with high level calculational results.

One field which is rapidly becoming important to organometallic chemists is electrochemistry.[1] This is a potentially very useful technique for this type of work; the metals used are generally available in different oxidation states, and being able to compare the redox properties as , for example, ligands are changed, can be quite informative. Quite often the species are stable in these different oxidation states, and examining relative stabilities of the different oxidation states while varying the ligand field is often quite useful.

The electrochemistry of a wide range of organic species has also been examined.[2] In some respects, the suitability of this technique for organic molecules is more limited, in that different oxidation states of organic molecules are generally more unstable and often will react further after the electron transfer. However, this property can make this a useful preparative technique, if the subsequent reactions are understood and controllable.

Electrochemistry of Cyclooctatetraene

One organic compound whose different oxidation states are stable enough to be studied electrochemically and which is of interest to this thesis is cyclooctatetraene and many of its substituted derivatives. The electrochemical reduction of cyclooctatetraene has been studied for many years, beginning in 1949 with Elofsen's polarographic work in aqueous ethanol.[3] This work, as well as subsequent work in 96% dioxane-water showed that the reduction was a two-electron process.[4] This reduction was later shown to proceed by two one-electron steps, when the process was studied in anhydrous dimethylformamide solution.[5]

The rate of the electron transfer process in these compounds has been studied and this work revealed that the first electron transfer step proceeds slowly, while the second proceeds rapidly.[5,6] One explanation put forth to explain this is that the first step requires the transformation of the tub-shaped neutral molecule to the planar state for the radical anion produced by the electron transfer, which should be energetically demanding and have an activation barrier (see Figure 4.1). Once the ring is in the

planar form of the the radical anion, however, there is no similar barrier for the transfer of the second electron, which can proceed more rapidly.

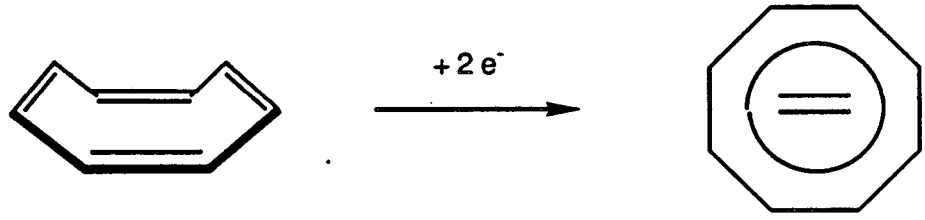

Figure 4.1

One of the leaders in the field of cyclooctatetraene chemistry has been Paquette of Ohio State University, and many of his publications have included electrochemical studies on his compounds. He has been interested in the radical anion, dianion and cation as well as the neutral molecules themselves. A few of his interesting results will be mentioned here, although this is by no means meant to be an exhaustive review.[7]

Perhaps the most interesting of his studies involved a systematic examination of a series of dimethyl substituted COT's.[8] Work had been done previously towards examining the electrochemical behavior of a broad range of substituted COT's, including methoxy-, benzo-, dibenzo-, and 1,3,5,7- and 1,2,4,7-tetraphenylcyclooctatetraene.[9] However, conditions used for these measurements varied a great deal, so a comparison of these results is not particularly meaningful. Paquette's series of Me_2COT's has the added advantage of using the same substituents, which should allow for a direct evaluation of the effect of the substitution pattern , rather than the type of substituent.

Using standard polarographic techniques under rigorously water and oxygen free conditions, he measured the half-wave potentials as shown in Table 4.1.[8] These values refer to the first electron transfer; the second waves are at significantly more negative values (~-3.0 V). The potentials for both sets of waves are all cathodic of COT itself, due in part to the inductive effects of the methyl groups. Further, if one plots the potential vs. the distance between the groups, it is evident that there exists a linear relationship. One rationale presented for this curious effect is based on a steric argument. The most cathodic of the reductions is in the case of the 1,2-dimethylcyclooctatetraene, which would be expected to have the most severe methyl-methyl interaction upon ring flattening. This effect however, should be diminished enough by the time the groups are as separated as in the 1,4- and 1,5- isomers as to be relatively unimportant. The difference observed in this case was explained by examining the orientations with which the molecules can interact with the electrode surface; the 1,5- isomer has a face free of substituents, whereas it is necessary for the 1,4- to approach with a methyl group sticking towards the surface. Although this explanation is mostly speculation, there is evidence of irreversibility for the first electron transfer step in all these cases, and the CV of the 1,5-isomer at low temperatures showed no evidence for formation of a reoxidizable product.

Table 4.1

Reduction Potentials of Isomers of Me_2COT

(THF solution, Volts vs SCE)

Compd.	$E_{1/2}$
1,2-Me_2COT	-2.33
1,3-Me_2COT	-2.255
1,4-Me_2COT	-2.227
1,5-Me_2COT	-2.145
MeCOT	-2.120
COT	-1.98

Taggart did a related study, examining a number of differently substituted compounds ranging from tetramethyl- to unsubstituted cyclooctatetraene in hexamethylphosphoramide solution, again free of water and oxygen.[10] These results are shown in Table 4.2, and this clearly shows the trends one would expect ; the most highly substituted rings, which should be the most difficult to flatten, are the most difficult to reduce.

Table 4.2

Reduction Potentials of Substituted COT's

(HMPA Solution, V vs SCE)

Compd	$E_{1/2}$	$\Delta E_{1/2}$
COT	-1.61	
MeCOT	-1.73	0.12
1,2 - Me_2COT	-1.95	0.22
1,2,3 - Me_3COT	-2.20	0.25
1,2,3,4 - Me_4COT	-2.54	0.34

Organometallic Electrochemistry

In the field of organometallic electrochemistry, there has been a fair amount of work done in order to examine a number of different properties. Although there are studies reported from as far back as 1949, most of the work in this area has been done in the last twenty years. One of the most productive of these researchers, R.E. Dessy, published a large series of articles in the mid-1960's. A brief discussion of some of the types of experiments performed by this group will give a good perspective on the types of studies that can be done with these compounds.

Dessy's earliest work was with a series of organometallic species of the Group IV-B metals, concentrating on tin and lead.[11] They were able to examine and identify a

number of the reactive intermediates in reactions of these metal compounds, producing species of the type $Ph_3M\cdot$. The next topic examined, by contrast, focussed on carbanion stabilities in transmetallation reactions of metals such as Li, Mg, and Hg.[12] He determined a correlation between the $E_{1/2}$ value for the process shown in Eq. [4.1] and log K_{ex} for the metal exchange, relating this back to pK_a values often out of range of standard techniques.

$$RHg \xrightarrow{e^-} R:^- + Hg \qquad [4.1]$$

Following these physical organic types of studies, Dessy and coworkers moved on to examine the standard redox properties of organic derivatives of group V metals, particularly compounds of the type Ph_2MX.[13] They reported the preparations of transient radicals which were found to then either hydrogen abstract (in the case of the phosphorous compounds), or undergo a radical coupling. These coupled products were found to react further to form new organometallic anions of the type $Ph_2M:^-$.

The next two reports by this group dealt with the transition series of metals, with a large number of different types of ligands.[14] The electrochemical properties of these complexes were studied in detail, with reference to features such as reversibility and stability. Following this was a study of the modes of decomposition for compounds containing metal-metal bonds as they were reduced electrochemically.[15] It was determined that there were two modes of decomposition, one involving the acceptance of two electrons and splitting into two anions, and the other involving acceptance of one electron, yielding a radical and an anion.

Other reports from this group include studies on the formation of metal-metal bonds, redistribution reactions in homo- and heterodimetallic compounds, nucleophilicities of anion derived from a number of different classes of metals, and the reactivity of organomagnesium reagents.[16] This is by no means an extensive review of the work done by this group, let alone of organometallic electrochemistry, but it should serve to give an indication of the type of information which can be obtained with these techniques. Information about reaction mechanisms, stability of short-lived intermediates, modes of decompositions, as well as more standard data on compound stability can all be determined electrochemically.

Sandwich compounds have also been the subject of many electrochemical studies, and much has been learned from these reports. For instance, ferrocene and its related compounds have been studied in great detail. Lemoine and coworkers have compared the redox properties of phosphaferrocenes (ferrocene with a CH ring group replace by a phosphorous atom) and ferrocene itself, and have found that there are major differences in the reduction potential, which are actually additive.[17] More traditionally substituted ferrocenes have been studied extensively and many effects have been examined in these molecules.[18] Similar metallocenes of other metals have been studied as well, including reports by Geiger on cobaltocene and its anion, and COT complexes with cyclopentadienyl cobalt species.[19]

In the field of f-element organometallics, however, the amount of work is more limited. There have been numerous reports of the redox properties of these metals of with a number of oxygen based ligands, but very few true organometallic species. Among those that have been examined, the Cp ligand is the most prevalent. Finke and coworkers published a report in 1982 of the one electron reduction of $(C_5Me_5)_2UCl_2$ to

its anion, and the lack of the analogous reaction in the thorium analog.[20] Reeb, Mugnier, Dormond, and Laviron have reported other work with Cp-uranium species, including additional work on the system Finke examined, in which they were able to help stabilize the anionic species by adjusting the supporting electrolyte and conditions of the reduction.[21]

There has only been one report on the electrochemistry of bis([8]annulene) actinide metallocenes, by Chambers and Pagni.[22] In this work, they were examining the oxidation properties of uranocene, and they saw evidence for the existence of the uranocene cation, at least as a short-lived species. There were also, however, rapid structural changes and electrochemical irreversibility which made it impossible to isolate and study the cation further.

Owing to the more limited number of oxidation states available to the lanthanides, the organometallic electrochemistry of these metals is even more scarce. There are reports of unpublished studies on the oxidation of bis(pentamethylcyclopentadienyl)ytterbium(II) and its europium and samarium analog,[23] but Bond and Deacon have the only published report on this class of molecule.[24] Their work consisted of the electrochemical reduction of tris(cyclopentadienyl)samarium(III), -ytterbium(III), and -europium(III) compounds. It was found that these complexes undergo reversible electrochemical reduction in THF at platinum, gold and mercury electrodes. The potentials they determined for these complexes are significantly more negative than the corresponding reduction potentials of the metal ions in aqueous solutions, and the predicted thermodynamic stability towards correlates with that observed chemically (Eu > Yb > Sm).

It is clear that there is much more work to be done in examining the electrochemistry of the f-block compounds, and as more of this chemistry in general is examined, there will certainly be more electrochemistry performed. In the course of our work with tetravalent cerium, it became of great interest to us to measure the reduction potential for our bis([8]annulene) cerium system. It was clearly of interest to see what sorts of effect the cyclooctatetraene ligands would have, since it was clear from the chemistry of this class of molecule that they were imparting some degree of stabilization to these metal complexes. An electrochemical study of the reduction potential of one of this class should help to give an indication of the strength of this stabilization.

Results and Discussion

Before the redox properties of this system could be examined electrochemically, several problems had to be solved. Due to the high air-sensitivity of these metallocenes, the electrochemical measurements must be made under conditions rigorously excluding oxygen. There have been two general approaches used to examine air-sensitive materials of this sort, either using air-tight vacuum line cells or doing the work inside an inert atmosphere glovebox. We chose the latter technique, as it seemed that manipulations of the compounds would be easier in that environment than on a vacuum line. Initially, measurements were made by making the electrical connections through the plug box of the glove box, but after some problems with electrical background noises were encountered, a direct connection was made through

the wall of the box. A small hole was drilled in a plug bolt through which were passed wires. This made it possible to use standard benchtop electrochemical cells and electrodes, attach wires from these electrodes to the wires passing through the wall of the box, and then to attach the potentiostat wires to the connections coming through the box wall. The results obtained using the connections through the wall of the glovebox were identical with the results obtained by using the plug box, prior to the electrical problems.

The second problem related to these measurements was the fact that the compounds to be studied could only be examined in a few non-aqueous solvents, which had to be kept rigorously free of water. The solvent we were basically required to use due to solubility properties was THF, which has very poor electrochemical properties (low dielectric constant). Acetonitrile was one other solvent tried, but the compounds decomposed even in rigorously water and oxygen free solvent. The THF solutions used had generally large amounts of uncompensated internal resistance, although our potentiostat was equipped with a feedback type of IR compensation loop, which was occasionally used.

