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[8]ANNULENE DERIVATIVES OF ACTINIDES AND LANTHANIDES

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December 1984

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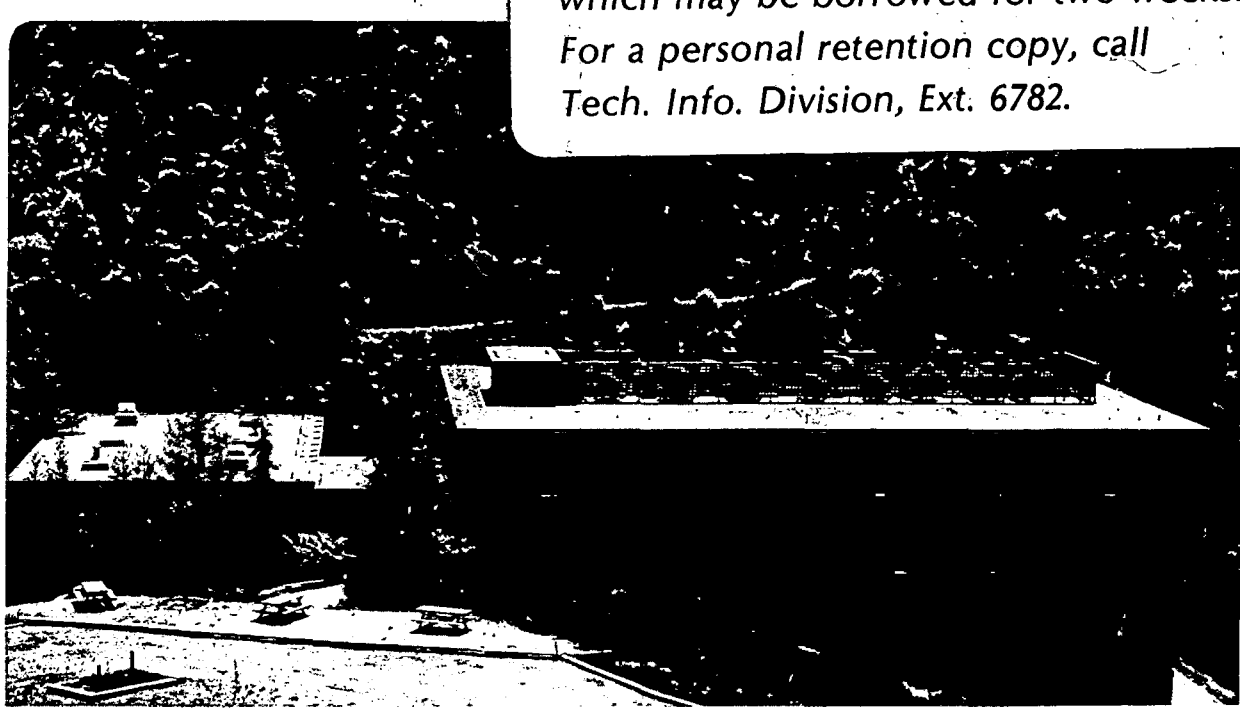

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[8]Annulene Derivatives of Actinides and Lanthanides

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[8]Annulene Derivatives of Actinides and Lanthanides

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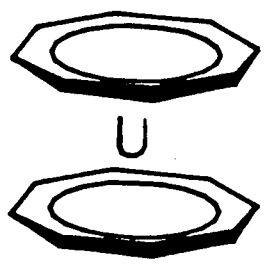
ABSTRACT. A number of [8]annulene actinide and lanthanide compounds are now known at oxidation levels of the central metal of +2, +3, and +4. Several structures have been established for these compounds. The [8]annulene ring is generally present as a planar octagonal ring of carbons with the metal centrally located. Many structures are those of sandwich compounds with the metal located between parallel rings. The original system, uranocene, is the most stable and the most thoroughly studied of these compounds. Only limited chemistry has been explored so far with these systems; in the sandwich compounds the large rings hinder coordination at the central metal. Uranocene is paramagnetic and shows a wide range of ^1H chemical shifts that have been particularly useful in studies of structure and electronic structure. Especially valuable are derived barriers for a number of dynamic processes. These energies provide significant new information concerning intramolecular interactions.

1. INTRODUCTION

Bis([8]annulene)uranium(IV)[1], uranocene, 1, was prepared as an expected f-orbital analogue to d-transition metal metallocenes.



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In d-transition metal complexes such as ferrocene, an important amount of ring-metal covalency is achieved by the interaction of the highest occupied ligand MOs (e_{1g}) of two cyclopentadienyl anions with the unoccupied $3d_{\pm 1}$ orbitals on Fe^{2+} (Figure 1). These orbitals share a common nodal plane and have the proper wave function phases for symmetry-permitted overlap.

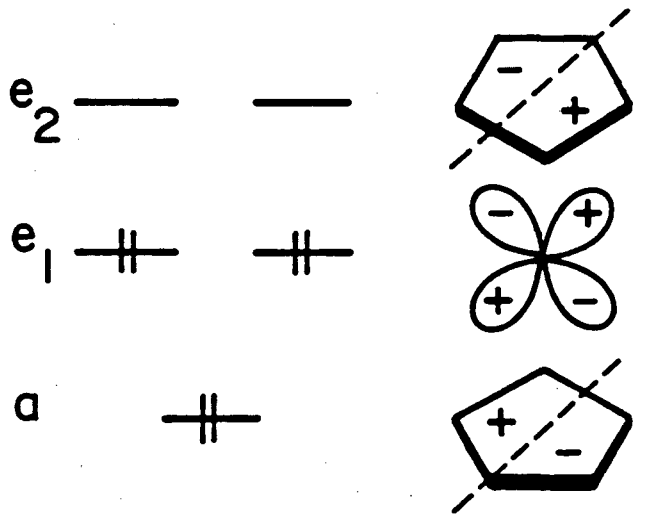


Figure 1. Ring-metal interaction between the HOMO e_{1g} π-MOs of two cyclopentadienyl anions and an e_{1g} d-orbital of the central metal.

By analogy, a ring-metal interaction is symmetry permitted between the highest occupied MOs of two [8]annulene dianions and two lanthanide or actinide metal f-orbitals (l = ±2). An empirical model depicting this interaction is shown in Figure 2. In this example, the central metal ion shown, uranium(IV), has two electrons remaining in metal f-orbitals; thus, the HOMO of uranocene is located on the metal.

Since the synthesis of uranocene,[2] there have been many other complexes synthesized involving a lanthanide or actinide element and one or more [8]annulene dianions. These complexes are generally unstable towards air (most are pyrophoric) and water; all handling of these complexes must be carried out in an inert atmosphere.

The first part of this paper reviews the synthesis and structures of the f-block metal [8]annulene dianion complexes. For the purpose of this paper, the [8]annulene dianion complexes of the actinides and lanthanides have been classified as bis- or mono-[8]annulene complexes and are further classified by oxidation state of the f-block metal (+3 and +4 for actinides, +2, +3, and +4 for lanthanides).

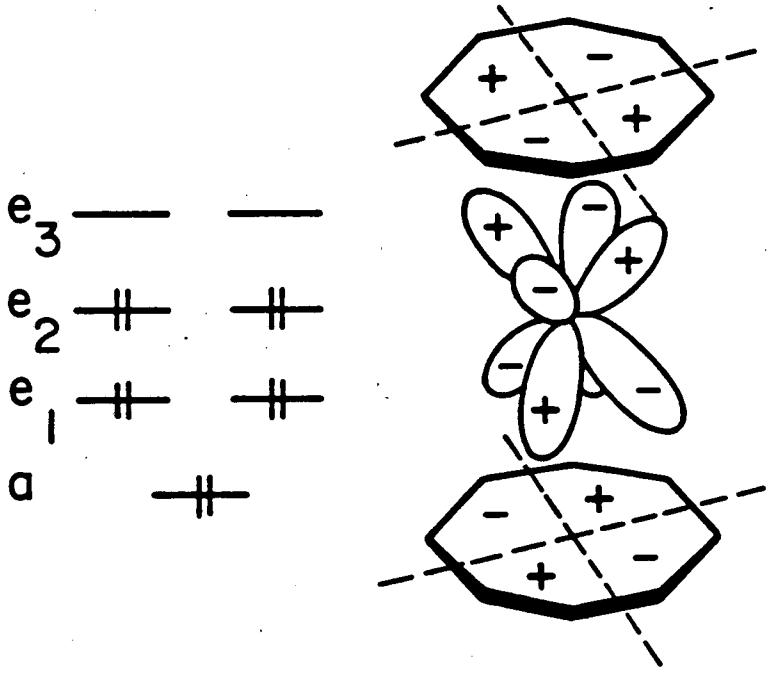


Figure 2. Analogous ring-metal interaction between the e_{2u} HOMOs of two [8]annulenes, with two nodes, and an e_{2u} f-orbital of the central metal.

2. STRUCTURES

2.1 *Bis([8]annulene)actinide(IV) complexes*

Uranocene and its ring alkylated,[3-7] arylated[8-10] and annulated[11-13] derivatives constitute the majority of the [8]annulene complexes known for the tetravalent actinides. The synthesis of the other bis([8]annulene)actinide(IV) complexes is similar to that of the uranium systems.

The most utilized route for the synthesis of bis([8]annulene)-actinide(IV) complexes is the reaction of a tetrahydrofuran (THF) solution of [8]annulene dianion with a stoichiometric amount of the actinide tetrachloride in THF. This method has been employed for the synthesis of bis([8]annulene)thorium(IV) (thorocene),[14] -protactinium(IV) (protactinocene),[15] -uranium(IV)[2] and -neptunium(IV) (neptunocene);[16] however, the yield of protactinocene by this method is low. Bis([8]annulene)plutonium(IV), plutonocene, was synthesized by the reaction of di(tetraethylammonium)plutonium(IV) hexachloride suspended in THF with a stoichiometric amount of [8]annulene dianion in THF.[16]

$$2\ K_2C_8H_8 + AnCl_4 \xrightarrow{THF} An(C_8H_8)_2 + 4\ KCl$$

An = Th, Pa, U, Np

$$2\ K_2C_8H_8 + (C_5H_5NH)_2PuCl_6 \xrightarrow{THF} Pu(C_8H_8)_2 + 4\ KCl + 2\ C_5H_5N^+Cl^-$$

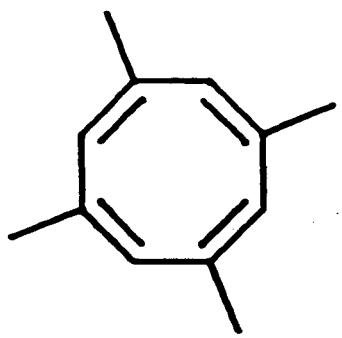
Curiously, attempts to synthesize plutonocene using dicesium- or dipyridinium- plutonium(IV) hexachloride, Cs_2PuCl_6 or $(C_5H_5NH)_2PuCl_6$, were unsuccessful, but the synthesis of uranocene from $(C_5H_5NH)_2UCl_6$ was successful.[16]

Thorocene, uranocene and plutonocene can also be synthesized by the reaction of cyclooctatetraene with the finely divided metals obtained by heating the metal hydrides.[17] In this reaction, a sealed Pyrex tube containing the actinide-cyclooctatetraene mixture was heated in a tube furnace at 150-160° C. The reaction product was isolated by sublimation. This preparative method provides demonstration of the thermodynamic stability of the bis([8]annulene)actinide complexes.

$$An^\circ + C_8H_8 \longrightarrow An(C_8H_8)_2$$

An = Th, U, Pu

The bis(1,3,5,7-tetramethyl[8]annulene)actinide(IV) complexes made from 1,3,5,7-tetramethylcyclooctatetraene, 2,[18,19] have been synthesized for many of the actinide elements.



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Treatment of 2 with two equivalents of potassium gives the corresponding [8]annulene dianion. 1,1',3,3',5,5',7,7'-Octamethylthorocene,[20] -uranocene,[19] -neptunocene[19,21] and -protactinocene[21] have all been synthesized by the addition of 1,3,5,7-tetramethyl[8]annulene dianion to the appropriate actinide salt.

$$2\ K_2(Me_4C_8H_4) + AnCl_4 \xrightarrow{THF} An(Me_4C_8H_4) + 4\ KCl$$

An = Th, Pa, U, Np

Attempts to make the octamethylplutonocene derivative by addition of tetramethyl[8]annulene dianion to the tetrachloride resulted in the reduction of Pu(IV) by the tetramethyl[8]annulene dianion to Pu(III).[19] When the borohydride complexes of neptunium and plutonium are used in place of the halide salts acceptable yields of the bis(tetramethyl[8]annulene) complexes were obtained.[21]

$$2\ K_2(Me_4C_8H_4) + An(BH_4)_4 \xrightarrow{THF} An(Me_4C_8H_4) + 4\ KBH_4$$

$$An = Np,\ Pu$$

Other substituted bis([8]annulene)actinide(IV) complexes of uranium,[3-13] thorium,[20] neptunium[4] and plutonium[4] have been prepared by the reaction of the substituted [8]annulene dianion with the appropriate actinide(IV) salt. X-ray diffraction data suggest that the alkyl-substituted neptunium(IV) and plutonium(IV) complexes are isomorphous with the corresponding uranium(IV) complex[4] but none of the structures of these complexes has yet been determined from single crystal x-ray diffraction.

