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I. Mono([8]annulene)Uranium(IV) Half-Sandwich Complexes
II. Novel Syntheses of Symmetrically Substituted Cyclooctatetraenes

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(Ph.D. Thesis)

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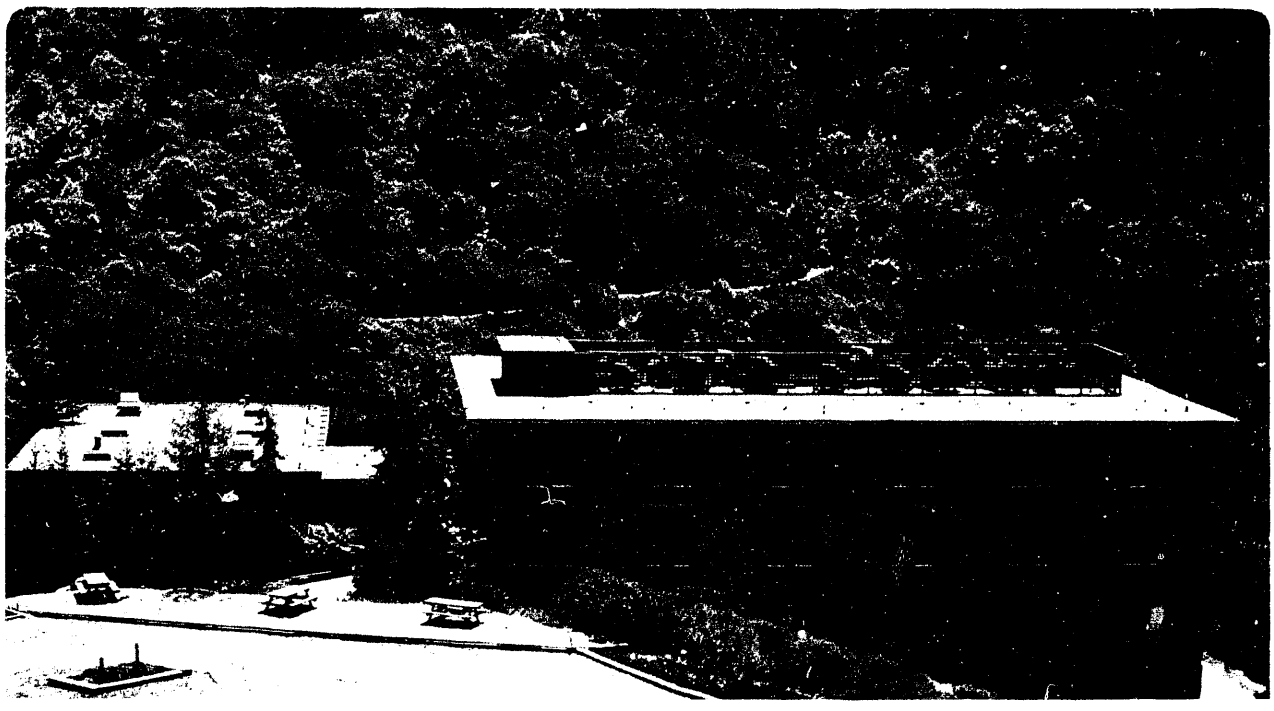

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by

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Abstract

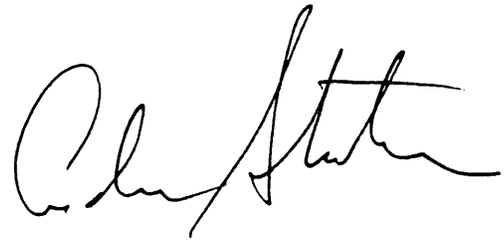
A reproducible, high-yield synthesis of mono([8]annulene)uranium(IV)dichloride (**1**) is reported, along with an X-ray crystal structural of the bis(pyridine) adduct. Metathesis reactions of the half-sandwich complex **1** with a variety of simple alkyl and alkoxy reagents failed to generate any isolable mono-ring complexes. Reactions of **1** with polydentate, delocalized anions did produce stable derivatives, including mono([8]annulene)uranium(IV)bis(acetylacetonate) (**4**). An X-ray crystal structure of **4** is reported.

Three novel syntheses of substituted cyclooctatetraenes are described. The first approach involves quenching of cyclooctatetraene dianion with trialkylsilyl chlorides, and subsequent conversion of the intermediate cyclooctatrienes to 1,4-di-silyl-substituted cyclooctatetraenes. The second approach exploits the Ni(0)-catalyzed cyclotetramerization of propargyl alcohol to tetrakis(hydroxymethyl)cyclooctatetraenes (THMCOT's). Following isolation of 1,3,5,7-THMCOT and 1,2,5,6-THMCOT and conversion to the corresponding tetrakis(bromomethyl)cyclooctatetraenes, reduction with LAH affords 1,3,5,7- and 1,2,5,6-tetramethylcyclooctatetrane, respectively. The third approach effects conversion of bulky mono-substituted acetylenes to 1,3,5,7-substituted cyclooctatetraenes.

$AlBr_3$-mediated dimerization of terminal acetylenes affords 1,3-substituted cyclobutadienes in high yield. Subsequent in situ dimerization of these 1,3-substituted cyclobutadienes to 1,3,5,7-substituted *syn*-tricyclo[4.2.0.$0^{2,5}$]octadienes is followed by thermal or photolytic ring-opening to the corresponding 1,3,5,7-substituted cyclooctatetraenes.

The syntheses of several mono([8]annulene)uranium(IV)dihalide complexes containing substituted [8]annulene rings is described. Three synthetic approaches are utilized, depending on the nature of the substituted-cyclooctatetraene ligand precursor. Direct synthesis via reduction by uranium trichloride is possible for silyl-substituted cyclooctatetraenes. Selective oxidation of a single ring of uranocenes with bromine or iodine affords mono-ring complexes for a variety of substituted cyclooctatetraenes. Finally, the direct synthesis of half-sandwich complexes containing very bulky substituted-[8]annulene rings from metathesis of substituted-cyclooctatetraene dianions with uranium tetrachloride is described.

An analysis of the structural parameters of [8]annulene lanthanide and actinide complexes is presented. This analysis concurs with the conclusions of an earlier analysis, and recognizes the importance of ligand-ligand steric interactions and Coulombic attractive and repulsive forces in determining the disposition of ligands around actinide and lanthanide metal centers.



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INTRODUCTION

The past twenty years have witnessed rapid development of the organometallic chemistry of the f-elements, both lanthanides and actinides. From this period of growth has emerged a more thorough understanding of the fundamental properties of these compounds, including thermodynamic and kinetic stabilities, bonding, and patterns of reactivity. The historical development of organo-f-element chemistry has been well reviewed in the past, both in the general chemistry literature[1] as well as in previous theses[2] in this group. No attempt at an in-depth review will be made here. Rather, the focus will rest on some of the salient features of f-element organometallic chemistry that have emerged from its historical evolution. Of particular consideration will be the chemistry of uranium, as it is the central subject of this Thesis. It should be noted that much of the development of organoactinide chemistry was inspired by parallel development within organometallic transition-metal chemistry. The chemistry of these two groups of metals reflects both similarities and striking differences. Where applicable, comparisons to analogous transition-metal chemistry will be drawn.

Initial attempts at the synthesis of actinide organometallic compounds predate World War II. These studies centered on the preparation of homolyptic alkyl complexes such as UMe_4 and UEt_4 in the hopes of generating volatile compounds for isotope separation. These early attempts were not successful. Wilkinson[3] isolated the first uranium organometallic complex, Cp_3UCl (where Cp is cyclopentadienyl anion), in 1956. The syntheses of a variety of cyclopentadienyl and related complexes followed, as did an understanding of the factors that govern the kinetic and thermodynamic stabilities of these compounds. Two themes emerged from this early work. First, that isolable complexes tend to have high coordination numbers relative to related transition-metal organometallic compounds; second, that barriers to ligand exchange in solution are relatively low.

Both of these features can be understood as resulting from the relatively large ionic radii of the actinides, and the diffuse and non-directional nature of the 5f and 6d valence orbitals.[4] Unlike transition metal complexes, for which virtually every aspect of structure and reactivity can be understood as arising from the strongly covalent (and therefore highly directional) nature of metal-ligand bonding, the valence shell of actinide ions is nearly spherical, leading to markedly different bonding behavior. In actinide cyclopentadienyl complexes, the disposition of ligands around the actinide ion is governed by the tendency to maximize the surrounding electron density. This is generally referred to as a propensity toward "steric saturation". Physically, this tendency can be viewed as a maximization of the electrostatic interactions between the highly charged metal ion and both negatively-charged and neutral coordinating ligands. High coordination numbers result simply because more ligands (or more generally, electron pairs) fit around actinide ions. Similarly, large ionic radii and shallow potential surfaces connecting various ligand arrangements likely contributes to a lowering of the activation energies for the dissociative and associative processes involved in ligand exchange reactions.

More recent advances in organoactinide chemistry have resulted in the isolation of a variety of complexes of widely differing structural types. Two important classes that grew directly from Wilkinson's early work are compounds derived from Cp_3UX[5,1b] and $Cp^*_2UX_2$[6,1a,1,e] structural units. In both cases the high kinetic stability of the Cp_3U- and Cp^*_2U- frameworks contributed to their robust chemistry. The kinetic stability of complexes of the sort Cp_3UX arises from the steric saturation associated with a very high coordination number (ten). In related complexes such as $Cp^*_2UX_2$, the lower coordination number (eight) is compensated by the kinetic stability provided by the bulky Cp^* ligands. The importance of the steric properties of ligands on the kinetic stability of organoactinide complexes is discussed more fully below.

The degree of kinetic stabilization associated with high coordination numbers is most dramatically demonstrated by the high thermal stability of complexes such as

$UMe_4(dmpe)_2$ [where dppe is bis(dimethylphosphino)ethane], synthesized and characterized by Andersen,[7] and $[Li(dioxane)]_3UMe_8$, isolated by Wilkinson.[8] The corresponding peralkyl complexes UMe_4 and UMe_5 are not isolable and are likely to be stable only at very low temperatures. That such extraordinary stabilization can be affected by blocking three or four coordination sites with non-labile ligands is quite remarkable.

A second important theme that has emerged from studies of actinide organometallic complexes is that sterically demanding ligands can be as effective in providing kinetic stability as high coordination numbers. This is illustrated by the isolation of complexes with very low formal coordination numbers such as $U[CH(SiMe_3)_2]_3$[9] and $U[N(SiMe_3)_2]_3$.[10] Kinetic stability is achieved in these complexes by enveloping the coordination environment of the metal ion with a small number of sterically demanding ligands. Dissociative pathways are inhibited by the strong metal-ligand bond strengths; associative processes are eliminated by blocking open coordination sites. The complexes are thermally stable because all low energy reaction pathways are blocked.

More typically, isolable complexes achieve steric saturation (i.e., kinetic stability) through a balance of high coordination numbers and ligand bulk. A classic example of this balance is found in bis(cyclopentadienyl) uranium complexes. The prototypical compound of this class, Cp_2UCl_2, has never been isolated. Under reaction conditions under which it might reasonably be expected to form, it instead undergoes disproportionation to Cp_3UCl and $CpUCl_3$. This process is dominated by the high kinetic stability of ten-coordinate Cp_3UCl. By substituting pentamethylcyclopentadienyl (Cp^*) for cyclopentadienyl, the bis-ring complex $Cp^*_2UCl_2$ becomes readily isolable. Because the steric bulk of Cp^* precludes formation of Cp^*_3UCl, the disproportionation pathway available to Cp_2UCl_2 is eliminated, thereby allowing isolation of $Cp^*_2UCl_2$. This example illustrates a dominant theme in organoactinide chemistry: the use of variable ligand steric properties to control the coordination environment, and in turn the thermal stability and relative reactivity, of metal

complexes. As will be seen in this Thesis, this constitutes an important theme in the chemistry of a related class of molecules, mono([8]annulene) uranium complexes.

A final note concerns the use of cyclooctatetraene dianion as a ligand in actinide organometallic chemistry. The first use of this ligand in the synthesis of uranocene was inspired by the possibility of observing covalent metal-ligand bonding involving f-orbitals.[11] Much subsequent effort, in these and other research groups, has been devoted to determining the nature of metal-ligand bonding among the f-block metals, in particular the degree to which covalent interactions are important. In the past, much of the research in these labs involving [8]annulene metal complexes has been directly or indirectly inspired by the study of the relative ionic/covalent character of the metal-ligand bonding. This is not true of the present study. Moreover, to avoid the semantical vortex of "ionic" versus "covalent" in the description of the bonding of these compounds, I feel that it is more productive to consider which model is of greater utility in describing the various aspects of their structure and reactivity. Thus, while f-block organometallic compounds may be formally considered to lie along the continuum between covalent and ionic bonding, it is clear that for all practical purposes (i.e., those of interest to synthetic chemists) their bonding can be considered as essentially ionic (see Chapter 4 of this Thesis). As such, the reaction chemistry of [8]annulene actinide complexes is best understood in terms of the principles of structure and reactivity that have emerged from studies of related actinide organometallic complexes, for example the extensive chemistry of cyclopentadienyl and substituted-cyclopentadienyl complexes. The principal concern of this Thesis is the synthesis of novel [8]annulene uranium complexes. These efforts should be considered within the context of related synthetic efforts involving other ligands, rather than within the traditional context of uranocene chemistry.

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CHAPTER 1

The Uranocene Half-Sandwich: Mono([8]Annulene)Uranium(IV) Dichloride and Some Derivatives

Introduction

The use of cyclooctatetraene (COT) dianion as a ligand in organoactinide chemistry began over twenty years ago with the synthesis of bis([8]annulene)uranium(IV), or uranocene.[1] Bis([8]annulene) complexes of several other tetravalent[2] and trivalent[3] actinides have since been prepared and their physical properties[4] have been thoroughly investigated. The use of this ligand has also been extended to the lanthanides and early transition metals in the preparation of mono- and bis([8]annulene) complexes as well as a slew of mixed ligand derivatives.[5] The focus of research in these labs has centered primarily on uranocene and thorocene, including the reactivity of these bis([8]annulene) complexes. Unfortunately, the reactivity of both with respect to ligand displacement has proven to be rather limited, in particular reactions involving controlled displacement of a single [8]annulene ring. The low reactivity arises from the high kinetic stability of these bis-ring metallocenes relative to their mono-ring counterparts. This stability is presumably the consequence of the inaccessibility of the metal metal center as a result of the steric constraints imposed by the [8]annulene rings.

As will be seen below, preparation of mono([8]annulene) thorium complexes is quite straightforward while analogous uranium complexes have proven much more elusive. As a result, isolation of uranium complexes containing a single cyclooctatetraene dianion ligand has been a synthetic goal in these labs for several years. Past synthetic efforts have focussed both on the removal of a single [8]annulene ring from uranocenes, as well as addition of a single cyclooctatetraene dianion to uranium tetrachloride and related uranium complexes. The evolution of the synthesis of the prototypical molecule of this class,

$(C_8H_8)UCl_2$, has been reviewed in the past,[6,7,8] but bears reappraisal in the light of more recent work.

Synthetic Approaches to Mono([8]annulene) Uranium(IV) Complexes

Addition of a Single Ring to UCl_4

Efforts to synthesize uranium compounds containing a single cyclooctatetraene ring focussed on $(C_8H_8)UCl_2(THF)_2$ (**1**) as a synthetic target based on the isolation of its thorium analog as well as its likelihood as a suitable precursor to more complex and interesting uranium complexes. Initial attempts to synthesize **1** centered on the addition of one equivalent of cyclooctatetraene dianion to UCl_4 in THF. Although the reaction appears to be complex and may involve U(III) intermediates, under various reaction conditions the only product isolated was uranocene (Eq. 1). This is in contrast to the analogous reaction between cyclooctatetraene dianion to $ThCl_4$ which cleanly generates[9] the mono([8]annulene) thorium(IV) dichloride "half-sandwich" $(C_8H_8)ThCl_2(THF)_2$ (**2**) in moderate yield (Eq. 2).

$$UCl_4 + K_2C_8H_8 \xrightarrow{THF} 1/2\ U(C_8H_8)_2 + 1/2\ UCl_4 \qquad (1)$$

$$ThCl_4 + K_2C_8H_8 \xrightarrow{THF} U(C_8H_8)ThCl_2(THF)_2 \qquad (2)$$

The difference in reactivity of $ThCl_4$ and UCl_4 in this reaction has been traditionally[6,7,8] ascribed to kinetic factors. Assumming stepwise, irreversible metatheses (based on the insolubility of KCl in THF),

$$MCl_4 + K_2C_8H_8 \xrightarrow{k_1} (C_8H_8)MCl_2(THF)_2 + 2\ KCl$$

$$(C_8H_8)MCl_2(THF)_2 + K_2C_8H_8 \xrightarrow{k_2} U(C_8H_8)_2 + 2\ KCl$$

it has been assumed that, for unknown reasons, $k_1(Th)>>k_2(Th)$ while $k_2(U)>>k_1(U)$. Speculation concerning the origin of the enhanced kinetic stability of **2** over **1** toward cyclooctatetraene dianion then focussed on differences in M-Cl bond lability or subtle electronic differences in the M-COT interactions.[6] Implicit in this scheme is the assumption that the reactions of UCl_4 and $ThCl_4$ with cyclooctatetraene dianion to form either mono- or bis([8]annulene) complexes proceed by the same mechanisms. As there is evidence to suggest that the initial step in uranocene formation is the reduction of UCl_4 to UCl_3 by cyclooctatetraene dianion,[10] and given the expected high reduction potential of $ThCl_4$,[11] this proposal now seems unlikely. It is more likely that the reaction of $K_2C_8H_8$ with UCl_4 proceeds by a mechanism entirely different than that of the reaction with $ThCl_4$, in which case **1**, or any such mono([8]annulene) uranium(IV) species, may not even appear on the reaction pathway of UCl_4 and $K_2C_8H_8$. Further evidence to suggest profoundly different reactivities of Th and U complexes toward cyclooctatetraene dianion is found in the reactions of **1** and **2** toward substituted-cyclooctatetraene dianions. Reaction of **1** results in ligand scrambling and a statistical distribution of substituted uranocenes,[7] while **2** reacts to yield only the mixed ring thorocene.[12] These reactions are discussed in greater detail later in this Chapter.

Redistribution[8,9] of thorocene and $ThCl_4$ in THF at reflux (Eq. 5) provides an alternative synthesis of **2**. Unfortunately, reaction of uranocene and UCl_4 under analogous conditions generates only small amounts of the uranium half-sandwich **1** (Eq. 6). The product **1** was observed by ^1H NMR but never isolated from the reaction mixture. It is likely, however, that Equation 6 does not represent a true equilibrium. For example, an attempt to approach the equilibrium from the opposite direction by heating the presumably more labile **1** in THF at reflux did not result in any observable disproportionation of **1** (Eq. 7).

$$Th(C_8H_8)_2 + ThCl_4 \xrightarrow[\text{reflux}]{\text{THF}} 2\,2 \qquad (5)$$

$$U(C_8H_8)_2 + UCl_4 \underset{\text{THF reflux}}{\rightleftharpoons} 2\,1 \qquad (6)$$

$$2\,1 \underset{\text{THF reflux}}{\rightleftharpoons} U(C_8H_8)_2 + UCl_4 \qquad (7)$$

Clearly, Equations 6 and 7 cannot both be true, and the true equilibrium position of this reaction is not known. The most that can be said is that the [8]annulene rings in **1** and uranocene are considerably less labile, at least at 67 °C, than those in **2** and thorocene. This difference in lability is reversed in the presence of cyclooctatetraene dianion (*vide infra*).

Coordination Stabilization of Mono-Ring Complexes

Attempts to stabilize mono-[8]annulene uranium complexes by replacement of coordinating chloride ligands with potentially polydentate borohydride ligands met with limited success. Marquet-Ellis[13a] reported ^1H NMR evidence for the half-sandwich compound $(C_8H_8)U(BH_4)_2$ in a reaction of UCl_4, $LiBH_4$ and $K_2C_8H_8$. Solar[8] showed that addition of cyclooctatetraene dianion to a THF solution of $U(BH_4)_4$ yielded uranocene as the only observed product. However, he found that low yields of $(C_8H_8)U(BH_4)_2$ could be generated from the slow addition of $K_2C_8H_8$ to a solution of $UCl_2(BH_4)_2$ generated *in situ*. In a related reaction, Cloke recently reported[13b] synthesis of $[(1,4\text{-}SiMe_3)_2C_8H_6]U(BH_4)_2$ from the reaction of $Li_2[(1,4\text{-}SiMe_3)_2C_8H_6]$ with $UCl_2(BH_4)_2$ in THF. The analogous mono([8]annulene) thorium(IV)bis(borohydride) half-sandwich has also been synthesized by several methods.[8,9]

Ken Smith[6] in these labs attempted to stabilize mono-[8]annulene uranium complexes toward uranocene formation through use of the strongly coordinating bidentate ligand TMEDA. He hoped to isolate a kinetically-stabilized, TMEDA-coordinated mono([8]annulene) complex from the reaction of $UCl_4(TMEDA)_2$ with cyclooctatetraene

dianion (Eq. 8). Instead he observed uranocene formation (Eq. 9) analogous to Equation 1.

$$UCl_4(TMEDA)_2 + K_2C_8H_8 \xrightarrow{\times} (C_8H_8)UCl_2(TMEDA)_x + 2\ KCl \qquad (8)$$

$$\downarrow \text{THF}$$

$$1/2\ U(C_8H_8)_2 + 1/2\ UCl_4(TMEDA)_2 + 2\ KCl + TMEDA \qquad (9)$$

The apparent failure of this approach is perhaps misleading. It has been determined that **1** is not appreciably complexed by TMEDA in THF (*vida infra*), which renders Equations 1 and 9 essentially equivalent. Had he used a bidentate ligand that better coordinates $(C_8H_8)UCl_2$, Smith's approach may well have worked.

Derivitization of Uranocenes

A second general approach to the synthesis of mono([8]annulene) metal complexes involves selective removal of one ring of the corresponding bis([8]annulene) metallocenes. One example of this approach is the reaction with protic acids. The reaction is general an has been applied to several metallocenes (Eq. 10). Reaction of $(C_8H_8)_2Zr$[14] or $(C_8H_8)_2Th$[8] with dry HCl generates the corresponding half-sandwich dichlorides in good yield. In the reaction of uranocene with dry HCl in THF, only moderate yields of the desired product **1** result. The reaction is complicated by the generation of large amounts of UCl_4 (from attack of HCl on **1**) and significant amounts of unreacted uranocene in the product mixture. Nevertheless, this reaction represented the most general and highest yield synthetic route to uranium(IV) half-sandwich complexes for some time.

$$M(C_8H_8)_2 + 2\,HCl \xrightarrow{THF} (C_8H_8)MCl_2(THF)_x \qquad (10)$$

M = Zr (79 %)
Th (70 %)
U (35 %)

In retrospect it can be seen that both of the above described approaches to the synthesis of **1** are inherently flawed. Addition of a single cyclooctatetraene dianion to UX_4 is complicated by the strong tendency of mono-[8]annulene uranium complexes to equilibrate to uranocenes in the presence of cyclooctatetraene dianion, possibly due to the availability of a U(III) oxidation state. Likewise, selective removal of a single [8]annulene ring from uranocene suffers the systemic failing that the mono-ring product is almost assuredly more reactive than its bis-ring predecessor, thereby almost guaranteeing low yields and complex product mixtures. As it turns out, the most successful approach to the synthesis of **1** involves a completely different approach, as will be seen below.

Reduction of Cyclooctatetraene by UCl_3 Complexes

In a study of the reaction of uranium(III) complexes as one-electron reducing agents, John Brennan[15] of the Andersen group found that reduction of cyclooctatetraene by $U[N(SiMe_3)_2]_3$ produces a mono([8]annulene) uranium(IV) complex (Eq. 11). Although the compound was not isolated, the U(IV)-bound [8]annulene protons were identified in the ^1H NMR spectrum. In the related reaction of tris(trimethylsilylcyclopentadienyl)uranium(III) with cyclooctatetraene, the products were isolated and characterized (Eq. 12).

$$U[N(SiMe_3)_2]_3 + C_8H_8 \xrightarrow{hexane} \text{COT-bound U(IV) compound} \qquad (11)$$

$$2\,U(C_5H_4SiMe_3)_3 + C_8H_8 \xrightarrow{hexane} (C_8H_8)U(C_5H_4SiMe_3)_2 + U(C_5H_4SiMe_3)_4 \qquad (12)$$

These reactions evidently proceed by electron transfer from U(III) to neutral cyclooctatetraene to form the cyclooctatetraene-bound uranium(IV) compounds. The synthesis of $(C_8H_8)U(C_5H_4SiMe_3)_2$ in this manner suggested a new approach to the synthesis of **1**. Bob Moore[7] in these labs showed that UCl_3 reacts with cyclooctatetraene in a fashion analogous to $U(C_5H_4SiMe_3)_3$ to form **1** and UCl_4 (Eq. 13).

$$2\,UCl_3 + C_8H_8 \xrightarrow{THF} \mathbf{1} + UCl_4 \qquad (13)$$

This approach avoids the failings of the previously described approaches by providing reaction conditions under which **1** is stable. However, it is handicapped by the generation of an equivalent amount of UCl_4 as a by-product. The similar solubility properties of **1** and UCl_4 render them difficult to separate. This problem was circumvented by using a reducing agent capable of selectively reducing UCl_4 to UCl_3 in the presence of cyclooctatetraene and **1**. In so doing, the UCl_4 generated by the reaction of UCl_3 and cyclooctatetraene is re-reduced to UCl_3 and cycled back into the reaction. A convenient such reducing agent is NaH (Scheme 1).

$$2\,UCl_4 + 2\,NaH \longrightarrow 2\,UCl_3 + 2\,NaCl + H_2$$
$$2\,UCl_3 + C_8H_8 \longrightarrow \mathbf{1} + UCl_4$$
$$\overline{\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad}$$
$$UCl_4 + C_8H_8 + 2\,NaH \xrightarrow{THF} \mathbf{1} + 2\,NaCl + H_2$$

Scheme 1

To test whether this approach could be applied to the synthesis of uranium half-sandwich complexes containing substituted [8]annulene ligands, Moore attempted the reaction of UCl_3 with *n*-butylcyclooctatetraene. After a prolonged reaction period, the only

product that he isolated was a trace amount of 1,1'-di(*n*-butyl)uranocene. The reduction potential of *n*-butylcyclooctatetraene is higher than that of unsubstituted cyclooctatetraene, both because of steric interactions in the planar dianion as well as the electron donating nature of the *n*-butyl substituent. It was theorized that this increase in the reduction potential inhibits the electron transfer from U(III) to the neutral alkyl-substituted cyclooctatetraene. This proposal was substantiated by the successful preparation of a half-sandwich compound containing a [8]annulene ligand substituted with the electron-withdrawing *m*-fluorophenyl group (Eq. 14).

$$UCl_4 + (m\text{-}F\text{-}C_6H_4)C_8H_7 + 2\ NaH \xrightarrow{THF} [(m\text{-}F\text{-}C_6H_4)C_8H_7]UCl_2(THF)_2 + 2\ NaCl + H_2 \qquad (14)$$

The electron-withdrawing effect of the *m*-fluorophenyl group apparently lowers the reduction potential of *m*-fluorophenylcyclooctatetraene sufficiently to allow electron transfer from U(III) to the substituted cyclooctatetraene.

Because the bulk of the commonly available substituted cyclooctatetraenes bear electron donating substituents [e.g. mono-, di- and tetra(alkyl)-substituted cyclooctatetraenes], the fact that this approach is not compatible with these ligands represents a fairly severe limitation. As a result, half-sandwich complexes bearing electron-donating ring substituents must be synthesized through derivatization of the corresponding uranocenes. However, discussion of the syntheses of these compounds, as well as the "direct" synthesis of half-sandwich complexes bearing electron-withdrawing ring substituents, will be deffered until Chapter 3.

Synthesis and Charcterization of $(C_8H_8)UCl_2(THF)_2$ (1)

Improvements To The Synthesis of 1

For some time after its discovery, the synthesis of **1** was plagued by variable and often low yields. A systematic investigation of the reaction was initiated in order to improve its reproducibility. It quickly became apparent that the yield of **1** from the reaction of UCl_4, cyclooctatetraene and NaH was highly dependent on the nature of the commercial NaH used. As mentioned above, a criterion for the *in situ* reductant of Scheme 1 is the capability of selectively reducing UCl_4 to UCl_3 in the presence of cyclooctatetraene and **1**. Alkali metal hydrides are attractive candidates because of the innocuous nature of their products (MCl and H_2). Schleyer[16] has described the preparation of "superactive" metal hydrides from the reduction by H_2 of metal alkyls. It was found that NaH prepared in this fashion was indeed "superactive", producing uranocene on reaction with UCl_4 and cyclooctatetraene. This is reminiscent of the reactivity of commercial KH (known to be capable of reducing cyclooctatetraene) which likewise produces uranocene in this reaction. It would appear then that kinetic factors dominate in these heterogeneous metal hydride reductions. After some experimentation, it was found that reproducibly high (>80%) yields of **1** were possible using commercial NaH that was treated by Sohxlet extraction with hexane (to remove the oil in which it is suspended) and grinding into a fine powder immediately before use. After the reaction was finished (generally by stirring 24 hours) residual unreacted UCl_4 could be effectively removed by addition of TMEDA to the product solution to form the hydrocarbon-soluble[17] $UCl_4(TMEDA)_2$. Extraction of the product mixture with hexane thus afforded UCl_4-free material. The only other significant side-product, uranocene, is somewhat hydrocarbon-soluble and was also removed by hexane extraction. The resulting crude material can be recrystallized from THF/toluene to afford pure **1**. Like its thorium analog **2**,[9] **1** was found to undergo desolvation on exposure to the glove box atmosphere, resulting in a variable THF content in the solid state. The rate of loss of THF from **1** is much greater than that of **2**, however, precluding isolation of dry crystalline, fully solvated material. This presented problems when a knowledge of the

exact stoichiometry of THF was needed. Accordingly, after recrystallization, **1** was subjected to a dynamic vacuum for several hours at room temperature and the THF stoichiometry of the resulting material was determined from C, H analyses. This green powder, $(C_8H_8)UCl_2(THF)_x$, x generally between 0.3 - 0.4, was then stored at ambient pressure in a glove box and used as needed.

^1H NMR of 1

The ^1H NMR of **1** in THF-d_8 at 30 °C shows a single resonance at -31.8 ppm with a line width of 18 Hz corresponding to the [8]annulene ring protons. The linewidth of the [8]annulene ring proton resonances is considerably more narrow than that of uranocene ($w_{1/2}$ = 90 Hz). A variable temperature ^1H NMR study of **1** reveals no dynamic processes operating on the ^1H NMR time scale within the temperature range studied (-80 - 80 °C). A plot of chemical shift versus 1/T is linear, exhibiting the expected Curie-Weiss behavior.

Crystal Structure of The Pyridine Adduct of 1

Considerable effort was directed toward obtaining crystals of **1** suitable for X-ray analysis. Appropriately sized crystals could be grown from toluene/THF solutions, but rapid desolvation and concomitant changes in crystal morphology while loading the crystals into capillaries was unavoidable. This desolvation behavior is in contrast to that of **2**, which also suffers loss of coordinating THF at ambient pressure, but at a much slower rate. Solvent loss is slow enough in **2** to allow X-ray structure analysis.[18a] Moore[7] showed that the IR spectrum of **1** from a rapid mull preparation is virtually superimposable with the IR spectrum of **2** similarly prepared, indicating that they are likely isostructural. The coordination sites on **2** may be "roomier" than those on **1** because of the larger ionic radius of Th(IV) over U(IV), allowing more tightly bound THF.