Since it was necessary that the system be kept completely free of water, we found it best to use a silver wire quasi-reference and add ferrocene to our solutions as an internal standard. Most of the well-determined reference electrode systems are aqueous based, but we were unable to use them because even the slow rate of leakage from the electrode to the bulk solution was enough to cause significant decomposition to our compounds. There is precedence for the use of ferrocene as a standard non-aqueous reference, as a result of its solvent-independent potential (0.4 V vs NHE).[25]

The full experimental details of the measurements are given in the experimental section at the end of the chapter. We used THF solutions which were on the order of 10^{-3} M in compound, with either tetra-n-butylammonium tetrafluoroborate or tetra-n-butylammonium hexafluorophosphate as the supporting electrolyte (0.1 - 0.4 M). The method used was cyclic voltammetry using a standard three-electrode configuration. As mentioned above, a silver wire quasi-reference was used, as well as a platinum wire counter electrode and Pt disk working electrode. After the properties of the waves for the compound being studied were examined, ferrocene was added to provide the reference needed. The appearance of the compound's voltammogram does not change, except for some shift in the apparent potential; the presence of the ferrocene does not interfere with the electrochemical processes of the compound of interest. Potentials were then measured vs. the ferrocene standard, and are reported vs the NHE potential (E^o = 0.400 V vs NHE).[25]

A representative cyclic voltammogram for $K[Ce(C_8H_8)_2]$ is shown in Figure 4.2. The voltammograms for these compounds are characterized by a well defined reduction peak in the negative potential direction and an oxidation peak on the reverse scan, both near the negative limit for the solvent breakdown. The peak to peak separation is a function of scan rate, as is the ratio of reduction peak current to oxidation peak current, although this is more difficult to quantify due to the solvent breakdown. In general, as the scan rate is slowed, the peaks approach each other and the oxidation peak becomes less distinct relative to the background current.

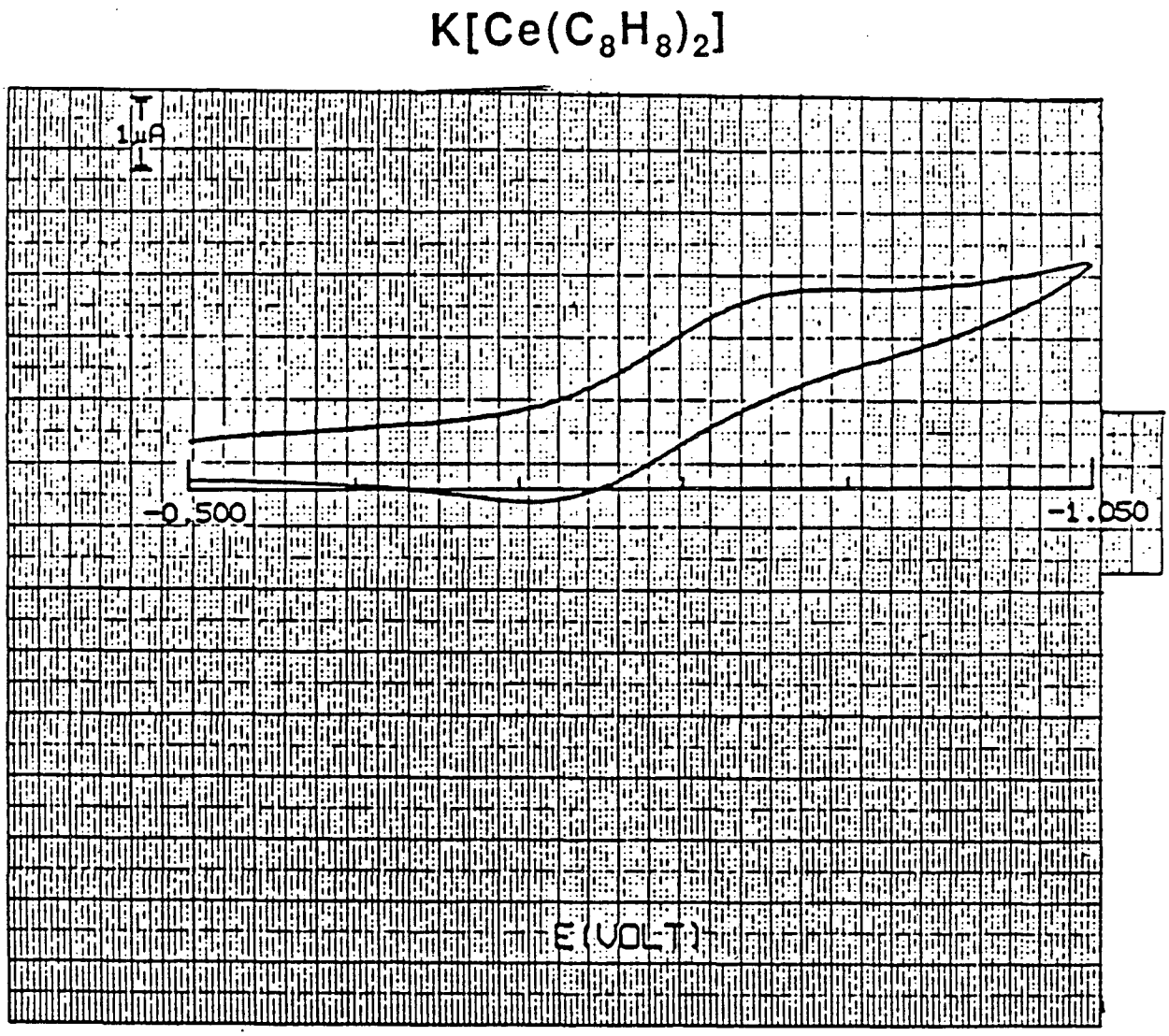

Figure 4.2: Cyclic Voltammogram of $K[Ce(C_8H_8)_2]$.

The full voltammogram after the addition of the ferrocene is shown in Figure 4.3. The ferrocene waves, located at the far left of the voltammogram, are normalized to give an $E^{o'}$ value of +0.400 V vs NHE. With this reference available, the value for the the cerium reduction potential can be determined as -1.28 V . This value is determined by taking the average of the potentials of the oxidation and reduction peaks, although using other accepted methods such as the average of the $E_{1/2}$ potentials for each wave gives essentially the same value. The $E^{o'}$ value obtained this way is generally independent of concentrations and scan rates, which do affect the positions of the individual oxidation and reduction peaks due to resistance effects. The peak to peak separation of the cerium wave closely matches that of the ferrocene waves, ranging from about 120 - 400 mV under the different conditions examined, suggesting that it is also a one-electron transfer process. Recent work on related compounds has supported this sort of relationship.[24, 26] There is a small irreversible wave at -0.75 V that is most likely due to an impurity of some sort; it is most prevalent in the case of material that had been stored for a while previous to use, and it was not present in some of the samples examined.

Examination of the voltammogram for the corresponding Ce(IV) species shows a similar result for the value of the potential, although the waves were not as well defined. This may be due to the fact that there is a tetra-n-butylammonium counterion present to help stabilize the reduced species rather than a potassium cation.

The significance of this potential has been discussed in previous chapters. It represents a reversal in the relative stabilities of these oxidation states as compared with the situation in aqueous solutions, and suggests that the COT rings are extremely effective in stabilizing the tetravalent cerium. An analysis similar to that carried out by

Raymond and coworkers on the tetracatechol species (see discussion in Chapter I, page 16). The ratio of the equilibrium constants of the cerium(IV)- and cerium(III) sandwich compounds for the following reaction can be determined:

$$Ce^{n+} + 2COT^{2-} = [Ce(COT)_2]^{n-4}$$

Since this is also a one-electron process, the same equation can be used and the ration can be determined to be $K_{IV} / K_{III} \cong 10^{50}$! This shows that the cyclooctatetraene rings are stabilizing the tetravalent oxidation state much more strongly than the trivalent; the chemistry we have seen for this molecule is consistent with such a difference in stabilization.

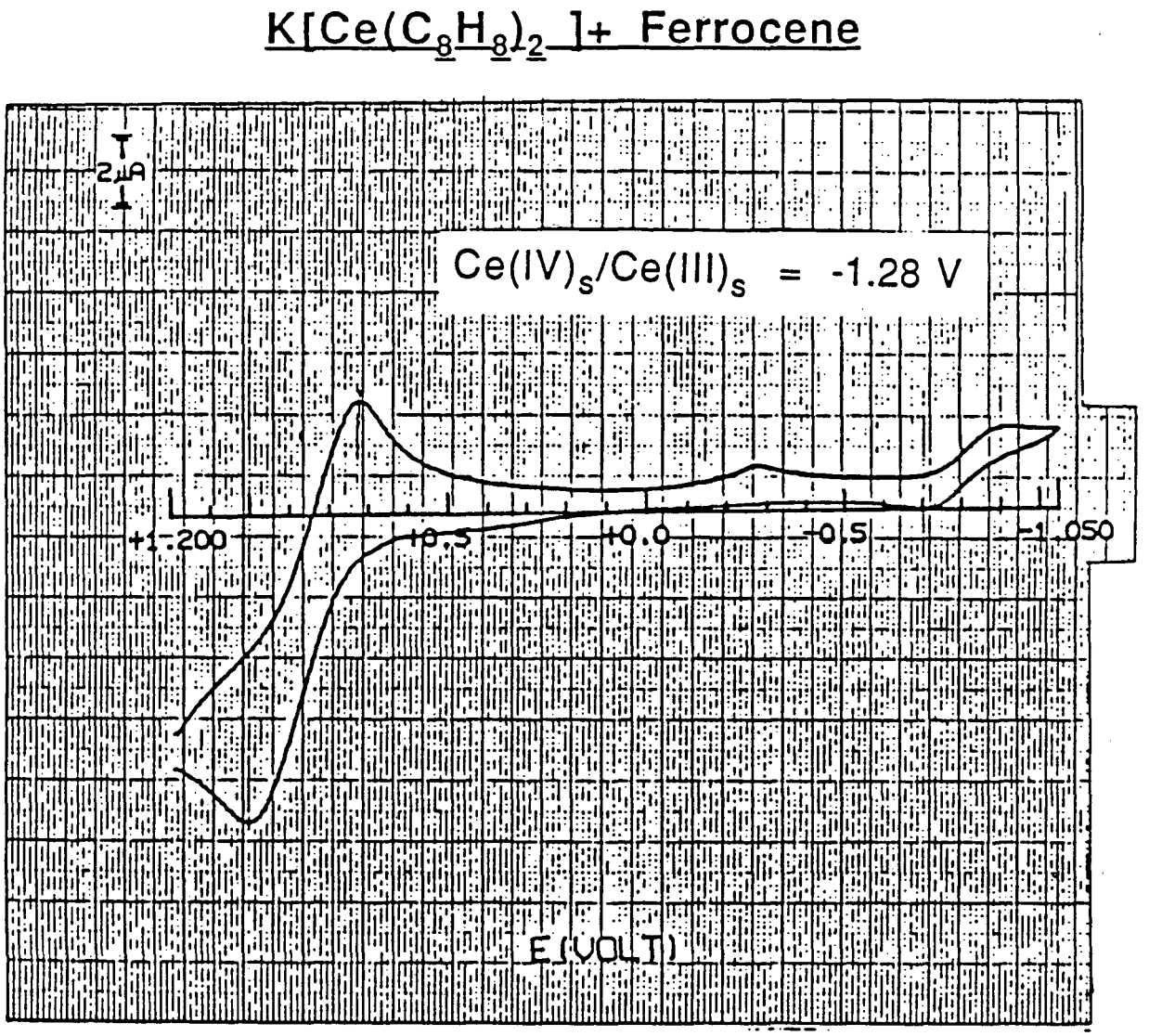

Figure 4.3: Cyclic Voltammogram of $K[Ce(C_8H_8)_2]$ + $Fe(C_5H_5)_2$.

As mentioned above, the electrochemistry of some substituted cyclooctatetraenes has been studied and has suggested that substituents can affect the potential for reduction of the rings. In addition, Hillard of this group has measured the reduction potentials of a series of cyclooctatetraenes in DMF; her results are shown in Table 4.3.[27] It is clear from these data as well that changing the type of substituents on the rings can change the measured reduction potential. We thought it would be of interest to see whether a corresponding change in the reduction potentials would be evident in the metallocenes of these substituted COT's.