The mechanism of the reaction to form the bis([8]annulene) complexes is not known. It is clear, however, that there are differences in the mechanism in the formation of uranocene compared to thorocene. When the reaction of two equivalents of n-butyl[8]annulene dianion with thorium tetrachloride was carried out in an NMR tube and monitored by ^{1}H-NMR, a resonance was observed which cannot be attributed to the bis([8]annulene) complex.[22] Further experiments showed that this apparent intermediate in the reaction is the mono-ring complex, [8]annulenethorium(IV) dichloride (*vide infra*).[22] The mechanism for the formation of bis([8]annulene)thorium evidently involves the stepwise substitution of [8]annulene dianion for two chloride ions.

$$K_2C_8H_8 + ThCl_4 \longrightarrow (C_8H_8)ThCl_2 + 2\ KCl$$

$$K_2C_8H_8 + (C_8H_8)ThCl_2 \longrightarrow Th(C_8H_8)_2 + 2\ KCl$$

In the analogous uranium system, however, no intermediate mono-ring complexes have been observed.

Uranium, unlike thorium, has an accessible trivalent oxidation state. It has been shown that uranocene can be reduced by lithium naphthalide to the bis([8]annulene)uranate(III) anion.[23] The same complex can be synthesized by the reaction of two equivalents of [8]annulene dianion with one equivalent of uranium trichloride.[23]

We have found that [8]annulene dianion reduces uranium tetrachloride to uranium trichloride when the reaction is carried out at -78° C.[24] When two moles of [8]annulene dianion in THF are added to one mole of uranium tetrachloride in THF at -78° C, the green color of uranium tetrachloride changes to the purple color of the trichloride. As this reaction mixture is warmed slowly to room temperature, the color of the reaction changes to the dark green color of uranocene. The yield of uranocene is not affected in this method of reaction. When one-half molar equivalent of [8]annulene dianion is added to uranium

tetrachloride at -78°C, no uranocene is formed upon warming the solution to room temperature.[25] These reactions indicate that the first step of the reaction to form uranocene is the reduction of the uranium tetrachloride.

Based on the existence of the bis([8]annulene)uranate(III) anion and the reduction of U(IV) to U(III) by [8]annulene dianion, the following mechanism has been proposed, as an alternative to simple ligand substitution, for the formation of uranocene:[26]

$$UCl_4 \cdot L_x + K_2C_8H_8 \longrightarrow UCl_3 \cdot L_x + KC_8H_8^-$$

$$UCl_3 \cdot L_x + K_2C_8H_8 \longrightarrow (C_8H_8)UCl \cdot L_x$$

$$(C_8H_8)UCl \cdot L_x + K_2C_8H_8 \longrightarrow (C_8H_8)_2U(III)$$

$$(C_8H_8)_2U(III) + UCl_4 \cdot L_x \longrightarrow (C_8H_8)_2U + UCl_3 \cdot L_x$$

$$(C_8H_8)_2U(III) + C_8H_8 \longrightarrow (C_8H_8)_2U + KC_8H_8^-$$

Clearly, more work is needed on the mechanism of the formation of bis([8]annulene)actinide(IV) complexes.

The crystal structures of some of the bis([8]annulene)actinide complexes are known. Uranocene[27,28] and thorocene[28] are isostructural (Figure 3) with the only major difference being the metal-to-carbon bond

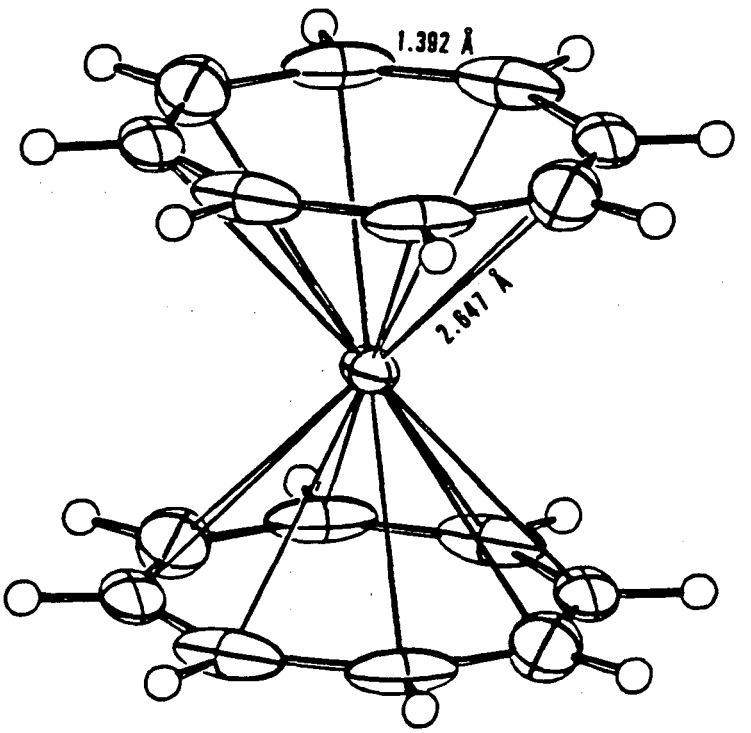


Figure 3. Structure of Uranocene (Ref. 27, 28).

lengths; this difference reflects the larger ionic crystal radius of thorium(IV) vs. uranium(IV).[29] Both of the molecules have D_{8h} symmetry; the carbon atoms of the [8]annulene rings are eclipsed. X-ray diffraction data and the infrared spectra of bis([8]annulene)neptunium and -plutonium suggest that these complexes are isostructural with uranocene and thorocene.[15]

The crystal structure of 1,1',3,3',5,5',7,7'-octamethyluranocene is also known.[30] This complex crystallizes as molecules in two rotomeric configurations (Figure 4).

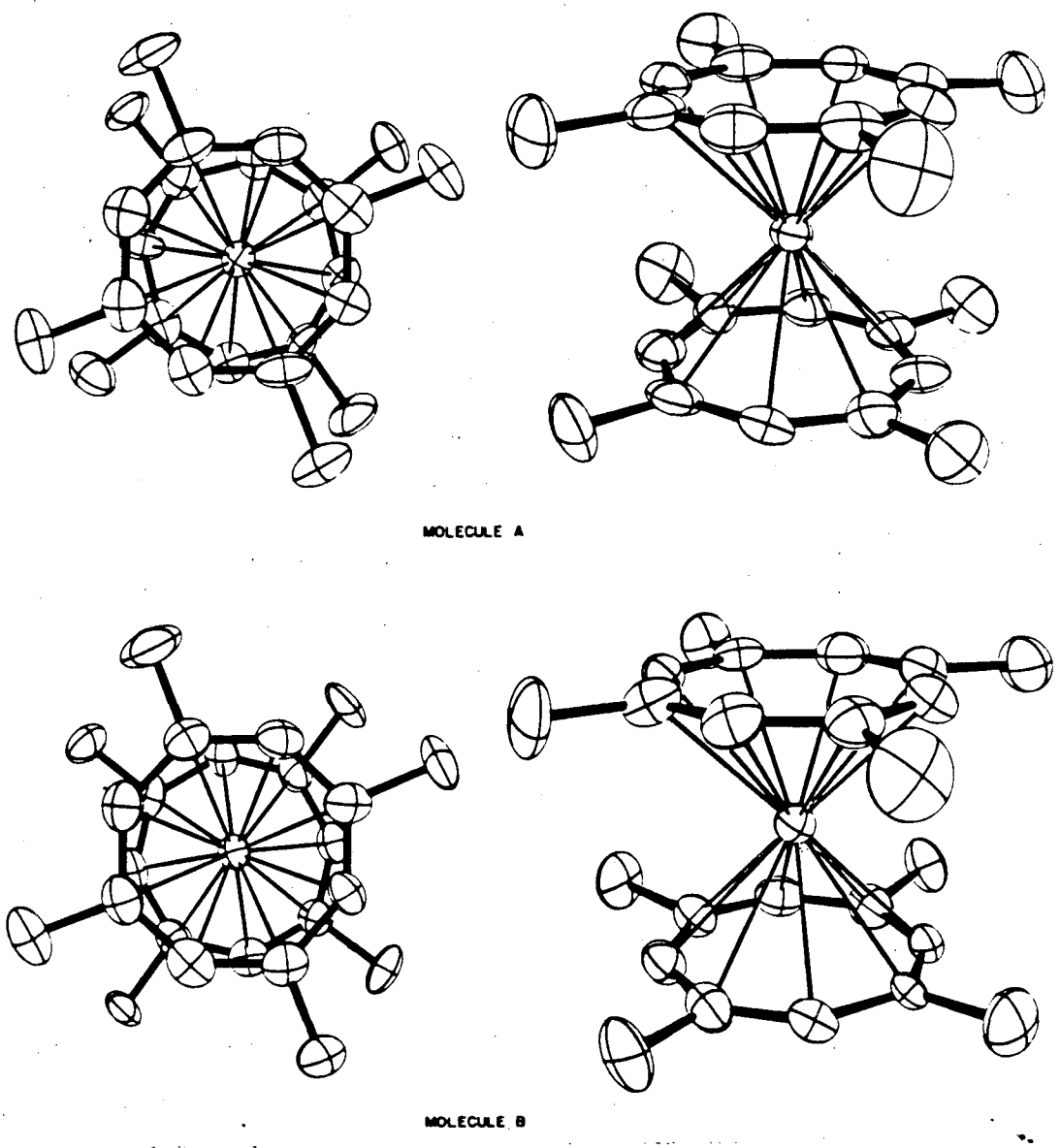


Figure 4. Structure of 1,1',3,3',5,5',7,7'-octamethyluranocene (Ref. 30).

In the A form the methyl groups are essentially eclipsed and in the B form the methyl groups are essentially staggered. The methyl groups on the [8]annulene rings are bent out of the plane of the ring by angles ranging from 0.8° to 6.5°. In the A form of this molecule, the methyl groups are separated by 3.76 Å as a result of this bending; this distance is within the Van der Waals contact distance for two methyl groups (4.0 Å).[31] One possible explanation for the bending of the methyl groups is the change in hybridization of the ring carbons to achieve better orbital overlap with the uranium 6d and 5f orbitals. This bending of the methyl group toward the uranium would result from such a change in hybridization (Figure 5).

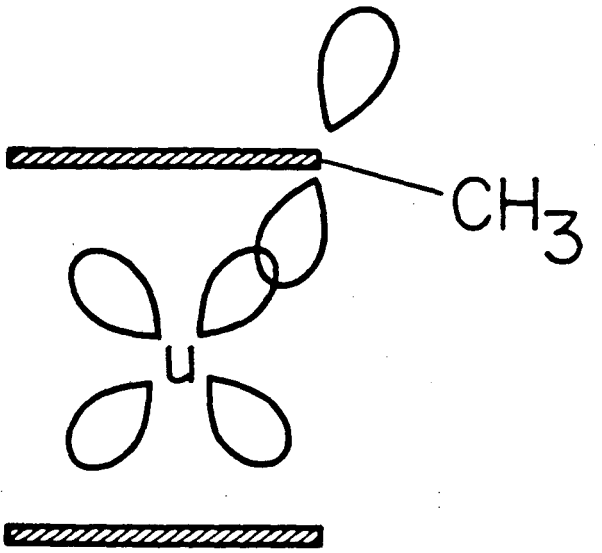


Figure 5. Bending in of a substituent enhances orbital overlap.

X-ray powder pattern data on 1,1',3,3',5,5',7,7'-octamethylprotactinocene, -neptunocene and -plutonocene indicate that these complexes are isostructural with the uranium complex.[21]

2.2 *Bis([8]annulene)lanthanide(IV) complexes*

Although the most stable oxidation state of the lanthanide elements is the +3 state, some of the lanthanides have an accessible tetravalent oxidation state. The lanthanide with the most stable tetravalent oxidation state is cerium. Cerium(IV), however, is a strong oxidizing agent (E°[aqueous] = 1.61 eV).[32] Since cerium(IV) is a strong oxidizing agent and [8]annulene dianion is a reducing agent, it was generally believed that bis([8]annulene)cerium(IV), cerocene, could not exist. Cerocene has been reported by two different methods. The reported products from these two methods differ differ completely.

Kalsotra, Multani and Jain reported that $Ce(C_8H_8)_2$ is a green, air-stable powder that can be synthesized by the reaction of two equivalents

of [8]annulene dianion with the cerium(IV) dipyridinium complex $(C_5H_5NH)_2CeCl_6$.[33]

$$2\ K_2C_8H_8 + (C_5H_5NH)_2CeCl_6 \xrightarrow{THF} \text{"}Ce(C_8H_8)_2\text{"} + 4\ KCl + 2\ C_5H_5N^+Cl^-$$

Their cerium complex is reported as stable to air and acid (although decomposed by hot nitric acid), properties which are not consistent with those of the known bis([8]annulene)actinide(IV) complexes. The infrared spectrum of their complex is also inconsistent with the presence of a planar [8]annulene ligand. We have attempted to duplicate the synthesis of cerocene by the method of Kalsotra, Multani, and Jain and have not been able to reproduce their reported results.

Greco, Cesca and Bertolini have reported that $Ce(C_8H_8)_2$ is an air-sensitive, brownish-red crystalline material that is synthesized in the reaction of cerium(IV) isopropoxide with triethylaluminum in cyclooctatetraene (COT).[34]

$$Ce(O\text{-}iC_3H_7)_4\cdot i\text{-}C_3H_7OH + Al(C_2H_5)_3 \xrightarrow[140°C,\ 2\ hr]{COT} \underset{\text{"Cerocene"}}{Ce(C_8H_8)_2}$$

The characterization of this complex, especially the infrared spectrum, x-ray powder pattern, mass spectrum and ^{1}H-NMR (Ce(IV) is diamagnetic) is consistent with a bis([8]annulene)cerium(IV) complex that is isostructural with uranocene. We have duplicated the work by Greco and co-workers and our results verify their work in every detail, except for the alcoholysis results, which will be discussed below.

The structure of cerocene has not yet been solved from single crystal x-ray data, but it can be concluded from x-ray powder data and infrared spectra that cerocene is isostructural with the bis([8]annulene)actinide(IV) complexes.[34]

We have found that a known complex, bis([8]annulene)cerate(III) anion, can be oxidized to cerocene by strong oxidizing agents.[35]

$$K[Ce(C_8H_8)_2] \xrightarrow{[O]} Ce(C_8H_8)_2$$

$$[O] = O_2,\ NOBF_4$$

Although the optimum reaction conditions of the oxidation reaction have not yet been determined, this method is potentially useful for the synthesis of substituted cerocenes.