In order to obtain a better behaved material, more strongly coordinating ligands for the uranium half sandwich were investigated. It was found that the bis(pyridine) adduct,

$(C_8H_8)UCl_2(NC_5H_5)_2$ (**3**), which can be readily synthesized from partially desolvated **1** (Eq. 15), does not lose coordinating pyridine on exposure to the glove box atmosphere.

$$(C_8H_8)UCl_2(THF)_x + \text{xs } C_5H_5N \xrightarrow{PhMe} (C_8H_8)UCl_2(NC_5H_5)_2 \qquad (15)$$

Single crystals of **3** were obtained by slow cooling of a saturated toluene solution, and the X-ray crystal structure of **3** was determined.[18b] The ORTEP plot of the molecular structure of **3** is shown in Figure 1. Positional parameters are listed in Table I with selected bond distances and angles listed in Table II. A summary of crystallographic and data refinement parameters are included as Supplementary Table I at the end of this chapter.

Figure 1 ORTEP of $(C_8H_8)UCl_2(NC_5H_5)_2$; Thermal ellipsoids at 50% probability level

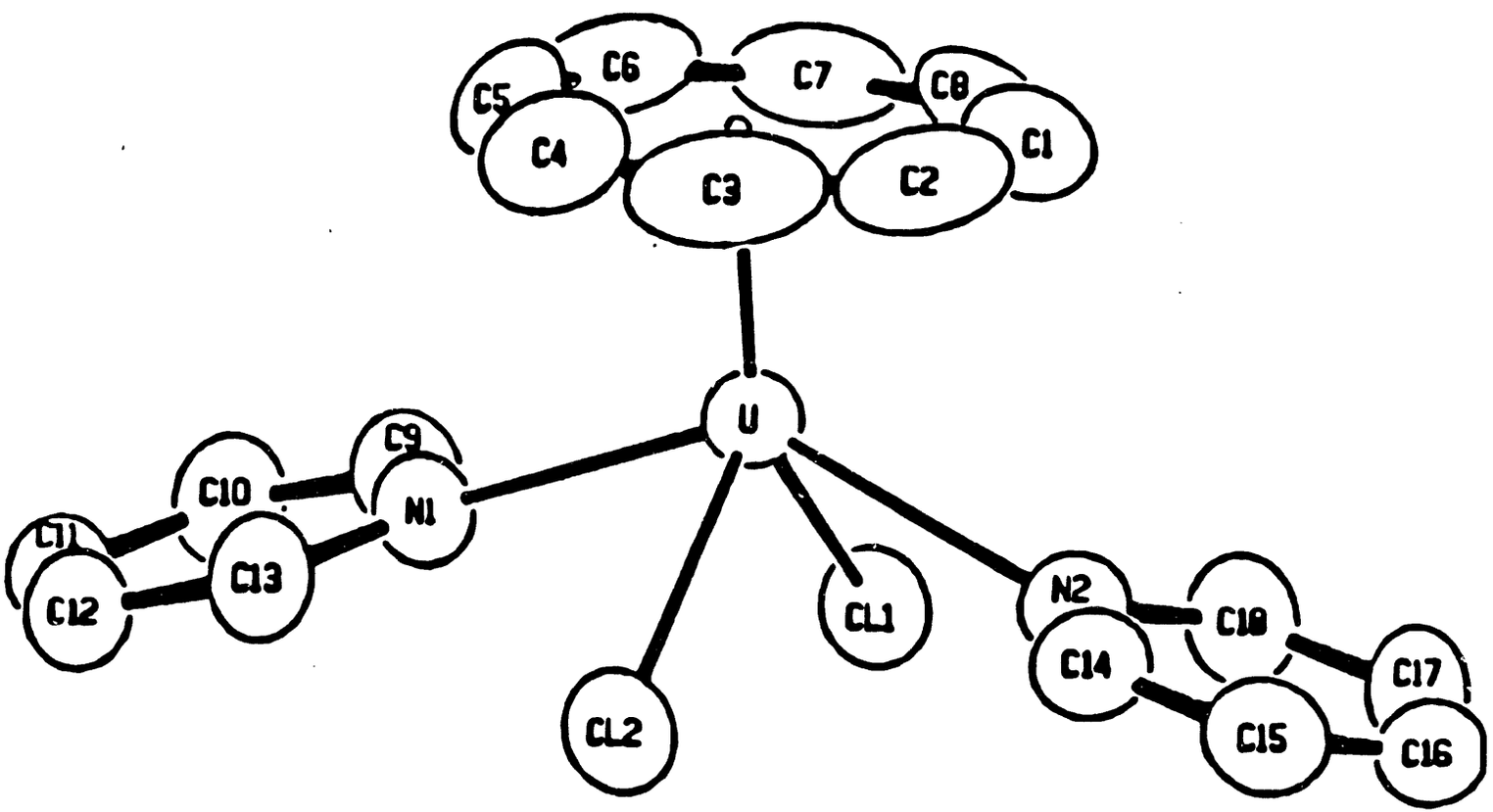

Table I Positional Parameters with Estimated Standard Deviations for $(C_8H_8)U(Cl)_2(NC_5H_5)_2$ (3)

Atom	x	y	z
U	0.25826(2)	0.05235(3)	0.01444(1)
Cl1	0.3853(1)	0.2449(3)	-0.0210(1)
Cl2	0.2136(1)	0.2455(3)	0.1355(1)
N1	0.3952(4)	0.0081(7)	0.1560(3)
N2	0.1643(4)	0.3099(7)	-0.0765(3)
C1	0.1540(8)	-0.069(1)	-0.1403(7)
C2	0.1011(7)	-0.076(1)	-0.082(1)
C3	0.1132(8)	-0.141(2)	0.004(1)
C4	0.183(1)	-0.229(1)	0.0631(8)
C5	0.269(1)	-0.285(1)	0.0606(7)
C6	0.3217(7)	-0.270(1)	0.0008(8)
C7	0.3101(7)	-0.190(1)	-0.0830(8)
C8	0.2389(8)	-0.110(1)	-0.1409(6)
C9	0.4769(5)	-0.025(1)	0.1463(5)
C10	0.5500(5)	-0.066(1)	0.2157(5)
C11	0.5384(6)	-0.069(1)	0.3003(5)
C12	0.4564(6)	-0.035(1)	0.3115(5)
C13	0.3871(5)	0.002(1)	0.2387(5)
C14	0.0858(5)	0.359(1)	-0.0628(5)
C15	0.0276(5)	0.474(1)	-0.1152(5)
C16	0.0517(6)	0.547(1)	-0.1865(5)
C17	0.1302(6)	0.496(1)	-0.2026(5)
C18	0.1832(6)	0.381(1)	-0.1470(5)

Table II Selected Bond Distances (Å) and Angles (°) for $(C_8H_8)UCl_2(NC_5H_5)_2$ (3)

U - Cl1	2.638(2)	Cl1 - U - Ct1	127.66
U - Cl2	2.649(2)	Cl2 - U - Ct1	131.75
U - N1	2.639(5)	N1 - U - Ct1	111.33
U - N2	2.644(6)	N2 - U - Ct1	110.21
U - C1	2.689(8)	Cl1 - U - Cl1	100.6(1)
U - C2	2.678(9)	Cl1 - U - N1	77.2(1)
U - C3	2.658(9)	Cl1 - U - N2	77.9(1)
U - C4	2.675(9)	Cl2 - U - N1	77.1(1)
U - C5	2.703(9)	Cl2 - U - N2	75.5(1)
U - C6	2.709(9)	N1 - U - N2	138.5(2)
U - C7	2.676(8)		
U - C8	2.683(7)		

The crystal structure of **3** is, as expected, structurally similar to its thorium relative **2**. The average U-C bond length in **3** (2.683 Å) is slightly shorter than the average Th-C bond length in **2** (2.72 Å). The difference is simply a reflection of the difference in metal ionic radii[19] between nine-coordinate U(IV) (1.05 Å) and nine-coordinate Th(IV) (1.09 Å). A similar difference between the M-Cl bond lengths between **3** (2.642 Å) and **2** (2.69 Å) are observed. As such, it is difficult to infer a plausible rationale for the enhanced kinetic stability of **2** over **1** based on a comparison of structural parameters of the uranium and thorium half-sandwich complexes. It is also of interest to compare the average U-C bond distances in nine-coordinate **3** with those of ten-coordinate uranocene.[4c] The U-C bond length would be expected to decrease on going from a ten- to nine-coordinate species, but in fact it increases from 2.647 Å in uranocene to 2.683 Å in **3**. A rationale for this observation as well a comparison of the structural parameters of **3** relative to other mono([8]annulene) U(IV) complexes is discussed in full in Chapter 4.

Metathesis Reactions of $(C_8H_8)UCl_2(THF)_2$

Reactions of 1 With Cyclooctatetraene Dianions

Initial reaction studies of **1** by Moore[7] showed that it shows no inherent instability in the presence of cyclooctatetraene dianion; i.e., it does not disproportionate to uranocene and UCl_4. Reaction of **1** with one-third equivalent of $K_2C_8H_8$ resulted in smooth conversion to one-third equivalent of uranocene (Eq. 16).

$$\mathbf{1} + 1/3\ K_2C_8H_8 \xrightarrow{THF} 1/3\ (C_8H_8)_2U + 2/3\ \mathbf{1} + 2/3\ KCl \qquad (16)$$

As mentioned earlier in this Chapter, the reaction of **1** with one equivalent of a substituted cyclooctatetraene dianion results in ligand scrambling and a statistical

distribution of substituted uranocenes (for example reacion with ^{t}BuCOT dianion, Eq. 17). This contrasts with the analogous reaction of **2** with a substituted cyclooctatetraene which leads exclusively to the mixed-ring thorocene (e.g. with PhCOT dianion,[12] Eq. 18).

$$\mathbf{1} + K_2{}^t\mathrm{BuC_8H_7} \xrightarrow{\mathrm{THF}} 1/2\ \mathrm{U(C_8H_8)(}{}^t\mathrm{BuC_8H_7)} + 1/4\ \mathrm{U(C_8H_8)_2} + 1/4\ \mathrm{U(}{}^t\mathrm{BuC_8H_7)_2} + 2\ \mathrm{KCl} \qquad (17)$$

$$\mathbf{2} + K_2\mathrm{PhC_8H_7} \xrightarrow{\mathrm{THF}} \mathrm{Th(C_8H_8)(PhC_8H_7)} + 2\ \mathrm{KCl} \qquad (18)$$

It is known that both uranocene and thorocene undergo ligand exchange with substituted cyclooctatetraene dianions to give mixed ring products at approximately the same rate.[12] Given this, it is surprising that no ligand scrambling is observed in Equation 18. This implies that the ligand scrambling observed in Equation 17 may not be occuring in the reaction of product uranocene with cyclooctatetraene dianion, but in reaction with an intermediate on the way to uranocene. One possible intermediate is a bis([8]annulene) uranium(III) complex, for which ligand exchange may be extremely rapid. The results of Equations 17 and 18 underscore the likelyhood that uranium and thorium complexes react with cyclooctatetraene dianion (and possibly with any highly reducing reagents) by entirely different mechanisms and that due caution should be exercised in comparing their reactivities.

Reactions of 1 With Monodentate Alkyl- and Alkoxy Anions

The preparation and study of the reactivity of σ-bonded alkyl, alkoxy, and amido uranium and thorium complexes has occupied a significant portion of the organoactinide literature over the past ten years.[20] Prominent among these studies are those of $Cp^*_2MCl_2$, M = U, Th, championed by Marks[21] and coworkers. One of the original goals of this research was to compare the reactivity of mono([8]annulene) complexes such as **1** with

bis(Cp^*) complexes such as $Cp^*_2UCl_2$. In this fashion we hoped to gain insight into the differences in steric and electronic properties of a single cyclooctatetraene dianion and two Cp^* anions, both in terms of the reactivity of the dichlorides as well as the kinetic stabilities of the products. To this end, the reaction of **1** with a variety of alkyl and alkoxy reagents were attempted, generally with disappointing results. These reactions are outlined below.

Alkylations of **1** with several alkyllithium and Grignard reagents were first attempted (Eq.17). In these reactions, the reagents were mixed at cold temperatures (-78 °C) and allowed to react for several hours before slowly warming to room temperature. Under these reaction conditions, only intractable products resulted. No organouranium complexes were isolated, neither complexes of the desired $(C_8H_8)UR_2$ stoichiometry, nor starting **1**, nor uranocene.

$$\mathbf{1} + 2\,RM \xrightarrow[-78\,^\circ C]{THF} \text{no isolated products} \qquad (17)$$

$M = Li,\ R = CH_3,\ C_6H_5,\ CH_2Si(CH_3)_3$

$M = MgCl,\ R = CH_3,\ CH_2C_6H_5,\ CH_2Si(CH_3)_3$

In addition, the reactions of **1** with dimethyl- and dibenzylmagnesium were attempted. In the reaction with $(CH_3)_2Mg$, the product appears (by ^1H NMR) to be chloro-bridged U-Mg dimer (Eq. 18).

$$\mathbf{1} + R_2Mg \xrightarrow{THF} (C_8H_8)U(THF)_x(\mu\text{-}Cl)_2Mg(CH_3)_2 \qquad (18)$$

Unfortunately, crystalline material was not isolated from this reaction. The assignment of the dimer structure to the product is speculative based on the ^1H NMR, which shows a [8]annulene resonance very near that of **1** as well as resonances for the methyl groups shifted significantly downfield (-1.7 ppm), although not shifted nearly as downfield as would be expected for complexes containing U-C bonds. There is precedence for this

assignment in the recently reported[22] "Grignard adduct" formed from the reaction of $(C_8H_8)(C_5Me_5)ThCl$ with benzylmagnesium chloride (Eq. 19). While not strictly analogous, this complex shares the actinide ion-bridging-chloride-magnesium ion core proposed in the product of Equation 18.

$$(C_8H_8)(C_5Me_5)ThCl + Me_3CCH_2MgCl \xrightarrow{THF} (C_8H_8)(C_5Me_5)Th(\mu\text{-}Cl)_2MgCH_2CMe_3(THF) \quad (19)$$

It was thought that this "dimethylmagnesium adduct" of **1** might represent an intermediate along the reaction pathway to a methyl-substituted half-sandwich complex, and that higher reaction temperatures were necessary to take it to product. However, heating of the complex in THF resulted in only decomposed material. In an attempt to remove the $MgCl_2$ from the aggregate at lower temperatures, 1,4-dioxane (1,4-DO) was added to an ether solution of the complex. The analogy is to the synthesis of dialkylmagnesium complexes from Grignard reagents by driving the Schlenk equilibrium through formation of the ether-insoluble $MgX_2(1,4\text{-DO})$ complex (Eq. 21). It was hoped that any solution equilibria between the half-sandwich-$Mg(CH_3)_2$ complex and methylated half-sandwich (for example, Eq. 20) could be driven to the right by addition of 1,4-dioxane to afford the dimethyl half-sandwich complex (Eq. 23). As in other other alkylation reactions, however, only intractable products resulted.

$$(C_8H_8)U(\mu\text{-}Cl)_2MgR_2 \rightleftharpoons (C_8H_8)URCl + RMgCl \quad (20)$$

$$2\,RMgX + 1,4\text{-DO} \xrightleftharpoons{Et_2O} MgR_2 + MgX_2(1,4\text{-DO})\downarrow \quad (21)$$

$$(C_8H_8)U(\mu\text{-}Cl)_2Mg(CH_3)_2 + 1,4\text{-DO} \not\longrightarrow (C_8H_8)U(CH_3)_2 + MgCl_2(1,4\text{-DO})\downarrow \quad (22)$$

$$(C_8H_8)U(CH_3)_2 \xrightarrow[\text{reflux}]{Et_2O} \text{decomposed material}$$

Curiously, there was no reaction between **1** and dibenzylmagnesium in THF, even at elevated temperatures. An NMR tube reaction showed unchanged resonances for both compounds even on heating at 50 °C for several days.

Reaction with sodium or potassium alkoxide reagents also failed to generate any isolable mono([8]annulene) uranium(IV) half-sandwich compounds (Eq. 23). The mixture of products obtained from the reaction of **1** with alkali metal alkoxides include cyclooctatetraene dianion and an array of mixed uranium(IV) alkoxides of unknown stoichiometry. No uranium complexes containing both [8]annulene and alkoxy ligands were detected by ^{1}H NMR.

$$\mathbf{1} + 2\,\mathrm{MOR} \xrightarrow[-78\,^\circ\mathrm{C}]{\mathrm{THF}} \text{no mono-COT U(IV) products} \qquad (23)$$

$\mathrm{MOR} = \mathrm{NaOC(CH_3)_3},\ \mathrm{KOC(CH_3)_3},\ \mathrm{NaOC_6H_5}$

Monitoring of Metathesis Reactions at Low Temperature

It is unclear whether our lack of success in isolating alkyl- or alkoxy-substituted uranium half-sandwich complexes is a result of some shortcoming in the synthetic approaches we have taken to date, or because of their inherent instability. It is conceivable that mono([8]annulene) actinide complexes are unstable in the presence of highly basic anions. Similarly it is possible that the dialkyl or dialkoxy derivatives form at low temperatures but are sterically unsaturated and possess low energy pathways to decomposition. Sattelberger[23] has also reported that the reactions of **1** and the thorium analogue **2** with alkyllithium and Grignard reagents lead to intractable products. The only σ-bound derivatives that he reports are $(C_8H_8)M[N(SiMe_3)_2]_2$, M = U, Th via the metatheses of **1** and **2** with two equivalents of $NaN(SiMe_3)_2$. Note that it is also likely that $(C_8H_8)U[N(SiMe_3)_2]_2$ is a product of Equation 11. The crystal structure of

$(C_8H_8)Th[N(SiMe_3)_2]_2$ shows evidence of an agostic interaction between one carbon on each of the $-N(SiMe_3)_2$ ligands and the thorium ion, a property Sattelberger ascribes to a coordination number deficiency in the compound. Given the sterically demanding nature of the $-N(SiMe_3)_2$ ligand and that a degree of steric unsaturation is observed in its half-sandwich derivative, it is likely that less bulky ligands fail to provide sufficient kinetic stabilization to allow observation of their half-sandwich derivatives, at least at room temperature.

To address the possibility that half-sandwich derivatives form at low temperatures but are thermally unstable, several low-temperature NMR-tube reactions of **1** with alkyl lithium and Grignard reagents were conducted, the results of which were unfortunately inconclusive. While the reactions clearly proceeded at low temperature (< –60 °C), the products could not be identified. The spectra were quickly obscured by precipitate formation and severe paramagnetic line broadening. Several possible paramagnetic side products are possible, including organic radicals, U(III) complexes and uranium metal. There is evidence from preparatory scale reactions of **1** with alkyl lithium reagents that small amounts of uranium metal are formed, at least after warming to room temperature. A low-temperature NMR tube reaction of **1** with the less reducing KO^{t}Bu was similarly inconclusive. Disappearance of the resonance of the [8]annulene protons of **1** was observed in conjunction with the appearance of a variety of paramagnetically shifted resonances, none of which could be easily assigned to mono- or bis(alkoxy) half-sandwich complexes.

Reactions of 1 with Multi-dentate Anions

Several examples of stable early transition metal and lanthanide complexes containing σ-bonded ligands with internal coordinating capability have been reported.[24] The reactions of **1** with two such ligands were attempted. These ligands are $LiCH_2C_6H_4$-o-$N(CH_3)_2$ and LiC_6H_4-o-$CH_2N(CH_3)_2$. No derivatives of the half-sandwich were

isolated; the products were thermally unstable and decomposed rapidly at room temperature both in solution and as solids.

The final set of reactions studied were those of **1** with delocalized bidentate anions. Metatheses of **1** with sodium acetylacetonate [Na(acac)],[25] sodium tropylate [Na(trop)],[25] and (methylenediphenylphosphoranyl)methyllithium [$Li(CH_2)_2PPh_2$][26] were attempted. Both Na(trop) and $Li(CH_2)_2PPh_2$ reacted to give a mixture of organometallic products. The major product was uranocene, but resonances for other organo uranium(IV) were observed. In both cases, attempts to isolate mono-ring complexes from the product mixtures were not successful. However, reaction of **1** with Na(acac) (Eq. 23) resulted in smooth conversion to bis-substituted product $(C_8H_8)U(acac)_2$ (**4**).

$$\mathbf{1} + 2\ \text{Na(acac)} \xrightarrow[-78\ ^\circ\text{C}]{\text{THF}} (C_8H_8)U(acac)_2 + 2\ \text{NaCl} \qquad (24)$$

Soluble in ethereal and hydrocarbon solvents, **4** proved also to be quite volatile; it can be sublimed without decomposition at 80 °C and 10^{-3} torr.

X-ray Crystal Structure of 4

An X-ray structure analysis was performed[18b] on single crystals of **4** obtained from slow cooling of a saturated pentane solution to -20 °C. The ORTEP plot of the molecular structure of **4** is shown in Figure 2. Positional parameters are listed in Table III and selected bond distances and angles are listed in Table IV. A summary of crystallographic and data refinement parameters for **4** are included with those of **3** in Supplementary Table I at the end of this chapter.

Figure 2 ORTEP of $(C_8H_8)U(acac)_2$; Thermal ellipsoids at 50% probability level

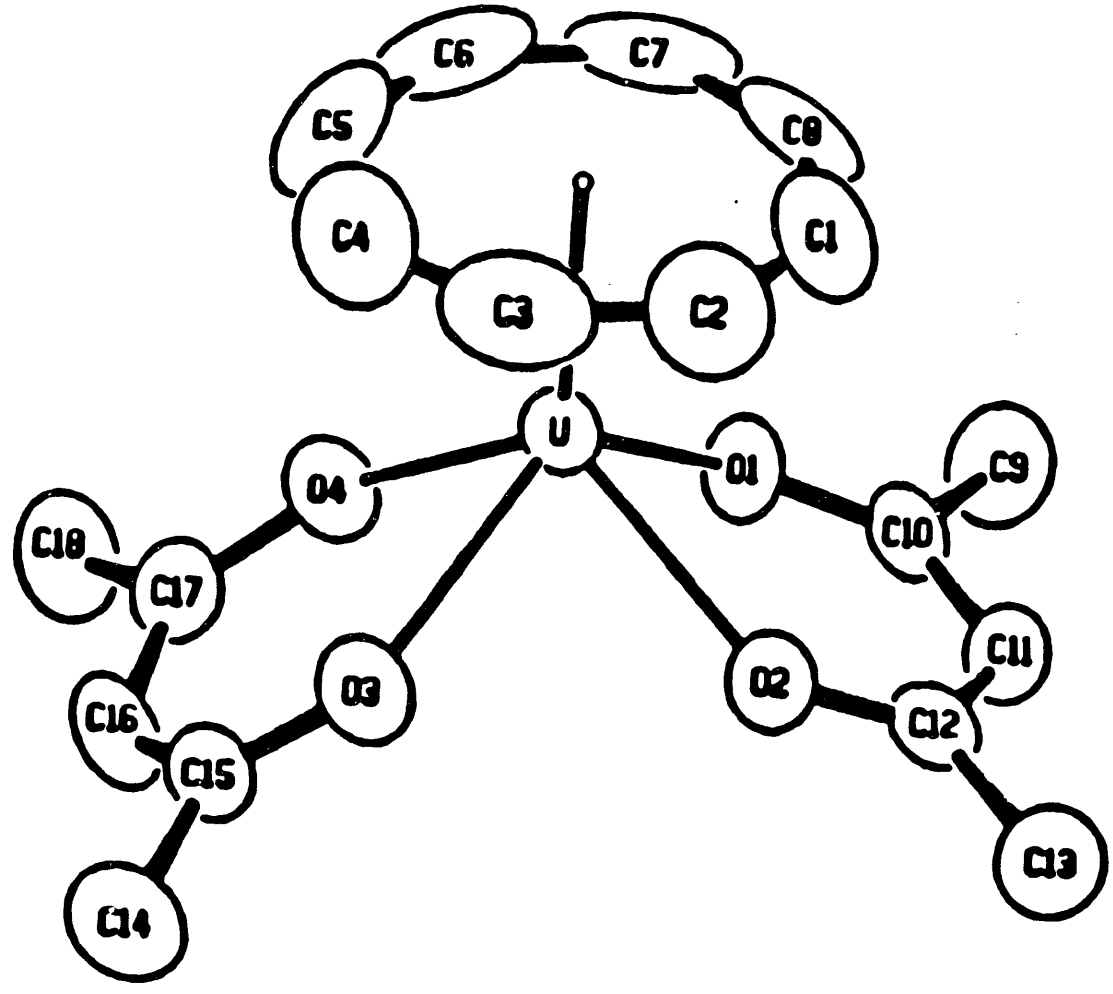

Table III Positional Parameters with Estimated Standard Deviations for $(C_8H_8)U(acac)_2$ (4)

Atom	x	y	z
U	0.11652(2)	0.20855(3)	0.23026(3
O1	0.0995(3)	-0.0119(5)	0.1868(5)
O2	-0.0024(3)	0.1741(5)	0.1639(5)
O3	0.0889(3)	0.3557(5)	0.0389(5)
O4	0.1894(3)	0.1702(5)	0.0533(5)
C1	0.0713(6)	0.201(2)	0.4939(9)
C2	0.0629(6)	0.330(1)	0.451(1)
C3	0.1059(7)	0.421(1)	0.399(1)
C4	0.1760(8)	0.422(1)	0.363(1)
C5	0.2302(6)	0.329(2)	0.368(1)
C6	0.2378(5)	0.200(2)	0.412(1)
C7	0.1938(8)	0.107(1)	0.468(1)
C8	0.1245(8)	0.111(1)	0.5005(9)
C9	0.0657(4)	-0.2307(8)	0.2098(9)
C10	0.0478(4)	-0.0879(7)	0.1938(7)
C11	-0.0216(4)	-0.0495(8)	0.1879(8)
C12	-0.0437(4)	0.0783(8)	0.1715(7)
C13	-0.1208(4)	0.1099(9)	0.1608(9)
C14	0.0801(5)	0.5070(9)	-0.1528(9)
C15	0.1137(4)	0.3907(8)	-0.0747(8)
C16	0.1684(5)	0.3283(8)	-0.1290(8)
C17	0.2050(4)	0.2224(9)	-0.0640(8)
C18	0.2637(4)	0.1615(9)	-0.1309(9)

Table IV Selected Bond Distances (Å) and Angles (°) for $(C_8H_8)U(acac)_2$ (**4**)

U - O(2)	2.313(5)	O(2) - U - Ct1	122.09
U - O(3)	2.339(5)	O(3) - U - Ct1	115.44
U - O(4)	2.310(5)	O(4) - U - Ct1	120.83
U - C(1)	2.682(8)	O(1) - U - O(2)	72.0(2)
U - C(2)	2.699(9)	O(1) - U - O(3)	119.4(2)
U - C(3)	2.712(9)	O(1) - U - O(4)	78.2(2)
U - C(4)	2.703(8)	O(2) - U - O(3)	77.1(2)
U - C(5)	2.686(9)	O(2) - U - O(4)	116.7(2)
U - C(6)	2.697(8)	O(3) - U - O(4)	71.2(2)
U - C(7)	2.700(8)	U - O(1) - C(10)	133.5(5)
U - C(8)	2.675(8)	U - O(2) - C(12)	134.7(4)
O(1) - C(10)	1.270(8)	U - O(3) - C(15)	138.0(5)
O(2) - C(12)	1.273(8)	U - O(4) - C(17)	138.8(5)
C(10) - C(11)	1.384(10)	O(1) - C(10) - C(9)	115.9(7)
C(12) - C(11)	1.387(10)	O(1) - C(10) - C(11)	125.0(7)
C(10) - C(9)	1.516(10)	O(2) - C(12) - C(13)	116.1(7)
C(12) - C(13)	1.504(10)	O(2) - C(12) - C(11)	124.0(7)
O(4) - C(17)	1.277(8)	C(10) - C(11) - C(12)	123.7(7)
O(3) - C(15)	1.256(8)	O(4) - C(17) - C(18)	116.3(7)
C(17) - C(16)	1.394(10)	O(4) - C(17) - C(16)	122.4(7)
C(15) - C(16)	1.376(11)	O(3) - C(15) - C(14)	116.5(8)
C(17) - C(18)	1.487(11)	O(3) - C(15) - C(16)	123.6(7)
C(15) - C(14)	1.502(10)		

The complex **4** assumes the expected C_{2v} symmetry and the bond lengths and angles within the acetylacetonate moiety compare with other bidentate acetylacetonate metal complexes.[27] The average U-C bond distance of 2.694 Å is slightly longer than that found in **3** and again longer than the U-C bond distance in uranocene. A full discussion of the bonding parameters of mono([8]annulene) complexes can be found in Chapter 4.

Experimental

Air and water sensitive compounds were handled under argon in a Vacuum Atmospheres glovebox or by using standard Schlenk line techniques. ^1H NMR spectra were obtained on UC Berkeley 200 and 250 MHz superconducting FT spectrometers equipped with Cryromagnets Inc. magnets and Nicolet model 1280 data collection systems. For variable temperature NMR spectra, temperatures were measured with a thermocouple mounted next to the NMR tube. Chemical shift values are reported in ppm with positive shifts reported for peaks downfield of TMS. Peaks are referenced to internal standards. UV-Visible spectra were obtained with an IBM model 9240 Ultra-violet/Visible Spectrophotometer. Values for λ_{max} are reported in nm. Infrared spectra were obtained with a Perkin-Elmer model 297 Infrared Spectrophotometer. All values are reported in cm-1. Tetrahydrofuran (THF), toluene, hexane, heptane, 1,4-dioxane (1,4-DO), and diethyl ether (Et_2O) were distilled from $LiAlH_4$ (LAH), CaH_2, or Na-benzophenone ketal. *tert*-Butanol was distilled and stored over 4 Å sieves. Cyclooctatetraene (COT, obtained from BASF) was stirred over activated 4 Å sieves overnight then vacuum transferred. Tetramethylethylenediamine (TMEDA) and pyridine were distilled from CaH_2. All liquids were degassed in three freeze-pump-thaw cycles and stored over 4 Å sieves before use. NaH (60% oil dispersion) was Soxhlet extracted with hexane overnight to remove oil and ground into a fine power immediately before use. Commercial potassium *tert*-butoxide (KO^{t}Bu) was sublimed before use. All other reagents, unless otherwise noted, were obtained from commercial suppliers and used without further purification.

"Superactive" Sodium Hydride, NaH[16a]

To a suspension of 4.81 g (50.0 mmol) of NaO^{t}Bu (prepared as described below) in 100 mL of dry hexane and 5.81 (50.0 mmol) of TMEDA at -25 °C was added dropwise 21.7 mL (50.0 mmol) of a 2.3 M solution of *n*-BuLi in hexane. After stirring for 15 min, dry H_2 gas was bubbled into the solution with vigorous stirring while the solution temperature

was raised to 0 °C. When absorption of H_2 ceased, the solution and ppt were transferred to centrifuge tubes sealed with septa. The solid was spun down and washed with several portions of dry hexane, combined, and dried *in vacuo*. The resultant white powder (0.95 g, 79.2 %) was stored in the glove box before use.