Table 4.3

Reduction Potentials of Substituted COT's

(DMF solutions, V vs SCE)

Compd	$E_{1/2}^1$	$E_{1/2}^2$
COT	-1.65	-1.90
ethylCOT	-1.76	-1.96
n-butylCOT	-1.79	-1.96
t-butylCOT	-1.90	-2.03
neopentylCOT	-1.77	-1.96
methoxyCOT	-1.76	-1.94
phenylCOT	-1.64	-1.74
triphenylCOT	-1.78	-1.91
naphthoCOT	-1.74	-1.91
benzyl ester of COT	-1.26	-1.58
t-butyl ester of COT	-1.34	-1.65

The voltammograms for the bis(n-butyl[8]annulene)- and bis(t-butyl[8]annulene) cerium(III) compounds were recorded, but there was no apparent difference in the observed potentials, at least within the limits of the experimental error in these measurements (± 100 mV). This may not be too surprising if one considers that much of the observed difference of 140 mV between the n-butyl and unsubstituted COT, and of an additional 110 mV for the t-butyl compound for the first electron transfer may be due to the difficulty involved with the flattening of the ring as discussed above. The differences in the second wave (60 mV and 130 mV for the n-butyl and t-butyl derivatives, respectively) may be a better representation of the electronic effects, and it is clear that these differences would be on the limit of our detection, even if the full effect were felt at the cerium center.

Preliminary examinations of other bis([8]annulene) sandwich compounds have also been attempted. The CV for $K_2[Yb(C_8H_8)_2]$ is shown in Figure 4.4, and it is clear that there is at least one reversible electrochemical process. However, when ferrocene was added to this sample, there was clearly some sort of reaction with the ferrocene going on, as the peaks corresponding to the Yb species could not be seen, and the ferrocene peaks were dramatically enlarged. It should be possible to find a different reference system for this system, and then the identity of the two sets of waves should be identified.

In the previous discussion of the (IV/III) reduction potentials of the lanthanides, it was pointed out that after cerium, the next most stable tetravalent ions are praseodymium and terbium, both with aqueous potentials around 3.0 V. If the same sort of stabilization as is seen in the cerium case is seen for the bis([8]annulene)

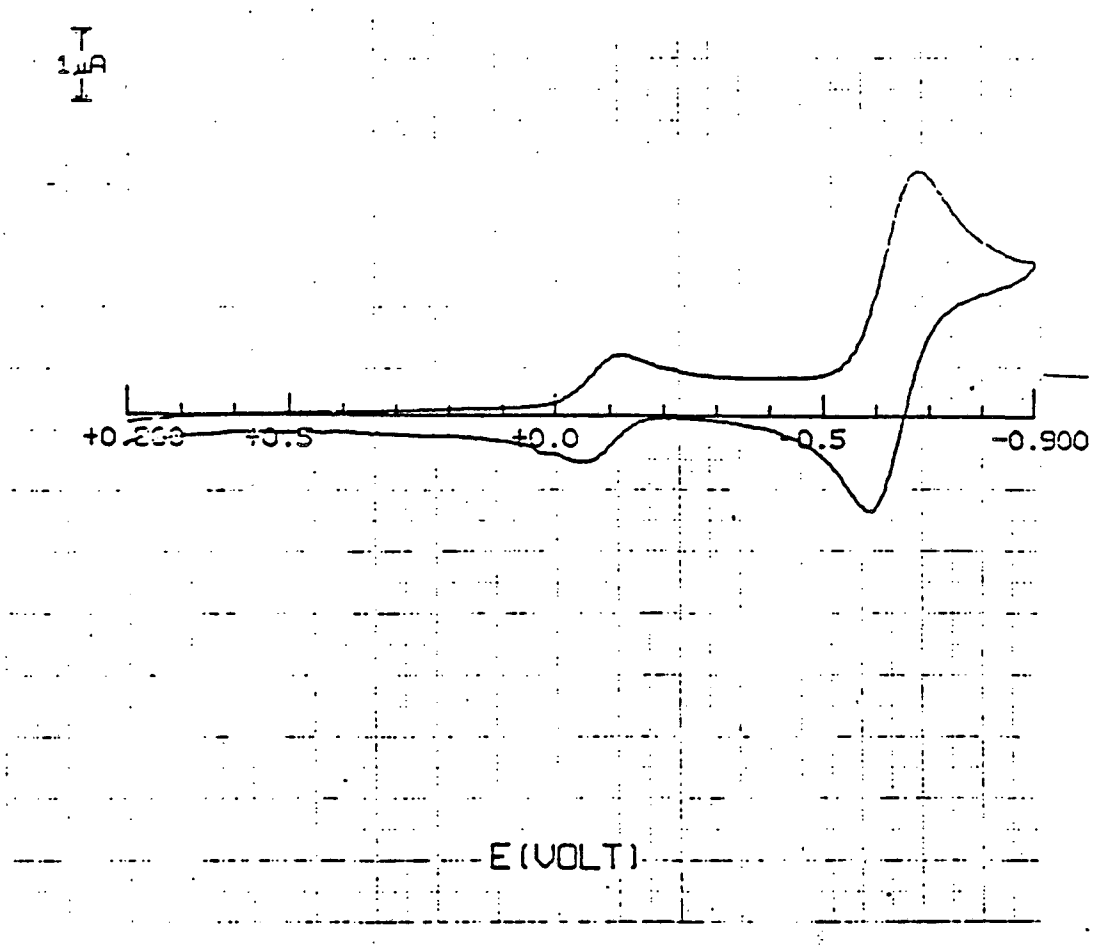

Figure 4.4: Cyclic Voltammogram of $K_2[Yb(C_8H_8)_2]$.

complexes of these tetravalent metals, it may be possible to isolate them as well. It was thought that an electrochemical examination would be the best way to see whether they are stable enough to be prepared, so the +3 salts of these compounds were prepared and their CV's recorded. Most of the work was done on the Pr salt, but the behavior of the Tb salt was quite similar.

Unfortunately, we were not able to get good voltammograms for these species. What we saw were irreversible oxidation waves, which would alter the electrode surface enough to prevent further examination of the properties of these waves. Whether these waves are due to a Pr(IV) sandwich compound, which then reacted with the electrode surface or some other material is just not clear at this point. This is an area which certainly warrants additional research, as the preparation of stable organometallic complexes of praseodymium or terbium would be completely unprecedented.

Experimental

Electrochemistry General

Electrochemical measurements were carried out with a Princeton Applied Research Model 173 Potentiostat / Galvanostat with a Model 175 Universal Programmer, or with a BAS-100 Electrochemical Analyzer in an argon glovebox equipped with electrical connections to the instrumentation outside the box. Voltammograms were recorded on a Houston Instruments Model 2000 X-Y Recorder. The electrodes used were a polished platinum disk (BAS) as the working, a platinum coil as the counter, and a polished silver wire as the reference, in a standard three-electrode configuration.

THF was distilled from K/benzophenone under argon, vacuum transferred and degassed for removal to an argon glovebox immediately prior to use. Tetra-n-butylammonium tetrafluoroborate was obtained from Fluka (puriss) and recrystallized from either ethyl acetate/hexane or acetone/ether and dried in vacuo, or prepared as given below. Tetra-n-butylammonium hexafluorophosphate was obtained from Fluka (puriss) and dried in vacuo prior to use. Ferrocene was obtained commercially (Aldrich) and sublimed prior to use. The preparations for the compounds studied are given elsewhere in this thesis.

Cyclic Voltammetry Methods

Approximately 10 mL of a stock solution of the electrolyte in THF (in the range of 0.1 - 0.4 M) was added to the electrochemical cell in an argon glovebox. The electrodes were then set up and the background voltammogram was recorded. If this is clear, the sample was added (in the general range of 1 x 10^{-3} M, although this is not critical and was usually not weighed out), and the appropriate sweeps were carried out. Scan rates were in the range of 50 - 500 mV / sec, with the majority of the measurements being made at 100 mV / sec. A small amount of ferrocene was added until the ferrocene peaks were clearly visible. Electrodes were wiped with Kimwipes and rinsed with THF between samples, unless they were dirty enough to require repolishing or cleaning, in which case they had to be removed from the glovebox.

Preparation of Tetra-n-butylammonium Tetrafluoroborate

In a 1L erlenmeyer flask was dissolved 50 g of tetra-n-butylammonium hydrogen sulfate (Alfa) in ~ 300 mL of distilled water. An excess of tetrafluoroboric acid (48 - 50 %, 50 mL) was slowly added with vigorous stirring and swirling. A heavy white precipitate formed immediately. The sides of the flask were frequently rinsed with additional water, resulting in a total volume at the end of the addition of ~ 750 mL. The product was filtered and rinsed with H_2O until the rinses were neutral.

The white powder was dissolved in 100 mL CH_2Cl_2 and molecular sieves were added to adsorb the water. The solution was swirled and then filtered off the sieves, which were rinsed with additional CH_2Cl_2, and the resulting solutions were combined and concentrated to ~ 100 mL. Ether was added (1 L) to precipitate the product which

came out as a white solid which was filtered and dried in vacuo; mp 159 - 161 °C (lit. mp 161 - 162 °C). If necessary, the material can be recrystallized as discussed in the general section.

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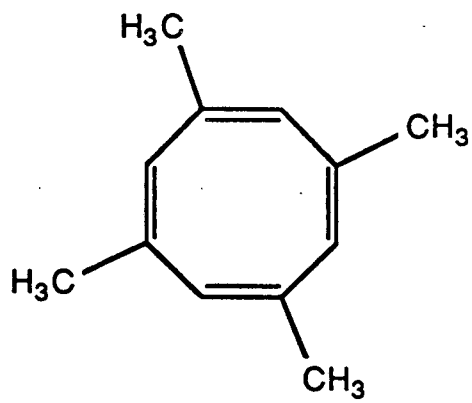
CHAPTER V:

TETRAMETHYLCYCLOOCTATETRAENE

The ligands attached to the central metal in these metallocenes have been found to have a great effect on many properties of these molecules. For instance, solubility, air and thermal stability, and spectroscopic properties can be modified by appropriate choice of substituents on the COT rings. One ligand of particular interest is 1,3,5,7-tetramethylcyclooctatetraene (TMCOT) (Figure 5.1), a highly substituted yet symmetric ligand.[1] This ligand is known to increase solubility while maintaining a high level of symmetry, and the steric bulk associated with this ligand may help to stabilize the sandwich compounds of this ligand.



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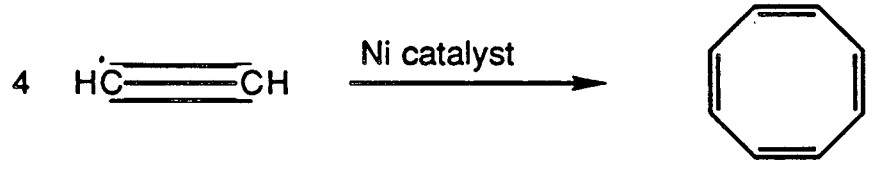
This ligand has been used in the field of the f-element metallocenes in the past; the crystal structure of the diglyme adduct of the dipotassium salt of TMCOT has been solved and showed that the ligand is, as expected, a planar aromatic system.[2] The sandwich molecules of several of the actinides have been prepared, including U, Th, Pa, Np, and Pu.[3] The crystal structure of bis(1,3,5,7-tetramethylcyclooctatetraene) uranium (IV) has been solved, and it showed a number of interesting features, which were discussed in Chapter III.[4] Among these features was the fact that the methyl groups were bent in towards the metal center. One of the postulated explanations for this was that the ring p-orbitals were rehybridizing to achieve better overlap with the metal orbitals. If this is the case, it had been anticipated that the cerocene analog, which had been thought to have less orbital overlap, might not show this same effect. If there were a difference between the actinides and lanthanides in terms of their orbital interactions with the ligands, this could be one structural manifestation.