Conversion of the bis([8]annulene)cerate(III) anion to cerocene can be accomplished electrochemically. The reversible half-wave potential for the Ce(IV)/Ce(III) couple in this system measured in THF solution is -1.28 eV vs SCE.[36]

2.3. *Theory of bis([8]annulene)metal(IV) complexes*

The existence of bis([8]annulene)actinide(IV) complexes does not by itself establish the existence of a ring-metal bond formed from the interaction of metal d and f orbitals with the ligand π orbitals. One method of establishing the importance of d and f orbital participation of bonding in these complexes is to compare experimental results, for example, photoelectron spectra, with predictions from calculational methods.

Early MO calculations (LCAO) by Hayes and Edelstein[37] on bis([8]annulene)actinide(IV) complexes did indeed indicate that there was significant interaction between the ligand e_{2u} orbitals and the metal $5f_{\pm 2}$ orbitals. In these calculations, only the ligand π orbitals and the metal f orbitals were used, since it was considered that the metal d-orbitals of the actinides were too high in energy to have significant interaction with the ligand MOs.

One important consequence of the early model of bonding is that the interaction of the metal f_2 orbitals with the e_2 ligand π-MOs leads to the energy level ordering $e_{2g} > e_{2u}$ for the bis([8]annulene) sandwich complexes. The first photoelectron spectra (PES) of thorocene and uranocene[38,39] were interpreted on this basis, but later work by Clark and Green,[40] in which the spectral changes due to He-I or He-II ionizing light were compared, led to the assignment of $e_{2u} > e_{2g}$. This assignment suggests that there is participation of the metal d orbitals in the bonding scheme.

A more complete bonding model from the Xα scattered-wave (SW) treatment of uranocene and thorocene was proposed by Rösch and Streitwieser.[41] Agreement with the PES was remarkably good, considering that relativistic effects had not been included in the calculations. These calculations supported the assignment of ionization potentials by Clark and Green and verified that the contribution of the metal d orbitals to the ring metal bond in these complexes is at least as important as the contribution of the metal f orbitals.

Recently, quasi-relativistic Xα SW MO calculations on uranocene, thorocene and cerocene were reported.[42] These calculations show remarkably good agreement with the photelectron spectra of uranocene and thorocene. As with the non-relativistic calculations, the calculated level ordering ($e_{2u} > e_{2g}$) from quasi-relativistic calculations confirms the PES interpretation of Clark and Green. The calculations also indicate that thorocene(IV) is more ionic than uranocene(IV).[41,42] One experiment which supports this idea is the slow reaction of 1,1'-di-*n*-butylthorocene with uranium tetrachloride to form 1,1'-di-*n*-butyluranocene.[20] The reverse reaction does not occur.

The quasirelativistic Xα calculations also suggest a similarity of cerocene to thorocene and uranocene. Indeed, when uranium tetrachloride was added to a THF-*d8* solution of cerocene, the slow formation of uranocene was monitored by NMR.[43] As an indication of the relative ionicity of thorocene and cerocene as compared to uranocene, the slow formation of uranocene in the above examples can be contrasted with the immediate reaction of the highly ionic bis[8]annulenecerate(III) anion with UCl_4 to form uranocene.[44]

2.4 *Bis([8]annulene)actinate(III) anions*

When two [8]annulene dianion rings complex a trivalent metal atom, the result is a bis([8]annulene) sandwich anion. There is one class of complexes involving the actinides and two classes of complexes for the lanthanide(III) ions which contain two [8]annulene dianions sandwiching a trivalent central metal ion.

The potassium salts of bis([8]annulene)uranate(III),[24] -neptunate(III),[45] -plutonate(III)[45] and -americiate(III)[46] anions have all been reported. These complexes have been synthesized by the reaction of two moles of [8]annulene dianion with one mole of the actinide trihalide.

$$2\ K_2C_8H_8 + AnX_3 \xrightarrow{THF} K[An(C_8H_8)_2] + 3\ KCl$$

$$An = U,\ Np,\ Pu,\ Am$$

The physical properties of these complexes are simular to those of the class $K[Ln(C_8H_8)]$.[44,47] Small amounts of oxidizing agents oxidize the trivalent central metal complexes to the corresponding tetravalent central metal complex.[45]

$$K[An(C_8H_8)_2] \xrightarrow{[O]} An(C_8H_8)_2$$

2.5 *Bis([8]annulene)lanthanide(III) anions*

The two classes of complexes containing a bis([8]annulene)-lanthanide(III) anion are those that contain an alkali cation and those that contain the complex [8]annulenelanthanide(III) cation. One of the classes, the alkali salts of the bis([8]annulene)lanthanide(III) anions, have been prepared by a variety of methods. The first of the methods, and the one which is of the most synthetic utility, is the direct reaction of the di-alkali salt of [8]annulene dianion with the anhydrous lanthanide trichloride. The synthesis can be accomplished either by the addition of a suspension of the lanthanide salt in THF to a THF solution of the dianion,[44,47] or by the reverse method, the addition of a solution of dianion to a suspension of the lanthanide(III) salt.[48]

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

The latter method is preferable, since in this manner of addition of the reagents the lanthanide trichloride is never exposed to an excess of reducing [8]annulene dianion. Bis([8]annulene)lanthanate(III) and -yttriate(III) anions have also been reported.[47] Similiarly, the bis([8]annulene)lanthanate(III) anion complexes from t-butylcyclooctatetraene[49] and 1,3,5,7-tetramethylcyclooctatetraene[50] have also been prepared the reaction of the substituted dianion with the lanthanide(III) chloride (eq. 3).[2,3]

Although the mechanism for the formation of the bis([8]annulene)-lanthanide(III) complexes is not known, the following equilibria have been established involving the lanthanide trichlorides, [8]annulene

dianion, the [8]annulenelanthanide(III) chloride and the bis([8]annulene)lanthanide(III) anion.[44]

$$2\ K_2C_8H_8 + 2\ LnCl_3 \longrightarrow [C_8H_8LnCl\cdot 2THF]_2 + 4\ KCl$$

$$[C_8H_8LnCl\cdot 2THF]_2 + 2\ K_2C_8H_8 \longrightarrow 2\ K[Ln(C_8H_8)_2] + 2\ KCl$$

$$K[Ln(C_8H_8)_2] + LnCl_3 \longrightarrow [C_8H_8LnCl\cdot 2THF]_2 + KCl$$

It is postulated from these equilibria that in the reaction of [8]annulene dianion with a lanthanide(III) chloride the [8]annulene-lanthanide(III) chloride is formed initially as a isolable intermediate of the reaction. The mono-ring intermediate then reacts with additional [8]annulene dianion to form the bis[8]annulene complexes.

The other preparations of the alkali bis([8]annulene)-lanthanide(III) salts are methods which are useful only for specific lanthanide elements. The bis([8]annulene)cerate(III) anion has been prepared by the reduction of bis([8]annulene)cerium(IV) with one equivalent of potassium:[34]

$$Ce(C_8H_8)_2 + K \longrightarrow K[Ce(C_8H_8)_2]$$

This method is only feasible for complexes which contain lanthanide ions that can exist in a 4+ oxidation state and thus only the cerium complex can be made in this manner.

The bis([8]annulene)ytterbate(III) anion has been prepared by reaction of two equivalents of neutral cyclooctatetraene with one equivalent of ytterbium metal and one equivalent of potassium metal in liquid ammonia.[51]

$$K + Yb + 2\ C_8H_8 \xrightarrow{NH_3} K[Yb(C_8H_8)_2]$$

This reaction is also of limited use; ytterbium and europium metals are the only lanthanides which dissolve in liquid ammonia solution to give divalent metal ions and solvated electrons.[52] In the above reaction, the initial product formed is probably an [8]annuleneytterbium(II) complex which then reacts with additional cyclooctatetraene to form the ytterbium(III) complex.

The bis([8]annulene)lanthanide(III) anions which are complexed by an [8]annulenelanthanide(III) cation are the only other class of complexes which contain two [8]annulene dianions in a sandwich arrangement about a lanthanide(III) ion. This class was first reported for the cerium(III) ion, from the reduction of a cerium(IV) alkoxide with triethylaluminum in the presence of cyclooctatetraene.[34]

$$Ce(OR)_4\ ROH + Al(C_2H_5)_3 \xrightarrow{C_8H_8} Ce_2(C_8H_8)_3$$

The green cerium complex was characterized by elemental analysis and infrared spectrum. The structure of this complex is not known, but its

infrared spectrum indicates that all of the ligands are present as the planar [8]annulene. Reaction of $Ce_2(C_8H_8)_3$ with cyclooctatetraene using a catalytic amount of triethylaluminum gave bis([8]annulene)cerium(IV).

A more general synthetic procedure for the synthesis of $Ln_2(C_8H_8)_3$ is by the reaction of neutral cyclooctatetraene with the lanthanide atom vapor at -198 °C.[53]

$$Ln^{\circ} + C_8H_8 \longrightarrow Ln_2(C_8H_8)_3$$

Crystallization of $Ln_2(C_8H_8)_3$ from THF gives the complex as its bis-THF adduct, $[(C_8H_8)Ln(OC_4H_8)_2][Ln(C_8H_8)_2]$.[53] The crystal structure of the THF adduct of the neodymium complex (discussed below) clearly shows that the bis([8]annulene)neodymate(III) anion is present in this structure.[53]

The structures of both classes of compounds involving bis([8]annulene)lanthanide(III) anions have been elucidated from single crystal x-ray diffraction studies on etherates of the complexes. The structure of the diglyme adduct of $K[Ce(C_8H_8)_2]$[54] shows a bis([8]annulene)cerate(III) anion which has the [8]annulene rings parallel planar and with a local symmetry of D_{8d} about the central metal atom (Figure 6). The anion is in a tight ion pair with a diglyme solvated potassium cation.

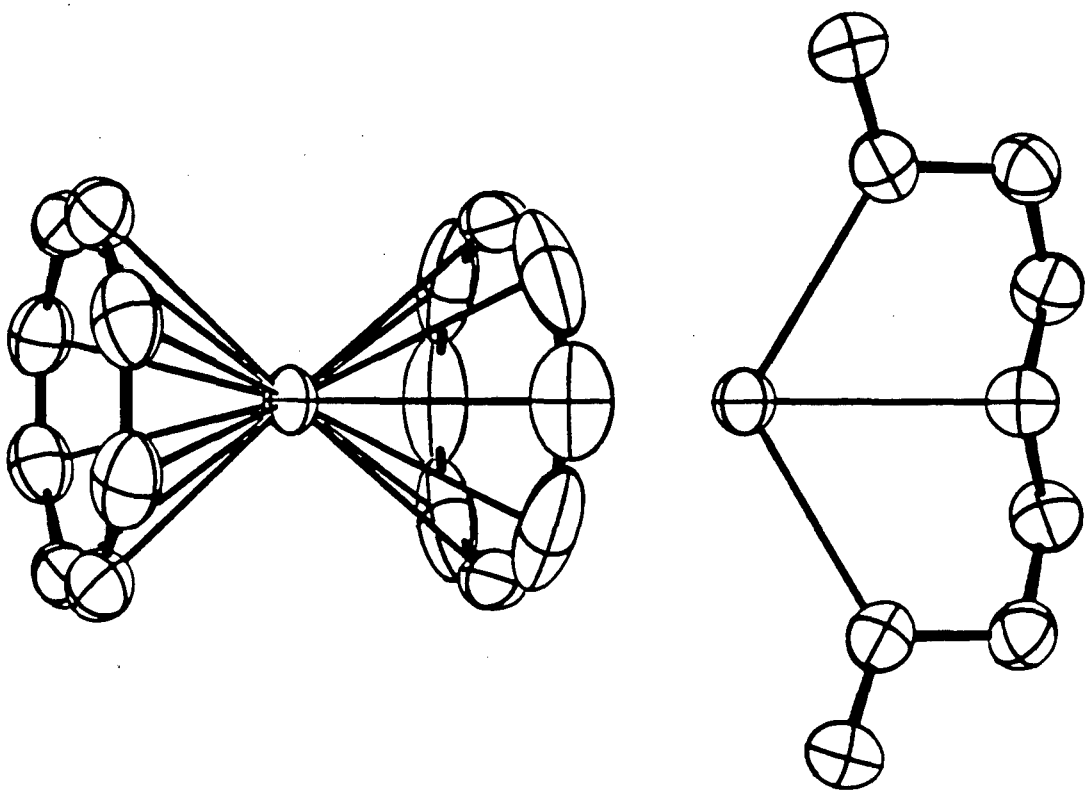


Figure 6. Structure of $[K(diglyme)][Ce(C_8H_8)_2]$ (Ref. 54).

The symmetry of $[K(diglyme)][Ce(C_8H_8)_2]$ is C_s; the potassium ion, cerium ion, two ring carbons and the central oxygen of the diglyme all lie on the mirror plane of this molecule.

The structure of the bis-THF adduct of $Nd_2(C_8H_8)_3$[53] shows a bis([8]annulene)neodymate(III) anion where the local symmetry of the anion is C_1. The carbon atoms of the two [8]annulene rings (A and B) are almost eclipsed, but the rings are not parallel planar and these planes intersect at an angle of 7.28°. The complex anion is an ion pair with a bis-THF solvated [8]annuleneneodymium cation. The metal-ring carbon distances shown in Figure 7 illustrate the effect of the presence of two trivalent atoms in this molecule.