([8]Annulene)U(IV) Dichloride, $(C_8H_8)UCl_2(THF)_x$. To a solution of 5.00 g (13.2 mmol) of UCl_4 and 1.37 g (13.2 mmol) of COT in 100 mL of THF was added 1.0 g (42 mmol) of commercial NaH and the suspension was stirred for 24 h at 25 °C. The solution was filtered, 5 mL of TMEDA was added, and the solution was stirred for 1 h. The THF and excess TMEDA were removed from the filtrate *in vacuo*, and the resultant powder was extracted with hexane in a Soxhlet extractor to remove uranocene and $UCl_4(TMEDA)_2$. After subjecting the resultant solid to a dynamic vacuum for several hours to remove coordinating THF, the residual THF content was determined by C, H analyses. The yield varied from 3.85 - 4.10 g (70-75%) and the number of coordinating THF molecules was generally between 0.3 - 0.5. ^1H NMR (THF-d_8, 30 °C) δ -31.5 (s, $w_{1/2}$=18 Hz); Visible (THF) 454 (ε 281), 500 (ε 249), 518 (ε 227), 570 (ε 206), 582 (ε 188), 596 (ε 174), 742 (ε 32); IR (as bis-THF complex **1**, Nujol) 1340 m, 1259 m, 1163 m, 1070 m, 1032 sh, 1008 s, 920 m, 900 m, 840 s, 805 s, 720 s, 660 m.

([8]Annulene])U(IV)dichloridebis(pyridine), $(C_8H_8)UCl_2(NC_5H_5)_2$ (3). To a solution of 10 mL of pyridine and 100 mL of toluene was added 1.00 g (2.24 mmol) of $(C_8H_8)UCl_2(THF)_{0.45}$. After stirring for 24 h, the solution was filtered and the solution volume was reduced to approximately 50 mL. Cooling to -20 °C afforded 1.2 g (94 %) of **3** as dark red crystals. ^1H NMR (THF-d_8, 30 °C) δ -31.6 (s, $w_{1/2}$=16.2 Hz, 8H), 6.4 (broad s, 4H), 6.6 (m, 4H), 7.4 (t, 4H); Visible (toluene) 342, 446; IR (Nujol) 1350 m, 1310 s, 1225, m, 1080 m, 1023 s, 1004 sh, 970 s, 845 m, 800 m, 767 s, 698 m, 633 s,

550 m.; Anal. Calcd. for $C_{18}H_{18}N_2Cl_2U$: C, 37.85; H, 3.17; N, 4.90. Found: C, 37.48; H, 3.35; N, 5.02.

Reactions of 1 with Commercial Alkyllithium and Grignard Reagents

In a 100 mL Schlenk flask capped with a septum was dissolved 2.25 mmol of $(C_8H_8)UCl_2(THF)_x$ (approximately 1.0 g) in 40 mL of THF. To this solution cooled to -78°C was added dropwise 4.6 mmol of the appropriate alkyllithium or Grignard reagent [3.3 mL of CH_3Li as a 1.4 M solution in Et_2O; 2.3 mL of C_6H_5Li as a 2.0 M solution in cyclohexane/Et_2O; 4.6 mL of $(CH_3)_3SiCH_2Li$ as a 1.0 M solution in pentane; 1.5 mL of CH_3MgCl as a 3.0 M solution in THF; 4.6 mL of $(CH_3)_3SiCH_2MgCl$ as a 1.0 M solution in Et_2O]. After stirring for 6-8 h the solution was warmed to room temperature and the volatiles were removed *in vacuo*. The crude product mixtures were then examined by ^1H NMR (in THF-d_8 and toluene-d_8 solutions). The hexane-soluble component of the product mixtures was also examined by ^1H NMR. No resonances in paramagnetic regions of the spectrum were observed.

Reaction of 1 with Neopentylmagnesium Chloride

To 0.22 g (9.0 mmol) of Mg turnings in 5 mL of anhydrous Et_2O was added dropwise 0.49 g (4.6 mmol) of neopentyl chloride in 10 mL of Et_2O and the solution was stirred for 4 h. The grey solution was cannulated from the remaining Mg into a 100 mL Schlenk flask containing a solution of 1.00 g of $(C_8H_8)UCl_2(THF)_{4.5}$ (2.25 mmol) in 40 mL of THF at -78 °C. After stirring for 6 h the solution was warmed to room temperature and the volatiles were removed *in vacuo*. Examination of the ^1H NMR (THF-d_8) of the crude product mixture revealed no resonances in paramagnetic regions of the spectrum.

Dimethylmagnesium, $(CH_3)_2Mg$[28]

A flame-dried 500 mL Schlenk flask equipped with a 100 mL dropping funnel and a magnetic stir bar was charged with 5.6 g (230 mmol) of Mg turnings and 400 mL of anhydrous Et_2O. A solution of 28.40 g (200 mmol) of CH_3I in 50 mL of Et_2O was added dropwise over 1 h, then stirred for an additional 6 h. The dropping funnel was replaced with a septum and the grey solution of CH_3MgI was then cannulated off the remaining Mg into a 500 mL Schlenk flask capped with a septum. To this solution was added 18.5 g (210 mmol) of 1,4-dioxane dropwise over 1 h. The solution was stirred for 18 h while a heavy ppt formed. The solution and ppt were transferred to centrifuge tubes sealed with septa, the solid was spun down, and the supernatant liquid was collected and combined. The volatiles were then removed *in vacuo* to give 4.7 g (87%) of $(CH_3)_2Mg$ as a fine white powder. ^1H NMR (THF-d_8) δ 0.35 (s, 3H).

Dibenzylmagnesium, $(C_6H_5CH_2)_2Mg$

Following the procedure for the synthesis of $(CH_3)_2Mg$ described above, 4.86 g (0.200 mmol) of Mg and 17.10 (0.100 mmol) of benzyl bromide were allowed to react in 200 mL of Et_2O, and to the resulting solution of $C_6H_5CH_2MgBr$ was added 9.69 g (110 mmol) of 1,4-dioxane. After centrifugation and removal of the ppt, the combined supernatants were distilled to dryness to afford a yellow oil. Vacuum sublimation (70 °C, 0.1 torr) afforded 4.5 g (44%) of $(C_6H_5CH_2)_2Mg$ as a waxy white solid. ^1H NMR δ 1.82 (s, 2H),

Reaction of 1 with Dimethylmagnesium

A 100 mL Schlenk flask capped with a septum was charged with a solution of 1.0 g (2.2 mmol) of $(C_8H_8)UCl_2(THF)_{0.37}$ in 40 mL of THF and cooled to -78 °C. To this solution was added dropwise a solution of 0.12 g (2.2 mmol) of $(CH_3)_2Mg$ in 10 mL of THF. After complete addition, the mixture was stirred for 3 h at -78 °C and allowed to warm to room temperature. Upon removal of the volatiles *in vacuo*, the resultant material was found to be insoluble in both hexane and toluene. The material was dissolved in 30 mL of

THF, then sufficient toluene (approximately 5 mL) was added to just begin precipitation. The solution was filtered and cooled to -20 °C to afford a black oily material. ^{1}H NMR (THF-d_8, 30 °C) δ -1.7 (s, $w_{1/2}$=15 Hz, 6H), -36.3 (s, $w_{1/2}$=70 Hz, 8H).

Sodium *tert*-Butoxide, $NaOC(CH_3)_3$ and Sodium Phenoxide, $NaOC_6H_5$

In a 500 mL RBF equipped with a reflux condenser and a magnetic stir bar was mixed 11.50 g (500 mmol) of Na metal, 40.77 g (550 mmol) of *tert*-butanol and 250 mL of anhydrous heptane. The mixture was heated at reflux with rapid stirring until the Na was consumed. The ppt was collected by vacuum filtration, washed with several portions of hexane, and dried *in vacuo* to afford 45.1 g (93.8%) of $NaOC(CH_3)_3$ as a white powder. By an analogous procedure, 2.30 g (100 mmol) of Na metal and 10.35 g (110 mmol) of phenol were heated at reflux in 100 mL of heptane to give 10.5 g (90.4%) of $NaOC_6H_5$ as a white powder.

Reactions of 1 with $KOC(CH_3)_3$, $NaOC(CH_3)_3$, and $NaOC_6H_5$

In a 100 mL Schlenk flask capped with a septum was dissolved 2.25 mmol of $(C_8H_8)UCl_2(THF)_x$ (approximately 1.0 g) in 30 mL of THF and the solution was cooled to -78°C. To this solution was slowly added via cannula a slurry or solution of 4.6 mmol the appropriate alkoxide or aryloxide reagent in 20 mL of THF [0.52 g of $KOC(CH_3)_3$, 0.44 g of $NaOC(CH_3)_3$, 0.53 g of $NaOC_6H_5$]. After stirring for 3 h at -78 °C, the solution was allowed to warm slowly to room temperature. Removal of the THF afforded green to black colored solids that proved insoluble in hexane or toluene. Examination of these materials by ^{1}H NMR (THF-d_8) revealed no resonances in the paramagnetic region of the spectra attributable to uranium-bound [8]annulene protons. They appeared to be mixtures of compounds of the general stoichiometry $U(OR)_xCl_y$, x+y=4.

2-[(N,N-Dimethylamino)methyl]phenyllithium, LiC_6H_4-*o*-$CH_2N(CH_3)_2$ and *ortho*-N,N-Dimethylaminobenzyllithium, $LiCH_2C_6H_4$-*o*-$N(CH_3)_2$[24a]

In a 100 mL Schlenk flask capped with a septum was mixed 40 mL anhydrous Et_2O, 1.35 g (10.0 mmol) of $C_6H_5CH_2N(CH_3)_2$, and 4.8 mL (10 mmol) of 2.1 M *n*-BuLi in hexanes. The solution was stirred for 18 h with formation of a white ppt. The ppt was collected by vacuum filtration, washed with several portions of hexane, and dried *in vacuo* to afford 1.30 g (92.2%) of LiC_6H_4-*o*-$CH_2N(CH_3)_2$ as a fine white powder.

By an analogous procedure, 1.35 g (10.0 mmol) of N,N-dimethylaminotoluene was mixed with 4.8 mL (10 mmol) of 2.1 M *n*-BuLi in hexanes in 50 mL of hexane and stirred for 48 h. The ppt was collected by vacuum filtration and washed with hexane to afford 1.39 g (98.6%) of $LiCH_2C_6H_4$-*o*-$N(CH_3)_2$ as a yellow powder.

Reaction of 1 with LiC_6H_4-*o*-$CH_2N(CH_3)_2$

In a 100 mL Schlenk flask capped with a septum was charged with a solution of 0.5 g (1.12 mmol) of $(C_8H_8)UCl_2(THF)_{0.45}$ in 30 mL of THF and cooled to -78 °C. To this solution was added dropwise a solution of 0.33 g (2.4 mmol) of LiC_6H_4-*o*-$CH_2N(CH_3)_2$ in 20 mL of THF; the resulting solution was stirred at -78 °C for 3 h, then allowed to warm slowly to room temperature. After removal of THF, the solid was extracted into toluene, filtered, and the toluene was removed *in vacuo*. After removal of toluene, the material proved no longer soluble in toluene. A ^1H NMR (THF-d_8) revealed no resonances in the paramagnetic regions of the spectrum. In a repeated attempt of this reaction, a ^1H NMR was recorded of the crude product immediately after removal of THF. No paramagnetic resonances were observed under these conditions either.

Reaction of 1 With $LiCH_2C_6H_4$-*o*-$N(CH_3)_2$

In a procedure analogous to the reaction of **1** with LiC_6H_4-*o*-$CH_2N(CH_3)_2$ described above, 0.5 g (1.12 mmol) of $(C_8H_8)UCl_2(THF)_{0.45}$ and 0.33 g (2.4 mmol) of

$LiCH_2C_6H_4$-*o*-$N(CH_3)_2$ were allowed to react in 30 mL of THF at -78 °C for 3 h, then warmed to room temperature. Following removal of THF *in vacuo*, a ^1H NMR (THF-d_8) of the crude product mixture was recorded. No resonances in the paramagnetic region of the spectrum were observed.

Sodium Acetylacetonate, $Na[(CH_3C(O)CHC(O)CH_3]$ and Sodium Tropylate, $Na(C_7H_5O_2)$

To a mixture of 1.68 g (70.0 mmol) of NaH in 30 mL of THF was added dropwise over 1 h a solution of 5.01 g (50.0 mmol) of acetylacetone in 20 mL of THF. After complete addition, the mixture was stirred for 18 h, filtered, and the solid washed with 2 10 mL portions of THF. The THF was removed from the combined filtrates and the resultant solid was washed with hexane and dried *in vacuo* to give 5.1 g (84%) of Na(acac) as a fine white powder.

By an analogous procedure, 6.11 g (50.0 mmol) of tropolone was allowed to react with 1.68 g (70.0 mmol) of NaH in 50 mL of THF; the suspension was filtered and the THF was removed from the filtrate to give 5.5 g (76%) of Na(trop) as a white powder.

(Methylenediphenylphosphoranyl)methyllithium, $Li[(CH_2)_2P(C_6H_5)_2]$[26]

Into a 100 mL septum-capped Schlenk flask containing 40 mL of anhydrous Et_2O was added 0.78 g (5.5 mmol) of CH_3I followed by 1.00 g (4.99 mmol) of $(C_6H_5)_2PCH_3$. The solution was stirred for 3 h, then the volatiles were removed *in vacuo*. The resultant $(C_6H_5)_2P(CH_3)_2I$ was dissolved in 50 mL of E_2O and to this solution was added dropwise 6.6 mL (11 mmol) of 1.6 M *n*-BuLi in hexanes. After stirring for 2 h, the ppt was collected by vacuum filtration and washed with 3 20 mL portions of Et_2O (to remove LiI) to afford 0.84 g (75.8%) of $Li[(CH_2)_2P(C_6H_5)_2]$ as a white powder.

Reaction of 1 with Sodium Tropylate

A 100 mL septum-capped Schlenk flask containing a solution of 0.75 g (1.7 mmol) of $(C_8H_8)UCl_2(THF)_{0.45}$ in 30 mL of THF and cooled to -78 °C, and to this solution was added dropwise a slurry of 0.51 g (3.5 mmol) of sodium tropylate in 30 mL of THF. This solution was stirred at -78 °C for 6 h, then allowed to warm slowly to room temperature. After removal of THF, the solid was extracted into toluene, filtered, and the toluene was removed *in vacuo*. A ^1H NMR (THF-d_8) revealed a forest of resonances in the paramagnetic region of the spectrum (between -15 and -40 ppm). The major peak was that of uranocene. Additional resonances could not be assigned because of the complexity of the spectrum. Attempts to fractionally recrystallize the product failed to isolate any products other than uranocene.

Reaction of 1 with $Li[(CH_2)_2P(C_6H_5)_2]$

A 100 mL septum-capped Schlenk flask was charged with a solution of 0.50 g (1.1 mmol) of $(C_8H_8)UCl_2(THF)_{0.37}$ in 40 mL of THF and cooled to -78 °C. To this solution was added dropwise a solution of 0.49 g (2.2 mmol) of $Li[(CH_2)_2P(C_6H_5)_2]$ in 20 mL of THF. After complete addition, the mixture was stirred for 3 h at -78 °C and allowed to warm to room temperature. After removal of the THF, the solid was extracted into toluene, filtered, and the volatiles were removed from the filtrate *in vacuo*. A ^1H NMR (THF-d_8) of the toluene-soluble material showed several resonances between -25 and -40 ppm, with a large peak corresponding to uranocene. Additional resonances could not be assigned to any mono-ring uranium complexes. Attempts to fractionally recrystallize the product failed to isolate any products other than uranocene.

([8]Annulene)U(IV)bis(acetylacetonate), $(C_8H_8)U(O_2C_5H_7)_2$ (4).

A 250 mL Schlenk flask capped with a septum was charged with a solution of 1.00 g (2.24 mmol) of $(C_8H_8)UCl_2(THF)_{0.45}$ in 50 mL of THF and the solution was cooled to -78 °C. To this solution was added via cannula a slurry of 0.59 g (4.84 mmol) of sodium

acetylacetonate in 50 mL of THF. The mixture was stirred at -78 °C for 3 h, then warmed to room temperature and stirred an additional 14 h. The THF was removed *in vacuo* and the orange solid was dissolved in 150 mL of toluene. The solution was filtered, then was concentrated and cooled to afford 1.21 g (92.5%) of **4** as orange crystals. ^{1}H NMR (Toluene-d_8, 30 °C) δ -29.6 (s, $w_{1/2}$=13.1 Hz, 8H), -10.0 (s, $w_{1/2}$=6.6 Hz, 12H), 10.2 (s, $w_{1/2}$=3.5 Hz, 2H); Visible (THF) 382 (sh), 458, 531 (sh), 572 (sh); IR (Nujol) 1355 s, 1288 s, 1201 m, 1145 m, 1075 m, 1010 m, 990 s, 984 sh, 870 m, 850 m, 805, m, 763 s, 710 m, 665 m, 650 s, 600 m, 580 m, 550 w; Anal. Calcd. for $C_{18}H_2O_4U$: C, 40.01; H, 4.10; Found: C, 40.33; H, 3.98.

Crystal Structures[18b]

The air sensitive crystals, sealed inside quartz capillaries, were mounted on a modified Picker FACS-1 automated diffractometer equipped with a molybdenum X-ray tube (λ $K\alpha_1$ = 0.70930 Å) and an oriented graphite monochromater. A set of θ-2θ scanned intensities were collected and processed. The structures were solved by Patterson and Fourier methods and refined by full-matrix least squares. Anisotropic thermal parameters were assigned to all non-hydrogen atoms, and isotropic thermal parameters to the hydrogen atoms. In the $(C_8H_8)UCl_2(NC_5H_5)_2$ complex, the hydrogen atomic parameters were all refined in an unrestrained manner. In the $(C_8H_8)UCl_2(CH_3COCHCOCH_3)_2$ complex, the hydrogen atomic parameters were restrained to their estimated values because the data would not support an unrestrained refinement of them. Atomic scattering factors for all atoms were taken from values in the International Tables.[29] The experimental details of the data collection and the least-squares refinements are tabulated in Table IV.

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Supplementary Table I

Crystallographic Summary and Data Processing for

	$(C_8H_8)UCl_2(NC_5H_5)_2$	$(C_8H_8)U(acac)_2$
a, Å [a]	15.431(3)	19.166(4)
b, Å	7.744(2)	10.312(2)
c, Å	15.665(3)	9.227(2)
β, °	105.69(2)	97.10(2)
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/n$
Volume, A^3	1802.2	1809.6
d(calcd), g/cm^3	2.105	1.983
Z	4	4
temp (°C)	23.0	23.0
empirical formula	$C_{18}H_{18}N_2Cl_2U$	$C_{18}H_{22}O_4U$
f(000)	1064	1016
fw	571.29	540.40
color	red	orange
reflection rules	h0l:l=2n,0k0:k=2n	h0l:h+l=2n,0k0:k=2n
crystal size (mm)	0.12x0.25x0.50	0.15x0.18x0.22
abs coeff, cm^{-1}	88.38	85.18
abs corr range	1.63-6.14	2.67-4.20
cryst decay corr range	0.98-1.02	0.94-1.03
2θ limits, °	5.4-55.1	6.5-55.1
sinθ/λ, min,max	0.066, 0.651	0.080, 0.65
hkl limits	h±20;k-9,10;l±20	h±24;k-0,13;l-12,23
scan width, °2θ	1.50+0.693tanθ	1.30+0.693tanθ
no. of standards	3	3
no. of reflections between stds	250	250
variation of standards (%)	1.32, 1.56, 1.11	1.96, 1.84, 2.03
no. of scan data	11614	8351
no. of unique reflections	4106	4184
Rint[b]	0.039	0.048
no. non-zero weighted data	2638 ($F^2>2\sigma$)	2442 ($F^2>2\sigma$)
pc	0.035	0.025
extinction k[d]	$7.46x10^{-6}$	$1.22x10^{-4}$
max % extinction corr	11.7 %	34.1 %
no. parameters	280	208
R (non-zero weighted data)[e]	0.030	0.030
Rw[f]	0.028	0.027
R (all data)	0.068	0.083
Goodness of fit[g]	1.02	1.04
Max shift/esd in least-square	0.017	0.0002
max/min in diff map (e/A^3)	1.52, -1.35	1.27, -1.24

(a) Unit cell parameters were derived by a least-squares fit to the setting angles of the

unresolved MoKa components of 31 reflections ($20<2\theta<30$) for $(C_8H_8)UCl_2(NC_5H_5)_2$ and 30 reflections ($20<2\theta<29$) for $(C_8H_8)U(CH_3COCHCOCH_3)$.

(b) R_{int} = agreement factor between equivalent or multiply measured reflections = $\Sigma[I(hkl)-\langle I(hkl)\rangle]/\Sigma[\langle I(hkl)\rangle]$

(c) In the least-squares, the assigned weights to the data are $4F^2[\sigma^2(F^2)+(pF^2)^2]^{-1}$.

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

(e) $R = \Sigma[|Fobs|-|Fcal|]/\Sigma|Fobs|$

(f) $Rw = \{\Sigma[w|Fobs|-|Fcal|]^2/\Sigma(wF^2)\}^{1/2}$

(g) $\sigma_1 = \{\Sigma(w[|Fobs|-|Fcal|]^2)/(no-nv)\}^{1/2}$, where no is the number of observations and nv is the number of variables

CHAPTER 2

Syntheses of Substituted Cyclooctatetraenes as Ligand Precursors

Introduction

Studies of the reactivity of $(C_8H_8)UCl_2(THF)_2$ with respect to displacement of the chlorides by σ-bound alkyl and alkoxy ligands (Chapter 1) indicate that the presumed products, $(C_8H_8)UR_2$ and $(C_8H_8)U(OR)_2$, are unstable. One explanation of the instability of these derivatives is that the uranium atom is coordinatively unsaturated. In complexes such as $(C_8H_8)UX_2$, where X is mono-dentate, the coordination number of the uranium is seven; this is considerably smaller than the coordination numbers of 9-12 more commonly found for U(IV).

Three approaches can be taken to increase the coordination environment of the uranium atom in these half-sandwich complexes. The first is to use multidentate ligands. This approach has provided the bulk of the half-sandwich derivatives thus far isolated. They include complexes incorporating multidentate, delocalized anions such as cyclopentadienyl,[1] borohydrido[2] or acetylacetonate,[3] the exception being the parent dichloride (which also contains two neutral coordinating ligands to bring the coordination number to nine) and the bis(trimethylsilyl)amido derivative.[4]

The second approach is to provide stabilization through the use of bulky mono-dentate ligands. In the complex $(C_8H_8)U[N(SiMe_3)_2]_2$ the bis(trimethylsilyl)amido ligands are apparently bulky enough to provide adequate kinetic stabilization, although even in this example there is evidence from both solid and solution state data of agostic ligand-metal interactions, indicative of coordination unsaturation. The analogous approach utilizing bulky alkyl and alkoxy ligands has been explored to some degree but has not as yet provided stable mono- or disubstituted half-sandwich derivatives. It is clear that even if

stable complexes of this type can be isolated, it will be through incorporation of very bulky pendant ligands. This approach is thus clearly limited in scope and flexibility.

The third approach is to increase the effective coordination environment around the metal center through use of substituted [8]annulene ligands. This approach is appealing because of the potential for controlling the steric and electronic properties of the [8]annulene ligand through judicious choice of substituted cyclooctatetraene ligand precursor. Moreover, the use of bulky carbocyclic anions to kinetically stabilize metal complexes has much precedent in organometallic cyclopentadiene chemistry,[5] to which the ubiquity of pentamethylcyclopentadienyl (Cp^*), 1,3-bis(trimetylsilyl)cyclopentadienyl (Cp''), and related complexes attests. Our efforts to develop stable mono[8]annulene uranium half-sandwich systems have therefore focussed on this approach: increasing the kinetic stability of low-valent complexes through use of sterically-demanding [8]annulene ligands. This approach requires syntheses of appropriate substituted cyclooctatetraenes to serve as ligand precursors, as well as development of new synthetic methodologies toward mono-ring complexes. New syntheses of substituted cyclooctatetraenes are the subject of this Chapter. Synthetic approaches to mono-ring complexes incorporating these ligands are detailed in Chapter 3.

Substituted Cyclooctatetraenes as Potential Half-Sandwich Ligand Precursors

The synthesis of half-sandwich complexes bearing "bulky" [8]annulene ligands is necessarily contingent on the availability of the corresponding substituted cyclooctatetraenes. While cyclooctatetraenes with degrees of substitution ranging from one through eight (curiously excepting seven) have been reported,[6] many of these compounds are unsuitable for our purposes. This unsuitability arises from the fact that the cyclooctatetraene precursor must be stable in its reduced dianion form. In addition to limiting the type of allowed substituent, this restriction places an upper limit on the degree,

as well as the pattern, of substitution on the ring. Because of the small internal angle between adjacent substituents (45°, compared to 72° in Cp anion), steric repulsions among substituents can become prohibitively large in the planar dianion. Thus, for example, 1,2,3-substituted cyclooctatetraenes cannot in general be reduced to their corresponding dianions while their 1,3,5-substituted analogs can. This restriction places an upper limit of four on the number of substituents; furthermore, these substituents are limited to 1,2,5,6- and 1,3,5,7-substitution patterns.

The lower limit of effective substitution is best assessed in terms of the steric bulk of the ligand with respect to unsubstituted cyclooctatetraene. One method that allows quantification of steric bulk is through calculation of the "cone angle" of a ligand.[7] The cone angle is an approximation of the solid angle formed by a set of vectors from the metal center to the van der Waals surface of the ligand. One component of this angle is shown as θ_R in Figure 1.

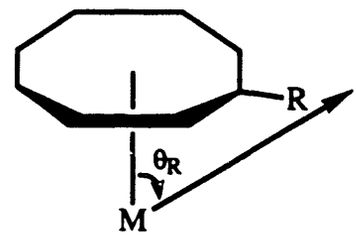


Figure 1. Component of Cone Angle in [8]annulene Complexes

Table 1 lists the cone angles of a variety of substituted cyclooctatetraene dianions at a distance from the metal center of 2.00 Å [the metal-ring centroid distance in $(C_8H_8)UCl_2(py)_2$]. The values were calculated from AM1-optimized structures of the cyclooctatetraene dianions as: cone angle = $(\Sigma\theta_i)/4$. To better approximate the van der Waals surface of the ligand, values of θ_H of ring hydrogens adjacent to substitutent groups were taken as the average of θ_H and $\theta_{substituent}$.

Table 1. Cone Angles for Some Substituted [8]annulenes

Dianion	Cone Angle at 2.00 Å (°)
C_8H_8	116
MeC_8H_7	124
$^tBuC_8H_7$	135
$Me_3SiC_8H_7$	136
1,4-$^tBu_2C_8H_6$	154
1,4-$(Me_3Si)_2C_8H_6$	156
1,3,5,7-$Me_4C_8H_4$	142
1,3,5,7-$Ph_4C_8H_4$	162
1,3,5,7-$^iPr_4C_8H_4$	170
1,3,5,7-$^tBu_4C_8H_4$	174

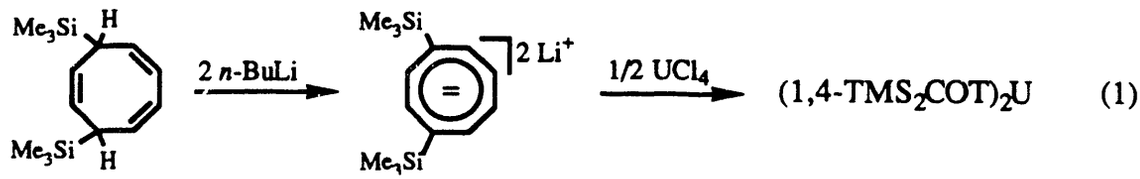
As can be seen from Table 1, mono-substituted cyclooctatetraene dianions, even those substituted with relatively bulky *tert*-butyl and trimethylsilyl substituents, do not represent a significant increase in steric bulk over unsubstituted cyclooctatetraene dianion. Thus, while mono alkyl-substituted cyclooctatetraenes are relatively easy to synthesize from the reaction of alkyllithium reagents with cyclooctatetraene[8] or bromocyclooctatetraene,[9] these ligands are of limited utility for our purposes. On the other hand, disubstituted cyclooctatetraenes, particularly those bearing bulky substituents, would seem to be appropriate candidates. Similarly, tetrasubstituted cyclooctatetraene dianions possess cone angles that are significantly larger than that of unsubstituted cyclooctatetraene dianion. Moreover, their high symmetry and large and variable steric properties and potentially variable electronic properties render them ideal as half-sandwich ligands.

In exploring new substituted-cyclooctatetraene syntheses, the focus has thus been on these two classes of compounds, di- and tetra-substituted cyclooctatetraenes, with particular focus on the development of straightforward, flexible syntheses starting from

readily available starting materials in as few steps as possible. What follows is a brief review of available syntheses of di- and tetra-substituted cyclooctatetraenes, as well as rationale for the new synthetic approaches described in this Chapter.

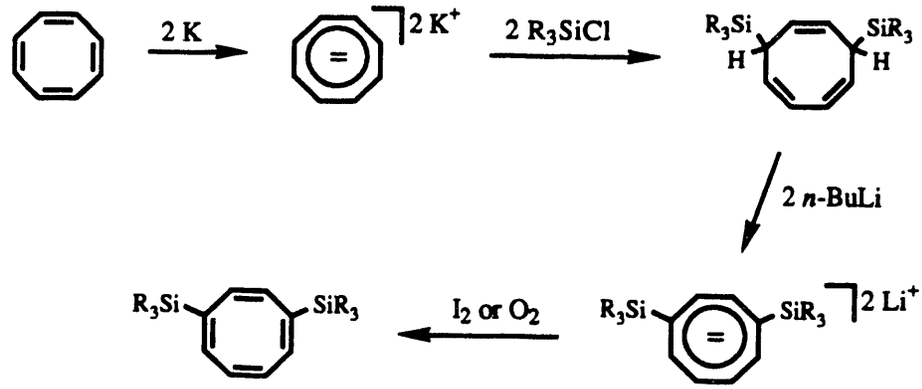
Synthetic Approaches to Disubstituted Cyclooctatetraenes

Because of the low degree of ring substitution in disubstituted cyclooctatetraenes, only compounds with bulky substituents represent appropriate candidates as ligand precursors (see Table 1). Syntheses of 1,4-di-*tert*-butylcyclooctatetraene[10,8] have been reported, as has the synthesis of its corresponding 1,1',4,4'-tetra(*tert*-butyl)uranocene.[11] The substituted cyclooctatetraene is available either from the reaction of cyclooctatetraene with excess *tert*-butyllithium, or through a multi-step synthesis starting from cyclooctatetraene oxide; the later synthesis is unsuitable for large scale syntheses. Recently, Cloke and coworkers[12] reported the syntheses of several organometallic complexes of 1,4-bis(trimethylsilyl)cyclooctatetraene dianion, including the 1,4,1',4'-tetrakis(trimethylsilyl)uranocene and the bis(borohydride) half-sandwich complex. Cloke did not isolate the corresponding 1,4-bis(trimethylsilyl)cyclooctatetraene (referred to herein as 1,4-TMS_2COT, rather than COT", as suggested by Cloke). Instead he generated the 1,4-TMS_2COT dianion in situ by twice deprotonating 1,4-bis(trimethylsilyl)-2,5,7-cycloctatriene, available[13] from quenching cyclooctatetraene dianion with trimethylsilyl chloride, with *n*-BuLi followed by addition of the appropriate metal chloride (UCl_4 in Eq. 1).



(1)

As it is known that cyclooctatetraenes can be recovered from their corresponding dianions through oxidation with I_2[10] or O_2,[8] conversion of 1,4-bis(trimethylsilyl)-2,5,7-cycloctatriene to 1,4-TMS_2COT was expected to be straightforward. Moreover, it was expected that this reaction could be extended to incorporate other alkyl- and aryl silyl chlorides. This suggested a new and general approach to the synthesis of 1,4-disubstituted cyclooctatetraenes (Scheme 1).