The synthesis of this ligand is, however, not straightforward. The syntheses of many types of substituted COT's have been worked out.[5] For instance, bromocyclooctatetraene[6] is a convenient precursor for a large number of monosubstituted COT's , treating it with alkyl-lithium or organocuprate reagents.[7] The yields on these reactions are variable, but they are in the range to make them useful for preparative scale. In several instances, the alkyl lithium reagents can be used directly on the unsubstituted COT, generally resulting in low yield.[8] One reason for this reduced yield is that there is frequently contamination of the product with multiply substituted rings, only some of which are readily separated from the monosubstituted derivatives. Using this method to prepare disubstituted analogs, however, has the problem that the reactions usually produce a mixture of the isomers; generally, these are much more difficult to separate, so alternate methods are needed, frequently involving

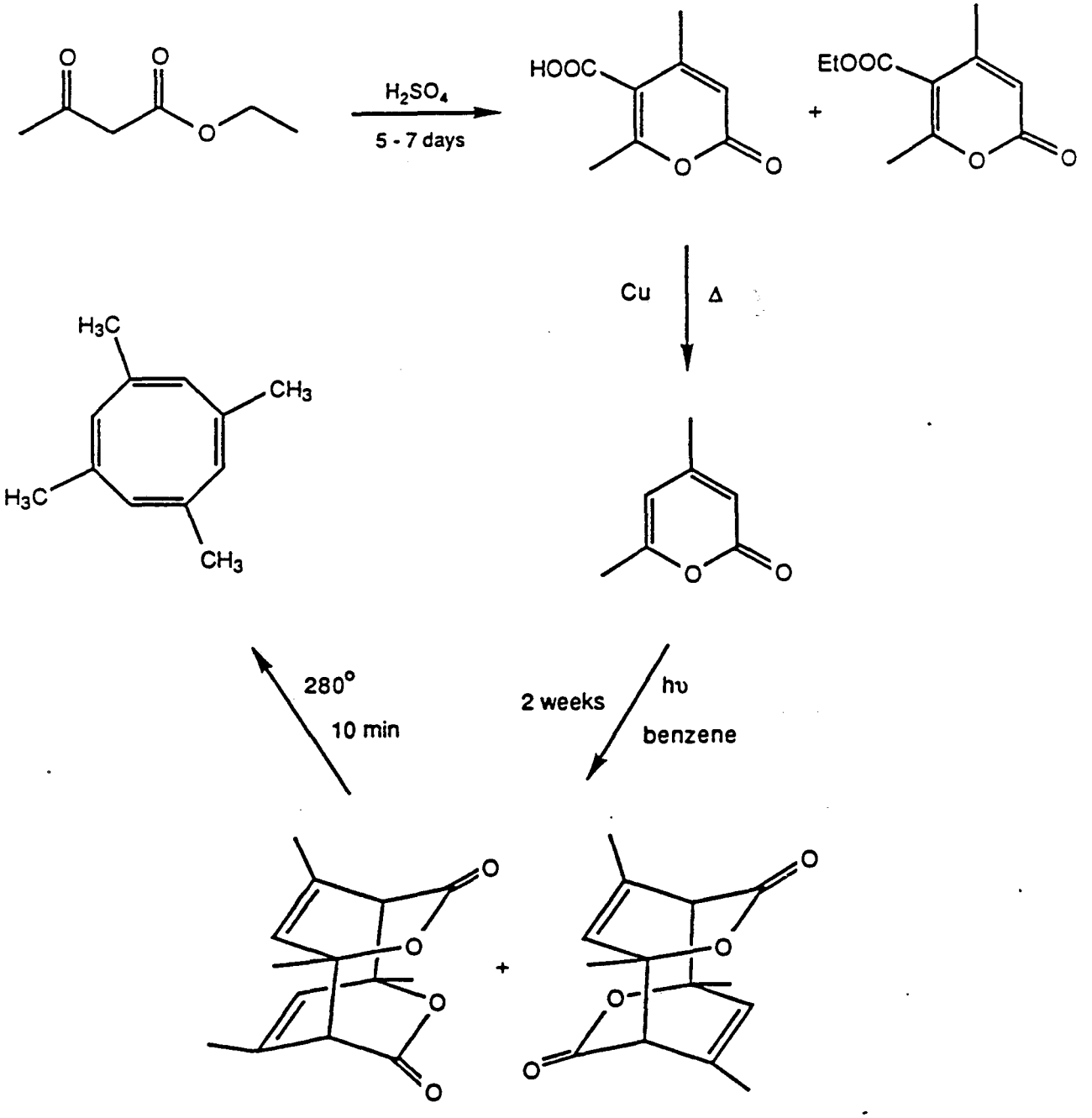
skeletal transformations.[9] The problem is clearly even more complicated when trying to synthesize tetrasubstituted derivative, and past approaches have focussed on making skeletal transformations.

De Mayo and Yip have developed the synthesis of the 1,3,5,7-tetramethylcyclooctatetraene which has been used most frequently (See Scheme 5.1).[10] Their approach starts with the conversion of ethyl acetoacetate into 4,6-dimethyl coumalic acid[11], which is then reacted with a Cu catalyst to yield the 4,6-dimethylcoumalin.[12] The coumalin is photolyzed to give the mixture of dimers shown, which can then be thermally decarboxylated to yield the symmetric TMCOT. The first two steps proceed in good yield, but the photolysis is a relatively poor yield reaction, with a reported yield of 26%, based on unrecovered starting material.

One other approach which could be envisioned for preparing substituted COT's is based on the early work of Reppe and co-workers at BASF in 1940.[13] They found that COT could be prepared by the tetramerization of acetylene in yields up to 70% (see Eq. [5.1]). The reaction is run in dry tetrahydrofuran or dioxane at elevated temperature and pressure in the presence of a nickel(II) catalyst. It was found that a number of Ni(II) compounds, including the cyanide, acetylacetone, and salicylaldehyde were effective. The reaction produces a fair number of side products, including benzene and styrene, but as mentioned above, conditions have been found which favor the formation of the tetramer product.



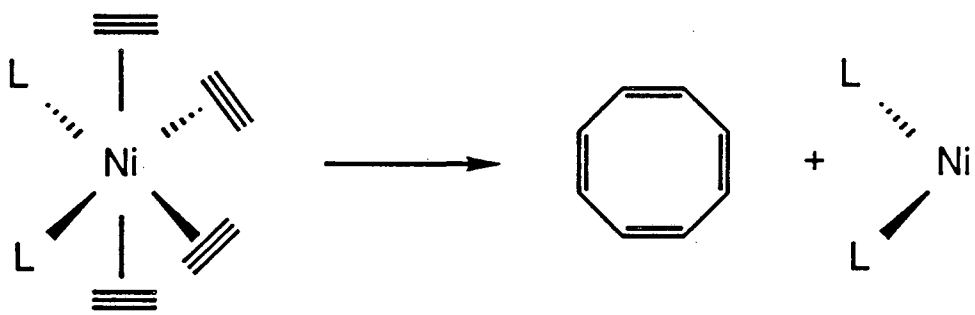
[5.1]



Scheme 5.1: De Mayo and Yip's Preparation.

The mechanism of this reaction has been a matter of considerable debate over the years. Recent work by Colborn and Vollhardt has suggested that the reaction proceeds by one of two of the postulated mechanisms.[14] The first is the mechanism espoused by Schrauzer, which involves the coordination of four molecules of the acetylene to a nickel metal center.[15] The molecules are then in the appropriate geometry to yield the COT in a concerted reaction (see Eq. [5.2]).

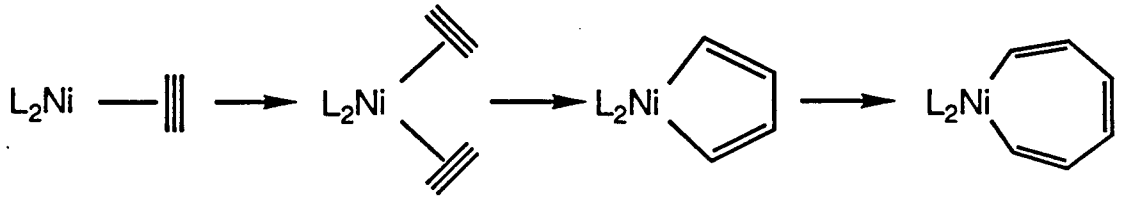
Concerted Mechanism:



[5.2]

The second postulated mechanism involves the coordination of each molecule in an individual step. The subsequent molecule of acetylene then inserts to expand the ring until the COT finally dissociates from the metal (see Eq.[5.3]). Metallacycloalkanes such as the postulated intermediates are known, and the experimentally observed products are consistent with this mechanism.[16] Whitesides and Ehmann have performed a labelling study to show that analogous cyclotrimerization catalysts gave product distributions which can be explained with a mechanism of this sort.[17]

Stepwise Mechanism:

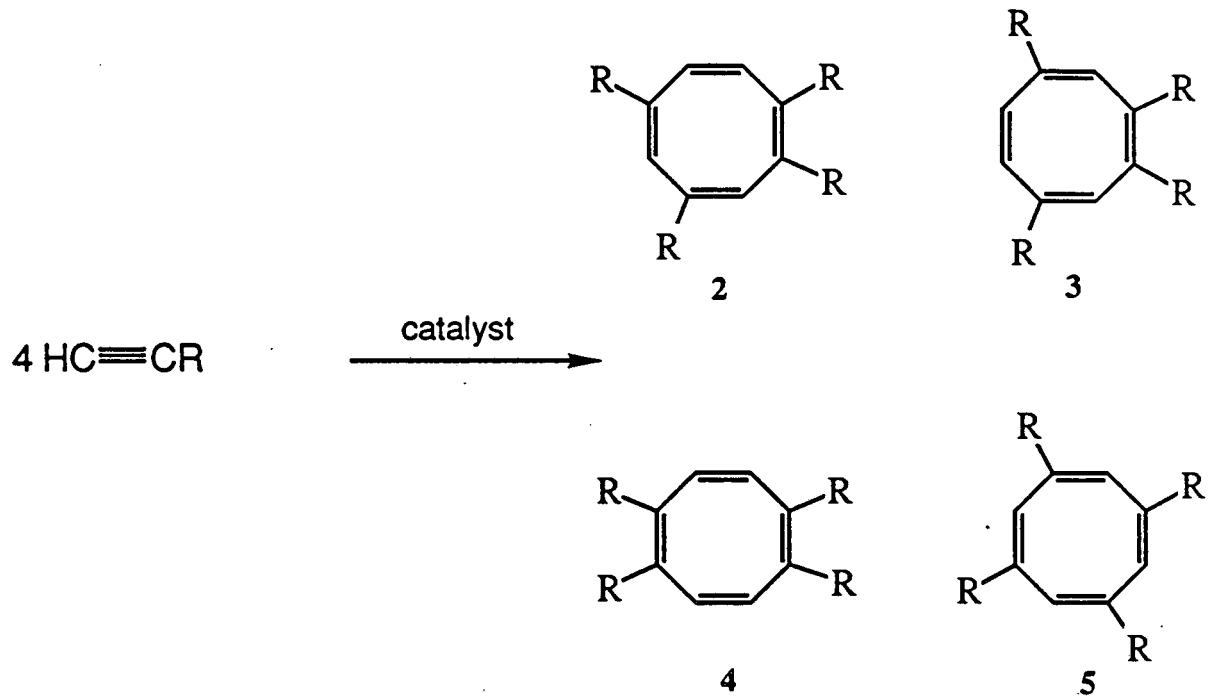


[5.3]

The tetramerization of substituted acetylenes has been tried and it has been found to go as well. The co-tetramerization of three molecules of acetylene with one of a substituted acetylene has produced various monosubstituted COT's, although the yields are greatly reduced from the Reppe synthesis itself.[18] The tetramerization of a disubstituted acetylene with three unsubstituted molecules has been found to proceed also, although in low yield.[19]

Theoretically, one could extend this procedure to cyclizing varying numbers of monosubstituted acetylenes with unsubstituted, but in actuality the product mixtures usually become much too complex to separate. In general, separating substituted COT's is a problem, and trying to separate the different isomers obtained in this type of reaction is unfeasible.