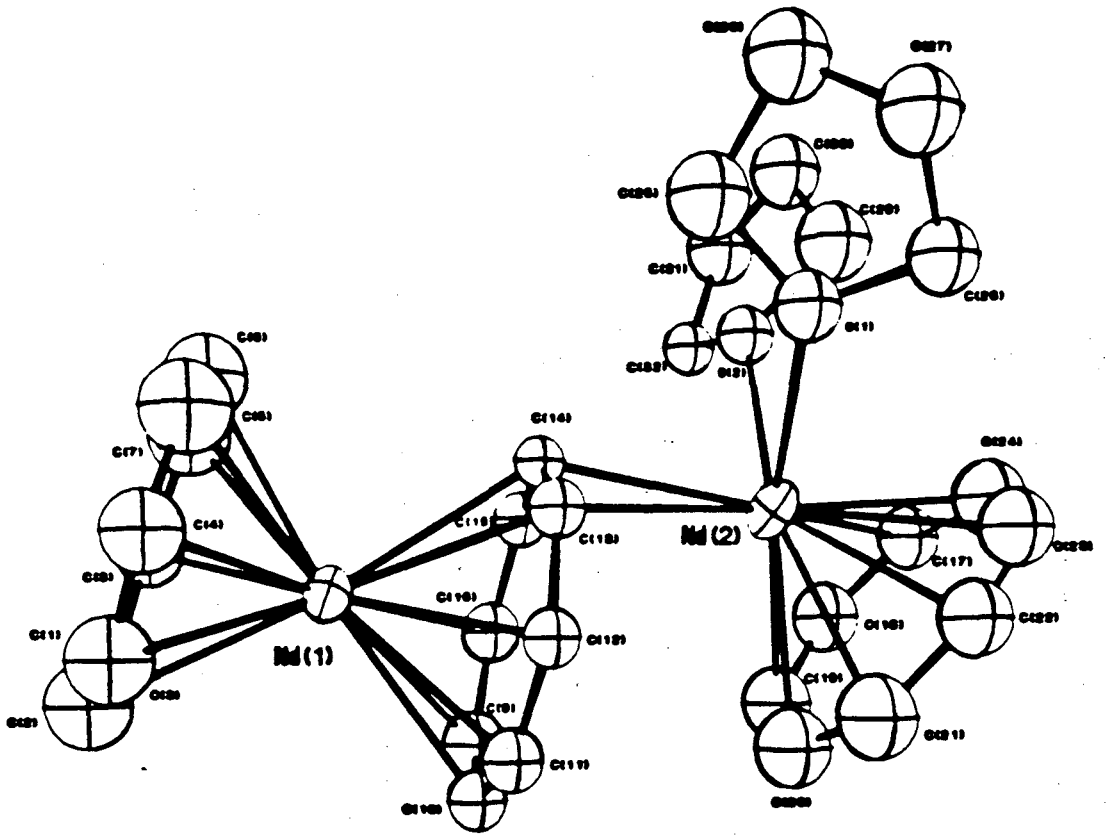


Figure 7. Structure of $[(C_8H_8)Nd\ 2THF][Nd(C_8H_8)_2]$ (Reproduced with permission from Ref. 53).

Carbon 14 of ring B is within bonding distance of both neodymiums. The presence of two neodymium atoms does not break the planarity of the rings, but it does cause distortions in the bis([8]annulene)neodymate anion.

The structure of $[(C_8H_8)Nd(OC_4H_8)_2]\ [Nd(C_8H_8)_2]$ can be contrasted with the structure of $Ti_2(C_8H_8)_3$.[55,56] In the titanium structure, both titaniums are complexed by one [8]annulene, but they share a third cyclooctatetraene that has a twisted structure; that is, the cyclooctatetraene acts as two diene units in coordinating to the two titaniums.

In the neodymium complex, the presence of a second lanthanide(III) only distorts the bis([8]annulene)lanthanide(III) ion. The thermodynamic driving force for neodymium to form a covalent π-bond with cyclooctatetraene is not sufficient to overcome the coulombic attraction between [8]annulene dianion and a lanthanide(III) ion.

2.6 *Bis([8]annulene)lanthanide(II) dianions*

The reported synthesis of $K_2[Ce(C_8H_8)_2]$ from the reduction of $Ce(C_8H_8)_2$ by two equivalents of potassium in 1,2-dimethoxyethane[34] is the first example of a bis[8]annulene compound with a central metal atom in a formal 2+ oxidation state.

$$2K + Ce(C_8H_8)_2 \longrightarrow K_2[Ce(C_8H_8)_2]$$

In this complex, the bis([8]annulene)cerate(II) complex is formally a dianion. The cerium complex as its di(1,2-dimethoxyethane) adduct was characterized by elemental analysis and infrared spectrum. The structure of $[K(C_4H_{10}O_2)]_2[Ce(C_8H_8)_2]$ is not known, but the infrared spectrum of the cerium complex does contain bands (887 and 682 cm^{-1}) which are consistent with the presence of an [8]annulene dianion.[57] Although there are reports of Ce(II) from the reduction of Ce(III) in other systems,[58,59] the presence of the cerium(II) ion in $[K(C_4H_{10}O_2)]_2[Ce(C_8H_8)_2]$ has not been shown by chemical or spectroscopic methods.

In order to study a bis[8]annulene compound with a divalent central metal atom we have synthesized and characterized the divalent ytterbium complex $K_2[Yb(C_8H_8)_2]$, $K_2[Yb(C_8H_8)_2]$, and its calcium analogue, $K_2[Ca(C_8H_8)_2]$.[51] These compounds were prepared by a reaction which utilizes the solubility of ytterbium and calcium metals in liquid ammonia. Reaction of cyclooctatetraene, potassium and either ytterbium or calcium, in liquid ammonia solution, gives the desired potassium salt of the complex dianion.

$$2K + M + 2\ C_8H_8 \xrightarrow{NH_3} K_2[M(C_8H_8)_2]$$

$$M = Ca,\ Yb$$

The physical properties for $K_2[Yb(C_8H_8)_2]$ and $K_2[Ca(C_8H_8)_2]$ are similar to the properties reported for the trivalent lanthanide complexes, $K[Ln(C_8H_8)_2]$.[44,47] The dimethoxyethane adducts of $K_2[Yb(C_8H_8)_2]$ and $K_2[Ca(C_8H_8)_2]$ are crystalline and have similar x-ray powder patterns; $K_2[Yb(C_8H_8)_2]$ and $K_2[Ca(C_8H_8)_2]$ have identical infrared spectra. Except for the differences that can be attributed to either the difference in the number of electrons between ytterbium and calcium, or to the availability of a trivalent state for the ytterbium complex, $K_2[Yb(C_8H_8)_2]$ and $K_2[Ca(C_8H_8)_2]$ behave as identical complexes. Since it is highly unlikely that the 4f and 5d orbitals are involved in the ring-metal interaction of $K_2[Ca(C_8H_8)_2]$, these orbitals also undoubtedly play no major role in the ring-metal interaction of $K_2[Yb(C_8H_8)_2]$; that is,

both compounds undoubtedly involve essestially wholly ionic ring-metal bonding.

X-ray structure analysis of $[K(C_4H_{10}O_2)]_2[Yb(C_8H_8)_2]$[51] shows planar parallel eclipsed [8]annulene rings sandwiching a centrosymmetric ytterbium. A potassium coordinated with dimethoxyethane is at the opposite side of each ring (Figure 8).

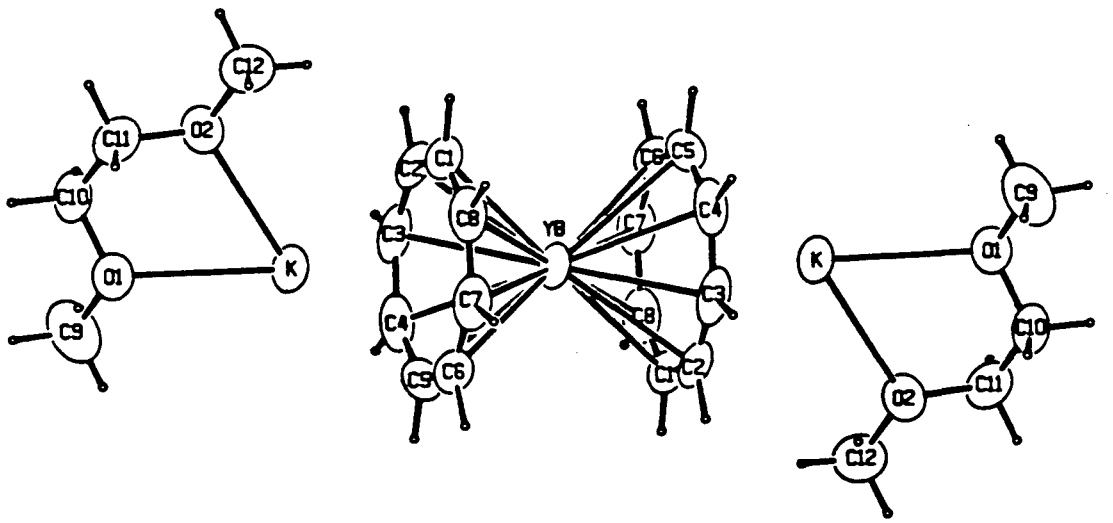


Figure 8. Structure of $[K(C_4H_{10}O_2)_2]_2[Yb(C_8H_8)_2]$ (Ref. 51)

Although the ring-metal interaction in the bis([8]annulene)lanthanide complexes is essentially ionic, the bis([8]annulene)calcate dianion and bis([8]annulene)ytterbate(III) anion do not undergo ring exchange in THF-$d8$ on the NMR timescale.[60] We have, however, observed an exchange process that does time-average the ring's environment between ytterbium(II) and ytterbium(III) ions in the ^{1}H-NMR spectrum of a mixture of $K_2[Yb(C_8H_8)_2]$ and $K[Yb(C_8H_8)_2]$ in THF-$d8$.[60] The coalescence temperature of this system is 0 °C. From the chemical shifts of the proton resonances for the ytterbium(II) and ytterbium(III) complex, a rate constant of $k \approx 10^6$ M^{-1} sec^{-1} is calculated. The same type of exchange phenomenon is seen between bis(t-butyl[8]annulene)ytterbate(II) and bis(t-butyl[8]annulene)ytterbate(III); in this system, however, rate constant is $k \approx 10^5$ $M^{-1}sec^{-1}$.[60] The exchange process occurring in the ytterbium(II)/(III) system is best viewed as an electron transfer between the two complexes. The rapid exchange process is observable by NMR only because of the great difference in chemical shifts of the ring proton resonances of the complexes (for the unsubstituted system $\Delta\delta \approx 60$ ppm).

2.7. *Mono-[8]annuleneactinide(IV) complexes*

The [8]annulenethorium(IV) "half-sandwich" complexes are the most extensively studied of the mono-[8]annulene complexes. [8]Annulenethorium dichloride can be synthesized as a bis-THF adduct by the stoichiometric reaction of [8]annulene dianion with thorium tetrachloride or by the equilibrium reaction between $ThCl_4$ and $Th(C_8H_8)_2$.[23,61]

$$K_2C_8H_8 + ThCl_4 \xrightarrow{THF} (C_8H_8)ThCl_2 + 2\ KCl$$

$$ThCl_4 + Th(C_8H_8)_2 \xrightarrow{THF} 2\ (C_8H_8)ThCl_2$$

The related compounds from alkyl substituted cyclooctatetraenes can be best prepared by refluxing bis(alkyl[8]annulene)thorium(IV) with excess thorium tetrachloride in THF or DME until the yellow color of the thorocene disappears. [8]Annulenethorium(IV) dichlorides can also be prepared by reaction of thorocene with anhydrous hydrogen chloride.[23]

$$Th(C_8H_8) + 2\ HCl \xrightarrow{THF} (C_8H_8)ThCl_2 + C_8H_{10}$$

The preparation of [8]annulenethorium(IV) bis-hydroborates have been achieved by several routes.[62] The alkyl-substituted complex, *n*-butyl[8]annulenethorium(IV) bis-hydroborate, is prepared by the reaction of thorium tetrahydroborate with bis(*n*-butyl[8]annulene)thorium(IV) in refluxing THF (eq x). Due to the low solubility of the unsubstituted thorocene in THF, the unsubstituted mono-ring complex is best prepared by the reaction of thorium tetrahydroborate with an equimolar amount of dipotassium [8]annulene in THF at room temperature.

$$Th(BH_4)_4 + Th(n\text{-}BuC_8H_7)_2 \longrightarrow 2\ (n\text{-}BuC_8H_7)ThCl_2$$

$$K_2C_8H_8 + Th(BH_4)_4 \longrightarrow (C_8H_8)Th(BH_4)_2 + 2\ KBH_4$$

Similar reactions to those shown above on the analogous uranium systems give poorly characterized products which suggest the existence of mono-[8]annuleneuranium(IV) bis-borohydrides.[62]

The structure of the bis-THF adduct of [8]annulenethorium(IV) dichloride is known (Figure 9).[61]

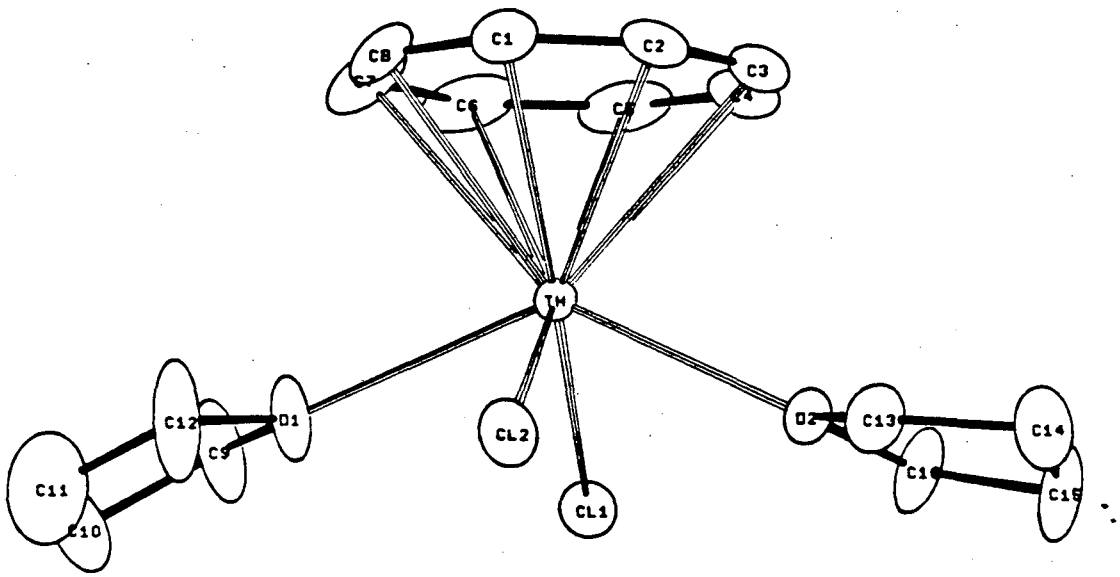


Figure 9. Structure of $(C_8H_8)ThCl_2 \cdot 2THF$ (Ref. 61)

The mono-ring dichloride crystallizes in two modifications. In both the α and β forms the thorium atom is complexed by one [8]annulene ring, two chlorine atoms and two THF molecules. The [8]annulene ring is centrally located on the thorium atom. The chlorine atoms and THF molecules are in a trans configuration on the side of the thorium atom opposite the ring. The α form of the complex crystallizes in space group $P2_1/n$ and the β form crystallizes in space group $P2_1/c$. The only significant geometrical difference between these two forms is the larger Cl-Th-Cl and smaller O-Th-O angles that the α form exhibits relative to the β form. The existence of two forms of mono-ring thorium complex is adequately explained by crystal packing forces acting on a highly ionic system.