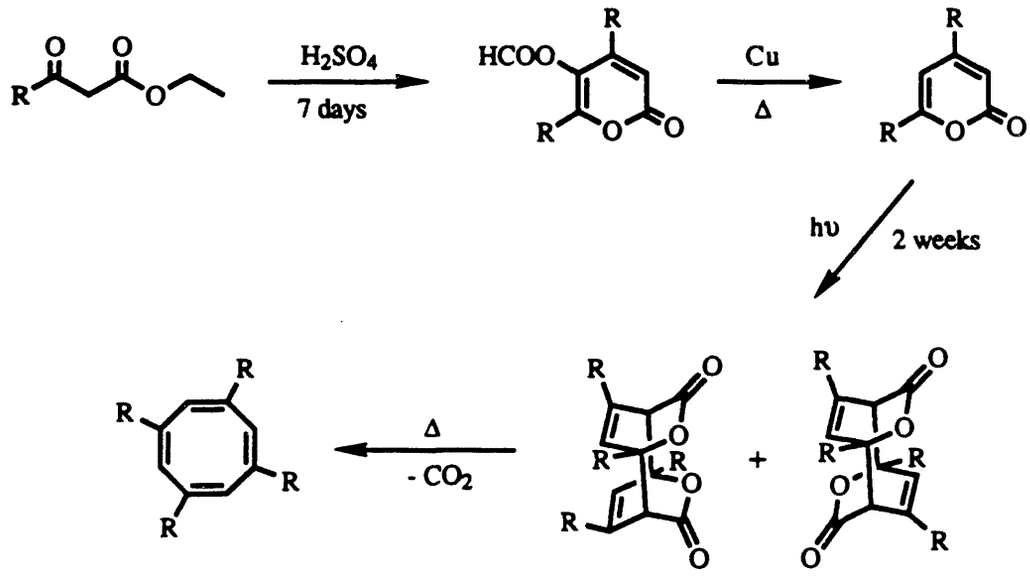


Scheme 1. Synthesis of 1,4-Di-silyl-substituted Cyclooctatetraenes

This approach involves only two steps and allows flexibility in the choice of R_3Si substituent. For these reasons, efforts toward developing syntheses of disubstituted cyclooctatetraenes focussed on this class of di-silyl-substituted cyclooctatetraenes.

Synthetic Approaches to Tetrasubstituted Cyclooctatraenes

Tetrasubstituted cyclooctatetraenes represent the most attractive, and challenging, class of ligand precursors. In the past, three general approaches have been taken to their synthesis. The most popular approach was developed by DeMayo and Yip[14] for the synthesis of 1,3,5,7-tetramethylcyclooctatetraene (1,3,5,7-TMCOT) (Scheme 2, R = Me).

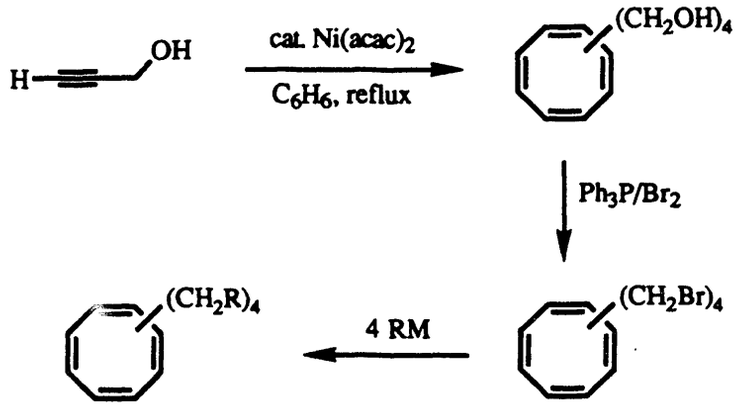


Scheme 2. DeMayo and Yip's Synthesis of 1,3,5,7-Substituted Cyclooctatetraenes

The approach suffers three serious limitations. First, photodimerization of 4,6-substituted coumalins goes slowly and in low yield (<40%), which brings the overall yield of the reaction sequence to under 20%. Second, the generality of the approach is limited by the availability of appropriate starting materials. For the synthesis of 1,3,5,7-TMCOT, the intermediate 4,6-dimethylcoumalin is readily accessible from commercially-available ethyl acetoacetate; other 4,6-substituted coumalins require more extensive syntheses, generally adding two or more steps to the reaction sequence depicted in Scheme 2. Third, the photodimerization of 4,6-substituted coumalins bearing bulky substituents may not proceed. As demonstrated by Miller et al.[10] in their attempt to synthesize 1,3,5,7-tetra-tert-butylcyclooctatetraene (Scheme 2, R = *tert*-butyl), photolysis of 4,6-di-*tert*-butyl coumalin produced dimers that were thermally unstable relative to the starting pyrone. This

limitation, coupled with the low-yield, multi-step nature of the approach, limits its attractiveness as a source of ligand precursors.

The second general approach to tetrasubstituted cyclooctatetraenes involves cyclotetramerization of "activated" acetylenes. One example is the tetramerization of propargyl alcohol to tetrakis(hydroxymethyl)cyclooctatetraene (THMCOT) and subsequent derivatization (Scheme 3).

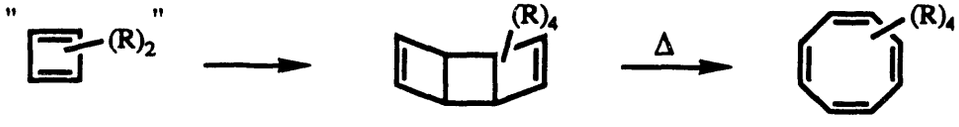


Scheme 3. Conversion of Propargyl Alcohol To Tetrasubstituted Cyclooctatetraenes

John Rigsbee[15] in these laboratories was the first to demonstrate the feasibility of this approach in the conversion of propargyl alcohol to 1,2,5,6-TMCOT. The critical limitation of his approach lay in the synthesis of the 1,2,5,6-THMCOT. Heating propargyl alcohol with $Ni(acac)_2$ in benzene at reflux for a week affords only 10% of cyclotetramers. Fortunately, under these reaction conditions one cyclotetramer isomer predominates. It was identified by the original workers[16] as 1,3,5,7-THMCOT, but impossible to differentiate by their analysis from the other highly symmetric 1,2,5,6-THMCOT isomer. By reduction to the corresponding 1,2,5,6-TMCOT, Rigsbee was able to provide evidence

that the primary cyclotetramer isomer produced under these conditions is in fact 1,2,5,6-THMCOT. The low yield of the $Ni(acac)_2$-catalyzed tetramerization of propargyl alcohol seriously limits the viability of this approach. However, recent availability of a high-yield synthesis of 1,3,5,7- and 1,2,5,6-THMCOT from propargyl alcohol (*vida infra*) makes this approach much more attractive. The promise of a three-step synthesis of a wide variety of 1,3,5,7-tetrasubstituted cyclooctatetraenes (by varying R in Scheme 3) stimulated further development of this synthetic approach.

The last general approach to the synthesis of tetrasubstituted cyclooctatetraenes involves Diels-Alder dimerization of disubstituted cyclobutadienes, followed by thermal ring opening of the intermediate *syn*-tricyclo[4.2.0.$0^{2,5}$]octadienes (Scheme 4).



Scheme 4. Dimerization of Disubstituted Cyclooctabutadienes

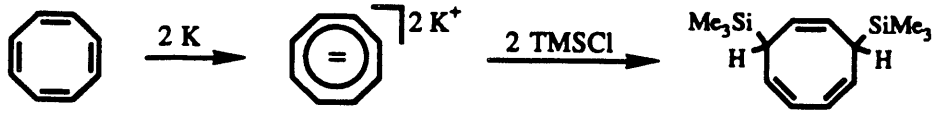
This approach has been limited to two examples, primarily due to the unavailability of 1,3-substituted cyclobutadiene precursors. However, development of synthetic methodology that allows ready generation of 1,3-substituted cyclobutadienes has facilitated development of this approach.

The remainder of this Chapter details the development of three synthetic approaches to substituted cyclooctatetraenes represented in Schemes 1, 3, and 4.

Syntheses of 1,4-Di-silyl-Substituted Cyclooctatetraenes

Synthesis of 1,4-Bis(trimethylsilyl)cyclooctatetraene (1,4-TMS_2COT)

The synthetic approach to 1,4-di-silyl-substituted cyclooctatetraenes is outlined in Scheme 1. The prototypical molecule of this class is 1,4-TMS_2COT (R = Me in Scheme 1). Starting from cyclooctatetraene, reduction to the dianion with potassium followed by quenching with two equivalents of trimethylsilyl chloride[13] afforded 1,4-bis(trimethylsilyl)-2,5,7-cyclooctatriene (1,4-TMS_2COTriene) in good yield (Eq 2). Surprisingly, this compound is quite oxygen sensitive, with a half-life in air of two days or so. By working quickly and by using degassed recrystallization solvents decomposition could be kept to a minimum.



(2)

Once isolated, 1,4-TMS_2COTriene could be deprotonated with KH or *n*-BuLi in THF to generate the dipotassium or dilithio salts 1,4-TMS_2COT dianion. Quenching the dianion with I_2 followed by a standard workup afforded 1,4-TMS_2COT in 50% overall yield from cyclooctatetraene.

Reaction of Cyclooctatetraene Dianion With Bu^tMe_2SiCl, Ph_3SiCl, and Ph_3SnCl

Following the successful preparation of 1,4-TMS_2COT, the syntheses of several additional 1,4-di-silyl-substituted cyclooctatetraenes were attempted. To this end, the reactions of cyclooctatetraene dianion with Bu^tMe_2SiCl, Ph_3SiCl, and Ph_3SnCl were undertaken.

Reaction of $K_2C_8H_8$ with $^tBuMe_2SiCl$ does not proceed appreciably at room temperature, and in refluxing THF led to a complex mixture of products. The desired 1,4-

substituted cyclooctatriene could not be isolated from the product mixture. The reaction of Ph_3SiCl with $K_2C_8H_8$ similarly lead to a mixture of products; however, 1,4-bis(triphenylsilyl)-2,5,7-cycloctatriene (1,4-TPS_2COTriene) could be isolated by column chromatography. Deprotonation of 1,4-TPS_2COTriene with *n*-BuLi followed by quenching of the resultant dianion with I_2 gave 1,4-bis(triphenylsilyl)cyclooctatetraene (1,4-TPS_2COT). The overall yield from cyclooctatetraene is considerably lower (20%) than that for 1,4-TMS_2COT. Reaction of the related Ph_3SnCl with $K_2C_8H_8$ led only to the quenching of the cyclooctatetraene dianion and formation of $(Ph_3Sn)_2$.

Nickel-Catalyzed Cyclotetramerization of Activated Acetylenes

Mechanism of Ni-catalyzed Cyclotetramerization of Acetylene

The most straightforward approach to tetrasubstituted cyclooctatetraenes is through the direct cyclooligomerization of mono-substituted acetylenes. While tetramerization of acetylene by Ni(II) catalysts was first reported by Reppe[17] in 1948, under the reaction conditions whereby commercial cyclooctatetraene is produced from acetylene only linear polymers and benzenes are produced from substituted acetylenes.[18]

Cooligomerizations[19] of acetylene with mono- and di-substituted acetylenes under Reppe's reaction conditions do give rise to substituted cyclooctatetraenes, but incorporation of only one substituted acetylene unit into the product cyclooctatetraene is observed. Direct cyclotetramerization of both acetylene[20] and propyne[21] by finely divided Ni metal have been reported. For propyne, linear polymers and benzenes represent less than half of the product distribution. However, within the major cyclotetramer fraction little regioisomer selectivity is observed; roughly equal amounts of three tetramethyl-substituted cyclooctatetraenes are formed.

Several pathways for the cyclotetramerization of acetylene by nickel catalysts have been envisioned. Initially a metal-mediated [2+2+2+2] "zipper" mechanism was proposed by Schrauzer,[22] followed by suggestions of the involvement of metal-cyclobutadiene,[23] and binuclear metalocyclobutadiene[24] intermediates. In a clever experiment, Colborn and Vollhardt[20] examined the ^{13}C distribution in the products of the cyclotetramerization of labelled acetylene, $HC^{13}CH$. Of the three suggested mechanisms, the experimental product distribution is best rationalized by the "zipper" mechanism, at least when the catalyst is finely divided nickel metal. No conclusive mechanistic evidence has been reported for the reaction under Reppe's reaction conditions. Moreover, while the mechanism has been much discussed in the literature, little discussion has been devoted to the basic question of why under the same reaction conditions unsubstituted acetylene gives rise to

cyclooctatetraene while alkyl-substituted acetylenes do not. At present the "zipper" mechanism, where the metal serves as a template to bring four acetylene units together, remains most popular. The presumed octahedral Ni(II) and tetrahedral Ni(0) intermediates are shown schematically in Figure 2.

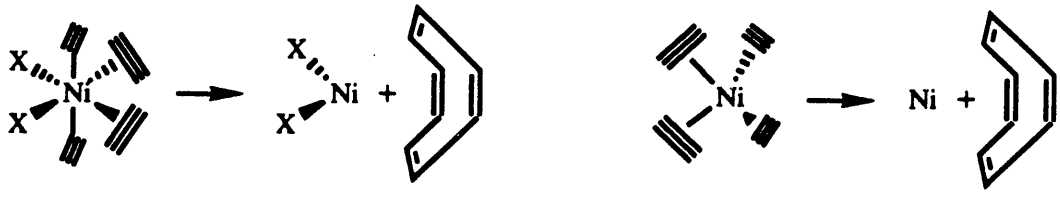


Figure 2. "Zipper" Mechanism For Ni(II) and Ni(0) Catalysts

Mechanism of Cyclotetramerization of Activated Acetylenes

Cyclooligiomerizations of "activated" acetylenes (such as propargylic acetylenes) mediated by transition metal catalysts have been long known to produce cyclotetramers. Particularly effective catalysts are those derived from Ni(II) and Ni(0). Cyclotetramerizations by other transition metal catalysts, including complexes of Fe, Co and Pt, have been reported. Generally, these reactions produce benzenes as the the primary products; cyclooctatetraenes are typically observed only in trace amounts. Within the cyclotetramer fraction, four isomers are possible. The isomers are depicted in Figure 3.

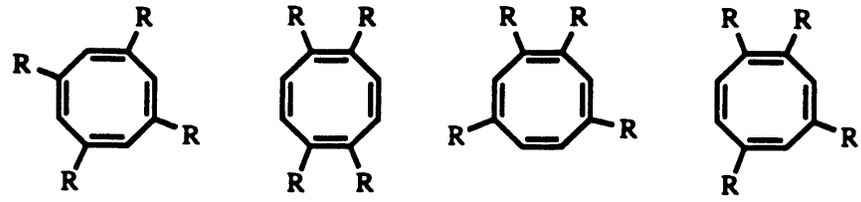


Figure 3. Isomeric Cyclooctatetraenes From Mono-substituted Acetylene Cyclotetramerization

A collection of catalysts, acetylene reactants, and reaction products for for a variety of Ni-catalyzed acetylene cyclotetramerization reactions are compiled in Table 2. Nickel catalysts for the cyclotetramerization of both "activated" and "unactivated" acetylenes have been included in Table 2 for for the sake of comparison.

Table 2. Cyclotetramerization of Acetylenes by Nickel Catalysts

Acetylene (HCCR)	Catalyst/conditions	Products	Ref.
HCCH	$Ni(acac)_2$/ THF, 90 °C, 15-20 atm HCCH	COT (70%) benzene (30%)	17
HCCH	Ni(0) (from $NiCl_2$ + K) in THF	benzene (80%) COT (20%)	20
3 HCCH + RCCH	$Ni(acac)_2$	1,2-R_2COT (20-50%) + benzenes + linear polymers	19
HCC-CH_3	Ni(0), 60 °C, dioxane	1,2,4,6 + 1,2,4,7 + 1,3,5,7 (55%) + linear polymers (35%) + benzenes (10%)	21
HCC-$C(CH_3)_2OH$	$Ni(acac)_2$ or $NiCl_2/NaBH_4$	1,2,4,7 (primary) + 1,2,5,6 + 1,2,4,6 + 1,3,5,7	25
HCC-CH_2OH	$Ni(acac)_2/C_6H_6$ reflux	1,2,5,6 (primary) + trace 1,2,4,7+ 1,2,4,6 + 1,3,5,7	16
HCC-CH_2OH	$Ni(DAD)_2$/THF	1,3,5,7 (primary) + 1,2,5,6 + trace 1,2,4,7+ 1,2,4,6	26a
HCC-CH_2OH	(DME)$NiBr_2/NaBH_4$	1,3,5,7 (primary) + 1,2,5,6 + trace 1,2,4,7+ 1,2,4,6	27
HCC-COOR	$Ni(PCl_3)_4$	1,2,4,6 (30%) + benzenes (70%)	28
HCC-COOR	$Ni(DAD)_2$	1,2,4,7	26b
HCC-CH_2O-*p*-Tol	$Ni(DAD)_2$	1,2,5,6	26c

As sources of potential ligand precursors, several of the reactions listed in Table 2 are of interest because the products are tetrasubstituted cyclooctatetraenes, often in good yield. Unfortunately, in most examples high yields are matched by a marked lack of regioisomer control. This is not always the case, however. Of particular relevance to us

was the work of tom Dieck and coworkers[26] detailing the catalytic tetramerization of propargyl alcohol, propargyl ethers and related acetylenes by bis(diazadiene)nickel(0) [Ni(DAD)$_2$] complexes. In the reaction of propargyl alcohol, they report essentially quantitative yields (>95%) of cyclotetramers, the majority of which is the 1,3,5,7-substituted isomer. They were also able to isolate this product, tetrakis(hydroxymethyl)cyclooctatetraene (1,3,5,7-THMCOT), and obtain an x-ray crystal structure[26a] to confirm its substitution pattern.

These Ni(DAD)$_2$ complexes are also active catalysts for the cyclotetramerization of other propargylic acetylenes such as propargyl ethers, propargyl esters and propargyl acid. The distribution of isomeric cyclooctatetraene products that result is highly dependent on the nature of the acetylene reactant. For example, for propargyl alcohol all possible isomers form with the 1,3,5,7-substituted isomer in excess; for propargyl *p*-tolyl ether the 1,2,5,6-substituted isomer is nearly the exclusive product; for propargyl esters and propargyl acid the 1,2,4,6-substituted isomer predominates.

For these Ni(DAD)$_2$-catalyzed cyclotetramerization reactions, tom Dieck proposed an alternative to the "zipper" mechanisms of Schrauzer and of Vollhardt. From the reaction of methyl propargyl ether with a Ni(DAD)$_2$ complex, tom Dieck isolated and structurally characterized[26d] a butadiene-bridged, nickel-nickel bonded complex (Figure 4).

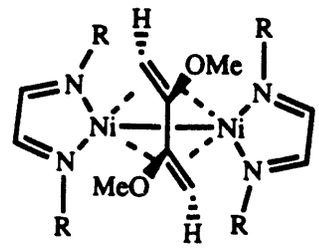


Figure 4. Product of the Reaction of Ni(DAD)$_2$ With Propargyl Methyl Ether

This complex proved to be an active tetramerization catalyst, prompting tom Dieck to suggest that such a complex is an intermediate in the catalytic cycle (Figure 5).

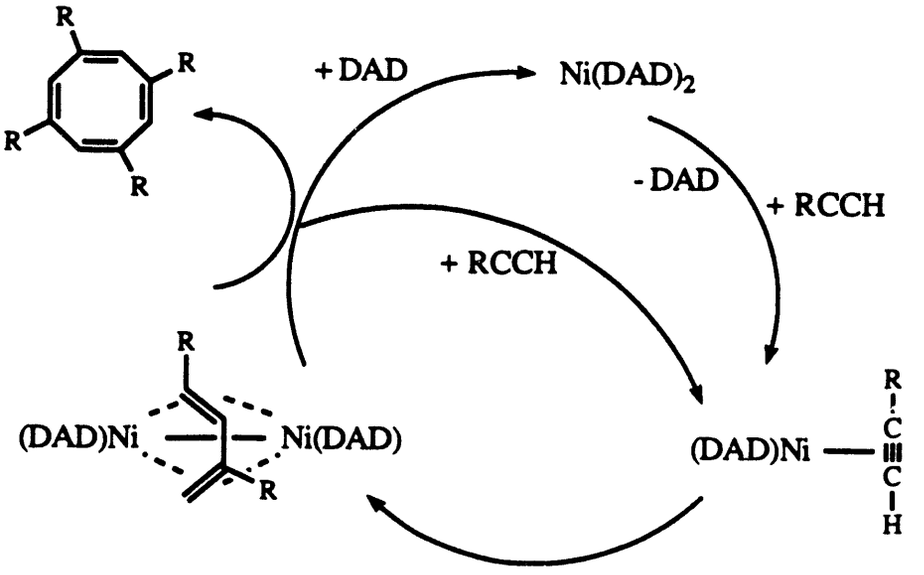


Figure 5. Proposed Mechanism for Ni(DAD)-Catalyzed Cyclotramerization of Propargylic Acetylenes

An acetylene cyclotetramerization pathway involving a butadiene-bridged metal dimer was not considered as a mechanistic possibility in Colborn and Vollhardt's original analysis. As it turns out, such a mechanism predicts the same product distribution as Schrauzer's "zipper" mechanism; Vollhardt's analysis cannot distinguish them. For the cyclotetramerization of propargyl alcohol by $Ni(DAD)_2$ complexes, however, there is compelling evidence to argue against tom Dieck's proposed mechanism (Figure 5), as will be seen below.

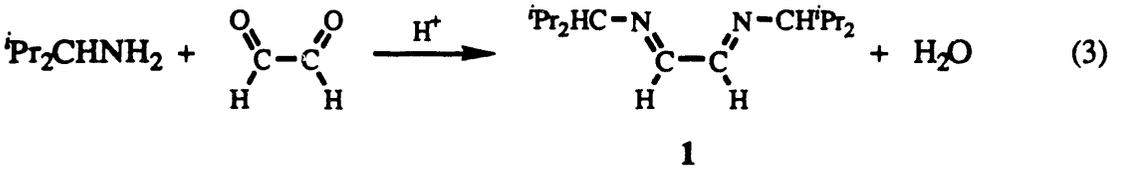
The details of the mechanism aside, this tetramerization reaction provides an entry into 1,3,5,7-THMCOT in high yield from inexpensive and commercially-available propargyl alcohol. It was hoped that this ready availability of 1,3,5,7-THMCOT would

allow full exploitation of Rigsbee's synthetic approach to tetrasubstituted cyclooctatetraenes (Scheme 3).

Cyclotetramerization of Propargyl Alcohol By Ni(DAD)$_2$

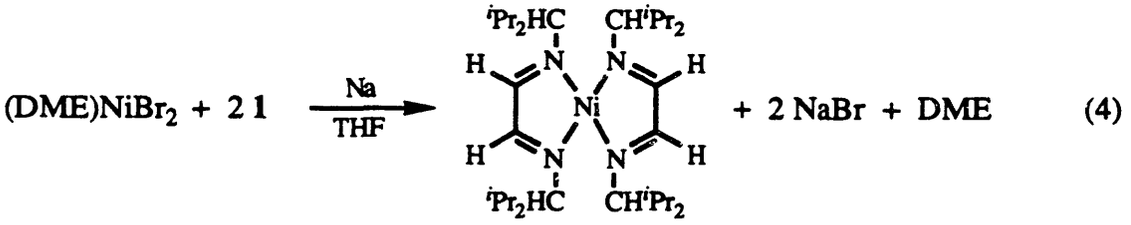
Initial efforts focussed on repeating tom Dieck's catalytic tetramerization of propargyl alcohol with Ni(DAD)$_2$ complexes. The objectives of these efforts were twofold. In addition to the specific goal of obtaining tetrakis(hydroxymethyl)cyclooctatetraenes (THMCOT's) for use as precursors to substituted cyclooctatetraenes, we also had the more general goal of developing a better understanding of this interesting catalytic reaction. It was hoped that greater insight into the role of the Ni(DAD)$_2$ catalyst, particularly within tom Dieck's proposed mechanism, would allow rational control of the various aspects of the reaction, including catalyst turnover rates, tetramer/trimer ratios, and distribution of isomeric tetramers. It was further hoped that this, in turn, would allow the ability to "tune" the reaction with appropriate choice of DAD ligand and acetylene to generate, for example, a specific isomeric cyclotetramer. These efforts will be discussed in greater detail later in this chapter; the first order of business was reproducing the THMCOT synthesis.

As part of his study of Ni(DAD)$_2$ complexes as catalysts for the cyclotetramerization of propargyl alcohol,[26a] tom Dieck studied the catalytic efficiency (in turnover rates and tetramer/trimer ratios) of a number of Ni(DAD)$_2$ complexes over a variety of reaction conditions. He reported that the catalyst derived from DAD = bis(diisopropylmethyl)diazadiene (**1**) demonstrated the highest catalytic efficiency. It was this system that we in turn chose for our initial studies. Synthesis of **1** is straightforward,[29] the product of the acid-catalyzed condensation of two equivalents of isopropyl)methyl amine with glyoxal (Eq. 3).



1

The corresponding $Ni(DAD)_2$ complex of **1** (**2**) is available through several routes,[26a] the simplest of which is the in situ reduction of $(DME)NiBr_2$ in the presence of excess **1** (Eq. 4). Although air- and water-sensitive, **2** can be isolated by recrystallization from pentane.



2

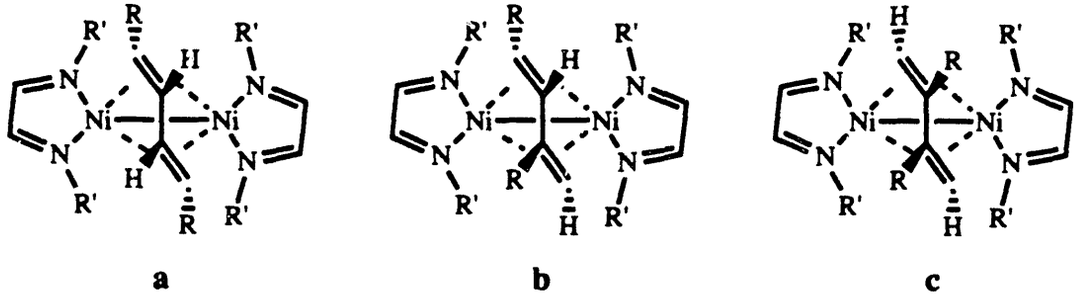
Addition of propargyl alcohol to a THF solution of **2** at 0 °C (per tom Dieck's recipe) did result in cyclotetramer formation, as indicated by ^1H NMR. For the resultant mixture of THMCOT isomers, the ^1H NMR in D_2O shows two regions of interest. The allylic protons appear in the range 3.9-4.2 ppm, but because they are overlapping multiplets are of little diagnostic utility. The vinyl protons (all but one singlets) lie in the range 5.6-6.1 ppm (in D_2O), but are also overlapping and cannot be used to identify individual isomers or the constituent isomer distribution. Furthermore, despite considerable effort, neither the 1,3,5,7 isomer, nor any other isomer for that matter, could be recrystallized away from the mixture. The isomeric mixture also proved resistant to separation by column chromatography under a wide variety of eluent and support conditions.

A Closer Examination of tom Dieck's Mechanism

We attributed the difficulty of separating the mixture of THMCOT isomers both to their chemical similarity as well as to the fact that no single isomer sufficiently

predominates in the cyclotetramerization to allow facile isolation. In hopes of modifying the reaction to produce a greater preponderance of a single isomer (preferably the 1,3,5,7- or 1,2,5,6-substituted isomer), we turned to other DAD ligands as well as to other propargylic acetylenes.

A closer look at tom Dieck's proposed mechanism reveals the following observation. Within his mechanism, the various isomeric COT products must arise from intermediates having different substitution patterns on the bridging butadiene moiety. The three possible intermediates and the products of their combinations are depicted in Figure 6.



a **b** **c**

a + a ⟶ 1,2,5,6

a + b ⟶ 1,2,4,6

a + c ⟶ 1,2,4,7

b + b ⟶ 1,3,5,7 + 1,2,4,7

b + c ⟶ 1,2,4,6

c + c ⟶ 1,2,5,6

Figure 6. Combinations of Intermediates in tom Dieck's Mechanism

Again, within this mechanism, the fact that for R= CH_2OH the 1,3,5,7-substituted isomer predominates indicates that either intermediate **b** is intrinsically more reactive than intermediates **a** and **c**, or it is present in higher concentration, the result of thermodynamic

or kinetic factors. As there is no obvious difference in the reactivities of the three intermediates, the latter explanation seems more plausible. Likewise, the observation that cyclotetramerization of propargyl ethers (e.g. R = CH_2O*p*-Tol) produces predominantly the 1,2,5,6-substituted product is consistent with a predominance of either intermediate **a** or **c**. If this is in fact true, control of the product distribution might be possible through selectively favoring one intermediate through judicious choice of DAD ligand and propargylic acetylene.

To examine the relationship between DAD ligand and acetylene reactant, the following experiments were conducted. First, a series of DAD ligands was synthesized in which the size of the R' group was systematically varied. These included ligands derived from *n*-butyl-, isopropyl, *tert*-butyl- and the previously described di(isopropyl)methylamines. The corresponding $Ni(DAD)_2$ complexes were then used in the cyclotetramerization of propargyl alcohol. While some variation in tetramer/trimer ratio is observed, there was no apparent variation in the relative proportion of isomeric THMCOT products. In the appropriate regions of the ^1H NMR spectrum, the spectra of the crude product mixtures were essentially superimposable. Clearly, the nature of the DAD ligand, while it can affect the tetramer/trimer ratio and the catalyst efficiency, has very little effect on the proportion of cyclotetramers produced. Within tom Dieck's mechanism, this independence of THMCOT product distribution and DAD ligand implies that the predominance of intermediate **b** (Figure 6) is not related to the steric bulk of the R' group of the DAD ligand.

It would be expected that a bulkier R group on the acetylene reactant would attenuate any R-R' interactions. This enhanced interaction might be expected to result in a more pronounced relationship between the R' group on the DAD ligand and resultant cyclotetramer isomer distribution. To test this premise, the above experiment was repeated using the trimethylsilyl ether of propargyl alcohol. In this experiment the isomer distributions resulting from the cyclotetramerization of trimethylsilyl propargyl ether by the

four $Ni(DAD)_2$ complexes were compared. In each reaction a broad distribution of isomeric cyclooctatetraene products resulted. Surprisingly however, little variation in isomer distribution was observed (by ^1H NMR) in the products of these reactions.

It is possible that Ni(DAD)-catalyzed propargylic acetylene cyclotetramerizations proceed according to tom Dieck's mechanism, but that the relative abundance of intermediates **a**, **b** and **c** is insensitive to the nature of the DAD ligand. For our purposes it is clear that control over the distribution of isomeric cyclooctatetraene products is not to be found in systematic modification of the DAD ligand in these $Ni(DAD)_2$ catalysts. Moreover, it calls into serious doubt the accuracy of describing the DAD groups as "control ligands" (tom Dieck's phrase) in the cyclotetramerization of propargylic acetylenes.