In general, the tetra-substituted derivatives have been prepared by making use of some sort of a skeletal transformation.[20] Cyclizing four molecules of monosubstituted acetylene, however, has been tried and in some cases has been found to be possible. In this case, four different isomers are found, depending on the relative orientations of the acetylene molecules upon reaction (Eq. [5.4]). There is no apparent logic which can predict which acetylenes give which isomers or which catalyst system is best for any given tetramerization; it has basically been a matter of trial and error to find the best conditions to effect any particular reaction. (See Table 5.1)[21]



[5.4]

Table 5.1

R	Catalyst and conditions	Product	Yield
CH_2OH	$Ni(acac)_2$, C_6H_6, reflux	**5**	70%
$C(OH)Me_2$	$Ni(acac)_2$,[a] 90 - 120°	**2** + **3**	40%
CO_2Me	$Ni(PCl_3)_4$, C_6H_{12}, 22 - 50°	**2**	83%
CO_2Me	$PdCl_2$, NaOAC, HOAc, 80°	**4**	(very low)
CO_2Et	$Ni(PCl_3)_4$, C_6H_{12}, 25 - 46°	Mainly **2**	30%
OEt	$NaNH_2$, NH_3(liq.), -70°	**5**	10 - 24%
OPr^n	$NaNH_2$, NH_3 (liq.), -70°	**5**	9.5%

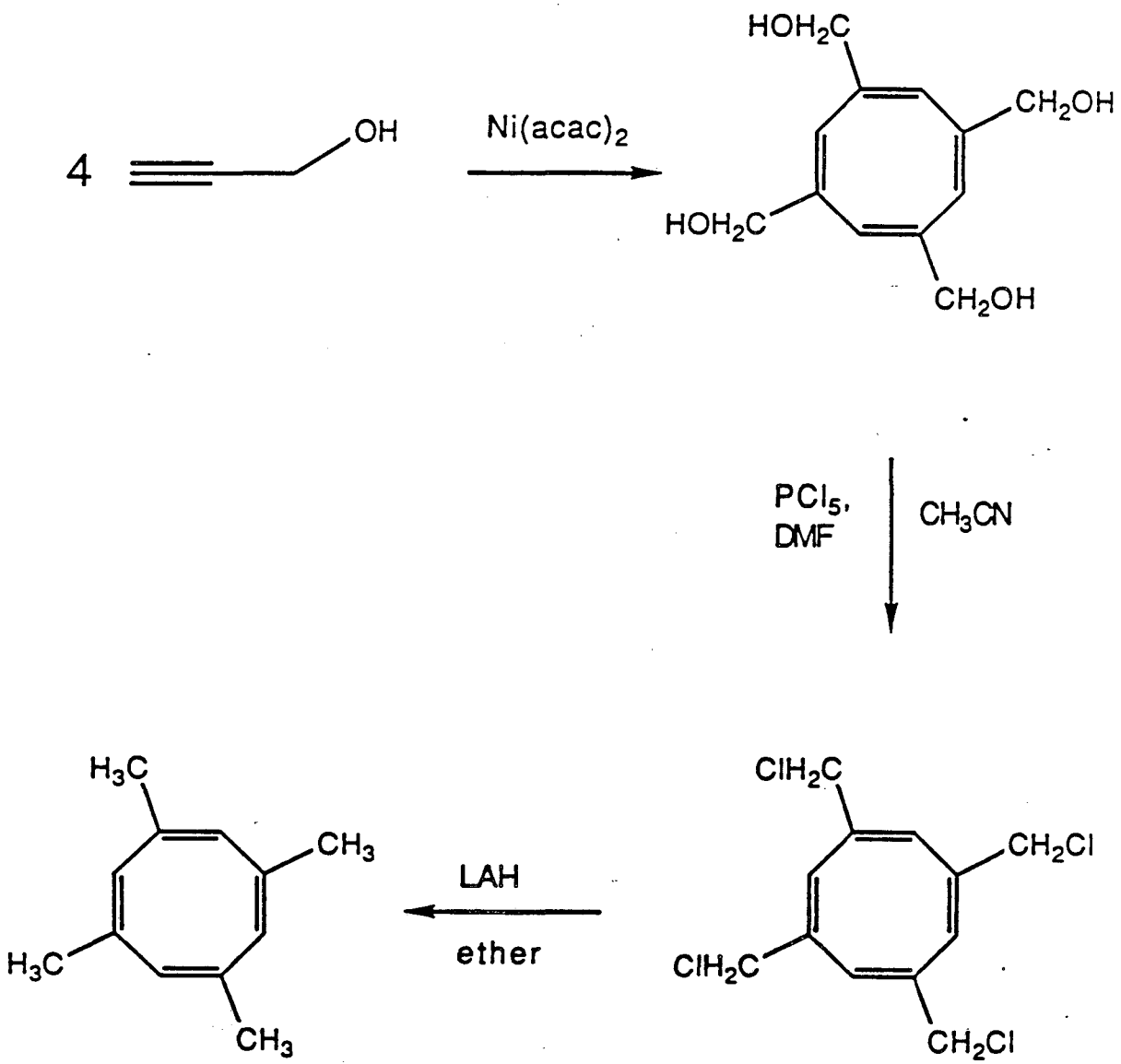
[a] The reaction is also catalyzed by $Ni(CO)_4$, $Ni(COD)_2$, $Ni(CN)_2$, $Ni(OEt)_2$, and $NiCl_2$-$NaBH_4$.

One of the reported results is of particular interest for this work. In 1974, Shitikov et al. reported that the reaction of propargyl alcohol with bis(acetylacetone)nickel (II) resulted in high yields of the 1,3,5,7 isomer of the tetraalcohol.[22] Although their experimental details are somewhat incomplete, we thought that if this tetramerization could be effected, then the subsequent conversion into the desired isomer of the tetramethyl compound should be feasible.

RESULTS AND DISCUSSION

The first step taken towards the synthesis of the ligand was an attempt to repeat the literature preparation of de Mayo and Yip (Scheme 5.1). The first two steps, the preparation of the dimethylcoumalic acid and the conversion into the coumalin both went quite well, with yields close to the yields reported in the literature.[11,12] The next step was the photolysis, and this step gave us much more trouble. Theoretically, the desired dimer will form on the wall of test tube after photolyzing for 1 - 2 weeks as a clear crystalline material. The solution can then be decanted and further photolysis should produce more of the dimer.[23]

When we attempted to repeat this, however, we obtained just trace amounts of a crystalline material after 2 weeks of photolysis. When this material was removed from the test tubes and the remaining solution was subjected to additional photolysis, other solids formed which neither physically nor spectroscopically resembled the desired product. The photolysis was carried out under conditions resembling those used previously in our group, and under slightly different reaction conditions with no better



Scheme 5.2: Proposed Synthesis of TMCOT.

result. The NMR spectra of these various attempts are listed in Table 5.2. The size of the peaks due to the desired dimer were usually much smaller than the other peaks visible. The origin of each entry is discussed in the Experimental Section.

Table 5.2

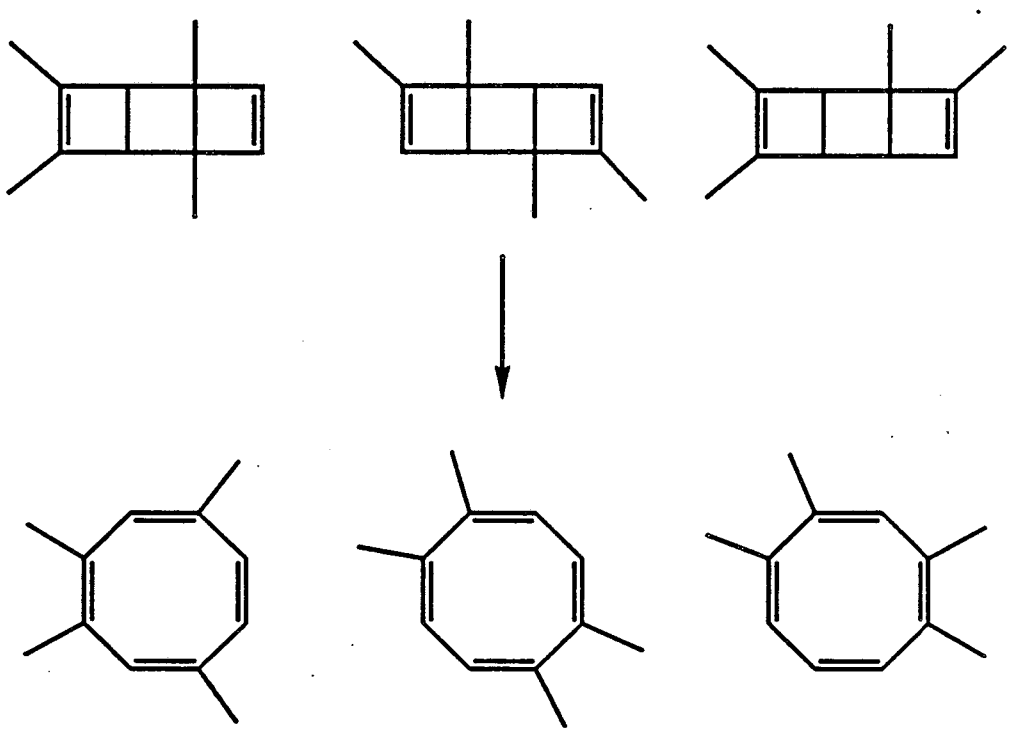
NMR of Photolysis Products

(Shifts in ppm)

Starting Material	Authentic Dimer	Trial 1	Trial 2a	Trial 2b
5.90	5.90	5.90	5.91	5.91
5.81				5.83
				5.73
		5.54		5.55
	3.23	3.23	3.24	3.24
		3.14		3.16
2.10				2.10
2.07				2.00
	1.75	1.75	1.75	1.75
		1.69		1.70
		1.56		1.57
	1.53	1.53	1.54	1.54

The identity of these undesired products was examined, in the hopes that it may have been possible to convert them to the TMCOT, but our efforts at this were unsuccessful as well. For instance, one possible product was the decarboxylated "tricyclic" dimer, which is simply a different isomer of the compounds which Criegee, Eberius and Brune were able to convert into differently substituted

tetramethylcyclooctatetraenes.[24] However, spectroscopic evidence and several attempts to effect this conversion, including pyrolysis of the neat material and a tube furnace pyrolysis, suggested that this was not our product. Another possibility was that it was another of the dimer products reported by de Mayo and Yip. According to their report, this material was readily converted into the desired dimer at 160 °C, although experimental details were lacking (see Eq. [5.5]). Our efforts to convert this material were also unsuccessful.



[5.5]

Details of the different trials are given in the Experimental section. The NMR of these products showed a number of similar peaks, but with the exception of the Trial 2a, the samples generally showed a mixture of products, of which the desired isomer was often in minor concentrations. Unfortunately, characterizations of the

intermediates of these reactions are scarce, so it is hard to determine exactly what is happening.

The reasons for the failure of this synthesis remain unclear to this point. However, independent efforts by Gilbert at Los Alamos Lab at about the same time as our work were encountering many of the same difficulties.[25] In his work, he got slightly higher yields of the desired photodimer, but yields which were still much below the reported yields, and which were so low as to make production of the ligand on a reasonable scale unfeasible. So, it was at this point at which we decided to try a new approach to synthesizing this ligand, based on the work of Shitikov, et al.

The report by the Russian group was somewhat less than convincing.[22] They claimed that only one isomer was formed, and that it was formed in ~ 70% yield. This claim was quite surprising in light of other results in this area, and would certainly have been remarkable if true. The experimental details in the paper were not complete, and the characterization of the product consisted of elemental analysis, ^{13}C and ^{1}H NMR, which left the identity of the compound less than certain. Gilbert at Los Alamos Laboratory was also interested in using this ligand, and repeated the Russian's work to see if it was accurate and found that although there were some inaccuracies in their report, it seemed promising enough to pursue. The first two steps in our proposed synthesis (see Scheme 5.2) were carried out in collaboration with Gilbert, with the best results being reported, and differences between our work mentioned where appropriate.