2.8. *Mono-[8]annulenelanthanide(III) complexes*

There are several types of lanthanide(III) complexes that contain only one [8]annulene ligand. The class of complexes $[(C_8H_8)LnCl\ C_4H_8O]_2$, which was shown earlier as an isolable intermediate in the formation of the bis([8]annulene)lanthanide(III) anion,[47] is made in good yield by the addition of one equivalent of [8]annulene dianion in THF to a suspension of one equivalent of anhydrous lanthanide trichloride in THF.[44,63,64] A good yield of the mono-ring cerium complex product is obtained by the reaction of bis([8]annulene)cerate(III) anion with one mole of cerium trichloride.

$$K_2C_8H_8 + LnCl_3 \xrightarrow{THF} 1/2\ [(C_8H_8)LnCl\cdot 2THF]_2$$

$$K[Ce(C_8H_8)_2] + CeCl_3 \xrightarrow{THF} [(C_8H_8)LnCl\cdot 2THF]_2 + KCl$$

The mono-THF adduct of [8]annulenescandium(III) chloride can be prepared by the addition of [8]annulene dianion to scandium trichloride.[65] Reaction of [8]annulenescandium(III) chloride with one equivalent of [8]annulene dianion gives bis([8]annulene)scandate(III) anion.[65]

The structure of $(C_8H_8)CeCl\cdot 2THF$ is known[66] and shows that [8]annulenecerium(III) chloride exists as a chloride-bridged dimer of the THF adduct (Figure 10).

Some mono-[8]annulenelanthanide(III) alkyl and aryls have been prepared from the corresponding chlorides by reaction with the corresponding organolithium reagents.[64]

$$1/2\ [(C_8H_8)LnCl\cdot 2THF]_2 + LiR \longrightarrow (C_8H_8)LnR\cdot xTHF$$

These derivatives were characterized by elemental analysis, infrared, ^1H-NMR and ^{13}C-NMR. The infrared spectra of the alkyl compounds indicate that the planar [8]annulene is present in these complexes. It is not known whether the mono-[8]annulenelanthanide(III) alkyls exist as monomers, dimers or as polymers.

A bimetallic mono-[8]annulene complex containing cerium(III) and aluminum(III) has been synthesized.[67] [8]Annulenecerium(III)-di-μ-isopropoxydiethylaluminum was synthesized by the reaction of cerium(IV) isopropoxide with triethylaluminum in the presence of cyclooctatetraene and toluene as the solvent.

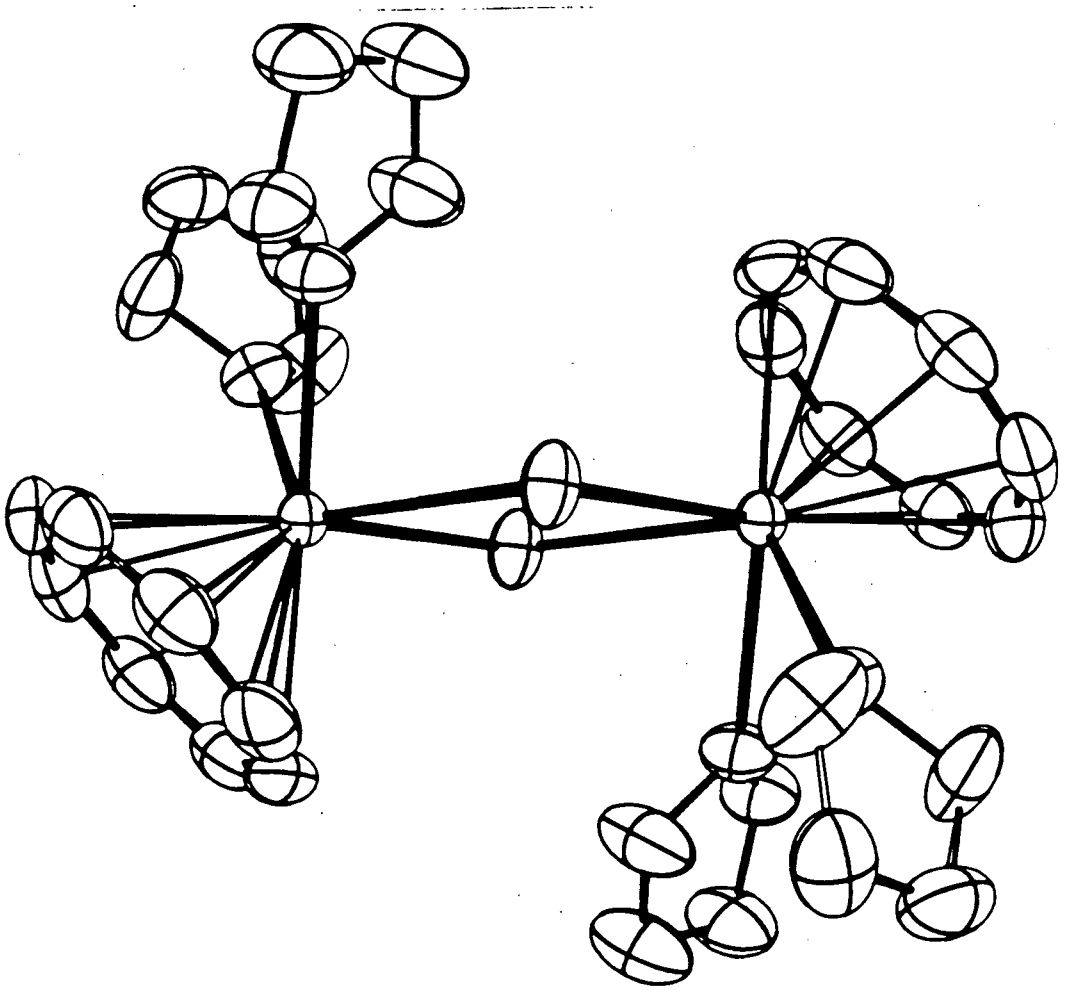


Figure 10. Structure of $[(C_8H_8)CeCl\cdot 2THF]_2$ (Ref. 66).

$$Ce(OR)_4 + Al(C_2H_5)_3 \xrightarrow[C_7H_8]{C_8H_8} (C_8H_8)Ce(OR)_2\cdot Al(C_2H_5)_2$$

This bimetallic complex was characterized by elemental analysis, infrared spectrum and mass spectrum. The infrared indicates that the eight-membered ring is present as [8]annulene. It was suggested from the mass spectrum and ^{1}H-NMR studies that this complex exists with the isopropoxide ligands bridging between the cerium and aluminum ions (Figure 11). The bimetallic [8]annulene complex has also been made as its acetonitrile adduct.[67]

The only other class of compound that contains a lanthanide(III) ion and one [8]annulene ligand is the "mixed sandwich" complex, the [8]annulenelanthanide(III) cyclopentadienides.[68] This class of complexes can be made either by the addition of cyclopentadienide to the mono-[8]annulenelanthanide chlorides or by the addition of [8]annulene dianion to cyclopentadienyllanthanide(III) dichloride. The yttrium[68] and scandium[64] members of this class have also been reported.

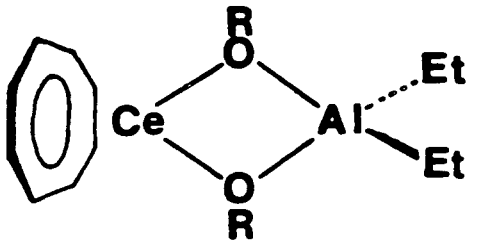


Figure 11. Proposed structure of $(C_8H_8)Ce\cdot(OR)_2\cdot Al(C_2H_5)_2$ (Ref. 67).

$$(C_5H_5)LnCl_2 + K_2C_8H_8 \longrightarrow (C_8H_8)Ln(C_5H_5)$$
$$(C_8H_8)LnCl + Na(C_5H_5)$$

These complexes were initially obtained as THF adducts, but lose THF *in vacuo* at 50 °C. The mass spectra of the complexes contain the parent $[MC_{13}H_{13}]^+$ as well as the fragments $[MC_8H_8]^+$ and $[MC_5H_5]^+$. The infrared spectrum of each complex contains absorbances which are attributable to [8]annulene and cyclopentadiene anion and the ^{1}H-NMR of the diamagnetic yttrium complex of this series contains resonances which can be assigned to the protons of [8]annulene and cyclopentadiene anion. In addition to characterization of the THF adduct, the complexes have also been characterized as 1:1 adducts with pyridine, ammonia, and cyclohexylisonitrile.[68]

2.9. *Mono-[8]annulenelanthanide(II) complexes*

The mono-[8]annulenelanthanide(II) complexes, $Ln(C_8H_8)$ (Ln = Eu, Yb),[69] were the first lanthanide complexes of [8]annulene dianion reported. The ytterbium(II) complex has also been synthesized by metal atomization.[53]

$$M + C_8H_8 \xrightarrow{NH_3} M(C_8H_8)$$

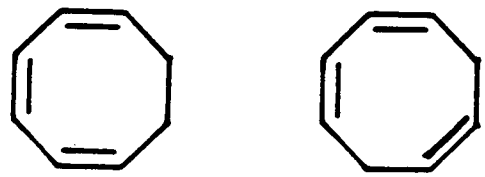
M = Eu, Yb

The characterization of the lanthanide(II) [8]annulene complexes is, however, limited. The infrared spectrum of $Yb(C_8H_8)$[12] suggests a highly symmetric complex (the only bands present between 1000 and 600 cm^{-1} occur at 888 and 678 cm^{-1}),[53] and the low solubility of the complexes in hydrocarbons, ethers and liquid ammonia suggests that the class $Ln(C_8H_8)$ is polymeric.[69]

3. REACTIONS

Few reactions have been noted for the [8]annulene compounds of actinides and lanthanides except for uranocene itself. The reactions of uranocene with nitro-compounds[70] and of some substituted uranocenes with or-

ganolithium compounds[5,71] have been reviewed previously.[72] One reaction that we have studied recently is the hydrolysis of uranocenes. Hydrolysis in wet THF is rather slow but can be followed kinetically by the change in color; the products are a mixture of cyclooctatrienes and uranium oxides. An interesting feature of this hydrolysis is proportion of cyclooctatriene isomers formed. Hydrolysis of the dipotassium salt of [8]annulene dianion in THF gives a 3:1 ratio of 1,3,5-cyclooctatriene to 1,3,6-cyclooctatriene, in the same direction as but a smaller magnitude than the equilibrium ratio 97:3; hydrolysis of uranocene, however, gives the opposite regiospecificity, a 1:2 ratio of 1,3,5 to 1,3,6.[73]



$K_2C_8H_8$	$\xrightarrow[THF]{H_2O}$	76	24
$U(C_8H_8)_2$	$\xrightarrow[THF]{H_2O}$	34	66
Equilibrium		97	3

Some rate constants[74] summarized in Table 1 show that electron-attracting groups, such as the ester group, increase the rate, whereas electron-donating groups slow the rate.