Cyclotetramerization of Propargyl Alcohol by "Naked Ni"

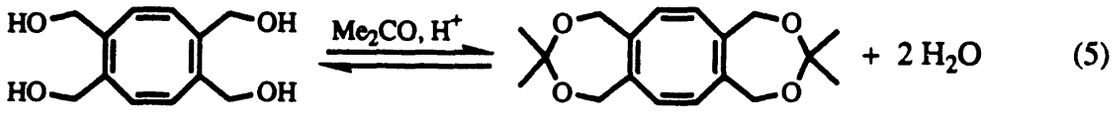
About the time we had confirmed that **2** and related complexes can be used as catalysts for the cyclotetramerization of propargyl alcohol, but had not yet developed an effective method for separating the isomeric products, we were made aware of another report in the literature of catalytic formation of THMCOT's from propargyl alcohol. Walther et al.[27] in 1989 published a remarkable study of the catalytic activity of "naked Ni" [Ni(0) generated in situ] and other finely divided zero-valent metals for this reaction. Intriguingly, they report that under the same reaction conditions (0 °C, THF) the distribution of THMCOT isomers that results from reaction with Ni(0) is the same as the isomer distribution reported by tom Dieck for the catalytic reaction with **2**. Moreover, Walther found that this isomer distribution is invariant over a range of solvent and temperature conditions, including neat propargyl alcohol. Additionally, he demonstrated that for tetramerizations run under the same conditions (neat propargyl alcohol, 114 °C) the proportion of 1,3,5,7-THMCOT produced is invariant with the source of Ni(0). These findings, coupled with our results showing the absence of a relationship between isomeric

product distribution and the nature of the DAD ligand of the $Ni(DAD)_2$ "catalysts", call into serious doubt the veracity of tom Dieck's proposed mechanism for the $Ni(DAD)_2$ catalyzed reaction (Figure 5). It would seem likely instead that the $Ni(DAD)_2$ is simply serving as an in situ source of low concentrations of Ni(0), and is not involved in the catalytic reaction per se at all. The enhanced effectiveness of $Ni(DAD)_2$ complexes bearing bulky substituents (such as **2**) as cyclotetramerization catalysts probably reflects the relative instability of these complexes with respect to ligand loss.

We were able to reproduce Walther's synthesis of mixed THMCOT isomers using Ni(0) obtained by the in situ reduction of $(DME)NiBr_2$. Addition of $NaBH_4$ to a dilute solution of $(DME)NiBr_2$ in propargyl alcohol resulted in an astonishingly exothermic reaction that boiled 30 mL of propargyl alcohol in seconds. The ^1H NMR spectrum of the crude product mixture is, as Walther reports, essentially superimposable on the spectra of the product mixtures resulting from catalysis by **2** and other $Ni(DAD)_2$ complexes. Unfortunately, these isomeric mixtures proved just as resistant to separation of their constituents by recrystallization as those obtained earlier. However, this method allows production of mixtures of THMCOT's on 20-50 g scale.

Separation of THMCOT Isomers by Selective Derivatization

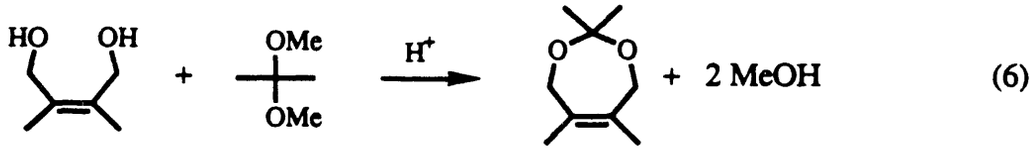
Examination of the four THMCOT isomers produced from the cyclotetramerization of propargyl alcohol (Figure 3, R = CH_2OH) reveals that, with the exception of the 1,3,5,7 isomer, each has a site of 1,2-di(hydroxymethyl) substitution. These 1,4-diols represent potential sites for chemical derivatization. John Rigsbee[15] has demonstrated that such diols can in fact be derivatized by conversion to the corresponding acetonides in the acid-catalyzed reaction with acetone. Specifically, Rigsbee was able to convert 1,2,5,6-THMCOT to the corresponding diacetonide in low yield through reaction with acetone and catalytic *p*-toluenesulfonic acid (Eq. 5).



(5)

Attempts to apply this approach to more complex mixtures of THMCOT isomers did not meet with encouraging results. At room temperature no reaction was detected while at reflux intractable polymeric product formation occured.

A better method[30] for acetonide formation from 1,4-diols is through acid-catalyzed reaction with dimethoxypropane (DMP) (Eq. 6). This reaction is thermodynamically downhill and does not require removal of water (as in Eq. 5) to shift the equilibrium to products.



(6)

This method proved to be better suited for application to mixtures of THMCOT isomers. Addition of DMP and catalytic *p*-toluenesulfonic acid to a concentrated solution of mixed THMCOT isomers (the crude product mixture from the Ni(0)-catalyzed propargyl alcohol tetramerization) in MeOH resulted in the formation of a white precipitate. Cooling of the solution followed by collection of the precipitate allowed isolation of a single product in high purity. This product was highly soluble in $CHCl_3$ and was shown by ^1H NMR to be identical to the diacetonide of 1,2,5,6-THMCOT (**3**, see Figure 7) synthesized and characterized by Rigsbee (Eq. 5). A tlc of the filtrate (alumina, 20% MeOH/$CHCl_3$) showed four spots. One spot (R_f = 1.0) corresponded to residual diacetonide. Two intermediate spots (R_f ~ 0.5) and a fourth spot (R_f = 0.3) followed. The last spot has the same approximate R_f value as the mixture of underivatized THMCOT isomers. Removal of MeOH from the filtrate and addition of more DMP initiated precipitation of a white powder

which could be collected by vacuum filtration. This product was soluble only in methanol and in water. The ^1H NMR in D_2O of this material showed two singlets, indicating a highly symmetric isomer. It was tentatively assigned as 1,3,5,7-THMCOT (**4**).

Reaction of mixed THMCOT isomers with DMP results in quantitative conversion of all 1,2-diols to the corresponding acetonides (Figure 7). This selective derivatization transforms the mixture of chemically similar (and therefore inseparable) tetraols into a mixture of chemically distinct (and easily separated) derivatives.

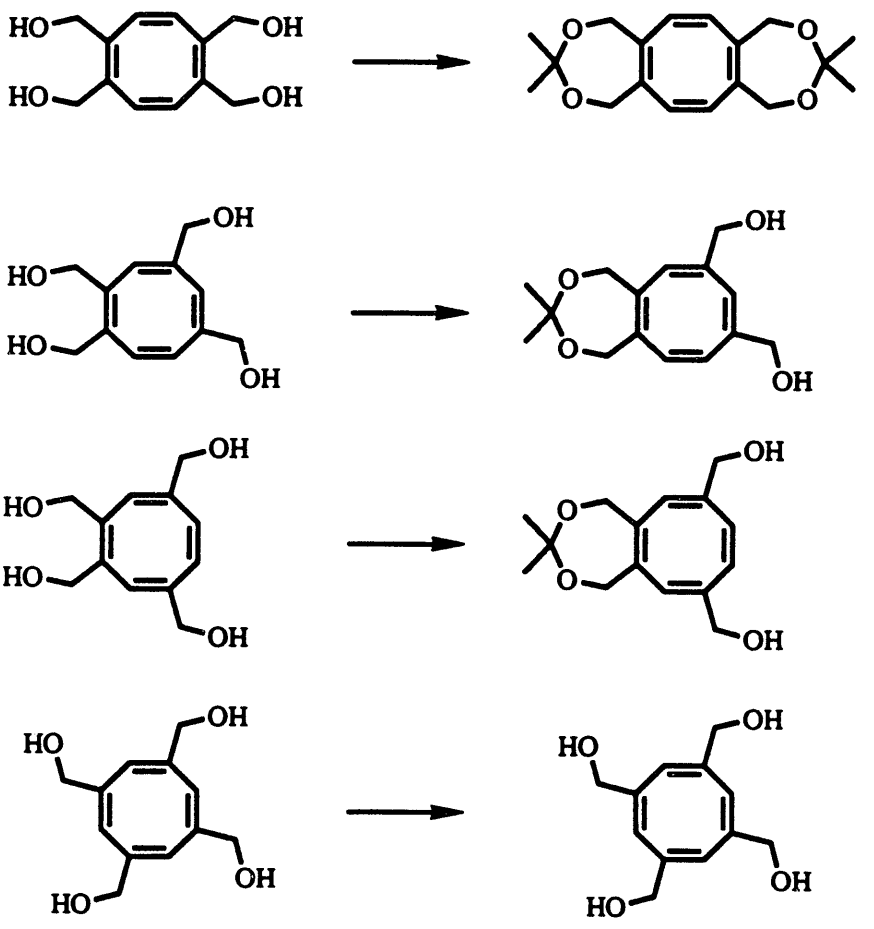
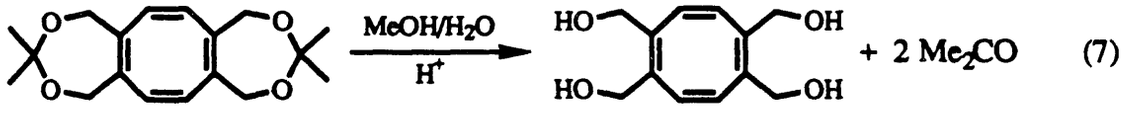


Figure 7. Reaction of THMCOT Isomers With DMP

^1H NMR of 1,2,5,6- and 1,3,5,7-THMCOT

Stirring **3** in acidic $MeOH/H_2O$ overnight results in the conversion to 1,2,5,6-THMCOT (**5**) in quantitative yield (Eq. 7).



(7)

The ^1H NMR spectra (D_2O, 250 MHz) of the crude product mixture of the Ni(0)-catalyzed cyclotetramerization reaction, as well as the isolated 1,3,5,7-THMCOT (**4**) and 1,2,5,6-THMCOT (**5**) are shown in Figure 8. In each spectrum the large peak at 4.67 ppm is due to protonated solvent.

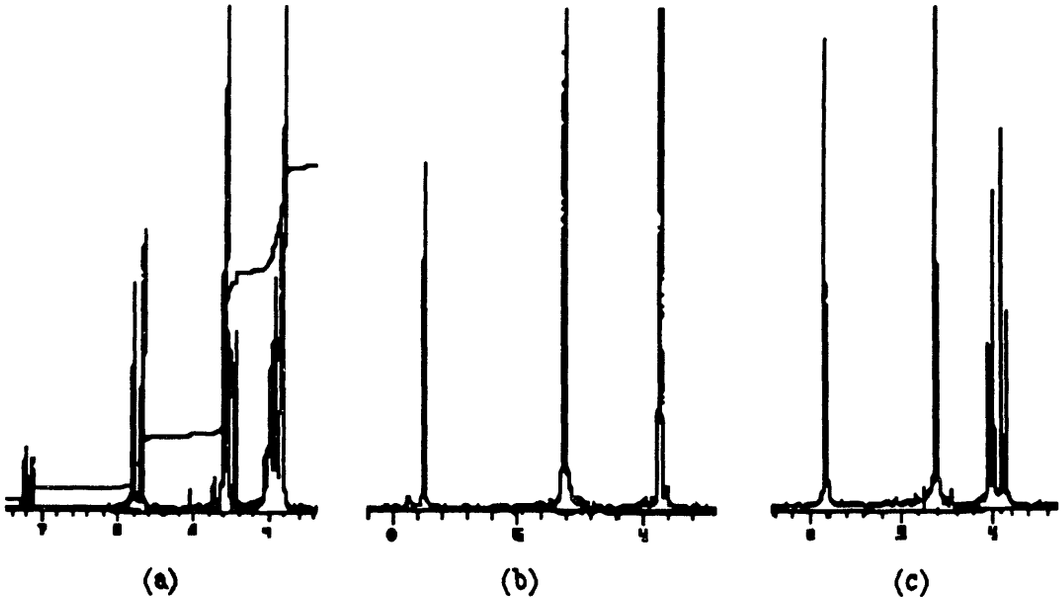


Figure 8. ^1H NMR (D_2O) of: (a) crude product mixture (b) **4** (c) **5**

The spectrum of the crude product mixture in D_2O shows resonances for both the tris(hydroxymethyl)benzenes (7.1-7.4 and 4.4-4.5 ppm) as well as the mixture of isomeric

THMCOT's (5.6-5.8 and 3.6-4.1 ppm). Isomeric **4** and **5** are easily differentiated, both by the resonances of the vinyl protons (5.75 ppm for **4**, 5.90 for **5**), as well as the splitting of the methylene protons (A_2 singlet, 3.91 ppm for **4**; AB pseuso-quartet, 4.08 and 3.98 ppm for **5**).

Examination of molecular models reveals that as a static molecule **4** has S_4 symmetry and that the methylene protons are chemically inequivalent; they should show an AB splitting pattern. Along with its X-ray structure, tom Dieck reports the ^1H NMR (360 MHz) spectra of **4** in both CD_3OD and in 5:1 CD_3OD/C_6D_6. In methanol, the spectrum of **4** consists of two singlets at 3.94 and 5.91 ppm, respectively. In methanol/benzene the methylene protons appear as the expected AB pattern. The equivalence of the methylene protons in the ^1H NMR spectra of **4** in methanol and in water is indicative of a dynamic solution process.

Two dynamic process are known for cyclooctatetraenes, inversion and bond shift isomerism.[31] These processes are shown in Figure 9 for COT itself. Inversion involves flipping of the COT ring from one "tub" conformation into another. Bond shift isomerism (BSI) converts one valence tautomer into another. The process can be thought of as resulting from the flattening of the tub-shaped COT to a planar structure, followed by shifting the single and double bonds around the ring, and reestablishment of the tub geometry.

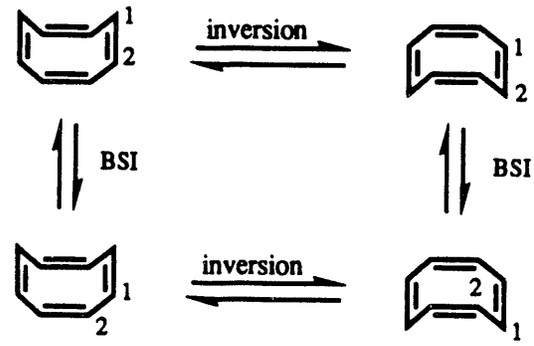


Figure 9. Inversion and Bond Shift Isomerism (BSI) in COT

Inversion is generally assumed to go through a planar transition state with alternating single and double bonds. The transition state for BSI is also planar, but with equivalent ring C-C bonds. Because the planar, delocalized structure is anti-aromatic, the activation energy for BSI is higher than that for inversion. In COT itself the barriers to both are quite low; $\Delta G^{\ddagger}$ values for BSI have been measured[32a] (13.7 kcal/mol) by ^{1}H and ^{13}C NMR and are in good agreement with calculated[32b] values for inversion. Because of steric effects in the planar transition state, inversion and BSI barriers in substituted COT's are significantly higher. For example, for 2-cyclooctatetraeneyl-2-propanol $\Delta G^{\ddagger}$ = 14.7 kcal/mol for inversion and $\Delta G^{\ddagger}$ = 15.1 kcal/mol for BSI.[33] These barriers increase with increasing ring substitution. The barrier to BSI in 1,3,5,7-tetramethylcyclooctatetraene (1,3,5,7-TMCOT) has been measured[34] as 22.5 kcal/mol. The barrier to inversion of octamethylcyclooctatetraene has been calculated[35] to be 94 kcal/mol. Barriers to inversion and BSI in substituted COT's are also dependent on patterns of substitution. For example, barriers are higher for 1,2,5,6-substituted COT's than for their 1,3,5,7-substituted isomers.[31] The dependence of the barrier to inversion on degree and pattern of substitution is reflective of trends in reduction potentials, and underscores the importance of steric factors in the planar eight-membered ring.

Both inversion and BSI interconvert the methylene protons of **4**. These processes for **4** are shown in Figure 10. Coupling of H_x with H_a and H_B is too small to be observed, and as a result the two processes cannot be distinguished by ^{1}H NMR. Because both BSI and inversion interconvert H_a and H_b, in a variable temperature ^{1}H NMR experiment in which the sample is cooled to reach coalescence, the dynamic process observed corresponds to the process with the lower activation energy. For reasons discussed above, inversion is presumed to have an activation energy lower than that of BSI and should be the process observed in a variable temperature NMR experiment.

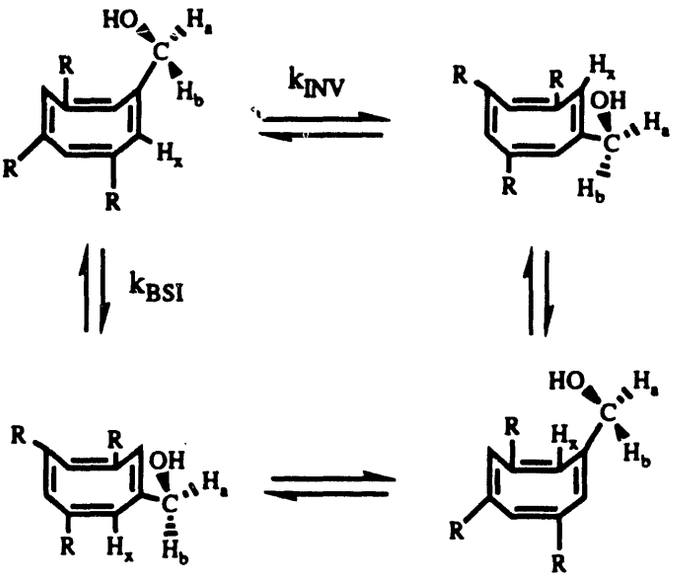


Figure 10. Inversion (INV) and Bond Shift Isomerism (BSI) in **4**

On cooling a sample of **4** in CD_3OD, the ^1H NMR (400 MHz) exhibits the following behavior. The A_2 singlet of the methylene protons broadens and two side peaks begin to grow in. On further cooling these side peaks increase in height while the center singlet broadens further and splits into a doublet. At -80 C the spectrum has resolved into a AB pseudo-quartet. Spectra at various temperatures are shown in Figure 11.

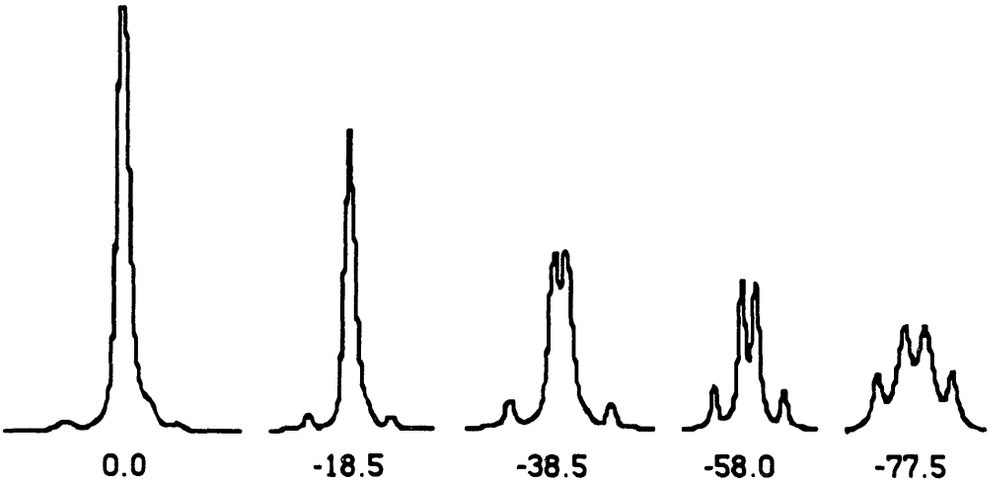


Figure 11. ^1H NMR of Methylene Protons of **4** at Various Temperatures (°C)

The rate of exchange (k_c) for coalescing spin-spin doublets[36] at the coalescence temperature (T_c) can be determined from Equation 8, where $\delta\nu$ is the difference in chemical shift between the exchanging protons and w is the line width at zero exchange. The free energy of activation can then be obtained from Equation 9.

$$k_c = \frac{\pi}{\sqrt{2}} \times \left[1 + \frac{3\sqrt{2}}{8}\left(\frac{w}{\delta\nu}\right) + \frac{21}{64}\left(\frac{w}{\delta\nu}\right)^2\right]^{-1} \times \delta\nu \qquad (8)$$

$$\Delta G^{\ddagger} = RT_c \ln\left(\frac{RT_c}{Nhk_c}\right) \qquad (9)$$

At 400 MHz, the coalescence temperature for **4** is -25 °C. The $\Delta G^{\ddagger}$ for inversion at -25 °C is 12.8 kcal/mol. At 300 MHz the coalescence temperature drops to -60 °C and the measured $\Delta G^{\ddagger}$ = 11.5 kcal/mol.

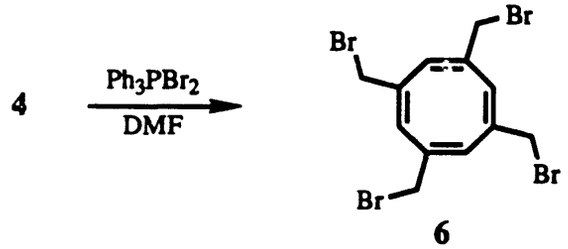
Although direct comparison of activation barriers for inversion of various cyclooctatetraenes should be done at the same temperature and in the same solvent, even qualitative comparison of values of $\Delta G^{\ddagger}$ for cyclooctatetraene (13.7 kcal/mol at -10 °C in CS_2), 1,3,5,7-TMCOT (22.5 kcal/mol at 120 °C in hexachlorobutadiene) and **4** (12.8 kcal/mol at -25 °C in methanol) indicate that the the barrier to inversion of **4** is anomalously low. Based on the similar steric demands of hydroxymethyl and methyl substituents, one might expect the barrier to inversion in **4** to be on the order of 20-25 kcal/mol. In 5:1 CD_3OD/C_6D_6 the methylene protons of **4** appear as a pseudoquartet in the temperature range 25-45 °C (at 300 MHz). Thus, addition of 20% benzene to the methanolic solution raises the coalescence temperature over 100 °C. This observation implicates hydrogen bonding as the source of the anomalously low activation barrier to inversion in **4**, although the exact mechanism is not clear. One possible explanation is that, for whatever reasons, hydrogen-bonding better stablizes the planar transition state than the tub-shaped ground

state. It could be that the hydroxy groups are more accessible in the planar structure, resulting in stronger hydrogen bonds and a net stabilization of the transition state.

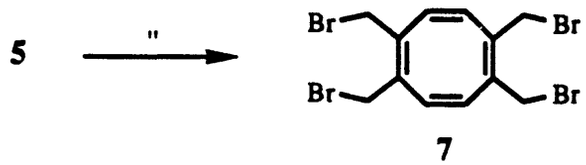
Conversion of 1,3,5,7- and 1,2,5,6-THMCOT to The Corresponding TMCOT's

In working with 1,2,5,6-THMCOT, John Rigsbee[15] found that conversion to the tetrakis(chloromethyl)- and tetrakis(bromomethyl) derivatives was possible by reaction with PCl_5 and Ph_3PBr_2, respectively. The 1,2,5,6-tetrakis(bromomethyl)cyclooctatetraene (1,2,5,6-TBrMCOT) proved to be better suited for further derivatization; for example, reduction of 1,2,5,6-TClMCOT gave a mixture of products containing both endo- and exo-double bonds, whereas 1,2,5,6-TBrMCOT could be reduced to 1,2,5,6-TMCOT. Our efforts thus focussed on use of bromo derivatives.

Both **4** and **5** can be readily converted to their corresponding tetrabromo derivatives 1,3,5,7-TBrMCOT (**6**) and 1,2,5,6-TBrMCOT (**7**) on reaction with Ph_3PBr_2 (Eqs. 10 and 11).

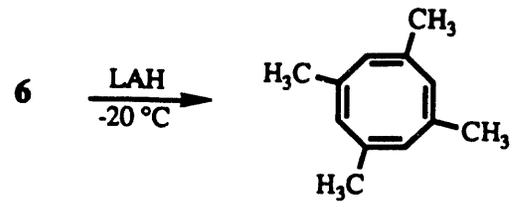


6 (10)

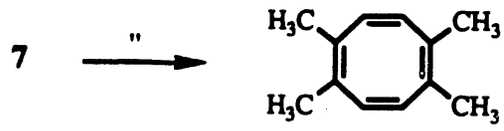


7 (11)

Reduction of **6** and **7** with LAH at -20 °C afforded the corresponding 1,3,5,7- and 1,2,5,6-TMCOT's in moderate yield (Eq. 12 and 13).



(12)



(13)

Some exocyclic reduction products are formed, but the TMCOT's can be isolated pure by flash chromatography.

Syntheses of Other Substituted Cyclooctatetraenes

The above-described syntheses of 1,3,5,7- and 1,2,5,6-TMCOT in three steps from propargyl alcohol demonstrates the viability of this synthetic approach to tetrasubstituted cyclooctatetraenes. Although unexplored at this point, it is anticipated that **6** and **7** can serve as versatile reagents for the syntheses of a variety of substituted cyclooctatetraenes. Such versatility in synthetic approach is a critical feature of any ligand synthesis for which control of steric and electronic properties is desired.

$AlBr_3$-Mediated Tetramerization of Mono-substituted Acetylenes

Dimerization of Disubstituted Cyclobutadienes

It has been known for 25 years that cyclobutadiene reacts with itself in a Diels-Alder fashion to yield *syn*-tricyclo[4.2.0.$0^{2,5}$]octadiene, which can in turn be thermally or photolytically ring-opened to cyclooctatetraene. Substituted cyclobutadienes react in an analogous fashion. For example, tetramethylcyclobutadiene (produced by a variety of means) dimerizes to give octamethyltricyclo[4.2.0.$0^{2,5}$]octadiene, which readily thermally ring-opens to octamethylcyclooctatetraene. It follows logically that dimerization of disubstituted cyclobutadienes leads to tetrasubstituted *syn*-tricyclo[4.2.0.$0^{2,5}$]octadienes, which in turn lead to tetrasubstituted cyclooctatetraenes (Scheme 3).

Starting from a 1,2-substituted cyclobutadiene, three isomeric *syn*-tricyclo[4.2.0.$0^{2,5}$]octadienes can form depending on the orientation of the reacting cyclobutadiene molecules. This leads to a mixture of three isomeric cyclooctatetraenes (Figure 12).

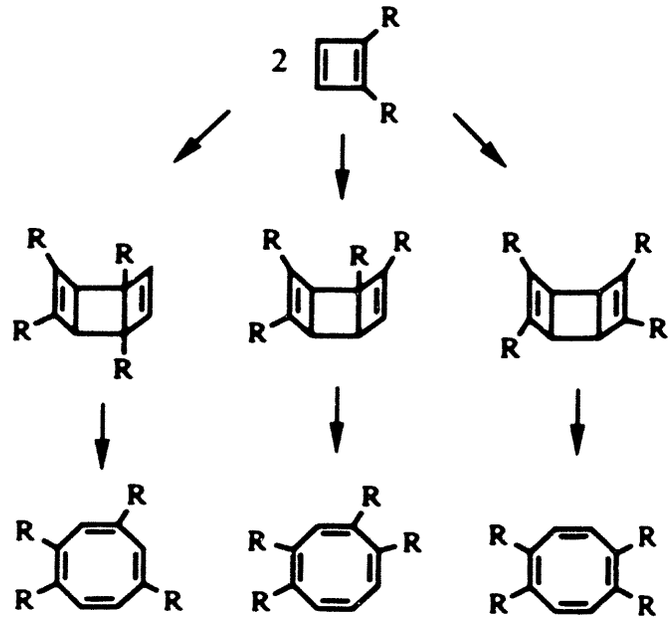


Figure 12. Dimerization of 1,2-Substituted Cyclobutadienes

This dimerization pattern has been demonstrated for 1,2-dimethylcyclobutadiene, generated both by the zinc reduction of 1,2-dichloro-3,4-dimethyl-3-cyclobutene[37] and, in lower yield, from the photolytic decarboxylation of dimethylcyclobutenedicarboxylic anhydride[38] (Figure 13).

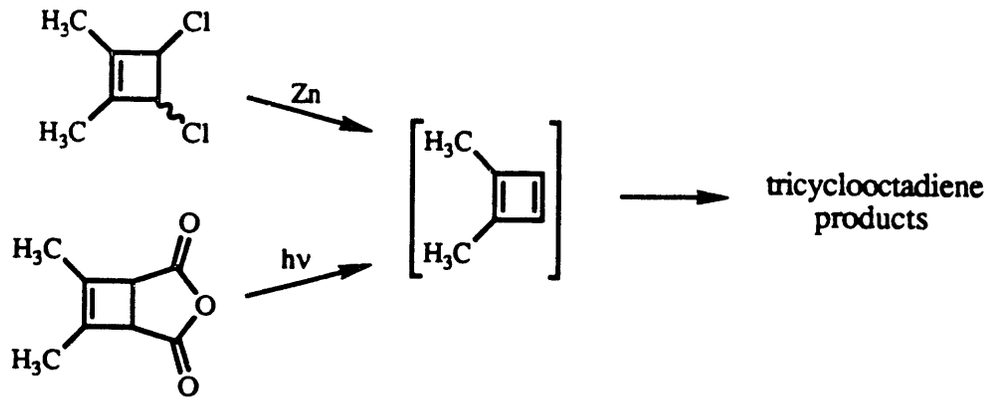


Figure 13. Generation of 1,2-Substituted Cyclobutadienes

Starting from 1,3-substituted cyclobutadienes, only two isomeric *syn*-tricyclo[4.2.0.0^{2,5}]octadienes can form, leading to a mixture of two isomeric cyclooctatetraenes. The Diels-Alder dimerization of a 1,3-substituted cyclobutadiene is shown in Figure 14, including the transition states leading to each product.

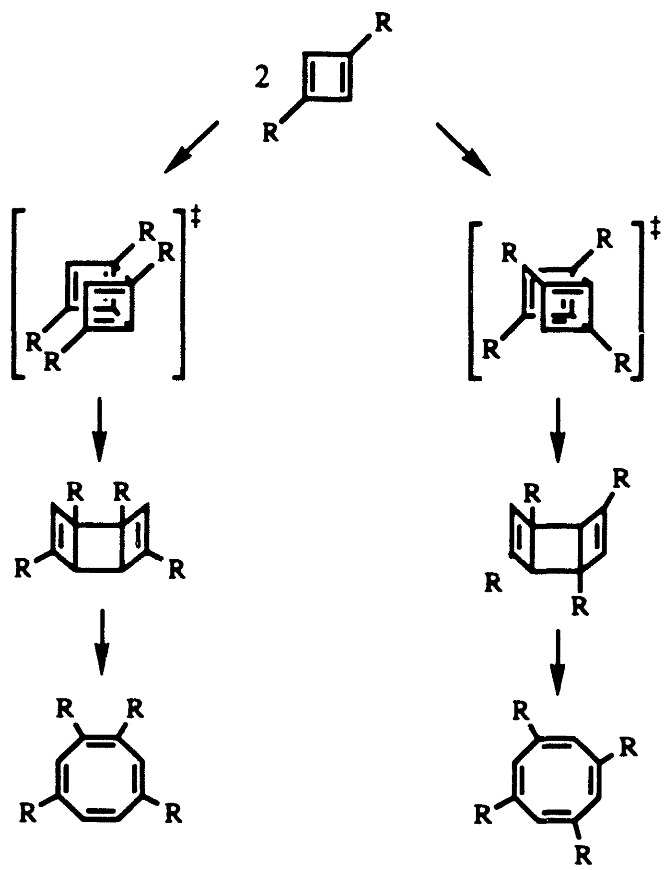
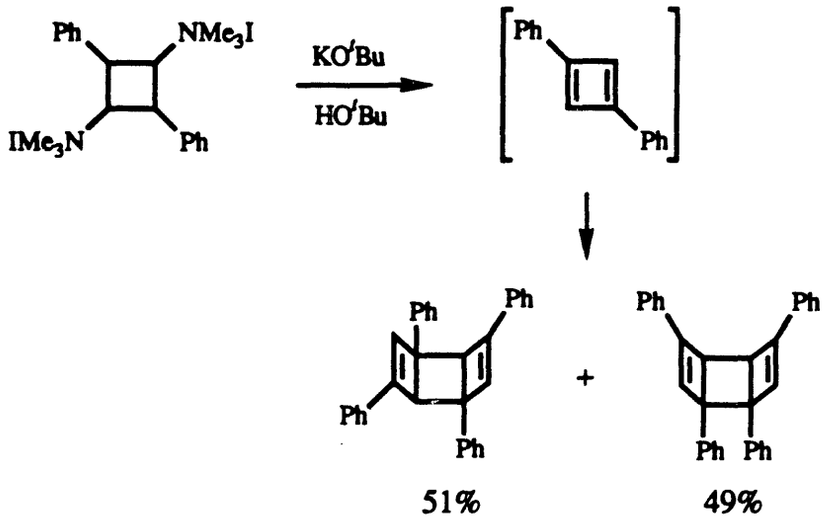


Figure 14. Dimerization of 1,3-Substituted Cyclobutadienes

The only example of this reaction in the literature is the dimerization of 1,3-diphenylcyclobutadiene generated from the Hofmann elimination of the bis-quaternary ammonium salt of diphenylcyclobutane (Eq. 14)



(14)

As an approach to the synthesis of tetrasubstituted cyclooctatetraenes, this method is attractive because of the small number of isomeric products formed. The critical limitation to this approach is the lack of a general route to 1,3-disubstituted cyclobutadienes.