Our reaction was set up using the amounts of reactants as reported by the Russians, and following as much of the experimental detail as was available. The reaction was monitored by GC, following the disappearance of the propargyl alcohol,

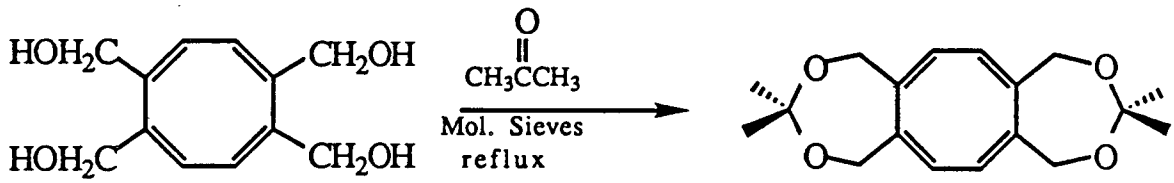
and although it was reported to be complete after 8 hours at the reflux temperature of the solvent, it was found that there remained significant quantities of the alcohol after 10-12 hours. After about 48 hours the concentration of the proparganol reached a constant, low level and the reaction was halted. After decanting the solvent, there remained a large amount of an extremely viscous, brown oil. NMR of this material in D_2O (not all of it dissolves, but the tetraalcohol does extract out to some extent) showed what looked to be a mixture of two isomers of the product (see below), as well as some other unidentified material.

In general, purifications of COT's have proven to be fairly difficult and this time was no exception. Numerous attempts to find a suitable solvent system to separate the isomers, both by TLC and by small test columns, could do no better than to separate a relatively fast moving spot from baseline material, presumably consisting of polymeric products. The best approach seemed to be to dissolve the oil in a minimum amount of ethanol, and to run this down a column of alumina. Much of the material remains on the column near the baseline, and what moves basically with the solvent front contains the COT material, although still not pure. This material is then taken up in a minimum amount of hot isopropanol to give a pale brown solution out of which, after standing for 4-7 days, crashes a white powder, which can be filtered and rinsed with additional isopropanol to give reasonably pure 1,3,5,7-tetrakis(hydroxymethyl)-cyclooctatetraene.[26] However, our yields by this method have ranged from about 5-10%, rather than the reported 70%.

Various attempts were made to improve the yield. Standard crystallizing methods were used to try to speed up and improve the crystallizing of the 1,3,5,7 isomer, including lowering the temperature, using mixed solvents, etc., but none of

these worked. One major problem with this molecule is its lack of solubility: It is poorly soluble in ethanol and isopropanol, but practically insoluble in other solvents. This obviously limits the possibility of techniques such as selective crystallizations, especially since most of the impurities seem to have similar limited solubility properties.

One other means was tried to help this separation, based on the belief that we were dealing mostly with a mixture of two TMCOT isomers, the 1,3,5,7- and the 1,2,5,6. This belief developed from the examination of the NMR spectrum of the reaction mixture, which appeared to have two sets of peaks, both from highly symmetric COT's. The observed splitting patterns were the same (a singlet and an AB quartet), with the major difference being the chemical shift; these two isomers seem to be the best fit with an NMR of this sort. Our approach was to try to remove the 1,2,5,6- isomer by converting the adjacent hydroxyl groups into an acetonide (see Eq. [5.6]). The hydroxyl groups on the 1,3,5,7-isomer should be separated by enough space that they would not be able to form a compound of this sort. This compound would then presumably have different solubility and chromatographic properties from the desired isomer, and thus separation would be possible. In order to test this idea, a small amount of the oil was taken up in hot acetone, and was refluxed over 3Å molecular sieves with a catalytic amount of *p*-toluenesulfonic acid. After reaction, the solution was cooled and crystals appeared which were collected. Elemental analysis and NMR were consistent with the structure proposed. Unfortunately, the reaction did not appear to convert the undesired isomer completely, and subsequent purification was not significantly improved.



[5.6]

Since this catalyst system was successful in the case of the propargyl alcohol, we decided to briefly investigate whether it could be used to tetramerize other substituted acetylenes as well. We decided first to try to tetramerize (trimethylsilyl)acetylene, in the hope that the additional steric bulk of the TMS groups would preclude the formation of any COT isomer except the 1,3,5,7; any other isomer would necessitate having two of these bulky substituent groups on adjacent ring carbons, which should be sterically unfavorable.

The reaction was carried out under much the same conditions as the propargyl alcohol run ($Ni(acac)_2$ in refluxing benzene) with minor modifications being made for the increased volatility of this acetylene. The reaction was monitored by GC, but other than a slight darkening of the solution, there appeared to be no significant amount of reaction even after several days. After workup, a small amount of black-brown tar was recovered out of which a number of small spots could be separated by TLC. Column chromatography of the reaction products , however, provided insufficient quantities of all but one of these spots to allow for any sort of characterization. NMR of the one available compound showed some peaks in the TMS region, but nothing indicative of a substituted COT. Most of the tar remained at the baseline, presumably as some sort of polymer. More vigorous conditions would probably lead predominantly to more polymeric product, so it appears that this tetramerization is not favored.

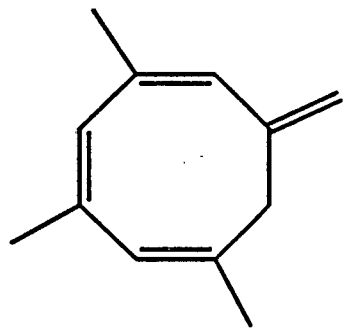
One other cyclization was tried with propargyl chloride to directly produce the second step in our projected synthesis, tetrakis(chloromethyl)COT. This tetramerization had been tried with $Ni(PCl_3)_4$ but without success;[27] however, it was thought that this might be a better catalyst system. The reaction was attempted twice, once in benzene, using the same conditions as in the propargyl alcohol reaction, and once in refluxing cyclohexane, but in no case did we observe any NMR resonances attributable to ring protons on a COT; there were, however, indications that a small amount of trimer product had formed.[28]

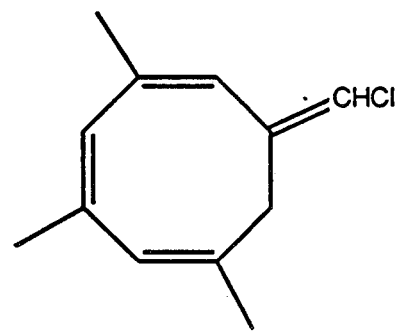
The subsequent step in our proposed synthesis was the conversion of the tetraalcohol into the corresponding tetra(chloromethyl) compound. This conversion was accomplished by using the Vilsmeier reagent, either generating it separately or in situ. The product was obtained in about 50 % yield as white crystals which analyzed after recrystallization from hot heptane.

It was at this point in the synthesis that serious problems arose. The conversion as reported by Gilbert was achieved by reaction of the tetra(chloromethyl) compound with LAH in ether. He was able to isolate an impure solid which he characterized as the 1,3,5,7-isomer. It was on this characterization, in fact, that the identity of the isolated tetra-alcohol isomer as the 1,3,5,7- was based. This will be discussed in more detail later.

When we attempted to repeat this procedure, however, our results were quite different. Instead of recovering what appeared to be an impure solid, our product was generally more of an oil. Examination of this material by ^1H NMR suggested that it was most likely a mixture of several products, including some of the type shown in Figure 5.2, with exocyclic double bonds. There is precedence fot the formation of

products of this sort with disubstituted COT's under similar reaction conditions.[29] What was not seen, however, were the resonances corresponding to the desired 1,3,5,7-tetramethylcyclooctatetraene. It was thought that the LAH used in this reaction was of higher quality than that used previously, and thus was essentially too strong for this system.





Varying the reaction conditions, including using low temperatures and shorter reaction times, seemed to have no effect on the results. We attempted next to deactivate the material by reacting the LAH with one equivalent of methanol, prior to the addition of the tetrakis-(chloromethyl)cyclooctatetraene. However, the material from this reaction had the same appearance as did that from the first reaction, an oily material, rather than the solid hoped for. ^{1}H NMR of this material showed it to be essentially the same as the material prepared from the non-deactivated reagent.

Following this same reasoning, then, it was thought that the reagent Red-Al, bis(2-methoxyethoxy)aluminum hydride should be further deactivated, and thus should

be a gentler reagent for this reaction. Unfortunately, reaction with this reagent gave the same results.

Several other reactions of this type were attempted. For instance, a titrated solution of LAH in THF was used as the reducing agent, in order to insure that the proper amount of the hydride was being used, in the belief that it was the excess of LAH that was causing the problem. This , however, did not improve the reaction either.

We became concerned that perhaps there was an equilibration occurring between the endo- and exocyclic double bonds, promoted by the aluminum chloride species produced by the reaction of the LAH with the tetrakis(chloromethyl)COT. For this reason, a different type of reagent was tried, tri-n-butyl-tin hydride. It was hoped that this different reaction mechanism might help to reduce the undesired reaction on the ring itself which were appeared to be encountering.

After ensuring that we were using a reactive sample of the tin hydride, the reaction was tried on our compound. In this case, the result was slightly different. After about 18 hours of reaction time, ^{1}H NMR showed that the starting material tetrakis(chloromethyl)COT was gone, but there was nothing that could be attributable to TMCOT. In fact, there were essentially no peaks in the COT region at all, so the compound appears to be unstable towards the tin hydride.

At this point, a whole range of alternative reagents was tried to effect this conversion but none of them proved to be successful. In general, if there was a reaction at all, it either went to the same sort of pattern as seen with the LAH, or it

apparently destroyed the COT ring itself, as evidenced by the lack of appropriate resonances in the NMR.

Our next approach was to replace the chloride leaving group with something which would be thought to be easier displace, with the hope that it would then be possible to use milder conditions, thereby avoiding the undesired side reactions. Bromide was chosen as the new substituent, since it should be easier to displace, but is still similar to the chloride. The first question to be answered is if this substituent would make the compound too unstable to be used.

The tetrakis(bromomethyl)cyclooctatetraene was prepared by the reaction of the tetrakis(hydroxymethyl)cyclooctatetraene with a mixture of bromine and triphenylphosphine (see Eq. [5.7]), following the preparation of the 1,2-disubstituted compound.[30] This reaction goes well, with a pale yellow solid being isolated in about 60 % yield. It appears to be a relatively stable material; it does not appear to decompose to any noticeable extent even after standing several days at room temperature.

$$C_8H_4(CH_2OH)_4 \xrightarrow[\text{DMF}]{Ph_3P\ /\ Br_2} C_8H_4(CH_2Br)_4 \qquad [5.7]$$

The question then became would the reaction to form the tetramethylcyclooctatetraene proceed cleanly. The reaction with LAH was tried, adding the reagents at -70 °C, then slowly warming to room temperature. After workup,

instead of a white solid, we were left with a pale yellow oil which did not solidify even after sitting overnight in a freezer. ^{1}H NMR of this material showed a singlet at δ 5.41 corresponding to olefinic protons, and a methyl singlet at δ 1.74. The splitting pattern of this material is appropriate for the desired 1,3,5,7-tetramethylcyclooctatetraene; however, the shifts are off. Luke reported shifts of δ 5.73 and δ1.73 ppm.[23] The methyl peak is a satisfactory match, but the olefinic resonance is 0.3 ppm off. Unfortunately, this spectrum corresponds well with that reported for the analogous 1,2,5,6-tetramethylcyclooctatetraene.[24, 31] That isomer is further characterized as a pale yellow liquid which melts at about -10 °C. In addition, the Paquette report on the NMR of this material mentioned small side peaks corresponding to the resonances from the related 1,4,5,8-tetramethylcyclooctatetraene, in ratios of about 10:1 in favor of the 1,2,5,6-; close examination of the spectrum of our material shows the presence of these peaks as well.

If this is the wrong isomer, the reaction to form the acetonide of this material should go as well. This was tried using the some conditions as used previously, and by NMR, there was some of the acetonide formed. It did not go completely, however, but it was more than a trace amount, and since the starting material was quite pure (by elemental analysis as well as NMR and melting point), it seems likely that the fact of the low conversion is a problem with the reaction conditions, rather than the wrong molecule.

If this material is in fact the wrong isomer of tetramethylcyclooctatetraene, as the evidence suggests, then the material isolated in the first step must have been the incorrect isomer. None of the experimental conditions used in the subsequent conversions was vigorous enough to cause this sort of structural transformation.