TABLE 1. Rates of hydrolysis of 1,1'-disubstituted uranocenes, $(C_8H_7Y)_2U$, in 1M water in THF, 25° C

Y	10^5 k, sec^{-1}
t-Bu	0.22
H	1.1
NMe_2	1.2
C_6H_5	44
O-t-Bu	6100
COO-t-Bu	110000

This trend is demonstrated more definitively by the hydrolysis rates of substituted 1,1'-di-phenyluranocenes. These rates follow a normal Hammett $\sigma\rho$ relation (Figure 12) with ρ=2.12; that is, electron-attracting groups clearly have a pronounced rate-accelerating effect.[73] One would expect that electron-attracting groups would tend to stabilize an

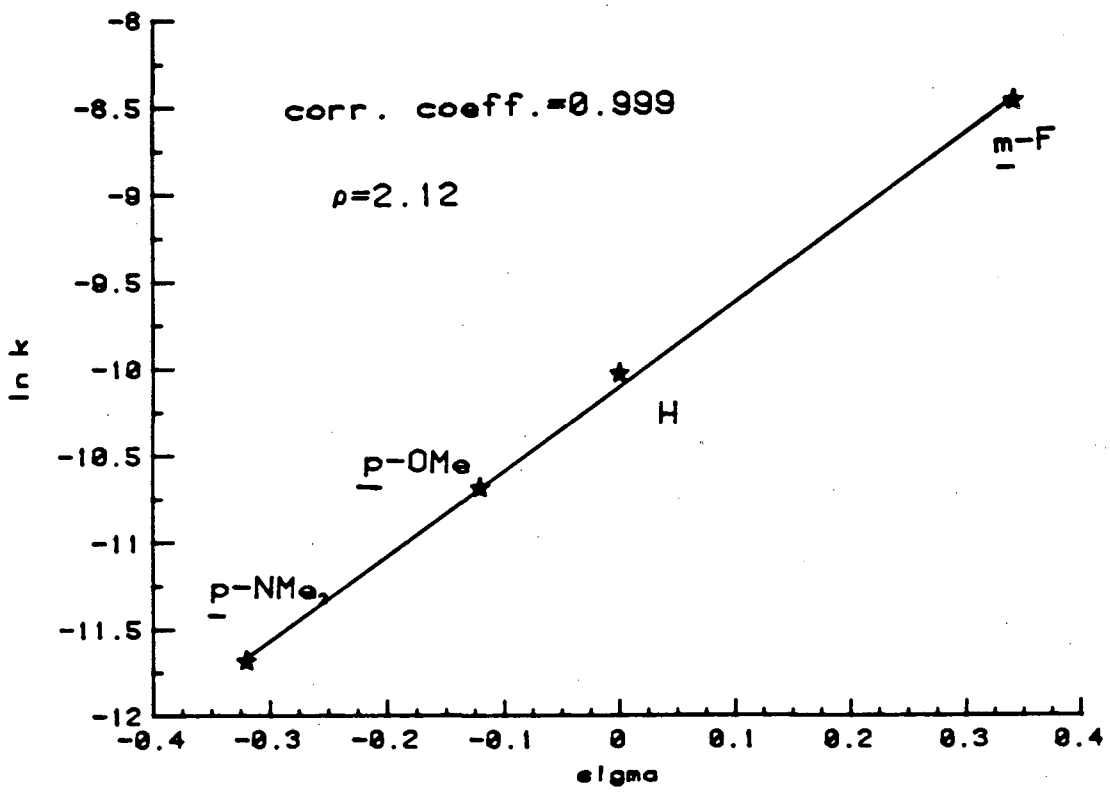


Figure 12. Hammett σρ plot for hydrolysis of substituted 1,1'-diphenyluranocenes in 1M water in THF at 25° C (Ref. 73).

[8]annulene dianion ring and make it less prone to add a proton. The reaction also shows pronounced primary isotope effects on replacing the H_2O by D_2O; k_H/k_D for uranocene at room temperature is 11.8.[75] We interpret these results with a mechanism (Figure 13) that involves a prior rapid equilibrium giving a small concentration of water coordinated with the uranium followed by rate-determining proton transfer from the coordinated water to one of the rings. Subsequent reactions follow rapidly. Uranium(IV) is expected to have Lewis acid properties but these are restrained by the close ring-ring distance that impedes attack by a base at the uranium. Spectral study, for example, showed no evidence for internal coordination of nitrogen with uranium in dimethylaminoalkyluranocenes.[5]

4. PROTON MAGNETIC RESONANCE

Uranocene has two f-electrons remaining on the central metal and is therefore paramagnetic. The theory behind chemical shifts of paramagnetic compounds has been developed in detail[76] and some applications to organoactinide nmr have been reviewed.[77,78] Accordingly, we give only a brief discussion of the theory here. The coupling of unpaired electrons with the nucleus being observed generally results in a shift in resonance frequency that is referred to as a *hyperfine isotropic* or

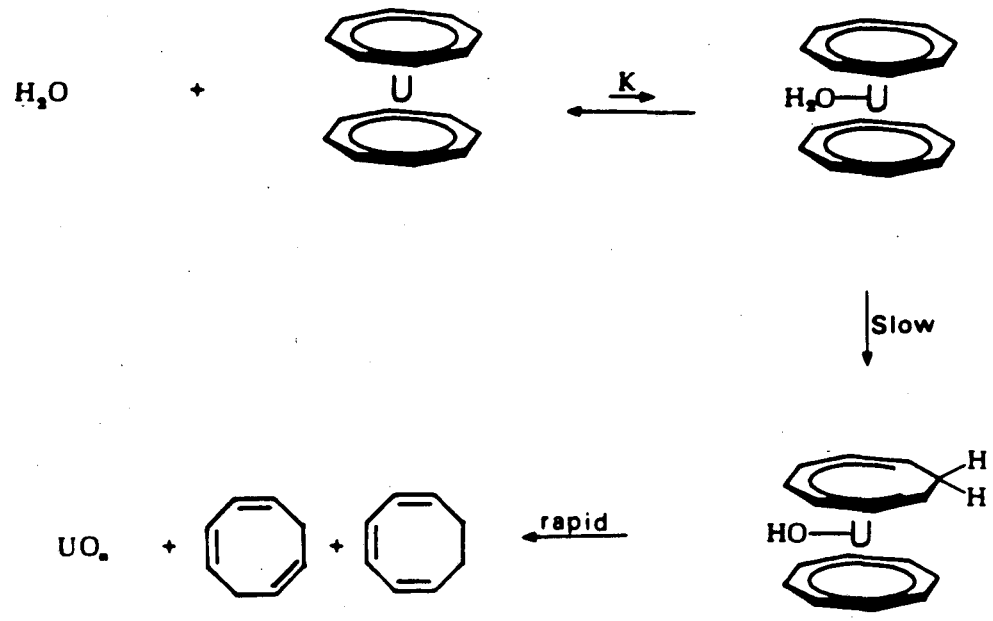


Figure 13. Proposed mechanism for hydrolysis of uranocene.

simply *isotropic* shift. This shift is defined relative to a diamagnetic standard and is usually dissected into two principal components.

$$\delta_{ISOTROPIC} = \delta_{CONTACT} + \delta_{DIPOLAR}$$

The *hyperfine contact*, also called the *Fermi contact* or simply the *contact*, shift derives from a transfer of spin density from the unpaired electrons to the immediate neighborhood of the nucleus being observed. The *dipolar* or *pseudocontact* shift derives from a classical dipole-dipole interaction between the electron magnetic moment and the nuclear magnetic moment and is geometry dependent. The isotropic shift for uranocenes may be obtained by comparison with the diamagnetic thorocene analogs but thorocene chemical shifts are generally rather similar to those of the corresponding [8]annulene dianions; accordingly, the uranium isotropic shifts have most often been obtained relative to the ligand dianions.

Expressions have been derived for the contact shift[79] but for uranocenes this term is normally obtained by subtracting a calculated pseudocontact shift from the experimental isotropic shift. The pseudocontact shift for uranocene is generally represented by the axially symmetric expression may be expressed as:[76,78]

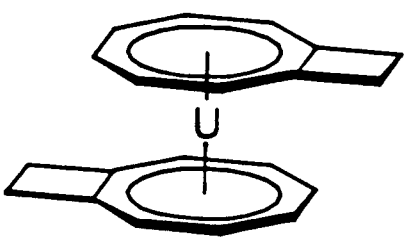
$$\delta_{DIPOLAR} = \frac{\chi_{\parallel} - \chi_{\perp}}{3} \cdot \frac{3\cos^2\theta - 1}{R^3}$$

in which $\chi_{\parallel}$ and $\chi_{\perp}$ are components of the magnetic susceptibility paral-

lel and perpendicular, respectively, to the ring-metal axis that is generally the principal magnetic axis of uranocene. This expression applies just as rigorously to substituted uranocenes having at least threefold axial symmetry but is usually assumed to apply to a sufficient approximation even to uranocenes having lower symmetry. The second part of this equation is called the geometric factor, $G_i = (3\cos^2\theta_i - 1)/R_i^3$.

The magnetic susceptibility of uranocene has been measured as a function of temperature and is approximately linear in 1/T except at rather low temperatures.[80,81] Over this temperature range, the proton chemical shift is also expected to be linear in 1/T; many such linear dependences have been documented.[77] Consequently, the anisotropy term, $\chi_{\parallel} - \chi_{\perp}$, is often replaced for convenience by the corresponding term involving magnetic moments, $\Delta\mu^2 = \mu_{\parallel}^2 - \mu_{\perp}^2$.

The nmr spectrum of uranocene was originally interpreted[19,82] on the basis of a $J_z = \pm 4$ ground state[4,37] for which $\chi_{\perp} = 0$. Fischer[78,83] has proposed useful and important methods for factoring the isotropic shifts of uranocenes into contact and dipolar components using a non-zero value for $\chi_{\perp}$. The methyl protons in 1,1'-bis(trimethylsilyl)-uranocene were assumed to have a negligible contact shift contribution. The experimental magnetic susceptibility and the calculated G term based on an assumed structure led to $\Delta\mu^2 = 8.78$ BM^2. We have determined a slightly different value for this quantity, 12.5 BM^2 from a different approach involving the assumption that the exo and endo protons in dicyclobutenouranocene, 3, have the same contact shift.[11]



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The geometric factors are quite different for these two protons and were calculated from the Xray crystal structure. The two values for $\Delta\mu^2$ do not differ seriously. Moreover, Fischer and Spiegl assumed a ring-silicon bond coplanar with the ring; this bond may actually be bent away from the ring (*vide infra*) which would have the effect of increasing the derived value of $\Delta\mu^2$.

Applied to uranocene, the value $\Delta\mu^2 = 12.5$ BM gives a dipolar shift of -8 ppm at 30° C based on a calculated geometric factor, $G = -2.34 \times 10^{21}$ cm^{-3} in which the hydrogens are assumed to be in the ring plane. The contact and dipolar shifts are therefore in the same direction for these hydrogens (Figure 14). A similar calculation applied to 1,1'-dimethyluranocene shows that the dipolar and contact shifts for the methyl protons are in opposite directions (Figure 14).

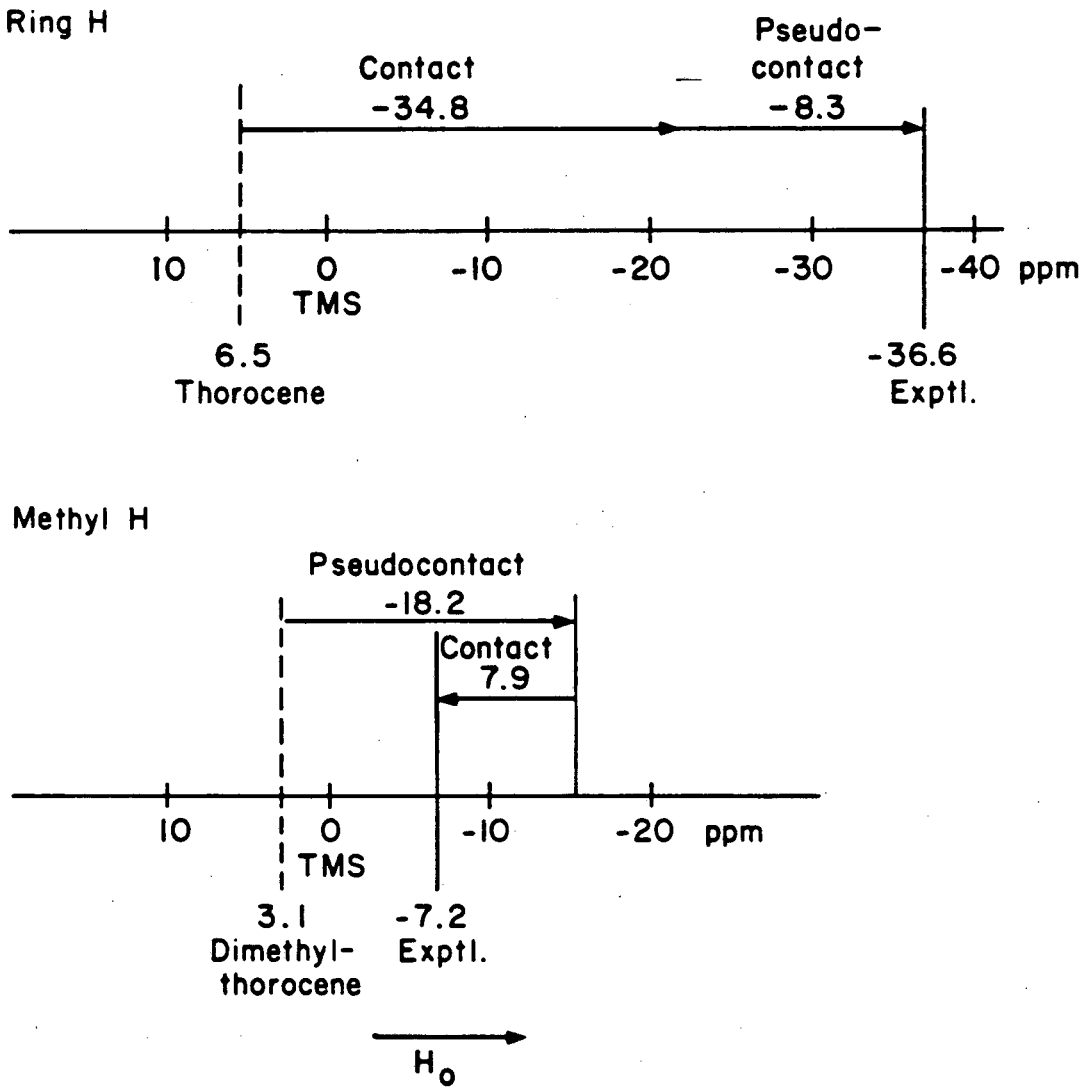


Figure 14. Contact and dipolar shifts in uranocene and 1,1'-dimethyl-uranocene. Thorocenes are used as the diamagnetic references.