$AlCl_3$ Salts of Tetrasubstituted Cyclobutene Cations

Aluminum halide salts of cyclobutene cations were first described[39] in the early 1970's, but it was not until a decade later that Hogoveen demonstrated the full range of their chemistry. The peralkylated compound is easily synthesized as its $AlCl_3$ salt through the reaction of two equivalents of a disubstituted acetylene with one equivalent of $AlCl_3$ in CH_2Cl_2. The crystal structure[40] of the tetramethyl complex indicates that the ring assumes a puckered geometry with the $AlCl_3$ σ-bound to one carbon of the ring and the other three carbons form a homocyclopropyl cation (Figure 15). Solution state dynamics have been investigated by ^1H and ^{13}C NMR and confirm the solid state structure. Variable temperature ^1H NMR shows that at 0 °C the $AlCl_3$ migrates around the ring in a series of 1,2-shifts.

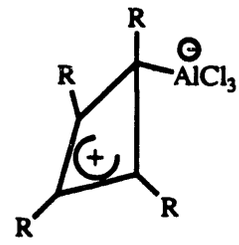
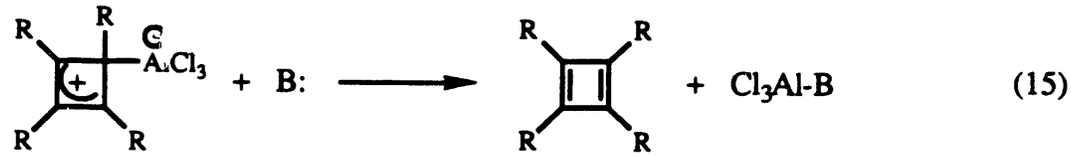


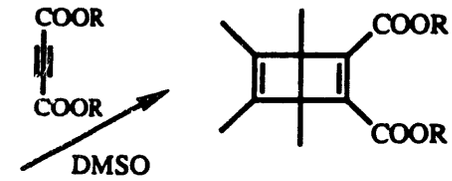
Figure 14. σ-Bound $AlCl_3$ Salt of Tetramethylcyclobutene Cation

These compounds are remarkably versatile synthetic reagents,[41] having been utilized in the syntheses of Dewar benzenes, bicyclohexenes, pyridines, pyrroles and a variety of other derivatives. One aspect of the reactivity of these compounds is that, in the presence of an appropriate Lewis base (such as DMSO), the $AlCl_3$ is complexed and cyclobutadiene is apparently liberated (Eq. 15).

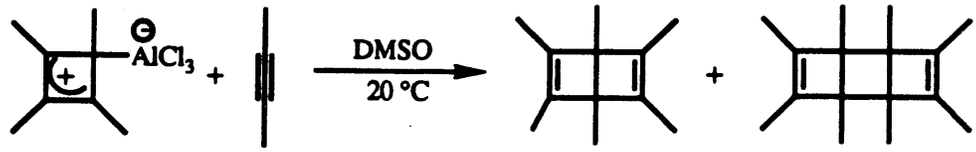


(15)

The cyclobutadiene thus generated has been trapped by a variety of dienophiles including acetylenes. The reaction of tetramethylcyclobutadiene with the weakly dienophilic 2-butyne is of particular interest.[42] In the presence of an activated dienophilic acetylene, over a wide temperature range, neither the 2-butyne nor tetramethylcyclobutadiene can compete and the Dewar benzene diester product is formed exclusively (Eq. 16). In the absence of such a reactive reagent, a temperature-dependent competition reaction between 2-butyne and tetramethylcyclobutadiene results. At room temperature the reaction affords a mixture of Dewar benzene and *syn*-tricyclo[4.2.0.$0^{2,5}$]octadiene products (Eq. 17); at -40 °C the product is exclusively that of self-condensation of tetramethylcyclobutadiene (Eq. 18).

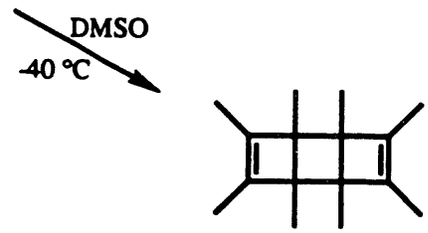


(16)



(17)

4 : 3

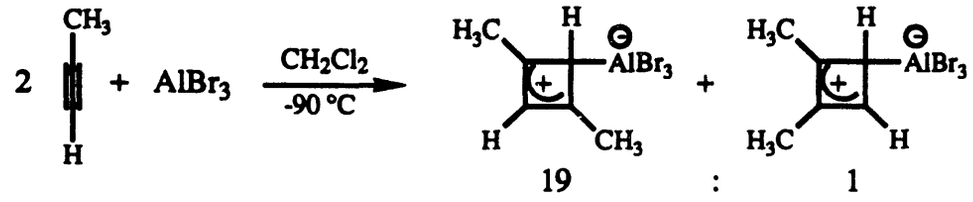


(18)

Although Hogeveen apparently was not interested in the synthesis of *syn*-tricyclo[4.2.0.0^{2,5}]octadienes, the results of Reaction 18 indicate that addition of base to the $AlCl_3$ salts of cyclobutene cations in the absence of a trapping agent affords these compounds in excellent yield.

$AlBr_3$ Salts of Disubstituted Cyclobutene Cations

Reaction of monosubstituted acetylenes with $AlCl_3$ in CH_2Cl_2 affords only polymeric material.[43] Hogeveen has shown, however, that disubstituted cyclobutene cations can be generated as their $AlBr_3$ salts by working at low temperatures. In addition, this acetylene dimerization shows remarkable regioselectivity. For example, the NMR tube scale reaction of propyne with $AlBr_3$ in CD_2Cl_2 is reported[43] to give 70% yield of cyclobutene cation salts, 95% of which is the 1,3-substituted complex (Eq. 19).



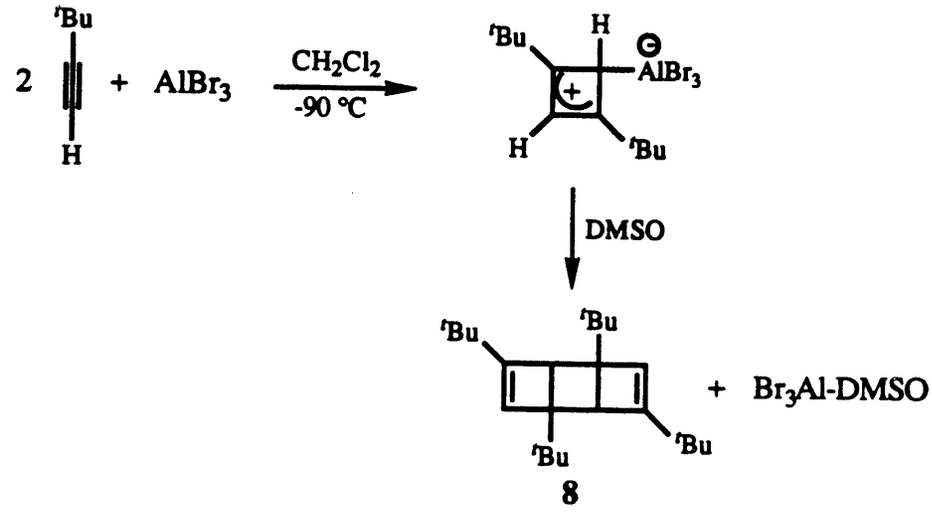
19 : 1 (19)

In preparative scale reactions, Hogeveen has used $AlBr_3$-cyclobutene salts derived from *n*-butylacetylene and isopropylacetylene in reactions resulting in final yields of 80% (based on the acetylene). Again, while Hogeveen has not reported using these reagents in the syntheses of substituted tricyclo[4.2.0.$0^{2,5}$]octadienes (except as undesired side products), their utility to this end, and to the subsequent conversion to substituted cyclooctatetraenes, is apparent.

Results of the Reaction of tert-*Butylacetylene With* $AlBr_3$

Our initial attempts to exploit $AlBr_3$-cyclobutene salts in the synthesis of tetrasubstituted cyclooctatetraenes focussed first on *tert*-butylacetylene as the starting acetylene. The rational for this was severalfold. It was expected that in the reaction of the acetylene with $AlBr_3$ the bulky *tert*-butyl substituent would provide the 1,3-substituted cyclobutene salt in large excess over the 1,2-substituted isomer (see Equation 19). It was further expected that in the subsequent dimerization of 1,3-di-*tert*-butylcyclobutadiene the steric demands of the bulky *tert*-butyl groups would favor one reaction pathway (to the right in Figure 14) and lead to the formation of a single product, the 1,3,5,7-substituted isomer. For practical reasons, *tert*-butylacetylene was attractive because of the relative ease of its synthesis and purification and, as a liquid, it more readily lends itself to the tricky, low-temperature reaction with $AlBr_3$. Finally, the desired products, the 1,3,5,7-tetra-*tert*-butyl-*syn*-tricyclo[4.2.0.$0^{2,5}$]octadiene and the corresponding 1,3,5,7-tetra-*tert*-butylcyclooctatetraene, had already been synthesized by another route[10] and could be identified by ^1H NMR.

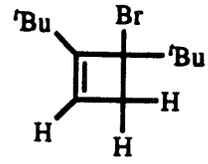
The reaction of *tert*-butylacetylene with $AlBr_3$ is shown in Eq. 20. In addition to low temperature, this reaction requires an inert atmosphere and use of oxygen- and water-free reagents; these are conditions familiar to most organometallic chemists.



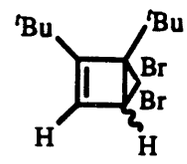
(20)

8

Slow addition of a 1:1 mixture of *tert*-butylacetylene and CH_2Cl_2 to a solution of $AlBr_3$ in CH_2Cl_2 at -90 °C led to the formation of a deep purple solution. Addition of DMSO effected an exothermic reaction and the formation of a white precipitate. Removal of the DMSO-$AlBr_3$ precipitate by filtration followed by a standard aqueous/organic work-up afforded the tricyclo[4.2.0.$0^{2,5}$]octadiene **8** in 70% yield. This product generally contained a small but variable amount of polymeric material and a significant amount of two other products (by tlc). These side products were identified by ^1H NMR as brominated cyclobutenes **9** and **10**.



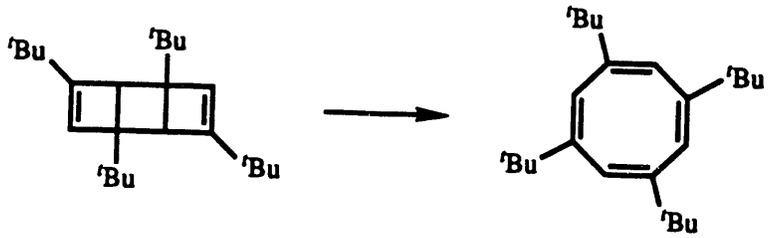
9



10

Product **9** presumably arises from addition of HBr (produced from hydrolysis of $AlBr_3$) to the cyclobutadiene. Product **10** may arise from the addition of Br_2 to the cyclobutadiene. The source of Br_2 is unknown, however. Hogeveen reports dibromocyclobutene products analogous to **10** in the reaction of $AlBr_3$-cyclobutene salts with excess SO_2.[44] In this case SO_2 is known to react with $AlBr_3$ to liberate Br_2. It may be that the Diels-Alder dimerization of the di-*tert*-butylcyclobutadiene is relatively slow, giving rise to competitive side reactions. The product **8** could be conveniently separated from these contaminants by flash chromatography on alumina with pentane eluent. It was identified by ^1H NMR as identical to the compound reported by Miller, et al.[10]

Conversion of **8** to 1,3,5,7-tetra-*tert*-butylcyclooctatetraene (**11**) (Eq. 21) was accomplished by heating **8** neat at 175 °C for one hour. Under these conditions, however, significant polymerization occurs. The product **11** could be separated from the majority of polymeric material by flash chromatography, then further purified by preparatory gas chromatography. Heating a dilute solution of **8** in DMF at reflux provides thermolysis conditions that result in significantly less polymerization. The reaction can be followed by tlc until conversion is complete; the DMF can then be conveniently removed by extraction into pentane/water.



(21)

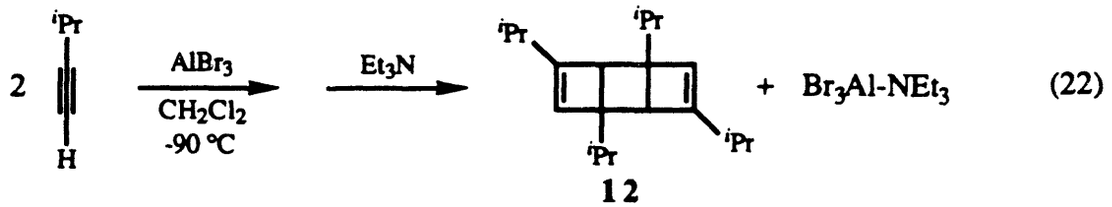
11

Preliminary studies of the suitability of **11** as a organoactinide ligand precursor had been undertaken in these labs in the past. Discussion of the current status of these

investigations, as well as the use of other substituted cyclooctatetraenes as organoactinide ligands, is presented in Chapter 3.

Results of the Reaction of Isopropylacetylene With $AlBr_3$

The reaction of isopropylacetylene with $AlBr_3$ proceeds in a manner analogous to the reaction of *tert*-butylacetylene to produce 1,3,5,7-tetraisopropyl-*syn*-tricyclo[4.2.0.$0^{2,5}$]octadiene (**12**). When DMSO is used as the base, brominated cyclobutenes analogous to **7** and **8** are formed. It was found, however, that these side reactions could be eliminated by using triethylamine (TEA) rather than DMSO as the base (Eq. 22).

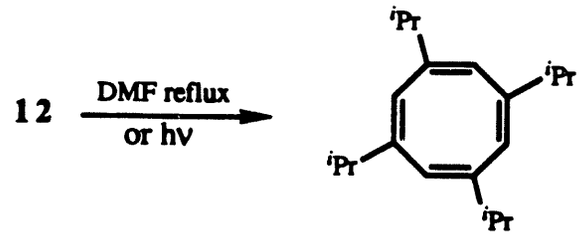


12

In addition to acting as a scavenger for HBr, TEA is more easily dried and probably introduces less water into the system than DMSO. Evidently, the side reaction leading to formation of dibromocyclobutenes is also shut down. TEA has the additional advantage of having a much lower melting point than DMSO and can be added to the $AlBr_3$-cyclobutene solution pre-cooled to -90 °C. The TEA-$AlBr_3$ complex, like DMSO-$AlBr_3$, has limited solubility in cold CH_2Cl_2 and can for the most part be removed by filtration.

Isolation of **12** is easily accomplished by flash column chromatography (alumina, pentane eluent) of the crude product mixture. The thermolytic ring opening of **12** to 1,3,5,7,-tetraisopropylcyclooctatetraene (**13**) proceeds in DMF at reflux (Eq. 22), or through photolysis with a 450 W medium-pressure mercury lamp for several hours. Some polymerization is observed in both cases. The majority of the polymeric material can be

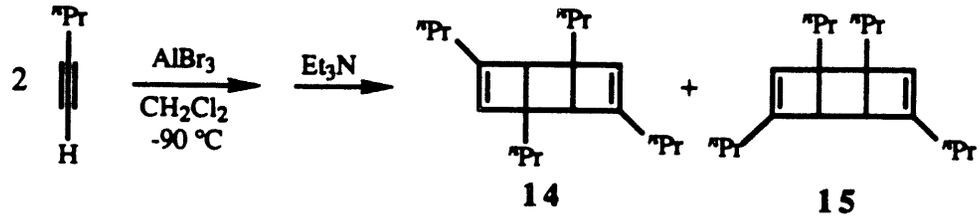
removed by flash column chromatography. The resulting product is suitable for successive reactions. Further purification by preparatory gas chromatography affords analytically pure material.



13 (23)

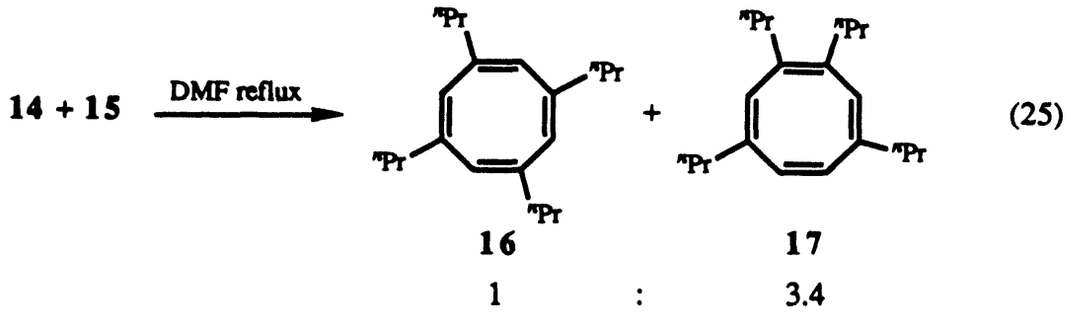
Results of the Reaction of n-*Propylacetylene With AlBr3*

In the reaction of *n*-propylacetylene with $AlBr_3$ and TEA two isomeric products are formed, the 1,3,5,7- (**14**) and 1,2,5,6-substituted (**15**) tricyclo[4.2.0.$0^{2,5}$]octadienes (Eq. 24).



14 15 (24)

The ^1H NMR of the mixture of **14** and **15** was complicated by overlapping resonances; as a result it was difficult to accurately determine the ratio of **14**:**15** from Equation 24. After isolating from polymeric byproducts, the mixture of **14** and **15** were thermally ring-opened to their corresponding 1,3,5,7- (**16**) and 1,2,5,6-substituted (**17**) cyclooctatetraenes (Eq. 25).



(25)

16 : **17**

1 : 3.4

The ratio of **16**:**17** (and at least approximately the ratio of **14**:**15** from Equation 24) was 1:3.4. This is analogous to the product mixture that results from the dimerization of 1,3-diphenylcyclobutadiene (Eq. 12), although the ratio of tetraphenylcyclooctatetraenes is 1:1. The rational for the difference in reactivity of the various acetylenes is quite simple. As shown schematically in Figure 14, there are two reaction pathways available in the Diels-Alder dimerization of 1,3-substituted cyclobutadienes. With bulky substituents (such as isopropyl and *tert*-butyl) it is likely that the transition state leading to the 1,2,4,6-substituted product is of significantly higher energy than the transition state leading to the 1,3,5,7-substituted product, resulting in the formation of a single product. For the less sterically demanding phenyl and *n*-propyl substituents both transition states are accessible and a mixture of products results. No attempt was made to separate **16** and **17**.

Results of the Reaction of Methylacetylene With $AlBr_3$

As mentioned above, Hogeveen reported yields by ^1H NMR of 70% for the formation of the $AlBr_3$ salt of 1,3-dimethylcyclobutene cation from the reaction of methylacetylene with $AlBr_3$ at -90 °C. He also reported similar yields (50-65%) in subsequent reactions of this salt. In our hands, repeated attempts to synthesize tetramethyl-*syn*-tricyclo[4.2.0.$0^{2,5}$]octadienes from the reaction of propyne with $AlBr_3$ followed by addition of DMSO or TEA resulted in the formation of polymeric material only. Disappointment occasioned by the failure of this reaction was tempered by the knowledge that, had the reaction been successful, an essentially equal (and likely difficult to separate)

mixture of 1,3,5,7- and 1,2,5,6-substituted tetramethyl-*syn*-tricyclo[4.2.0.$0^{2,5}$]octadienes would have resulted. Given the ease of synthesis of tetramethylcyclooctatetraenes from propargyl alcohol (described above), synthesis of 1,3,5,7-TMCOT through this route is rendered superfluous.

Experimental

General experimental details can be found in Experimental section of Chapter 1. Aluminum bromide received from a commercial supplier (Aldrich) required sublimation or Kugelrohr distillation before use. Commercial isopropylacetylene and 1-pentyne were distilled on a spinning-band apparatus immediately before use. Trimethylsilyl chloride (TMSCl) was distilled and stored over Mg turnings. Cyclooctatetraene (COT) was vacuum distilled and degassed immediately before use. Propargyl alcohol was vacuum distilled at temperatures <50 °C and stored under Ar. Tetrahydofuran (THF), diethyl ether (Et_2O), dimethoxyethane (DME), and methylene chloride (CH_2Cl_2) were dried by standard methods. All other reagents, unless otherwise noted, were used as received from commercial suppliers.

1,4-Bis(trimethylsilyl)-2,5,7-cyclooctatriene (1,4-TMS_2COTriene)[13]

A 500 mL 1-necked Schlenk flask capped with a septum was charged with 10.0 g (96.0 mmol) of COT, 75 mL of THF and 25 mL of Et_2O. To this solution was added 5.52 g (240 mmol) of freshly cut Na metal and the mixture was stirred (18 h) under Ar until most of the Na was consumed. Following removal of unreacted Na, the solution was cooled to -78 °C and 22.0 g (203 mmol) of TMSCl was added dropwise via syringe. After stirring for 2 h at -78 °C, the solution was warmed slowly to room temperature and the volatiles were removed *in vacuo*. Following addition of 100 mL of Et_2O and 50 mL of cold degassed H_2O, the organic layer was separated and washed with 2 50 mL portions of degassed H_2O. The combined organic fractions were dried over $MgSO_4$ in a stoppered flask, then the Et_2O was removed by rotary evaporation. The crude product was twice recrystallized from degassed acetone to afford 15.9 g (67%) of 1,4-TMS_2COTriene as

colorless crystals: mp 55-56 °C (lit.[13] 54.5-55.5 °C); ^{1}H NMR ($CDCl_3$) δ 0.05 (s, 18H), 2.76 (m, 8 lines, 2H), 5.45 (m, 4H), 5.74 (m, 2H) (matches reported[13] spectrum).

1,4-Bis(trimethylsilyl)cyclooctatetraene (1,4-TMS_2COT)

In a 250 mL 1-necked Schlenk flask capped with a septum was dissolved 5.00 g (20.0 mmol) of 1,4-TMS_2COTriene in 100 mL of Et_2O, and to this solution was added via syringe 30 mL (42 mmol) of 1.4 M MeLi in Et_2O. The solution was stirred until gas evolution ceased (6 h), then was quenched by addition of 5.3 g (21 mmol) of solid I_2 in small portions. Following addition of 50 mL of H_2O, the organic layer was separated and washed with with sat. $Na_2S_2O_3$ and 3 50 mL portions of 20% NaCl. After drying over $MgSO_4$, the ether was removed *in vacuo* to afford an orange oil. Flash column chromatography (pentane, 230-300 mesh silica) of this oil afforded, after removal of solvent, 3.8 g (77%) of 1,4-TMS_2COT as a yellow oil: ^{1}H NMR ($CDCl_3$) δ 0.015, 0.022 (2 s, 18H), 5.79 (m, 6H); Anal. Calcd. for $C_{14}H_{26}Si_2$: C, 67.12; H, 10.47. Found: C, 67.40; H, 10.19.

Glyoxal-bis(2,4-dimethyl-3-pentyl)imine (1)[29]

To 14.5 g (100 mmol) of a 40% solution of glyoxal in water, 50 mL of methanol, and 1 mL of formic acid at 0 °C was added dropwise a solution of 23.04 g (200 mmol) of 3-amino-2,4-dimethylpentane in 25 mL of methanol. After stirring at 0 °C for 2 h and at 25 °C for 18 h the methanol was removed and 100 mL of hexane was added. The hexane solution was washed with 2 50 mL portions of saturated brine and 2 50 mL portions of water. The combined organic layers were dried over $MgSO_4$ and evaporated to dryness. The resultant red oil was recrystallized from acetone to yield 23.0 g (45.6%) of **1** as colorless crystals: ^{1}H NMR ($CDCl_3$) δ 7.760 (s, 2H), 2.405 (t, J = 6.0 Hz, 2H), 1.976 (m, J = 6.75 Hz, 4H), 0.787 (d, J = 6.75 Hz, 12H), 0.780 (d, J = 6.75 Hz, 12H) (matches reported[29] spectrum).

Glyoxal-bis(*tert*-butyl)imine[29]

Following the procedure for glyoxal-bis(2,4-dimethyl-3-pentyl)imine above, 14.63 g (200 mmol) of *tert*-butylamine yielded, after recrystallization from acetone, 18.14 g (54.0%) of glyoxal-bis(*tert*-butyl)imine as colorless crystals: ^{1}H NMR ($CDCl_3$) δ 7.931 (s, 2H), 1.252 (s, 18H) (matches reported[29] spectrum).

Glyoxal-bis(isopropyl)imine[29]

Following the procedure for glyoxal-bis(2,4-dimethyl-3-pentyl)imine above, 11.82 g (200 mmol) of isopropylamine reacted with 14.5 g (100 mmol) of a 40% solution of glyoxal in water to yield a dark red oil from which crystalline material could not be isolated. Reduced-pressure distillation (10 torr, 55 °C) afforded 15.4 g (54.9%) of glyoxal-bis(isopropyl)imine as a viscous, colorless oil: ^{1}H NMR ($CDCl_3$) δ 7.885 (s, 2H), 2.863 (m, J = 6.5 Hz, 2H), 1.619 (m, J = 6.5 Hz, 6H), 1.615 (m, J = 6.5 Hz, 6H) (matches reported[29] spectrum).

Glyoxal-bis(*n*-propyl)imine[29]

Following the procedure for glyoxal-bis(isopropyl)imine above, 11.82 g (200 mmol) of *n*-propylamine yielded after distillation (10 torr, 70 °C) 5.4 g (19.3%) of glyoxal-bis(*n*-propyl)imine as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 7.933 (s, 2H), 3.035 (t, J = 6.0 Hz, 4H), 1.699 (m, 4H), 1.105 (t, J = 6.5 Hz, 6H) (matches reported[29] spectrum).

(DME)$NiBr_2$[45]

A solution of 127 g (approximately 500 mmol) of $NiBr_2(H_2O)_x$ in 200 g (1.35 moles) of triethyl orthoformate was heated at reflux (146 °C) for two h. The volume was reduced by distillation to the point of precipitation, then 250 mL (2.7 moles) of anhydrous DME was added and the solution was cooled to -20 °C. The product was collected by vacuum

filtration and washed with cold DME and pentane, then was dried *in vacuo* to yield 107g (69%) of (DME)$NiBr_2$ as small pink crystals.

Bis[glyoxal-bis(2,4-dimethyl-3-pentyl)imine]nickel (2)[29]

In a 250 mL Schlenk flask charged with 100 mL of anhydrous THF was dissolved 4.00 g (13.0 mmol) of (DME)$NiBr_2$ and 7.57 g (30 mmol) of glyoxal-bis(2,4-dimethyl-3-pentyl)imine. To the resultant solution was added 1.2 g (31 mmol) of freshly cut K metal and the mixture was stirred under Ar until the K was consumed (24 h). The dark brown solution was filtered and the THF was removed *in vacuo*. The solid was dissolved in pentane and the solution was cooled to -80 °C to yield 3.0 g (41%) of **2** as chunky brown, air- and water-sensitive crystals: ^{1}H NMR (toluene-d_8) δ 8.60 (s, 4H), 2.61 (t, J = 5.5 Hz, 4H), 2.20 (m, 8H), 0.72 (d, J = 6.7 Hz, 24H), 0.71 (d, J = 6.7 Hz, 24H).

Propargyl *p*-tolyl ether[26c]

A 500 mL 2-necked flask equipped with a reflux condenser and a magnetic stir bar was charged with 250 mL of absolute ethanol, and to this was added 5.75 g (250 mmol) of Na metal in small pieces. The mixture was heated at reflux until the Na was consumed, cooled to 25 °C, and 27.0 g (250 mmol) of *p*-cresol was added. After stirring for 3 h, propargyl bromide (23.8 g, 200 mmol) was added and the solution was heated at reflux for 4 h. After quenching with 100 g of ice, ether (200 mL) was added, the organic layer was collected and washed with 2 50 mL portions of 10% NaOH and 3 50 mL portions of water. The combined ether layers were dried over $MgSO_4$ and the ether was removed *in vacuo*. Reduced-pressure distillation (0.1 torr, 55-60 °C) afforded 25 g (85%) of propargyl *p*-tolyl ether as a colorless liquid: ^{1}H NMR ($CDCl_3$) δ 7.04 (d, J = 12.5 Hz, 2H), 6.82 (d, J = 12.5 Hz, 2H), 4.60 (2, J = 2.4 Hz, 2H), 2.44, (t, J = 2.4 Hz, 1H), 2.23 (s, 3H) (matches reported[26c] spectrum).

Propargyl trimethylsilyl ether[45]

To a 200 mL Schlenk flask charged with 50 mL of CH_2Cl_2 was added 8.61 g (154 mmol) of propargyl alcohol, 0.12 g (0.1 mmol) of DMAP and 11.80 g (161 mmol) of trimethylsilyl chloride and the solution was stirred for 30 min at 25 °C. After cooling to 0 °C, 18.6 g (184 mmol) of triethylamine was added dropwise to the solution via syringe, then warmed to 25 °C and stirred for 18 h. The $Et_3N{\cdot}HCl$ ppt was collected on a fritted-glass filter and washed with CH_2Cl_2. The filtrate was extracted with 2 50 mL portions of water, the organic layers were combined and dried over $MgSO_4$, and the CH_2Cl_2 was removed *in vacuo*. Fractional distillation on a spinning-band distillation apparatus afforded propargyl trimethylsilyl ether (10.1 g, 70.9%) as a colorless liquid: ^1H NMR ($CDCl_3$) δ 4.20 (d, J = 2.4 Hz, 2H), 2.33 (t, J = 2.4 Hz, 1H), 0.10 (s, 9H) (matches reported[45] spectrum).

Tetramerization of propargyl alcohol by $Ni(DAD)_2$ complexes

Procedure A - Reaction with isolated $Ni(DAD)_2$[26c]

To a solution of 0.28 g (0.5 mmol) of **2** in 30 mL of anhydrous THF under Ar was slowly added 10 g (178 mmol) of propargyl alcohol. The solution was stirred for 18 h and quenched by bubbling O_2 into the solution for several minutes. The solution was diluted with THF, filtered through a bed of Celite, and the THF and unreacted propargyl alcohol were removed *in vacuo* to yield 8.0-9.2 g (80-92%) of trimer and tetramer products. Isolation of products from this mixture is discussed in the text and below.

Procedure B - Reaction with $Ni(DAD)_2$ generated in situ[26a]

To a solution of 0.15 g (0.05 mmol) of $(DME)NiBr_2$ and 2.0 mmol of the DAD ligand in 20 mL of THF under Ar was added 0.04 (1.0 mmol) of $NaBH_4$ and then stirred until the color of the solution turned dark brown. The solution was then cannulated through a filter stick and diluted with 10 mL of THF. To this solution was added 10 g (178 mmol) of propargyl alcohol and the products were worked-up as described in Procedure A above.