If the isomer recovered in the first reaction is, in fact, the 1,2,5,6-isomer, it is important to examine Gilbert's characterization of his final product, to determine whether we isolated different isomers using the same procedure. Examination of his characterization, however, is not absolutely clear on this point. After carrying out the LAH reaction the first time, the ^{1}H NMR of the product was taken and along with a great deal of impurity, he observed small singlets at δ 5.5 and δ 1.76 which he attributed to the 1,3,5,7-tetramethylcyclooctatetraene. These shifts are slightly off from what Luke reported for this isomer , and they are quite close to those found in this work.

In his subsequent preparations of this ligand, Gilbert did not purify the material to any large extent. In general, he reacted the crude workup mixture with potassium to form the dianion, which he stored in an argon glovebox. He did not report characterization of this dianion. He then used this reagent directly to prepare a number of new organometallic complexes.

What evidence there is suggests that the isomer prepared by Gilbert is the isomer we prepared as well. The NMR shifts are slightly off, but they are closer to the reported shifts for the 1,2,5,6- than for the 1,3,5,7-isomer. In addition, our characterizations of the intermediates (the alcohol and the chloromethyl) match quite well with those reported by Gilbert , including the melting points, which would be thought to show a bigger change than does the NMR.

Paquette reported that this molecule exists as an equilibrium mixture of the 1,2,5,6- and the 1,4,5,8-isomers.[31] If the mixture was pyrolyzed in the gas phase or irradiated, the ratio could be altered. After standing at room temperature for several hours, however, both mixtures would revert to the original equilibrium ratio of 10:1.

This suggests that it should be possible to form the dianion of this molecule, since the change in configuration would necessitate that the molecule go through a planar transition state. In addition, as discussed above, Gilbert stored his material as the dianion, so it was important to make sure that our material would form the dianion.

To test this theory, a sample of the COT in THF-d_8 was made in an NMR tube. To this was added a small amount of potassium, and the spectrum was taken as a function of time. The solution slowly turned dark brown as the potassium reacted, and ^{1}H NMR showed the growing in of a peak at about δ 2.8, which, on the basis of the 1,2-disubstituted analog, most likely corresponds to the dianion. Thus, it appears that this molecule has the potential to be used as a ligand for these metallocenes; although it is not quite as symmetric as the 1,3,5,7-isomer, it may have properties which could be of interest.

EXPERIMENTAL

General

See Chapter 2, Experimental Section, General.

Elemental analyses were performed by the Microanalytical Laboratory of the College of Chemistry, University of California, Berkeley. Infrared spectra were recorded on a Perkin-Elmer Model 283 Infrared recording spectrophotometer. Melting points were determined with a Büchi ___ and are reported uncorrected.

Preparation of 1,3,5,7-Tetramethylcyclooctatetraene

I. Preparation of 4,6-Dimethylcoumalin

This material was prepared from 4,6-dimethylcoumalic acid[11] according to the procedure in *Organic Syntheses* .[12]

Additional characterization: ^{1}H NMR ($CDCl_3$): δ 5.90 (d, 1H), δ 5.81 (d, 1H), δ 2.18 (s, 3H), δ 2.07 (s, 3H).

II. Photodimerization of 4,6 - Dimethylcoumalin

The photolysis of the coumalin was carried out using a 450 - watt Hanovia mercury lamp, which was placed in a quartz sleeve and suspended on a ring stand. When a Pyrex filter was used, it consisted of a conventional Pyrex photoreactor placed around the sleeve. Two six inch rings were attached to the ringstand, encircling the lamp, with one ring about 3 inches above the other. Test tubes containing the coumalin

in benzene solution (see below) were then wired to the rings, and the entire ringstand was placed in a large plastic bucket which had had a hole cut out of the side, to which a draining tube was attached. A water hose was then placed in the bucket and turned on at such a rate that the drain tube kept the water level about 1 inch below the tops of the test tubes. With water flowing through the sleeve as well as the bucket, the temperature remained fairly steadily between 15 - 20 °C with the lamp turned on.

For each of the runs, some of the dimethylcoumalin was dissolved in a minimum amount of benzene and placed in the appropriate number of test tubes, which were flushed with N_2, capped with rubber septa and wired to the rings. After 2 days of photolyzing, the solutions turned pale yellow, and the solid material began to form after 2 days to 1 week.

In the first attempt, no Pyrex filter was used and it required two weeks for any solid at all to collect. The solution, however, had turned yellow and become extremely viscous. The solvent was removed, resulting in a pale yellow powder which had a mp of 110 °C and the NMR shown in Table 5.2 (Trial 1). IR of this material showed a stretch at 1740 cm^{-1}, possibly due to a carbonyl stretch, and an elemental analysis reasonably consistent with a compound still containing two CO_2 groups.

In the second attempt, a Pyrex filter was used. After 1 week, crystalline material appeared in the bottom of the two tubes used for this experiment. One of the tubes was removed, and the solution was decanted from the crystals; the solution was placed in another tube and allowed to photolyze one additional week, while the crystals were examined by NMR (Trial 2a in Table 5.2). After the additional reaction time, the undisturbed tube had more of the crystals, while the decanted solution had a white powder on the bottom (Trial 2b in Table 5.2).

Several other attempts were made with similar results.

Pyrolysis Attempt of Product 1

A 5.62 g portion of the original benzene solution from Trial 1 was placed in a 25 mL round bottom flask and flushed with nitrogen. An oil bath was heated to about 100 °C and the flask was immersed in it. The benzene boiled off, after which the temperature of the oil bath was slowly raised to about 170 °C, at which point the solution turned a deep red color. The material was placed on a silica gel column (2.7 x 24 cm) and the column was eluted with hexane. No material came off until the eluting solution had been increased to a 50:50 mixture, at which point a small amount of material came off. NMR of this material showed nothing identifiable. Since the desired TMCOT was described as a fast moving band on a column eluted with pure hexane,[23] further work with this was not attempted.

Tube Furnace Pyrolysis

A tube furnace apparatus was set up consisting of two small U-tubes attached to either end of a tube furnace. In one tube was placed a small sample of the material and the tube was immersed in an oil bath. The receiving tube was placed in a dry ice bath and the system was connected to a vacuum pump pulling about 0.5 torr. The temperature of the furnace was set at 220 °C, and the oil bath was heated to volatilize the material. At an oil bath temperature of about 120 °C, the material melted, at which point the temperature was allowed to stabilize, and the system was allowed to stand for

about 2 hours. During this time the material darkened, but nothing was collected in the receiving U-tube. NMR of the darkened starting material gave no evidence for any COT species.

Preparation of Tetrakis(hydroxymethyl)cyclooctatetraene

In a 500 mL three-necked flask fitted with a reflux condenser, a dropping funnel and a stopcock for gas inlet, 2.31 g (0.01 mol) of $Ni(acac)_2$ (Ventron/Alfa Inorganics, dried prior to use) was dissolved in 125 mL of benzene. Propargyl alcohol (50 mL, 0.86 mol) was added dropwise over a 75 minute period to the refluxing solution under nitrogen. The color slowly turned from dark green to brown. The reaction was stopped after the appropriate reaction time and washed three or four times with benzene to separate the nickel catalyst. The viscous product mixture was dissolved in a minimum amount of ethanol. A chromatographic column containing basic alumina (activity III/IV) was run with ethanol, with the size of the column dependent on the amount of material to be separated. The material was collected until the color of the solution coming off the column turned pale yellow. A large amount of brown material remained near the top of the column. About 1 - 2 L of yellow-orange solution was obtained, which was evaporated under reduced pressure, and the resulting red-brown oil was dissolved in hot isopropanol. Over a period of 1-2 weeks the $(CH_2OH)_4C_8H_4$ (1,3,5,7-isomer?) precipitated in low yield (3.5 g, 7%). ^{1}H-NMR (D_2O): δ 5.82 (s,1 H); δ 4.03 (d, J = 12.8 Hz, 1 H); δ 3.88 (d, J = 12.9 Hz, 1H).

Anal. Calcd. for $C_{12}H_{16}O_4$: C, 64.26; H, 7.21; O, 28.53. Found: C, 63.98; H, 7.15.

Preparation of Acetonide

In 100 mL of hot acetone was dissolved 4 g of the oil obtained in the tetramerization reaction of the propargyl alcohol prior to column purification. A few crystals of *p*-toluenesulfonic acid were added, as well as 3Å sieves. The solution was stirred at reflux overnight, then filtered from the sieves and allowed to cool to room temperature. White crystals appeared on cooling which were separated, washed with cold acetone, yielding 0.5 g of the white crystals; mp. 218 - 220 °C, ^{1}H-NMR ($CDCl_3$): δ 5.74 (s, 1H); δ 4.17 (d, J = 17.5 Hz, 1H); δ 3.91 (d, J = 17.5 Hz, 1H); δ 1.32 (s, 3H).

Anal. Calcd for $C_{18}H_{24}O_4$: C, 71.01; H 7.96. Found: C, 70.45; H, 7.99.

Attempted Preparation of Tetrakis(trimethylsilyl)cyclooctatetraene

A flask equipped with addition funnel, condenser and dry ice condenser was charged with 8 mL of benzene and 0.12 g of $Ni(acac)_2$ (4.5×10^{-4} mole). To this solution was added 4.5 g (0.0458 mole) of trimethylsilylacetylene (Aldrich). The system was flushed with nitrogen and heated to reflux under a nitrogen balloon, in order to minimize loss of the volatile acetylene. The reaction was followed by GC, but after 72 hours, there had been little change in the amount of the acetylene present. The reaction mixture was extracted with hexane and the solvent was removed. NMR of the crude material showed no resonances in the region expected for a COT.

Preparation of Tetrakis(chloromethyl)cyclooctatetraene

To 80 mL of acetonitrile stirring in a 250 mL round-bottomed flask under nitrogen was slowly added 10.42 g (50 mmol) of PCl_5. The solution was stirred for 4 hours and 2.24 g (10 mmol) of the putative 1,3,5,7-$(CH_2OH)_4C_8H_4$ was added slowly. The color turned from yellow to green. After 16 hours the reaction was stopped and poured onto 250 - 300 g of ice. After the ice had melted, CH_2Cl_2 was added and the layers were separated. The aqueous layer was extracted three times with 100 mL of CH_2Cl_2 and the combined organic extracts were washed with 70 mL of H_2O. The orange-brown solution was dried over $MgSO_4$, filtered and evaporated to a red-brown oil which was then digested in hot heptane. The material is not very soluble until the heptane is near boiling, but care must be taken to avoid heating the oil too much before it dissolves, as it does decompose at elevated temperatures. The hot heptane solution was filtered through a frit with silica gel , which was rinsed thoroughly with additional hot heptane, resulting in a colorless solution. White needles formed overnight in a refrigerator (0 °C), yield 42% (1.27 g). ^1H NMR ($CDCl_3$): δ 6.09 (s, 1H, ring proton); δ 4.24 (d, J = 12.2 Hz, 1 H); δ 4.08 (d, J = 12.2 Hz, 1H); mp 118-119 °C.

Anal. Calcd for $C_{12}H_{12}Cl_4$: C, 48.32; H, 4.06; Cl, 47.61. Found: C, 48.26; H, 4.14; Cl, 47.32.

LAH Reduction of Tetrakis(chloromethyl)cyclooctatetraene (Gilbert's method).[25]

In an argon glovebox, a slurry of tetrakis(chloromethyl)cyclooctatetraene (1.15 g, 3.86 mmol) in 50 mL of ether was treated with $LiAlH_4$ (Alfa, 0.732 g, 19 mmol) in small portions. The reaction flask was capped with a condenser and gas inlet, removed from the glovebox and placed under argon on a Schlenk line. The solution was allowed to reflux for 18 h, then was cooled in an ice bath. The reaction mixture was cautiously hydrolyzed with 40 mL of saturated NH_4Cl, followed by addition of concentrated HCl to bring the pH of the solution to about 1. A colorless organic layer separated from a gray heterogeneous aqueous layer. The layers were separated and the aqueous layer was extracted with ether (3 x 50 mL); the combined ether extracts were rinsed with 100 mL of water, dried over $MgSO_4$ and filtered, resulting in a clear, colorless solution. The solvent was removed *in vacuo* without warming, resulting in a pale yellow, semi-solid oil. ^1H NMR ($CDCl_3$) of the crude product was quite complicated, as mentioned in the text. The main features, were an apparent series of overlapping multiplets centered around δ 4.0 - 4.3, a series of possible singlets between δ 5.4 - 6.1, and a large group of overlapping peaks from δ 1.8 - 2.0. Attempts to purify the material (TLC, Column chromatography) were unable to simplify the spectrum much, although they did remove residual stopcock grease.