These results are in accord with a simple model (Figure 15).[4,84] In the ground state, orbital angular momentum dominates so the two f-electrons on the uranium have their magnetic moments opposed to the applied field. Electron density donated from filled ligand π-molecular orbitals to any vacant metal orbitals will be spin-polarized to give a net spin density in the ligand π-MOs with a magnetic moment alligned with the applied field. α-Protons as on methyl groups are part of the π-MO system by hyperconjugation and have the same electron magnetic moment in their immediate Fermi contact vicinity corresponding to deshielding and a downfield shift. A second spin-polarization is required to relay the spin density to the ring protons that are in the nodal plane of the π-system, which results in an electron moment opposing the applied field and an upfield shift.

The distribution of spin density within a ligand should, by this

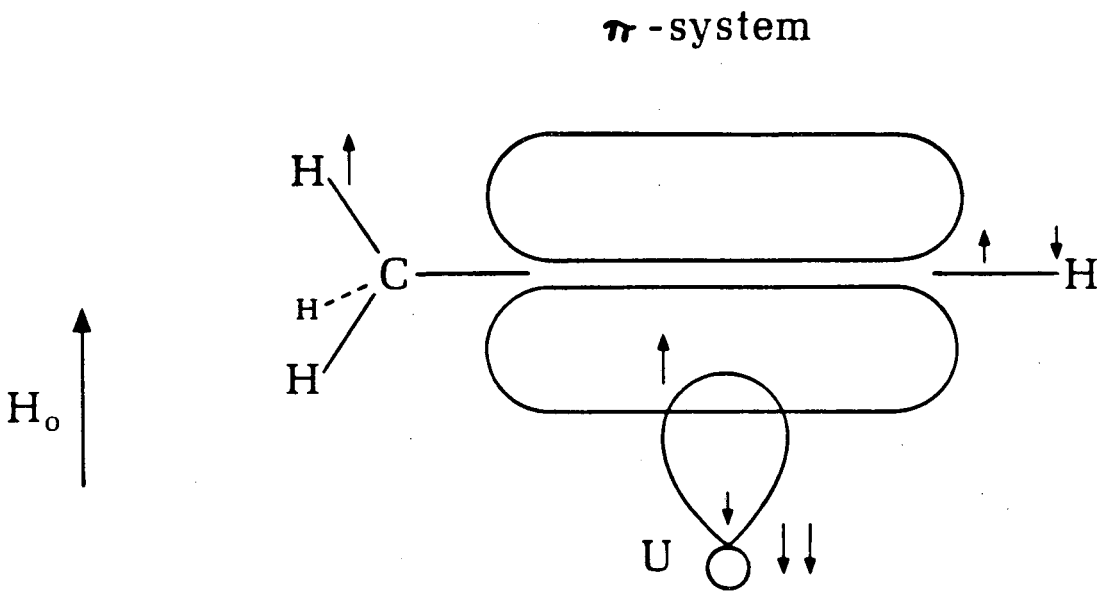
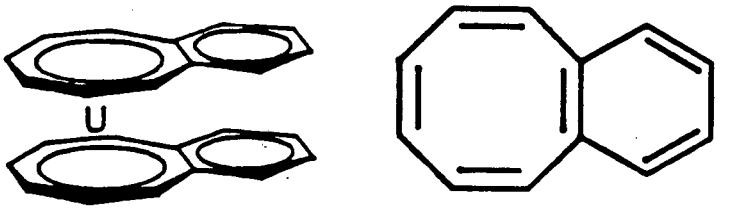


Figure 15. Spin polarization model for contact shifts in uranocenes.

type of mechanism, resemble that of a corresponding radical or ion radical. An interesting application of this concept has been applied to bis(benzo[8]annulene)uranium(IV), dibenzouranocene, 4.[13] Isotropic shifts were determined by direct comparison with the corresponding thorium compound and the geometry factors were computed from the Xray structure.[85] If the electronic structure of 4 can be regarded as one in which electron density is donated from ligand dianion to a central U^{+4}, the resulting spin polarization should give a spin density distribution in the ligand resembling that of the radical anion of benzocyclo-octatetraene, 5.



4 5

The same picture emerges from an electronic structure derived from interaction of the *u* and *g* combinations of the HOMOs of two molecules of 5 dianion and suitable f- and d- orbitals of U^{+4}. Accordingly, we expect a correlation between the contact shifts and the hyperfine coupling constant (hfcs)[86] of the radical anion. The comparisons in Table 2 show an excellent parallelism between the two sets of numbers.

The relationship between contact shift and esr hyperfine coupling constants found for the benzouranocene system does not apply straightforwardly to alkyluranocenes, perhaps because the alkyl groups

TABLE 2. Analysis of nmr spectrum of 4(30°C)

Pos.	δ	Isotropic shift[a]	G_i $10^{21}cm^{-1}$[b]	Contact shift	Dipolar shift[c]	α[d]
1	-47.88	-54.6	-2.34	-8.3	-46	0.183
2	-18.94	-25.2	-2.34	-8.3	-17	0.082
3	-24.28	-30.3	-2.34	-8.3	-22	0.125
7	-10.57	-18.3	-5.05	-17.9	0	0.019
8	-12.69	-19.7	-3.68	-13.1	-7	0.082

(a) Based on nmr of the thorium analog as the diamagnetic reference. (b) Geometric factor=$(3\cos^2\theta-1)/R^3$ using the Xray structure of 4 (ref. 85). (c) Calculated from G_i (ref. 77). (d) Hfsc from esf spectrum of radical anion of 5 (ref. 86).

do not introduce a sufficient perturbation of the [8]annulene system. There are large variations in contact shift for different hydrogens and these have been identified for primary alkyl substituents. Some examples are summarized in Figure 16. Other primary alkyl substituted uranocenes examined (n-propyl, n-butyl, neopentyl) show the same ring hydrogen pattern as ethyl in Figure 16. The 5-hydrogen is readily identified by its relative intensity. The line width of most uranocenes are too broad for spin-spin decoupling examination; hence, the remaining positions were assigned by deuterium labeling experiments.[77]

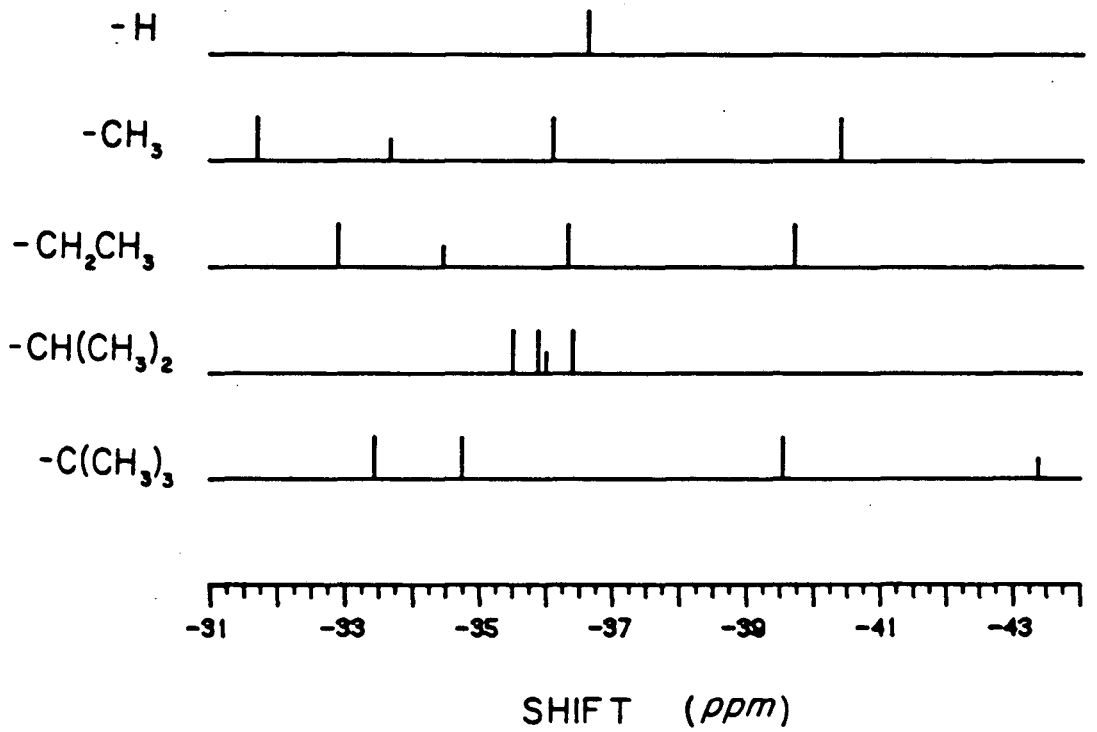


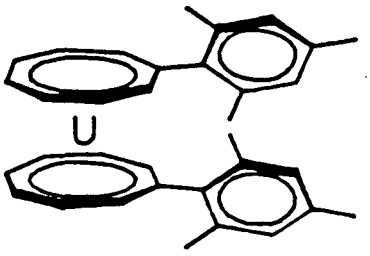
Figure 16. ^{1}H-NMR chemical shifts for the ring protons of several 1,1'-dialkyluranocenes at 30° C.

As shown in Figure 16, the pattern for the t-butyl substituent is much different. The highest field proton is now H-5 rather than the proton closest to the substituent, H-2. To assign the remaining positions, specifically deuterated t-butylcyclooctatetraenes were prepared and converted to the corresponding uranocenes.[87] The nmr results gave the assignments shown in Figure 16. These assignments confirm those made earlier[77] on a tentative basis.

The contrasting patterns of primary alkyl and t-butyl compared with the rather small effect of isopropyl suggest a steric source. It was mentioned earlier that the methyl substituent tends to bend towards uranium, apparently to provide more effective orbital overlap (Figure 5). Similar bending has been found in dicyclobutenouranocene, 5,[12] and dicyclopentenouranocene.[88] Models indicate that a similar bending for a t-butyl group would cause one of the substituent hydrogens to come within Van der Waals distance of a ring-hydrogen on the opposite ring. Accordingly, we suggest that the t-butyl group instead is bent away from the central metal. For isopropyl the two effects are equal and opposite and we suggest that such secondary alkyl substituents are bound in the 8-membered ring plane and are not bent appreciably up or down. Other bulky substituents show the same ring resonance pattern as t-butyl; a significant example is the trimethylsilyl group (*vide supra*).

Thus, the pattern of ring hydrogen chemical shifts appears to be dependent on whether the ring substituent is bent towards or away from the central uranium. Because the [8]annulene ring geometry remains essentially constant in all of these structures, the effect clearly is a contact shift effect that depends on spin density. Moreover, the average shift is little different from that of uranocene itself; that is, the total amount of spin density in the [8]annulene ring is essentially constant - it is simply redistributed depending on the bending of the ring alkyl substituent. The reason for this effect - that is, the mechanism coupling the alkyl bending to spin density distribution - is still unknown.

A dramatic demonstration of the validity of the phenomenological effect is found in some results with 1,1'-dimesityluranocene, 6.[8]



6

The NMR spectrum was especially distinctive. The two ortho-methyl groups had widely separated chemical shifts, endo at -46 ppm and exo at +24 ppm. Both remained as sharp resonances over a wide temperature range; thus, the mesityl ring must remain twisted with respect to the [8]annulene ring and the two ortho-methyls do not interconvert. This

result is not unexpected since the internal angle of the octagonal ring is greater than that of a six-membered ring and the barrier to rotation should be substantially higher than that of the corresponding biphenyl. For comparison, in 1,1'-di-o-tolyluranocene a methyl resonance appears only at δ +15 ppm; that is, in this compound the methyl group is locked into the exo-position.

The proton nmr resonances of several aryluranocenes are summarized in Table 3. It is especially noteworthy that the range of the [8]annulene resonances in phenyluranocene is rather small and reminescent of the pattern found above for the isopropyl substituent (Figure 16). According to the steric argument deduced above, this result suggests that the phenyl group, although undoubtedly twisted with respect to the [8]annulene ring, does not interact importantly with the opposite 8-membered ring and probably involves a phenyl-C_8 bond essentially coplanar with the C_8 ring. The o-tolyl group fits this same pattern and suggests strongly that with an exo-orientation of the ortho-methyl the interaction with the opposite ring is miminal.

TABLE 3. ^1H chemical shifts of C_8 protons of 1,1'-diaryluranocenes (δ, 30°C).

H		-36.6		
Phenyl	-34.4	-36.2	-36.5	-37.1(H5)
p-$Me_2NC_6H_4$	-34.3	-36.2	-36.5	-37.1(H5)
o-Tolyl	-33.3	-34.2	-37.1	-38.8(H5)
Mesityl	-15.0(H2)	-33.2(H3)	-54.3(H4)	-57.3(H5)

The mesityl group is dramatic in its contrast. At 30°C the range of C_8 proton chemical shifts is over 40 ppm. Yet, the weighted average of these shifts, -37.5 ppm, differs little from that of the other aryl substituents or of uranocene itself. This result must mean that the net amount of spin in the C_8 ring is unchanged but that its distribution has changed markedly; that is, the uranocene structure with parallel rings and centosymmetric metal is probably still retained. The obvious conclusion that the mesityl group must be markedly bent away from the opposite ring finds support in molecular models. The upfield position of H5, identified by its relative intensity, brings to mind the similar but less marked pattern for the t-butyl substituent. Indeed, the total pattern of C_8 ring hydrogen chemical shifts is similar to that of the t-butyl compound. Moreover, the relaxation time of dimesityluranocene, 6, is sufficiently high that normal spin decoupling could be applied. Irradiation of one hydrogen position caused a sharpening of the resonances of adjacent protons. All of the ring positions could be assigned directly (Table 3) and are found to be in the t-butyl pattern.