Tetramerization of propargyl alcohol by Ni metal generated in situ[27]

Procedure C - in THF solution

To a solution of 0.01 g (0.03 mmol) of (DME)$NiBr_2$ in 10 mL of THF was added 0.006 g (0.15 mmol) of $NaBH_4$ and the mixture was stirred until the solution was colorless. To the suspension was added 20 mL of THF and then 20 g (356 mmol) of propargyl alcohol. After stirring for 3 h the solution was diluted with THF, filtered through a bed of Celite, and the THF and unreacted propargyl alcohol were removed *in vacuo*. The resultant product mixture was then treated as described below.

Procedure D - in neat propargyl alcohol

A 100 mL 2-necked flask equipped with a reflux condenser capped with an Ar bubbler and a ground-glass stopper was charged with a solution of 0.01 g (0.03 mmol) of (DME)$NiBr_2$ in 30 g (534 mmol) of propargyl alcohol. To this solution was added 0.006 g (0.15 mmol) of $NaBH_4$ in several portions. Care must be taken as the reaction is extremely exothermic. After stirring for 1 h the solution was diluted with 100 mL of THF, and the products were worked-up as described in Procedure C above.

Treatment of mixed THMCOT isomers with 2,2-dimethoxypropane

Isolation of 1,2,5,6-THMCOT diacetonide (3)

To 10 g of the mixture of cyclotetramers and cyclotrimers resulting from the nickel-catalyzed reactions described above was added 30 g of 2,2-dimethoxypropane (DMP), 20 mL of methanol and 0.1 g of *p*-toluenesulfonic acid and the mixture was mechanically stirred for 18 h. The resulting suspension was cooled to 0 °C for 2 h, the precipitate was collected by vacuum filtration, and the filtrate was set aside (see below). Dissolution of the precipitate in $CHCl_3$ followed by filtration and evaporation of the filtrate to dryness yielded 3.0 g (22% based on 1,2,5,6-THMCOT) of **3** as a white powder: mp 121-122 °C; ^1H

NMR ($CDCl_3$) δ 5.71 (s, 4H), 4.12 (d, J = 12.6 Hz, 4 H), 3.87 (d, J = 12.6 Hz, 4 H), 1.27 (s, 12H). This material is identical to that isolated and characterized by Rigsbee.[15]

Isolation of 1,3,5,7-THMCOT (4)

The methanol and unreacted DMP were removed from the filtrate *in vacuo*, then 20 mL of DMP was added and the mixture was mechanically stirred for 4 h. Cooling of the resulting suspension at 0 °C for 24 h followed by collection of the precipitate by vacuum filtration afforded 4.3 g (43%) of **4** as a white powder. This material is suitable for subsequent reactions. Recrystallization from acetone yielded **4** as small, colorless crystals: mp >360 °C; ^1H NMR (D_2O, 25 °C) δ 5.75 (s, 4H), 3.91 (s, 8H); (CD_3OD, 25 °C) δ 5.84 (s, 4H), 3.95 (s, 8H); (CD_3OD, -77.5 °C) δ 5.81 (s, 4H), 3.95 (dd, J = 12.1, 14.6 Hz, 8H) (see text for discussion of variable temperature ^1H NMR). The spectrum in CD_3OD matches that reported[26a] by tom Dieck.

Conversion of 1,2,5,6-THMCOT diacetonide (3) to 1,2,5,6-THMCOT (5)

Into 50 mL of a solution of 10% water in methanol containing 0.1 g of *p*-toluenesulfonic acid was mixed 3.0 g (9.9 mmol) of **3**, and the suspension was stirred at 50 °C until a clear solution resulted (2-3 h). The solution was filtered and evaporated to dryness *in vacuo*. Recrystallization from methanol yielded 1.8 g (81%) of **5** as colorless crystals: mp 162-163 °C; ^1H NMR (D_2O, 25 °C) δ 5.90 (s, 4H), 4.08 (d, J = 12.8 Hz, 4H), 3.98 (d, J = 12.8 Hz, 4H); (CD_3OD, 25 °C) δ 5.90 (s, 4H), 4.10 (d, J = 12.8 Hz, 4H), 3.96 (d, J = 12.8 Hz, 4H). The spectrum in D_2O matches the spectrum reported by Rigsbee[15] for the compound he identified as 1,3,5,7-THMCOT.

1,3,5,7-Tetrakis(bromomethyl)cyclooctatetraene (6)

To a solution of 9.36 g (35.7 mmol) of PPh_3 in 200 mL of dry DMF at 0°C was added 11.41 g (71.4 mmol) of Br_2 dropwise over 1 h. After stirring for an additional 1 h, a suspension of 2.0 g (8.9 mmol) of **4** in 100 mL of DMF was added over 30 min. The solution was warmed to 25 °C and stirred for 18 h. After quenching with ice and extraction

with Et_2O, the organic layer was washed with 2 50 mL portions of saturated brine and 2 50 mL portions of water. The combined organic layers were dried over $MgSO_4$, the volume was reduced to ca. 40 mL and the solution was cooled to -20 °C to precipitate Ph_3PO. The solution was then pulled through a 10 cm plug of silica and washed with Et_2O. Removal of the Et_2O afforded 2.3 g (60%) of **6** as a white powder. ^1H NMR ($CDCl_3$) δ 6.13 (s, 4H), 3.98 (d, J = 10.1 Hz, 4H), 3.91 (d, J = 10.1 Hz, 4H).

1,2,5,6-Tetrakis(bromomethyl)cyclooctatetraene (7)

Following the procedure for the synthesis of **6** above, 2.00 g (8.9 mmol) yielded 1.7 g (45%) of **7** as a white powder. ^1H NMR ($CDCl_3$) δ 6.14 (s, 4H), 4.14 (d, J = 10.9 Hz, 4H), 4.00 (d, J = 10.9 Hz, 4H). This spectrum matches that reported by Rigsbee[15] for what he identified as the 1,3,5,7-substituted isomer.

Reduction of 6 to 1,3,5,7-TMCOT with $LiAlH_4$

To a suspension of 0.24 g (6.3 mmol) of $LiAlH_4$ in 25 mL of anhydrous ether at -20 °C was added a solution of 1.0 g (2.1 mmol) of **6** in 20 mL of ether over 1 h. After allowing to warm slowly to room temperature and quenching with I_2 (1.6 g, 25.2 mmol), 50 mL of water and 50 mL of ether was added, followed by 50 mL of 10% aqueous HCl. The organic layer was separated and washed with sat. $Na_2S_2O_3$ and 3 50 mL of 10% HCl. After drying over $MgSO_4$, the ether was removed *in vacuo* to afford a yellow oil. Flash column chromatography (pentane, 150 mesh alumina) of this material gave, after removal of solvent, 0.14 g (42%) of 1,3,5,7-TMCOT as a pale yellow oil, suitable for further reactions: ^1H NMR ($CDCl_3$) δ 5.40 (s, 4H) 1.66 (s, 12H) (matches reported[14, 34b] spectra).

Reduction of 7 to 1,2,5,6-TMCOT with $LiAlH_4$

By a procedure analogous to the reduction of **6** described above, 1.0 g of **7** afforded after chromatography 0.19 g (57%) of 1,2,5,6-TMCOT as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 5.50 (s, 1H), 1.75 (s, 3H).

Aluminum tribromide[47]

To a 250 mL 2-necked Schlenk flask equipped with a stir bar, condenser, and a 100 mL dropping funnel was added 6.0 g (222 mmol) of Al pellets. To the Al was added slowly with rapid stirring a solution of 50 g of Br_2 (313 mmol) in 25 mL of CH_2Br_2. After stirring at room temperature for 1 h, the condenser and dropping funnel were replaced by ground-glass stoppers and the CH_2Br_2 was removed *in vacuo*. The $AlBr_3$ was then flame distilled (at 1 torr) into a 50 mL receiving flask. The $AlBr_3$ was further purified by Kugelrohr distillation (100 °C, 1 torr) to yield a colorless solid (typically 35-40 g, 63-72%) that was stored in a glove box before use: mp 96-97 °C (lit.[47] 97 °C).

1,1'-Dichloro-3,3'-dimethylbutane and 2-Chloro-3,3'-dimethyl-1-butene[48]

Into a 3-L, 3-necked flask equipped with a mechanical stirrer, a 500 mL dropping funnel, and a thermometer was placed 500 g (2.40 mol) of PCl_5. The flask was cooled to -5 °C and 240 g (2.40 mol) of pinacolone was added dropwise at a rate such that the pot temperature remained < 0 °C. After complete addition, the slurry was stirred at 0 °C for 4 h, then was stirred a additional 14 h at 25 °C. The resultant solution was poured into a mixture of ice (800 g) and ether (500 mL). The ether layer was separated, washed with 3 100 mL portions of water, and dried over $MgSO_4$. The ether volume was reduced by rotary evaporation with the formation of heavy white ppt. The ppt was collected by vacuum filtration and the filtrate saved. The ppt was sublimed (0.1 torr, 40 °C) to afford 110 g (70.9%) of 1,1'-dichloro-3,3'-dimethylbutane as colorless plates: mp 150-151 °C (lit.[48] 151-152 °C); ^{1}H NMR ($CDCl_3$) δ 2.16 (s, 3H), 1.24 (s, 9H) (matches reported[49]

spectrum). The ether was removed from the filtrate and the resultant red oil was distilled to afford 60.3 g (21.2%) of 2-chloro-3,3'-dimethyl-1-butene as a colorless liquid: bp 97-99 °C (lit.[48] 97-99 °C); ^{1}H NMR ($CDCl_3$) δ 5.15 (d, J = 1.6 Hz, 1H), 5.11 (d, J = 1.6 Hz, 1H), 1.19 (s, 9H) (matches reported[49] spectrum).

tert-Butylacetylene[48,49]

A 250 mL 2-necked flask equipped with a stir bar, a reflux condenser, and a 100 mL dropping funnel was charged with a solution of 38.0 g (339 mmol) of KO^{t}Bu in 80 mL of DMSO. To this solution was added dropwise a solution of 25.0 g (161 mmol) of 1,1'-dichloro-3,3'-dimethylbutane in 25 mL of DMSO over 1 h. After heating at 100 °C for 4 h, the reflux condenser was replaced with a distillation head and the low boiling products (<80 °C) were removed. The crude distillate was fractionally distilled on a spinning band distillation apparatus. The fraction (11.0 g, 86%) collected between 36-38 °C (lit.[48] bp 36.5-38.5 °C) was saved: ^{1}H NMR ($CDCl_3$) δ 2.10 (s, 3H), 1.17 (s, 9H) (matches reported[50,51] spectrum). Note that 2-chloro-3,3'-dimethyl-1-butene can also be used in this procedure.

1,3,5,7-Tetra-*tert*-butyl-*syn*-tricyclo[4.2.0.0^{2,5}]octadiene (8)[52]

To 26.67 g (100 mmol) of $AlBr_3$ in a 250 mL 1-necked Schlenk flask equipped with a magnetic stir bar and capped with a septum was added 100 mL of CH_2Cl_2 (precooled to -78°C) and the resultant slurry was cooled to -90 °C. A solution of 8.22 g (100 mmol) of *tert*-butylacetylene in 10 mL of CH_2Cl_2 was added dropwise by syringe over 1 h. The solution was warmed to -78 °C and stirred for 30 min. Into this solution was cannulated 42 mL (300 mmol) of cold (-78 °C) TEA, and the resultant slurry was warmed slowly to room temperature. The ppt was collected by vacuum filtration and washed with CH_2Cl_2. The filtrate was washed with 2 50 mL portions of saturated NH_4Cl and 2 50 mL portions of water. The organic layers were combined, dried over $MgSO_4$, and evaporated to

dryness. The crude product was purified by flash chromatography (pentane, 150 mesh alumina) to yield 6.5 g (79%) of **8** as a colorless oil: R_f (pentane, silica tlc) = 0.95; ^1H NMR ($CDCl_3$) δ 5.63 (d, J = 3.3 Hz, 2H), 2.75 (d, J = 3.3 Hz, 2H), 0.97 (s, 18 H), 0.88 (s, 18 H) (matches previously reported[48,10] spectra).

1,3,5,7-Tetra-*tert*-butylcyclooctatetraene (11)

A solution of 2.0 g (6.09 mmol) of **8** in 30 mL of DMF was heated at reflux (153 °C) for 12 h, cooled to room temperature, and poured into 200 mL of a 1:1 mixture of pentane and water. The pentane layer was collected and washed with 4 50 mL portions of water. The combined pentane layers were dried over $MgSO_4$ and evaporated to dryness. The crude product was purified by flash chromatography (pentane, 150 mesh alumina) to yield 1.2 g (60%) of **11** as a colorless oil. This material was used for subsequent reactions. Further purification by prep. gc gave material that was pure by ^1H NMR standards: ^1H NMR ($CDCl_3$) d 5.67 (s, 4H), 1.52 (s, 36H) (matches previously reported[10] spectrum).

1,3,5,7-Tetraisopropyl-*syn*-tricyclo[4.2.0.0^{2,5}]octadiene (12)

Following the procedure for the synthesis of **8** above, 3.41 g (50 mmol) of isopropylacetylene yielded after chromatography 2.3 g (68%) of **12** as a colorless oil: R_f (pentane, silica tlc) = 0.95; ^1H NMR ($CDCl_3$) δ 5.62 (dd, J = 2.5 Hz, 2H), 2.44 (d, J = 2.5 Hz, 2H), 2.30 (m, 2H), 1.74 (m, J = 6.6 Hz, 2H), 1.02 (d, J = 6.6 Hz, 12 H) 0.93 (d, J = 6.6 Hz, 6 H), 0.89 (d, J = 6.6 Hz, 6 H).

1,3,5,7-Tetraisopropylcyclooctatetraene (6)

Following the procedure for **4** above, 2.0 g (7.3 mmol) of **5** yielded, after chromatography, 1.4 g (70%) of **6** as a colorless oil: ^1H NMR ($CDCl_3$) δ 5.45 (s, 4H), 2.21 (m, J = 6.8 Hz, 4H), 0.934 (d, 6.9 Hz, 12H), 0.925 (d, J = 6.8 Hz, 12 H).

1,3,5,7-Tetra-*n*-butylcyclooctatetraene (16) and

1,2,5,6-Tetra-*n*-butylcyclooctatetraene (17)

Following the procedure for the synthesis of **8** above, 3.41 g (50 mmol) of *n*-butylacetylene yielded after chromatography 1.9 g (56%) of a mixture of **14** and **15** as a colorless oil: R_f (pentane, silica tlc) = 0.95, 0.90. This material was heated at reflux in DMF for 5 h and worked up as described for **11** above to afford after chromatography 1.4 g (41% from *n*-butylacetylene) of a 1:3.4 mixture of **16** and **17**: ^{1}H NMR of **16** ($CDCl_3$) δ 6.22 (s, 4H), 2.45 (t, J = 8 Hz, 2H), 0.9 (overlapping m); ^{1}H NMR of **17** ($CDCl_3$) δ 6.80 (s, 2H), 6.72 (s, 2H), 2.52 (t, J = 8 Hz, 2H), 0.9 (overlapping m).

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CHAPTER 3

Half-Sandwich Complexes Bearing Substituted [8]Annulene Ligands

Introduction

An account of the development of a variety of synthetic approaches to mono([8]annulene)uranium(IV) half-sandwich complexes can be found in the introductory section of Chapter 1 of this Thesis. Two complementary synthetic approaches to this class of compounds have emerged from these studies. The first approach is the "direct" preparation from UCl_3 and an appropriate cyclooctatetraene. This method is described in some detail in Chapter 1 in the preparation of $(C_8H_8)UCl_2(THF)_2$ (**1**). A second, "indirect" approach, discussed briefly in Chapter 1, involves selective derivatization of uranocenes through reaction with protic acids. As will be seen, neither of these approaches provides sufficient generality to allow ready synthesis of mono([8]annulene) uranium complexes from available substituted cyclooctatetraenes. This chapter details both the extension of the direct synthetic approach to silyl-substituted cyclooctatetraenes as well as the development of two novel half-sandwich syntheses. Application of one of these three synthetic approaches now allows syntheses of mono([8]annulene)uranium(IV) complexes from a wide variety of substituted cyclooctatetraenes.

As described in Chapter 1, direct reduction of cyclooctatetraene by UCl_3 affords the mono([8]annulene) half-sandwich complex **1** in excellent yield. For the preparation of half-sandwich complexes bearing substituted [8]annulene ligands, however, this method is of limited utility. The approach is restricted to cyclooctatetraenes with relatively low reduction potentials, at or below that of cyclooctatetraene itself (-1.89 V vs SCE in DMF[1a], -1.98 V vs SCE in THF[1b]). This limitation is particularly severe as the majority of commonly available substituted cyclooctatetraenes contain simple alkyl- or aryl

substituents; these cyclooctatetraenes have reduction potentials considerably higher than that of cyclooctatetraene [e.g. 1,3,5,7-tetramethylcyclooctatetraene (1,3,5,7-TMCOT): -2.11 V vs. SCE in DMF[1a]]. Reduction potentials of substituted cyclooctatetraenes are generally higher than that of unsubstituted cyclooctatetraene as a result of destabilizing steric interactions in the planar dianion between the substituent and α-ring hydrogens. These destabilizing interactions can be mitigated to some degree by using ring substituents that stabilize the negative charge of the dianion. As an example, note that UCl_3 does not react with *n*-butylcyclooctatetraene but does reduce *m*-fluorophenylcyclooctatetraene to form the corresponding substituted half-sandwich complex.[2] Here the inductive stabilization of the dianion by the electron-withdrawing fluoro-substituted phenyl group apparently compensates for the steric destabilization of ring substitution. While syntheses of cyclooctatetraenes bearing bulky, electron-withdrawing substituents can be imagined, in particular by utilizing the synthetic methodologies described in Chapter 2, their preparations are not straightforward. Thus this direct method is not particularly amenable to the syntheses of half-sandwich complexes bearing bulky [8]annulene ligands.

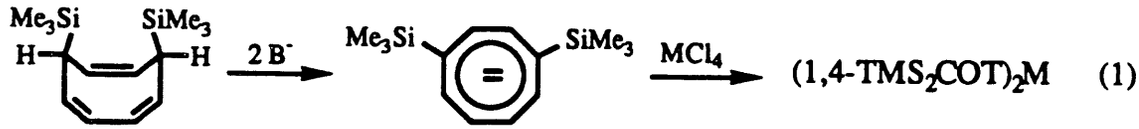
Removal by protonation of a single ring of uranocenes has been explored[3] by previous workers in these labs as another approach to mono([8]annulene) uranium complexes. This indirect method has been applied in the low-yield (<20%) synthesis of **1** and the moderate-yield (40%) synthesis of $(n\text{-}BuC_8H_7)UCl_2(THF)_x$ by reaction of the corresponding uranocenes with dry HCl in THF. The low yields of these reactions is attributable to a systematic failing of the approach: that the half-sandwich product of protonation of one ring of a uranocene is itself more reactive toward acid than its uranocene predecessor. This is presumably the result of the higher accessibility of the metal center in the mono-ring complexes. Compare the half-lives in 1 M H_2O/THF of uranocene (20 hours) with **1** (ca. 5 minutes).[2] It is possible that this limitation could be overcome by running the protonation reaction in a non-coordinating solvent such as pentane in which the mono-ring product is insoluble, thereby protecting it from further protonation (*vida infra*).

However, this reaction suffers a second limitation that uranocenes bearing even moderately bulky [8]annulene ligands are quite stable to acid. For example, the half-life of 1,1'-di-*tert*-butyluranocene in 1 M H_2O/THF increases to over five days. Moreover, more highly substituted uranocenes are quite unreactive toward moderately strong acids (e.g. trifluoroacetic acid).[2] The reactivity of highly substituted uranocenes toward HCl in either THF or other non-coordinating solvents is not known. It is likely that the rate of reaction is dependent on the degree and type of ring substitution, and that reaction may be prohibitively slow for uranocenes bearing bulky [8]annulene ligands. These potential problems aside, it is clear that selective removal of a single [8]annulene ring from uranocenes is a viable and potentially general approach to the synthesis of uranium half-sandwich complexes bearing substituted [8]annulene rings. As will be detailed later in this Chapter, slight modification of this approach - selective oxidation, rather than protonation, of a single ring of uranocenes - allows full exploitation of this synthetic method.

The Direct Synthesis of $(1,4\text{-}TMS_2COT)UCl_2(THF)_x$

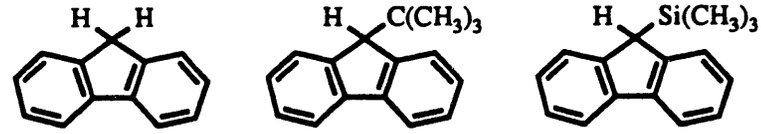
Rational For Using Silyl-substituted Cyclooctatetraenes in Half-sandwich Syntheses

In 1975 Bellema and Davison[4] reported the facile synthesis of 1,4-bis(trimethylsilyl)-2,5,7-cyclooctatriene (1,4-TMS_2COTriene) through quenching of cyclooctatetraene dianion with trimethylsilyl chloride. Recently Cloke[5] used 1,4-TMS_2COTriene as the starting material for the syntheses of 1,1',4,4'-tetrakis(trimethylsilyl)uranocene, the corresponding bis(borohydride) uranium half-sandwich complex, as well as several other related compounds. In these labs, Jensen[6] has similarly used 1,4-TMS_2COTriene in the syntheses of the the analogous cerate, $K[(1,4\text{-}TMS_2COT)_2Ce]$, and cerocene, $(1,4\text{-}TMS_2COT)_2Ce$, complexes. Each of these syntheses featured deprotonation of 1,4-TMS_2COTriene to the dianion followed by reaction with an appropriate metal chloride (Eq. 1.).



(1)

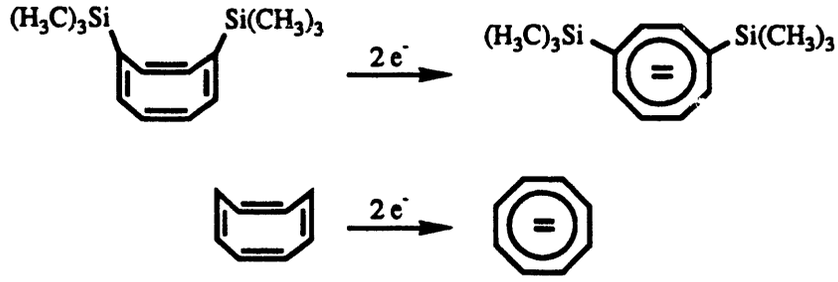
Isolation of the neutral 1,4-bis(trimethylsilyl)cyclooctatetraene (1,4-TMS_2COT) through oxidation of 1,4-TMS_2COT dianion with I_2 is described in Chapter 2. It was hoped that silyl-substituted cyclooctatetraenes would serve as appropriate ligands for the direct synthesis of uranium half-sandwich complexes, by virtue of the anticipated stabilization of the negative charge of the cyclooctatetraene dianion by the α-silyl substituents. As evidence of this stabilization, note that relative to hydrocarbon analogs, α-trimethylsilyl substitution results in an increase in the acidity of 2-3 pK_a units for delocalized carbanions. Compare the pK_a values in THF for the cesium salts of fluorene[7] (22.90), 9-(*tert*-butyl)fluorene[7] (24.39), and 9-(trimethylsilyl)fluorene[8] (21.32) (Figure 1).



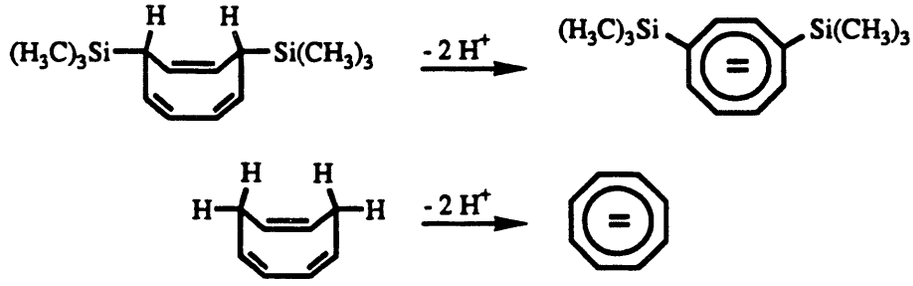
$pK_{Cs/THF}$ = 22.90 24.39 21.32

Figure 1. pK_a values for fluorene and substituted fluorenes

Strictly speaking, one cannot directly compare the effect of silyl substitution on carbon acidity with the effect on reduction potential of a neutral species. One should compare the reduction potentials of substituted versus unsubstituted cyclooctatetraenes:



rather than the difference in pK_a between substituted and unsubstituted cyclooctatrienes:



However, it is likely that the effects of silyl substitution on the ground states of both systems are approximately the same. For the present purposes, the qualitative correlation between the two processes is sufficient.

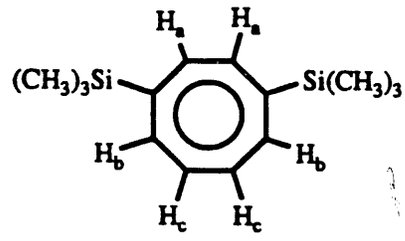
Synthesis of (1,4-TMS_2COT)$UCl_2(THF)_x$

Reaction of 1,4-TMS_2COT with UCl_4 and excess NaH in THF at room temperature (standard half-sandwich reaction conditions, see Chapter 1) afforded (1,4-$TMS_2COT)UCl_2(THF)_x$ (**2**) in moderate yield (Eq. 2).

$$1,4\text{-}TMS_2COT + UCl_4 + \text{xs NaH} \xrightarrow{THF} \underset{\mathbf{2}}{(1,4\text{-}TMS_2COT)UCl_2(THF)_x} \qquad (2)$$

There was generally more uranocene formation in this reaction than in the reaction with unsubstituted cyclooctatetraene. However, the high solubility of $(1,4\text{-}TMS_2COT)_2U$ in hexane rendered it easily separable from the mono-ring compound. Crystalline material was isolable from this reaction, but solvent loss was rapid even at ambient pressure (see Chapter 1 for a discussion of solvent loss associated with **1**) Accurate analyses were complicated by variable THF content in the solid state. Desolvated **2** is slightly soluble in toluene and insoluble in hexane.

The ^1H NMR of **2** in THF-d_8 at 30 °C shows a singlet for the trimethylsilyl protons and three peaks of equal integration for the ring protons in an overall integration ratio of 9:1:1:1. This is indicative of the following substitution pattern:



This pattern is observed in both 1,1',4,4'-tetra-*tert*-butyluranocene[9] (above -30 °C) and 1,1',4,4'-tetrakis(trimethylsilyl)uranocene.[5] The linewidths of the ring protons of **2** are considerably more narrow (23-29 Hz) than those of $(1,4\text{-}TMS_2COT)_2U$. Splitting of H_b and H_c is just resolved, allowing distinction of H_a (a singlet) from H_b and H_c (doublets). The upfield shift of the trimethylsilyl resonance (-3.15 ppm) is less pronounced than in $(1,4\text{-}TMS_2COT)_2U$ (-9.90 ppm) and in $(1,4\text{-}TMS_2COT)U(BH_4)_2$ (-7.78 ppm). See below for a more detailed discussion of the ^1H NMR chemical shift values for the trimethylsilyl protons in **2** and related silyl-substituted [8]annulene uranium complexes.

Syntheses of Mono-Ring Uranium Compounds Through Selective Oxidation of a Single Ring of Uranocenes

Chemical Oxidation of Uranocenes

The redox behavior of uranocenes with respect to both oxidation and reduction has been investigated in these and other labs. Reversible U(IV)/U(III) processes have been established,[10] as has isolation and characterization[11] of bis([8]annulene) U(III) complexes. A study[12] of the electrochemical oxidation of uranocene by Pagni revealed complicated, irreversible behavior. Some preliminary studies were undertaken to explore the possibility of isolating U(VI) or U(VII) [8]annulene complexes from chemical oxidations of uranocenes. It was found that reaction of substituted uranocenes with two-electron oxidants I_2 and Br_2 and the one-electron oxidant TCNQ in THF led, not to higher-valent uranium complexes, but to the rapid decomposition of the uranocenes and the liberation of neutral cyclooctatetraenes (Eq. 2).

$$(RCOT)_2U + Ox \not\longrightarrow Ox[(RCOT)_2U]^+$$
$$\xrightarrow{THF} 2\,RCOT + U(Ox)_4(THF)_X \qquad (2)$$

For reactions with I_2 and Br_2, the nature of the uranium-containing byproducts [presumably $UI_4(THF)_x$ and $UBr_4(THF)_x$] were not investigated. The product of oxidation with TCNQ was isolated as the tetrakis uranium salt $U(TCNQ)_4$. Interestingly, the rate of decomposition of the uranocenes was found to be qualitatively invariant with the steric bulk of the [8]annulene rings. This is in contrast to the marked dependence on the steric and electronic properties of ring substituents in the acidolysis of uranocenes (discussed briefly above). Hydrolysis of uranocenes is thought to involve pre-coordination of water followed by proton transfer to the [8]annulene rings; the effect of ring substitution

on the rate of hydrolysis can be easily rationalized within this mechanism. While the mechanism of reaction of uranocenes with one-electron oxidants can only be the subject of speculation, one can infer that it involves a rate-determining step that is either extremely rapid, or relatively insensitive to the nature of ring substitution, or both. For these highly ionic species, is not expected that ring substituents will have a significant effect on rates of simple electron transfer. Eisenberg[13] has attempted to measure rates of electron transfer in self-exchange reactions of bis([8]annulene) U(IV) and U(III) complexes. He found that electron exchange could not be frozen out on the 500 MHz ^{1}H NMR time scale, implying very rapid rates of electron-transfer. He also found that ring substituents have little effect on the rate of electron transfer in related systems.

Oxidations in a Non-coordinating Solvent

Studies of thorium half-sandwich dichloride complexes bearing substituted [8]annulene rings [e.g. (1,4-^{t}Bu$_2$C$_8$H$_6$)ThCl$_2$][14] indicate that these complexes are very poorly soluble in non-coordinating solvents and virtually insoluble in non-polar solvents such as pentane. Bearing this in mind, and assuming that the solubility properties of the analogous uranium complexes are likely to be similar, it was thought that oxidation of uranocenes by I_2 or Br_2 in non-coordinating solvents might allow isolation of the intermediate mono([8]annulene) dihalide complexes. It was anticipated that the precipitation of the mono-ring complex would protect it from further oxidation to UX_4. This is indeed the case. Reaction of 1,1'-dimethyluranocene with I_2 in hexane results in the immediate precipitation of a red solid whose ^{1}H NMR is consistent with the mono-ring uranium(IV) diiodide, $(CH_3C_8H_7)UI_2$ (Eq. 3).

$$(CH_3C_8H_7)_2U + I_2 \xrightarrow{\text{hexane}} (CH_3C_8H_7)UI_2 \Downarrow + CH_3C_8H_7 \qquad (3)$$

Dimethyluranocene reacts with Br_2 in an analogous fashion to yield the dibromo half-sandwich, $(CH_3C_8H_7)UBr_2$ (Eq. 4).

$$(CH_3C_8H_7)_2U + Br_2 \xrightarrow{\text{hexane}} (CH_3C_8H_7)UBr_2\Downarrow + CH_3C_8H_7 \qquad (4)$$

This approach can be extended to uranocenes bearing bulky [8]annulene ligands for which selective ring protonation is probably not feasible. For example, (1,4-$TMS_2COT)_2U$ reacts instantly with both I_2 and Br_2 in pentane to generate what appears by ^1H NMR to be the corresponding half-sandwich dihalides (1,4-$TMS_2COT)UI_2$ and (1,4-$TMS_2COT)UBr_2$, respectively (Eq. 5).

$$(1,4\text{-}TMS_2COT)_2U + X_2 \xrightarrow{\text{pentane}} (1,4\text{-}TMS_2COT)UX_2\Downarrow + 1,4\text{-}TMS_2COT \qquad (5)$$
$$X = I, Br$$

The oxidation of uranocenes by Br_2 and I_2 in non-coordinating solvents represents the most general approach to the synthesis of mono([8]annulene)uranium dihalides developed to date. It is particularly amenable to the syntheses of half-sandwich complexes bearing substituted [8]annulene rings. An additional feature of this reaction is control of halide substituent. This capability should facilitate further study of the metathesis chemistry of this class of compounds. Single-ring oxidation of uranocenes may also allow entry into new classes of [8]annulene uranium complexes incorporating such ligands as oxo (through reactions with nitro- or nitrosobenzene) and sulfide (through oxidation with S_8). The controlled reaction of uranocenes with other easily reduced small molecules is also of interest.