Attempts with other Reducing Agents

A wide range of other reducing agents was tried to effect this reduction, as discussed in th text. Experimental conditions used were standard for the types of reagents, with temperatures and reaction times varied as appropriate. The physical

appearance and ^1H NMR of the products were similar to those mentioned above for the reagents which did not destroy the COT ring system, as evidenced by peaks in the δ 5.5 - 6.0 region.

Preparation of Tetrakis(bromomethyl)cyclooctatetraene

To a solution of 7.5 g (0.0286 mol) of triphenylphosphine in 150 mL of anhydrous dimethylformamide (freshly distilled from CaH_2) stirred under nitrogen in an ice bath was slowly added 4.56 g (0.0285 mol) of bromine. To this bright yellow-orange mixture was added 0.8 g (0.0036 mol) of $C_8H_4(CH_2OH)_4$ in about 50 mL of dimethylformamide over a period of 30 minutes. The ice bath was removed and the solution was allowed to stir for 4 hours at room temperature. After this time, the solution was poured into 200 mL of cold water and extracted with ether (3 x 100 mL). The combined extracts were rinsed with water followed by saturated sodium bicarbonate solution, dried over $MgSO_4$ and evaporated under reduced pressure to give a pale yellow solid.

This solid was digested with a large volume of hot pentane (approximately 500 mL) and filtered through silica which had been deactivated with one equivalent of water. After the extractions, the silica was rinsed with hot heptane to remove the last of the desired compound. The resulting solutions were evaporated to yield a pale yellow solid (0.99 g, 57 %). ^1H NMR ($CDCl_3$): δ 6.12 (s, 1H); δ 4.11 (d, J = 10.9 Hz, 1 H); δ 3.97 (d, J = 10.9 Hz, 1 H).

LAH Reduction of Tetrakis(bromomethyl)cyclooctatetraene

A solution of 0.8 g (0.0017 mol) of tetrakis(bromomethyl)cyclooctatetraene in 15 mL of ether was added during 20 minutes to a suspension of $LiAlH_4$ (Alfa, 0.65 g, 0.017 mol) in 30 mL of ether stirring in a dry ice bath. The bath was removed and the solution was allowed to come to room temperature while stirring for about 2 hours. Following the cautious hydrolysis of the reaction mixture with 20 mL of saturated NH_4Cl solution, it was diluted to about 100 mL with dilute hydrochloric acid. After the layers were separated, the organic layer was extracted with ether (3 x 50 mL), the combined organic extracts were washed with saturated sodium chloride solution, dried over $MgSO_4$ and filtered. The solvent was removed *in vacuo* without heating, resulting in a pale yellow oil (0.16 g, 0.001 mol, 59%). This oil was placed on a short silica gel column and eluted with hexane. A pale yellow liquid was collected and a dark yellow layer remained at the top of the column. The solvent was removed from the collected material, resulting in a pale yellow liquid. ^1H NMR ($CDCl_3$): δ 5.49 (s, 1H); δ 1.75 (s, 3H); (CCl_4): δ 5.42 (s, 1H); δ 1.74 (s, 3H). The reported singlets at δ 5.52 and δ 1.63 are also present, although the integration on these was not accurate.[31]

Formation of the Dianion of the Reduction Product.

In an argon glovebox, a degassed sample of the TMCOT isomer prepared above was placed in an NMR tube equipped with a stopcock joint. THF-d_8 was added, and a small piece of potassium (freshly shaved) was placed in the top of the tube, such that it was not in contact with the solution. The tube was then removed from the glovebox and sealed under vacuum on a Schlenk line. A spectrum of the

TMCOT in THF-d_8 was taken, then the tube was inverted so that the potassium metal was dislodged and dropped into the solution. The solution immediately started turning a dark brown in the area of the metal. After 4 hours, with intermittent shaking of the tube, the potassium metal had disappeared, and a ^{1}H NMR was taken. ^{1}H NMR (starting material, THF-d_8): δ 5.48 (s, 1H); δ 1.73 (s, 3H). ^{1}H NMR (after 4 h reaction time, THF-d_8): δ 5.48 (s); δ 2.74 (s); δ 1.73 (s).

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CHAPTER VI:

CONCLUSIONS

It was discussed in the previous chapters that one of the principal reasons for investigating the properties of the bis([8]annulene) complexes of the lanthanides was to compare them to the analogous and more thoroughly studied actinide series. It was thought that the lanthanide series should provide a good ionic analog to the actinocenes, thus perhaps revealing information about the relative degree of covalency in these two classes of molecules.

The chemistry of the first series of bis([8]annulene)lanthanide complexes examined, $K[Ln(C_8H_8)_2]$, did show the expected differences between the two classes. The lanthanide metallocenes show properties consistent with a highly ionic system, especially in comparison to the relatively stable properties of uranocene. However, at least a part of this difference was thought to be the result of comparing the lanthanide anion salts with the neutral uranocene and thorocene molecules; the fact that these compounds are potassium salts definitely biases their chemistry towards the ionic. Thus, it was hoped that cerocene, as the one likely stable neutral lanthanide metallocene of this class, could provide the comparisons hoped for.

As more information was learned about this molecule, however, questions arose as to the nature of the bonding in it. The initial reports on its preparation were greeted with some skepticism, with the report by Kalsotra, et al., especially

questionable as a result of the refutations mentioned before.[1] Although there is now some debate as to the appropriateness of the Xα method for this system, the results determined from these calculations suggest that not only should cerocene be a ground state and potentially be stable enough to be isolated, but that it may have a much higher degree of covalency than had been expected. The subsequent reconfirmation of the Greco synthesis under conditions which might have been thought to be too vigorous for its preparation suggest that the molecule is definitely more stable than might have been expected.[2]

The work reported in this thesis further supports this apparent stability of cerocene. Rather than being an intermediate which would rapidly undergo intramolecular electron transfer, this is a remarkably robust organometallic species. Surprisingly, many of its properties more closely mimic those of uranocene or thorocene than those of other lanthanide species, and since uranocene has generally been observed to be the most stable of this class of metallocene, this suggests an unusual amount of stability in this molecule as well. The electrochemical work has given a more quantitative measure of this stabilization and is consistent with the chemical evidence; the conditions necessary to effect the oxidation of the cerate complex are surprisingly gentle.

The nature of this stabilization is, as in the case of uranocene itself, difficult to determine. The Xα calculations would suggest that much of the stabilization comes from overlap of metal and ligand orbitals, but whether these results can be trusted is not yet clear. This amount of participation by the lanthanide's orbitals in the bonding of the compound is certainly unusual, especially as it would appear to approach the amount in the actinide cases.

Recently, Fragalà and Marks have reported the preparation and examination of a second type of tetravalent cerium organometallic species, $(C_5H_5)_3CeO\text{-}i\text{-}C_3H_7$ and comparisons of the properties of this compound and cerocene are quite interesting.[3] Greco originally reported the preparation of this complex in poor yield, as discussed in Chapter I. Fragalà and Marks have developed a much improved method for obtaining this compound in up to 69 % yield (see Eq. [6.1]). The NMR yields using both the methyl and the n-Bu derivative of the tin reagent appeared to be essentially quantitative, with the methyl being the preferred because the volatility of the $Me_3Sn(O\text{-}i\text{-}Pr)$ produced helps in the work-up. Further work suggests that this same approach will work with $Me_3Sn(C_5H_4Me)$ as well. Their NMR data are consistent with a diamagnetic Ce(IV) complex, and they are in reasonable accord with what the Greco group reported.

$$Ce(O\text{-}i\text{-}Pr)_4 + 3R_3SnCp \xrightarrow[\text{toluene}]{65\ ^\circ C} Cp_3Ce(O\text{-}i\text{-}Pr) + 3R_3Sn(O\text{-}i\text{-}Pr) \qquad [6.1]$$

$$R = CH_3,\ n\text{-}Bu$$

The electrochemistry of this compound was explored, and the data was consistent with a one-electron, reversible process as in the case of cerocene. The reported $E_{1/2}$ value is about +0.5 V (vs NHE) , as compared with -1.3 V for cerocene; there is clearly a dramatic difference between the two compounds in this respect.

Calculations were performed on the related compound $(C_5H_5)_3CeOMe$ using the non-relativistic $X\alpha$ formalism.[4] The photoelectron spectra of the corresponding

isopropyl compound were measured using both He-I and He-II radiation. The results of these two studies are presented in Table 6.1.[3]

Table 6.1

Comparison between Xα and PES Results

MO	TSIE[a] (-eV)	IE (expt)[b] (-ev)	Composition (%) Ce s	p	d	f	Cp_3	O	CH_3	Predominant Character
20a"	7.31	7.41	0	0	2	25	66	6	1	π - Cp
26a'	7.32		0	1	0	6	83	8	2	π - Cp
19a"	7.43	7.76	0	0	0	21	79	0	0	π - Cp
25a'	7.49		0	0	2	15	77	5	1	π - Cp
18a"	8.26		0	0	5	4	62	23	6	π
24a'	8.59	8.47	0	0	4	3	41	43	9	O_{2p}
17a"	8.81		0	0	10	3	38	40	9	O_{2p}
23a'	8.92	9.41	0	0	7	2	69	18	4	π

[a] Calculated values for Cp_3CeOMe.

[b] Experimental PES data from $Cp_3Ce(O\text{-}i\text{-}Pr)$.

The calculated results show that the MO's can be grouped into three main types based on their composition: a) π orbitals predominantly derived from the Cp; b) lone pair orbitals derived from the O_{2p} orbitals; and c) lower energy π- and σ-ligand orbitals which are essentially uninvolved in the bonding. It is also clear from this table that they determined a significant amount of both f- and d-orbital involvement (see, for example, 20a", 19a", and 25a').

The results are then compared with the PES work, and there appears to be reasonable agreement. There are four main bands in the region below about 10.5 eV, which are assigned as shown in the Table 6.1. Of particular interest to this discussion is the observation that there is very little difference in the relative intensities of the bands when the radiation is changed to He-II. This PES behavior is typical of the trivalent cyclopentadienyl lanthanide complexes,[5] but stands in contrast to this group's results on Cp_3UOEt. Marks and Fragalà suggest that this difference may reflect the reduced metal involvement in the lanthanide case relative to the actinide. In addition, they also mention that the intensity changes in the Cp_3Ce(O-i-Pr) spectra are smaller than those observed in the spectra of $Ce(COT)_2$, possibly suggesting a higher degree of metal involvement in the latter case.

This study shows that the field of tetravalent cerium organometallic chemistry is one which needs to be explored. Rather than being too unstable to exist in organometallic species, there have now been two examples of relatively stable complexes which have been prepared in good yields; the possibility of others is now clearly present. The difference in values for the Ce(IV)/Ce(III) couple suggests that the stability imparted by the COT ligands is greater than that imparted by the ligands in the other molecule, but the Cp's and isopropyl group still provide enough support to allow

the molecule to be isolated and studied. If a similar Nernstian analysis is made of this data as was made in Chapter IV for the cerocene, it can be seen that whereas the K_{IV} / K_{III} for the cyclooctatetraene system is about 10^{50}, in Marks' compound the ratio is closer to 10^{20}; there is still a higher relative stabilization of the tetravalent cerium, but not to the same degree as in cerocene. The PES and calculational work suggests that although there may be a different mode of bonding in the two compounds, there does appear to be some degree of orbital overlap between the metal and ligands in each of these cases. If this is the case, it will be interesting to explore the chemistry of tetravalent cerium, to try to understand what ligands can provide the needed stability for the isolation of these compounds, and explore the effects of a range of different types of ligands.

References

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4. Pitzer's results as discussed in Chapter I have suggested that the Xα calculations are not suitable for uranocene, and presumably its derivatives; Whether they can be trusted for other f-element systems must still be determined.

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