As an nmr sample of 6 is cooled the resonances at first all show normal 1/T behavior. Below about -30°C, however, H2, H3 and H4 show typical coalescence behavior, first broadening and fading into the baseline, and, below about -100°C re-emerge as pairs of peaks which again show linear 1/T dependence. This behavior is summarized in Figure 17. Note that H5 remains sharp and normal throughout this entire range. Clearly, some dynamical process is involved. The most reasonable such

process is based on a ground state conformation in which the two mesityl rings are close to each other as diagrammed in the structural representation shown for 6. This structure is chiral and we suggest that the dynamical process involved above is a rotation about the ring axis that interconverts the R- and S-enantiomers. All seven ring hydrogens on each C_8 ring are distinct but the rotation interverts the pairs 2 and 8, 3 and 7, 4 and 6. The two aryl rings are held together presumably by van der Waals forces. The magnitude of this interaction was determined by line shape analysis of the coalescing bands. In line shape analysis of such paramagnetic systems it is important to use the appropriate $\Delta\delta$ for each temperature. The rates found lead to the activation parameters $\Delta H^{\ddagger}$ =9.9 Kcal mol^{-1} and $\Delta S^{\ddagger}$ = 11.3 e.u. The positive entropy is consistent with the proposed process but the enthalpy value found is surprisingly high for the aryl ring-ring interaction. This result suggests that related studies could prove useful in determining such interaction parameters for other systems. The wide range of chemical shifts and the symmetry of the uranocene system are singularly effective for such applications. A schematic representation of the potential surface for rotation about the uranocene ring axis is shown in Figure 18.

A conclusive demonstration that the dynamical process involves interaction between the two mesityl rings is found in an equilibration experiment. Addition of [8]annulene dianion to 6 gave some uranocene together with the mixed ring system, mesityluranocene, whose NMR spectrum showed no coalescence even down to -109°C. Moreover, the fact

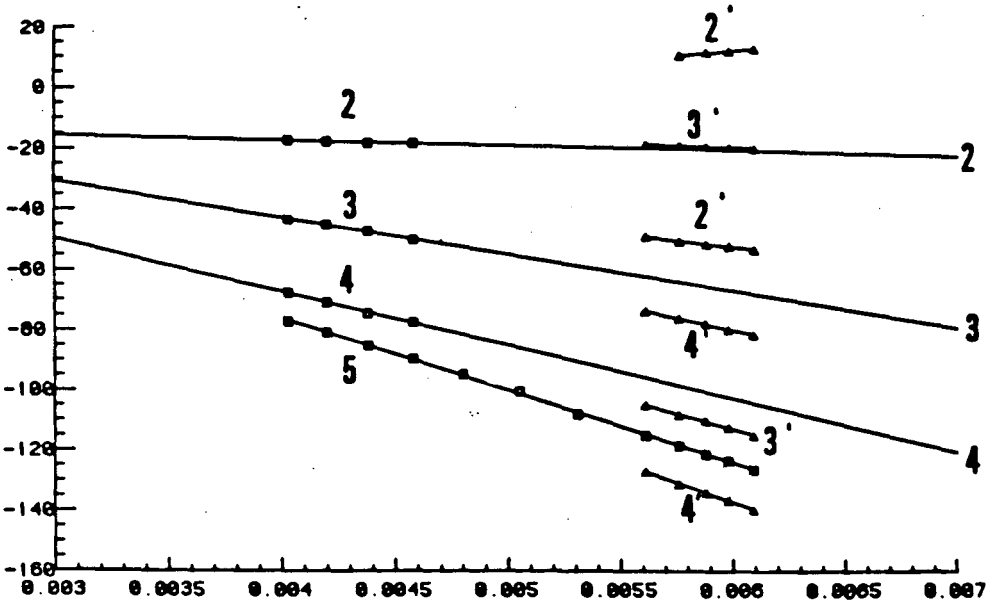


Figure 17. Chemical shifts of C_8 ring resonances of dimesityluranocene, 6, as a function of 1/T. Numbers show the ring proton assignments from spin decoupling experiments. Primed numbers show the assignments below the coalescence temperature.

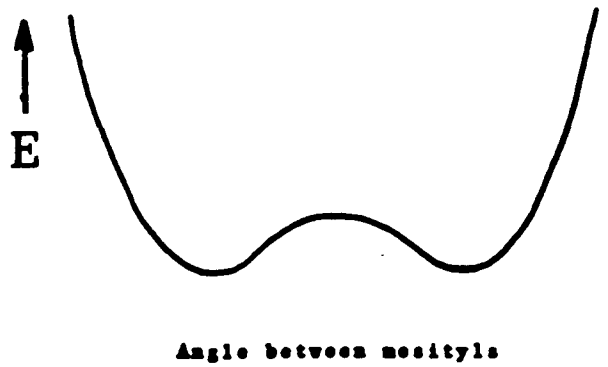


Figure 18. Schematic potential diagram for rotation of dimesityl-uranocene interconverting R- and S-enantiomers.

that all three uranocene systems were present means that the equilibrium constant cannot differ in magnitude much from unity. Thus, the attraction between the aryl rings in 6 must be comparable to the steric strain involved between one mesityl ring and the opposite C_8 ring. In the ring rotation process, of course, the strain effect is approximately constant.

In 1,1'-diphenyluranocene the barrier for rotation about the uranocene-phenyl bond is much less than in the mesityl case. This rotation equilibrates the exo- and endo-ortho phenyl protons (Figure 19).

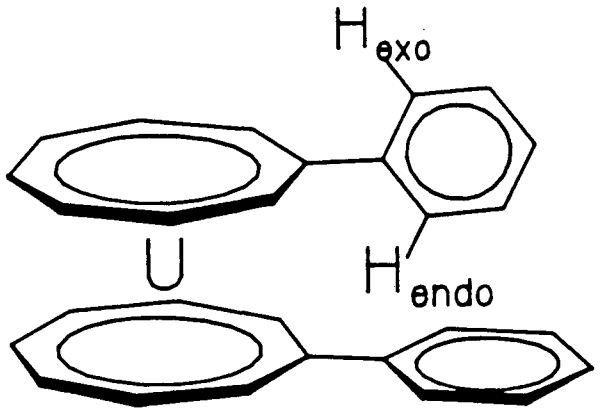


Figure 19. Phenyluranocene showing exo- and endo-ortho positions.

The energy barrier for this process is sufficiently low that coalescence cannot be observed before solubility becomes too low at low temperature. The ortho-proton resonances do broaden, however, at low temperature and permit line shape analysis. The $\Delta\delta$ between the endo- and exo-ortho positions was estimated with the help of o-tolyluranocene. The results give $\Delta H\ddagger$ = 4.4 Kcal mole^{-1} and $\Delta S\ddagger$ = -4.7 e.u.[89] This barrier is about 2 Kcal mole^{-1} higher than that for rotation about the ring-ring bond in biphenyl. This difference is in the expected direction considering that the larger internal angle of the 8-membered ring compared to a 6-membered ring will lead to greater hydrogen repulsions in the coplanar conformation.

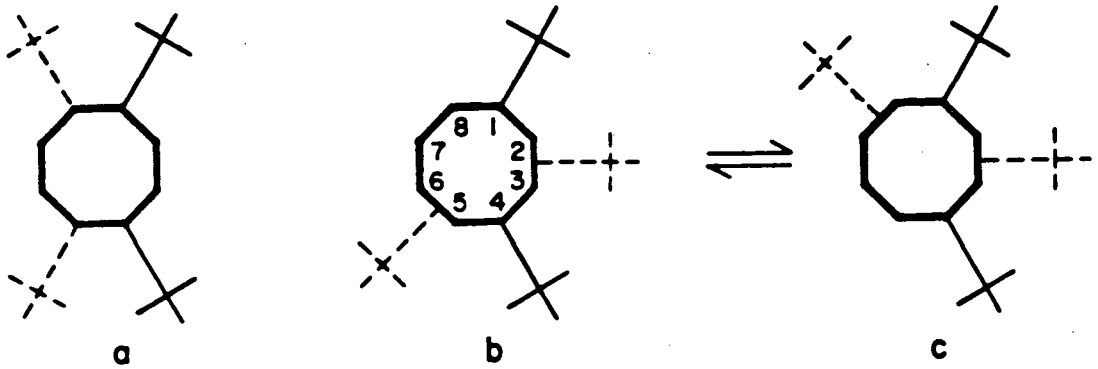


Figure 20. Possible conformations of 1,1',4,4'-tetra-t-butyluranocene.

A related application is in the rotation about the ring-metal bond in bis(1,4-di-t-butyl[8]annulene)uranium(IV).[90] Two possible conformations of this compound are shown in Figure 20. In conformation (a) all t-butyl groups are equivalent whereas in conformation (b) they are of two types. Only one kind of t-butyl group resonance is found at room temperature, but as the temperature is lowered, first coalescence is seen and then two t-butyl resonances appear as singlets. Similarly, the ring protons show corresponding behavior (Figure 21). All of the resonances both before and after coalescence show linear 1/T behavior. These results show that conformation (a) in Figure 20 is not important. The results also give $\Delta G^{\ddagger}$ of rotation of 8.3 Kcal mole^{-1}. In the rotation process a t-butyl group must slide past another t-butyl on the opposite ring. This process is easier in uranocene with its larger ring-ring distance than in the corresponding ferrocene. A comparable study gave $\Delta G^{\ddagger}$ = 13.1 Kcal mole^{-1} for 1,1',3,3'-tetra-t-butylferrocene. Once again, the large $\Delta\delta$ values in uranocene compounds permit dynamic NMR studies even with relatively low energy barriers.

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1. Controversy exists in naming sandwich organometallic actinide and lanthanide compounds of cyclooctatetraene dianion; [8]annulene dianion and [8]annulene-metal(X) complex are chosen here because these names properly describe the delocalization of charge in the ligand and also emphasize the formal oxidation state of the metal in the complex.

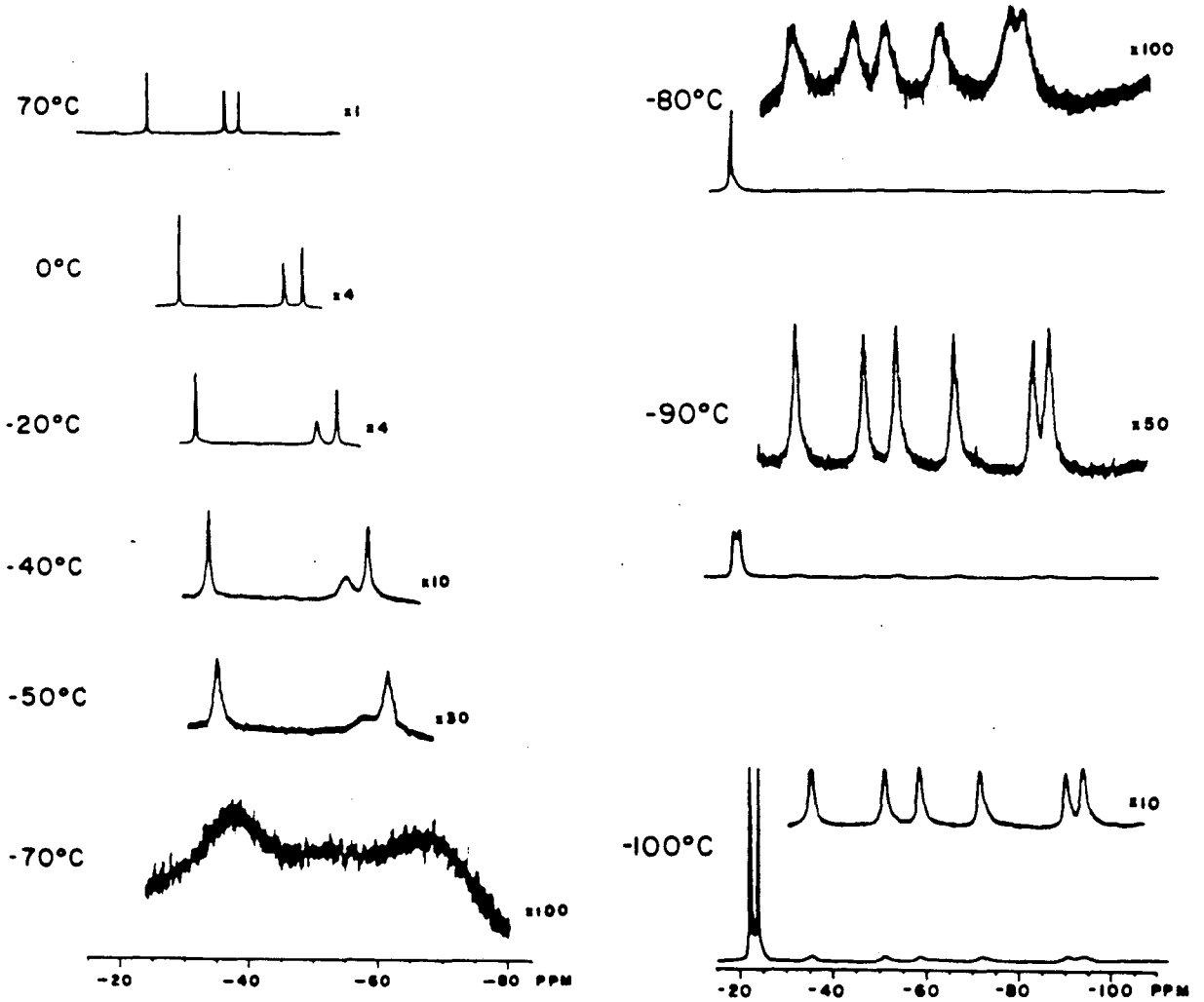

Figure 21. ^{1}H NMR spectra of 1,1',4,4'-tetra-t-butyluranocene as a function of temperature. The spectra at low temperatures show the t-butyl resonances as well as the ring protons.

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