Reactions of Very Bulky Cyclooctatetraene Dianions With UCl_4

*1,3,5,7-Tetra-*tert*-butylcyclooctatetraene Dianion*

The synthesis[15] of 1,3,5,7-tetra-*tert*-butylcyclooctatetraene (TTBCOT) as well as some preliminary studies[16] of the reaction of TTBCOT dianion with UCl_4 have been carried out by previous workers in these labs. This ligand system was not more fully investigated, not only because of the previous difficulty of synthesizing TTBCOT (four steps, 20% overall yield from *tert*-butylacetylene and pivaloyl chloride), but also because no organometallic products were isolated from the reaction of TTBCOT dianion and UCl_4. There were lingering questions about these reactions, however, and recent development of a high yield, two-step synthesis of TTBCOT from *tert*-butylacetylene (Chapter 2) has facilitated a reexamination of TTBCOT dianion as an organoactinide ligand precursor.

Reduction of TTBCOT to its dianion can be carried out in the standard fashion through reaction with potassium metal in THF. Cyclic voltametric measurements of the reduction of TTBCOT indicate that it has a very high reduction potential - too high to measure in DMF.[1a] Optimized structure calculations at the AM1 level bear this observation out. Large internal ring bond-angle alterations within the calculated structure of the planar dianion (133.3 ° and 136.8 °) indicate significant steric interactions between the *tert*-butyl substituents and α-ring hydrogens. The high reduction potential also manifests itself in the slow reaction with potassium; complete reaction requires stirring with excess potassium metal in THF for 24 hours. Addition of two equivalents of K_2TTBCOT to a THF solution of UCl_4 at room temperature (standard uranocene reaction conditions) resulted in formation of a black precipitate and a purple-colored solution. Examination of the THF-soluble material from this reaction by ^1H NMR did not reveal any resonances in the paramagnetic region of the spectrum. Neutral TTBCOT was the only characterizable product. The UV-Visible spectrum confirmed the presence of UCl_3. Evidently, K_2TTBCOT simply reduces UCl_4 to uranium metal and UCl_3. Repetition of the reaction by introducing the reactants at

-78 °C and allowing them to warm slowly to room temperature resulted in similar observations. So too did reaction of equimolar amounts of K_2TTBCOT and UCl_4 at room temperature.

The reaction of K_2TTBCOT with $ThCl_4$ was also examined. It was hoped that $ThCl_4$ might prove more resistant to reduction. However, reactions of K_2TTBCOT with both one-half and one equivalents of $ThCl_4$ in THF led only to isolation of neutral TTBCOT and an insoluble material assumed to be thorium metal.

1,3,5,7-Tetraisopropylcyclooctatetraene Dianion

In order to design a ligand system less reducing than TTBCOT dianion, other alkyl substituents were considered. Preliminary calculations showed that considerable stabilization of TTBCOT dianion could be afforded by removing one methyl from each of the *tert*-butyl substituents. The most stable conformation (at the AM1 level) of the resultant 1,3,5,7-tetraisopropylcyclooctatetraene (TIPCOT) dianion is one in which the methyl groups are locked above and below the plane of the ring, thereby diminishing steric interactions with α-ring hydrogens (Figure 2).

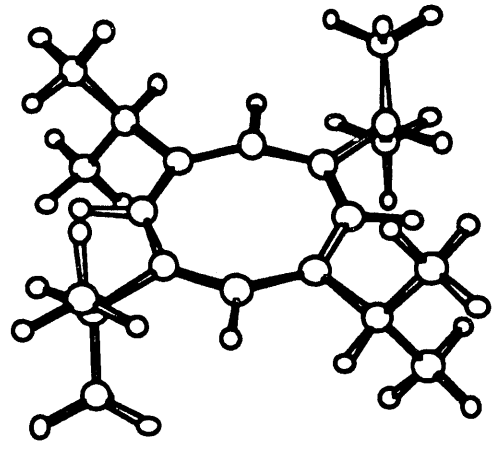


Figure 2. AM1 Optimized Structure of TIPCOT Dianion

The enhanced stability of TIPCOT dianion is also manifested in less pronounced internal bond-angle alternations in its calculated structure than those observed in the calculated structure of TTBCOT dianion. These results suggested that TIPCOT dianion, whose steric properties are quite similar to TTCOT (the calculated cone angles are 170 ° and 174 °, respectively), might prove to be considerably less reducing toward substrates such as UCl_4 and $ThCl_4$

The synthesis of TIPCOT was analogous to the synthesis of TTBCOT (see Chapter 2). Reduction to the dianion on reaction with potassium in THF was straightforward. The addition of K_2TIPCOT to one-half equivalent of UCl_4 in THF (in an attempt to synthesize the uranocene) resulted in the formation of a red solution from which a brown solid was isolated. This solid was moderately soluble in toluene but nearly insoluble in hexane. The ^1H NMR in THF-d_8 revealed three singlets at -6.03, -11.95, and -33.87 ppm, respectively, in a integration ratio of 6:1:1, indicative of formation of a uranium [8]annulene complex. These values can be compared to the isopropyl resonances of 1,1'-diisopropyluranocene[9] at -9.89 (CH_3) and -14.47 ppm (CH). While these NMR data are consistent with both the mono- and bis-ring complexes, there is other evidence to suggest that the product is the (TIPCOT)$UCl_2(THF)_x$ or half-sandwich complex. For example, the relatively narrow line width of the ring proton resonance (30 Hz) is suggestive of a mono-ring compound. Additionally, the material is highly reactive toward O_2; decomposition on exposure to the atmosphere is nearly instantaneous. This is in contrast to the high O_2-stability of highly substituted uranocenes, e.g. octaphenyluranocene, which is air stable. Furthermore, molecular models indicate that the large cone angle of TIPCOT dianion likely precludes bis-ring complex formation. Efforts to better characterize this product are currently underway.

Comparison of ^1H NMR Spectra of Mono- and Bis(1,4-TMS_2COT) U(IV) Complexes

The synthesis of (1,4-$TMS_2COT)_2U$ and the series of homologous half-sandwich dihalide complexes (1,4-$TMS_2COT)UX_2(THF)_x$, where X = Cl, Br, I allows comparison of the ^1H NMR chemical shifts of both the trimethylsilyl and ring protons (Table 1).

		Chemical Shifts (ppm) at 30 °C				
Compound	Solvent	TMS	Ring Protons			Ave. Ring
(1,4-$TMS_2COT)_2U$	PhMe	-9.96	-29.85	-35.54	-42.17	-35.85
"	THF	-9.26	-24.44	-38.21	-44.36	-35.67
(1,4-$TMS_2COT)U(BH_4)_2$	C_6D_6	-7.78	-29.85	-30.66	-32.61	-31.04
(1,4-$TMS_2COT)UCl_2$	THF	-3.15	-26.91	-36.35	-44.77	-36.01
(1,4-$TMS_2COT)UBr_2$	THF	-5.29	-24.08	-40.09	-41.93	-35.37
(1,4-$TMS_2COT)UI_2$	THF	-8.28	-31.16	-36.87	-43.06	-37.03

Table 1. ^1H NMR Chemical Shifts For 1,4-TMS_2COT U(IV) Complexes

The isotropic shift associated with a paramagnetic ion (in this case U^{4+}) is the sum of its component contact and pseudocontact shifts. The former is associated with the transfer of spin density from the unpaired electrons of the paramagnetic ion to the nucleus (in this case ^1H) being observed. The latter arises from a through space dipole-dipole interaction between the electron magnetic moment of the paramagnetic ion and the nuclear

magnetic moment of the observed nucleus. For actinide organometallic complexes, the contact ($\delta_{contact}$) and pseudocontact ($\delta_{pseudocontact}$) shifts take the form:

$$\delta_{contact} = \frac{A_i(g_J - 1)\chi}{Ng_J\beta_e g_N\beta_N}$$

$$\delta_{pseudocontact} = \frac{\chi_z - 1/2(\chi_x + \chi_y)}{3N} \cdot \frac{(3\cos^2\theta - 1)}{R^3} + \frac{(\chi_x - \chi_y)}{2N} \cdot \frac{\sin 2\theta \cos 2\omega}{R^3}$$

where A_i is the hyperfine coupling constant, g_J' is an electronic g value evaluated from a crystal field model, β_e is the Bohr magneton, g_N and β_N are the corresponding nuclear constants; θ, ω, and R are the angles and distance of the nucleus from the paramagnetic center and χ_x, χ_y and χ_z are the components of the magnetic susceptibility as depicted in Figure 2.

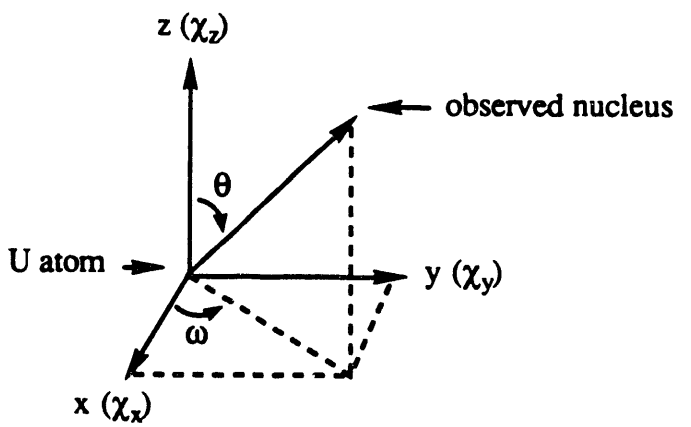


Figure 2. Coordinate System for Uranocenes

Edelstein[17] has proposed an approximation for the isotropic shifts in uranocenes:

$$\delta_{isotropic} = \delta_{pseudocontact} + \delta_{contact} = \frac{\chi_{\parallel} - \chi_{\perp}}{3} \cdot \frac{3\cos^2\theta - 1}{R^3} + \frac{A_i}{3} \cdot \frac{16g_j^2 b_e}{5kT} \qquad (6)$$

where the z axis is oriented along the ring-centroid-U-ring-centroid vector (Figure 2) and, as a result of the axial symmetry of uranocene, $\chi_{\parallel} = \chi_z$ and $\chi_{\perp} = \chi_x \approx \chi_y$. While this approximation applies only to uranocenes with three-fold or higher axial symmetry, both Luke[18] and Fischer[19] have demonstrated that for uranocenes of formally lower axial symmetry (e.g. 1,1-disubstituted and 1,1',4,4'-tetrasubstituted uranocenes) the perturbations of the crystal field imposed by the lower symmetry are sufficiently small that they can be ignored; to a first approximation, Eq. 6 applies. As will be seen below, this approximation does not apply to half-sandwich complexes.

Ring Proton Shifts

Significant effort has been directed toward determining the magnitudes of the contact and pseudocontact components of the isotropic shifts of ring protons in uranocene and substituted uranocenes.[8,18,20] Despite these efforts, a clear understanding of the relationship between ring substitution and the isotropic shifts of specific ring protons is as yet forthcoming. Even less is known about the isotropic shifts of ring protons in substituted half-sandwich complexes and no effort at serious analysis will be made here. It might be noted that there is no obvious pattern in the shifts of the ring protons in the series of halide-substituted 1,4-TMS_2COT half-sandwich complexes listed in Table 1. The average values are very similar, as has been observed in the weighted averages of the ring protons in substituted uranocenes.

Trimethylsilyl Proton Shifts

There is a clear trend in the magnitudes of the upfield shifts of trimethylsilyl protons in the complexes listed in Table 1. Because these protons are significantly removed from

the [8]annulene ring, the analysis of the origin of their paramagnetic shift is greatly simplified. In general, for a nucleus separated by three or more atoms from the paramagnetic center, it can be assumed that the contact shift component of the isotropic shift is effectively zero. Fischer[18] has applied this assumption to the trimethylsilyl protons in in 1,1'-bis(trimethylsilyl)uranocene, i.e. that the upfield shift of these protons arises only from the pseudocontact component of the isotropic shift and that the contact shift component can be neglected. He applied Edelstein's approximation of the ^1H isotropic shift in uranocenes and omitted the contact shift component. The isotropic shift then becomes:

$$\delta_{isotropic} = \delta_{pseudocontact} = \frac{\chi_{||} - \chi_{\perp}}{3} \cdot \frac{3\cos^2\theta - 1}{R^3} \qquad (7)$$

Fischer then used the observed values of $\delta_{isotropic}$ for the trimethylsilyl protons, coupled with calculated geometric parameters R and θ to estimate a value of $\chi_{||} - \chi_{\perp}$ for uranocenes

The absence of axial symmetry in mono[8]annulene complexes precludes application of Edelstein's approximation. The isotropic shifts of the trimethylsilyl protons in $(1,4\text{-}TMS_2COT)UX_2$ complexes instead takes the general form of $\delta_{pseudocontact}$:

$$\delta_{isotropic} = \frac{\chi_z - 1/2(\chi_x + \chi_y)}{3N} \cdot \frac{(3\cos^2\theta - 1)}{R^3} + \frac{(\chi_x - \chi_y)}{2N} \cdot \frac{\sin 2\theta \cos 2\omega}{R^3}$$

where the variables are as described above. For a given set of χ_x, χ_y and χ_z, the magnitude of the downfield shift of the trimethylsilyl protons is a function of the average distance, R, of the proton from uranium, and the angles θ and ω, as depicted in Figure 2. As such, these downfield shifts become a sensitive probe of molecular geometry. It is tempting to assume that the steady progression of isotropic shifts of the trimethylsilyl protons across the series of $1,4\text{-}TMS_2COT$ U(IV) dihalide complexes is a reflection of

increasing metal-ring distance. An increase in metal-ring-carbon distance produces changes in $1/R^3$, $\cos^2\theta - 1$, and $\cos 2\theta$ that are consistent with a decreasing isotropic shift. However, it is quite likely that the relative values of χ_x, χ_y and χ_z differ significantly through the series. Certainly the anisotropy in the x,y plane, as reflected in $\chi_x - \chi_y$ is dependent on the nature of the halide substituent. As such, attribution of changes in $\delta_{isotropic}$ to changes only in R and θ is rendered highly speculative. These differences may also reflect changes in halide substitution. Clearly, more data, including magnetic susceptibility measurements, crystal field calculations, and X-ray structural data are necessary to fully dissect the relative effects of geometric changes and magnetic anisotropy on the isotropic shifts observed in these complexes.

Acknowledgement

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Experimental

General experimental details can be found in Experimental section of Chapter 1, as are details of the treatment of NaH, and solvents tetrahydofuran (THF), diethyl ether (Et_2O), tetramethylethylenediamine (TMEDA), toluene, hexane, and pentane. Substituted cycloctatetraenes were synthesized by methods described in Chapter 2. 1,1'-dimethyluranocene was synthesized by a literature method. All other reagents, unless otherwise noted, were used as received from commercial suppliers.

[1,4-Bis(trimethylsilyl)[8]annulene]uranium(IV) Dichloride, (1,4-TMS_2COT)$UCl_2(THF)_x$ (2)

To a solution of 1.53 g (4.02 mmol) of UCl_4 in 40 mL of THF was added 0.50 g (21 mmol) of NaH and 1.00 g (4.02 mmol) of 1,4-TMS_2COT and the resultant slurry was stirred at 25 °C for 24 h. The solution was filtered and the THF was removed from the filtrate *in vacuo*. The solid was strirred in a solution of ca. 5 mL of TMEDA in 50 mL of hexane for 3 h. The solid was then collected by vacuum filtration and washed with hexane. Recrystallization of this material from 1:1 THF/toluene afforded red microcrystalline material that quickly desolvated on exposure to a glove box atmosphere. The solid was subjected to a dynamic vacuum (0.1 torr) for 24 h at 25 °C to afford 1.5 g (65%) of a brown solid. ^{1}H NMR (THF-d_8, 30 °C, 250 MHz) δ -3.15 (s, 18H), -26.91 (s, 2H), -36.35 (s, 2H), -44.77 (s, 2H). Anal. Calcd. for (1,4-TMS_2COT)$UCl_2(THF)_{0.21}$ ($C_{14.84}H_{27.68}Cl_2O_{0.21}Si_2U$): C, 30.83; H, 4.53. Found C, 30.80; H 4.54.

(Methyl[8]annulene)uranium(IV) Diiodide, $(CH_3C_8H_7)UI_2(THF)_x$

To a rapidly stirred solution of 0.50 g (1.05 mmol) of 1,1'-dimethyluranocene in 25 mL of hexane at 0 °C was added slowly via syringe a solution of 0.25 g (1.00 mmol) of I_2 in 25 mL of hexane. After complete addition the color of the solution was still faintly green. The

resultant ppt was collected by vacuum filtration and washed with hexane. This material was dried *in vacuo* for several hours to afford 0.5 g of a red solid. ^{1}H NMR (THF-d_8, 30 °C, 250 MHz) δ -8.75 (s, 3H), -31.52 (s, 1H), -32.63 (s, 2H), -38.48 (s, 2H), -39.31 (s, 2H).

(Methyl[8]annulene)uranium(IV) Dibromide, $(CH_3C_8H_7)UBr_2(THF)_x$

In a procedure analogous to that for the synthesis of $(CH_3C_8H_7)UI_2(THF)_x$ described above, 0.50 g (1.05 mmol) of 1,1'-dimethyluranocene was allowed to react with 0.16 g (1.00 mmol) of Br_2 to afford after drying 0.4 g of a brown solid. ^{1}H NMR (THF-d_8, 30 °C, 250 MHz) δ -7.44 (s, 3H), -29.45 (s, 1H), -31.07 (2, 2H), -34.10 (s, 2H), -42.31 (s, 2H).

1,1',4,4'-Tetra(trimethylsilyl)uranocene, $(1,4\text{-}TMS_2COT)_2U$[5]

To a solution of 3.00 g (12.0 mmol) of 1,4-TMS_2COT in 30 mL of THF was added 18 mL (25 mmol) of a 1.4 M solution of MeLi in Et_2O and the resultant solution was stirred for 18 h. This solution was added via cannula to a solution of 2.3 g (6.0 mmol) of UCl_4 in 20 mL of THF. After stirring for 2 h, this deep green solution was filtered and the THF and Et_2O were removed *in vacuo*. The resulting solid was extracted into pentane and the volume was reduced to ca. 25 mL. Cooling to -20 °C afforded 3.4 g (78%) of (1,4-$TMS_2COT)_2U$ as small green plates. ^{1}H NMR (Toluene-d_8, 30 °C, 250 MHz) δ -9.96 (s, 18H), -29.85 (s, 2H), -35.54 (s, 2H), -42.17 (s, 2H) (matches reported[5] spectrum).

[1,4-Bis(trimethylsilyl)[8]annulene]Uranium(IV) Diiodide, $(1,4\text{-}TMS_2COT)UI_2(THF)_x$

To a solution of 0.50 g (0.68 mmol) of (1,4-$TMS_2COT)_2U$ in 10 mL of pentane cooled to 0 °C was added via syringe a solution of 0.16 g (0.65 mmol) of I_2 in 20 mL of pentane. After complete addition, the ppt was allowed to settle and the supernatant liquid was

removed via syringe. The solid was washed with 2 10 mL portions of pentane and was dried *in vacuo* to afford 0.4 g of a red oil. ^{1}H NMR (THF-d_8, 30 °C, 250 MHz) δ -8.28 (s, 18H), -31.16 (s, 2H), -36.87 (s, 2H), -43.06 (s, 2H).

Mono[1,4-Di(trimethylsilyl)[8]annulene]Uranium(IV) Dibromide, (1,4-TMS_2COT)$UBr_2(THF)_x$

By a procedure analogous to the synthesis of (1,4-TMS_2COT)$UI_2(THF)_x$ described above, 0.10 g (0.65 mmol) of Br_2 in 20 mL of pentane was added to 0.50 g (0.68 mmol) of (1,4-TMS_2COT)$_2$U in 10 mL of pentane at 0 °C to afford after work up 0.3 g of a brown solid. ^{1}H NMR (THF-d_8, 30 °C, 250 MHz) δ -5.29 (s, 18H), -24.08 (s, 2H), -40.09 (s, 2H), -41.93 (s, 2H).

(1,3,5,7-Tetraisopropyl[8]annulene)uranium(IV) Dichloride, (TIPCOT)$UCl_2(THF)_x$

In 10 mL of THF at 25 °C, 0.2 g (0.73 mmol) of TIPCOT was stirred with 0.11 g (2.8 mmol) of freshly cut K metal for 24 h. The excess K was removed and the solution of K_2TIPCOT was added slowly to a solution of 0.27 g (0.70 mmol) of UCl_4 in 10 mL of THF. After stirring for 1 h, the solution was filtered and the THF was removed *in vacuo*. The resultant solid was washed with hexane, and extracted into hot toluene; the toluene solution was filtered and the toluene was distilled from the filtrate at reduced pressure to afford 0.2 g of a red solid. ^{1}H NMR (THF-d_8, 30 °C, 250 MHz) δ -6.03 (s, 24H), -11.95 (s, 4H), -33.87 (s, 4H).

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CHAPTER 4

Structural Effects in [8]Annulene Metal Complexes

Introduction

In the late 1970's Raymond published two papers[1] that undertook an analysis of the structural parameters of actinide and lanthanide cyclopentadienyl and [8]annulene complexes, including an assessment of the the structural manifestations of ionic and covalent bonding in these complexes. In order to facilitate direct comparison of metal-ligand bonding in a series of metal complexes containing the same ligand, he introduced the concept of a ligand "radius". Based on Pauling's definition[2] of the distance, R, between univalent metals and ligands in ionic compounds as the sum of the cationic and anionic radii:

$$R_{C\text{-}A} = r_C + r_A$$

Raymond proposed that this approach could be generalized to describe the bond distances in any ionic complexes, including those with multivalent metals, M, and polydentate and polyanionic ligands, L:

$$\text{M-L distance} = r_M + r_L$$

The ligand radius, r_L, is thus defined as the metal-ligand distance minus the metal ionic radius:

$$r_L = \text{M-L distance} - r_M$$

To determine values of ligand radii, metal-ligand distances were obtained from X-ray structural studies. For carbocyclic ligands such as cyclopentadienyl and cyclooctatetraene dianion, the metal-ligand distances were defined as the average metal-carbon bond distance. Metal ionic radii were taken from the tables of Shannon.[3] Raymond was thus able to generate a set of values of r_{Cp} and r_{COT} from a variety of metal complexes that were normalized for differences in metal charge and coordination number. This allowed direct

comparison of metal-ligand bonding among different metals in a variety of oxidation states and over a range of structural motifs. His conclusions include the following.

(1) Within a purely ionic model, a graph of metal ionic radius versus metal-ligand distance for a set of metal complexes should be linear with a slope equal to unity. For first-row transition metal Cp_2M complexes such a correlation did not exist. The deviation from linearity could be understood within a covalent bonding model. Metal ionic radii for divalent, six-coordinate metals decrease going from left to right across the first transition series. After Cp_2Fe, however, population of metal-ligand antibonding orbitals tends to increase the metal-ligand distance. This results in an anomalously high (as predicted by an ionic model) value of r_{Cp} for the later transition metal complexes. [This is also illustrated in the comparison of the metal-ligand distances in ferrocene[4] and ferrocenium[5] cation. The metal-carbon distance is shorter in ferrocene despite the fact that the ionic radius of six-coordinate Fe(III) is smaller than that of six-coordinate Fe(II). A rationalization based on a covalent model suggests that oxidation of ferrocene removes an electron from a metal-ligand bonding orbital, resulting in an increase in the metal-carbon distance.]

(2) Within lanthanide and actinide cyclopentadienyl complexes, there is a high correlation between metal ionic radius and metal-ligand distance. This results in a very small variation in the calculated values of r_{Cp}. Raymond argued that this constitutes structural evidence for the predominance of ionic bonding in lanthanide and actinide cyclopentadienyl complexes.

(3) There is little variation in values of r_{COT} among [8]annulene complexes of a wide variety of metals, including those of alkali metals, early transition metals, lanthanides, and actinides. Additionally, Raymond pointed out that the r_{COT} for $(C_8H_8)_2U$ is the same as that for $K_2C_8H_8$·(diglyme); this argues strongly that there is no structural evidence for covalency in lanthanide and actinide [8]annulene complexes.

Recently, Stockwell and Hanusa[6] updated the analysis of cyclopentadienyl complexes to include the large number of compounds structurally characterized since

Raymond's study was first published. They compiled an exhaustive survey of structural data of alkaline-earth and f-element cyclopentadienyl compounds and performed a statistical analysis on the cyclopentadienyl ligand radii of these complexes. They found that Raymond's simple ionic model is insufficient to rationalize all of the observed structural trends among these complexes. Regressive analysis indicated that metal-Cp distances showed a strong dependance on metal oxidation state. In fact, analysis of the structural trends of the complexes segregated by metal valency revealed that r_{Cp} (taken as 1.651 Å) is a strong predictor of metal-Cp distances only among divalent metal complexes. For tri- and tetradentate complexes, they found that there is not a simple correlation between metal ionic radius and metal-ligand distance. They concluded that for higher valent complexes both steric interactions among ligands as well as metal ionic radii are important in the determination of metal-ligand distances. Clearly, ligand-ligand interactions, which were not incorporated into Raymond's ionic model, must be considered in any structural analysis of metal-ligand bonding in lanthanide and actinide cyclopentadienyl complexes.

Analysis of [8]Annulene Metal Complexes

Modifications of Raymond's Analysis

We endeavor here to update Raymond's analysis of the structural parameters of [8]annulene metal complexes. In the ten years since his argument was presented, structural analyses of several additional [8]annulene complexes have been obtained. We have updated Raymond's analysis to include these additional structures. Data from representative structures are summarized in Table 1. In the discussion that follows, specific compounds are referred to by the number assigned to them in Table 1. Table 1 does not represent an exhaustive survey of [8]annulene complexes for which structural data is known; we have chosen to include only those compounds whose coordination numbers are relatively unambiguous. Metal coordination numbers are calculated as the sum of electron pairs involved in interaction with the metal center. Thus, cyclooctatetraene dianion

is considered to contribute five to the coordination number count whereas cyclopentadienyl anion contributes three. Neutral coordinating ligands contribute one per coordinating heteroatom. Structures containing agostic interactions or fractional coordination numbers were omitted from this analysis in order to facilitate direct comparison of structural parameters. Metal ionic radii are taken from the tables of Shannon.[3] It should be noted that accurate ionic radii for some metals in some coordination numbers are not known. In his papers, Raymond calculated these metal radii from known radii at different coordination numbers using the relationship:[2]

$$\left(\frac{r_{II}}{r_I}\right) = \left(\frac{CN_{II}}{CN_I}\right)^{1/n-1}$$

where n is the Born exponent. We have found this method to be unsatisfactory as it often gives calculated metal radii that are discontinuous with radii at higher and lower coordination numbers. For metals considered in this analysis, plots of metal ionic radius versus metal coordination number are not linear; they tend to flatten out at high coordination numbers. However, these data can be fit to second-order polynomial equations from which metal ionic radii at unknown coordination numbers can be readily extrapolated. For example, a plot of ionic radius versus coordination number for U(IV) (Figure 1) gives an extrapolated value of 1.09 Å for the ionic radius of ten-coordinate U(IV).

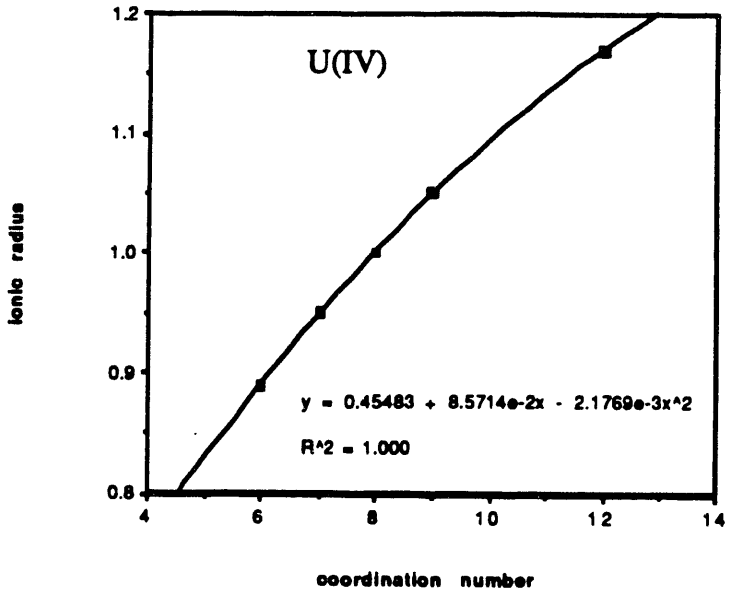

Figure 1. Graph of Ionic Radius Versus CN For U(IV)

A final note on comparisons on structurally related compounds. We compare structures of bis[8]annulene complexes differing both in oxidation state of the central metal and in substitution of the [8]annulene rings with the implicit assumption that substitution on the rings does not significantly affect the parameters we will be comparing, i.e. average metal-ligand bond distances. As evidence of this assumption, note that the structures of substituted uranocenes **2** and **3** (Table 1 below) are essentially the same as that of unsubstituted uranocene (**1**) with respect to metal-ring carbon distance and ring planarity. In the structures of all complexes containing substituted [8]annulene ligands (**2, 3, 5, 12, 24**) the ring C-C(R)-C is contracted from the normal value of 135° to 130 - 132° and the substituents are to differing degrees bent out of the plane. MNDO optimized structures of methylcyclooctatetraene dianion and tetramethylcyclooctatetraene dianion reproduce these ring C-C(CH_3)-C angle contractions; presumably they arise from enhanced steric interactions between the methyl group and adjacent ring hydrogens resulting from the rather

large interior angle of the 8-membered ring. A reduction of the ring angle results in separating adjacent substituents. In the comparison of metal structures that follows, this angle contraction has only a small effect on the average M-C bond distances.

Analysis of Compounds in Table 1

There is significantly greater variation in the values of r_{COT} in the complexes listed in Table 1 than within the set of complexes originally evaluated by Raymond. The range of r_{COT} reported in his original study was 1.49 - 1.60 Å. In this study, the range of values of r_{COT} derived from lanthanide, actinide, and early transition metal metal-carbon distances increases to 1.46 - 1.67 Å. If the r_{COT} values derived from K-carbon distances in Table 1 are included, this range further increases to 1.43 - 1.75 Å. While the range of values of r_{COT} is this study is quite large, it should be noted that within roughly homologous compounds there is much closer agreement. For example, the bis([8]annulene) uranium(IV), thorium(IV) and cerium(IV) complexes **1** through **5** show values of r_{COT} in the range 1.57 - 1.62 Å. Note also the similarity in values of r_{COT} within structurally related half-sandwich compounds **6** through **8** (1.63 - 1.64 Å). Similar agreement is evident in mixed-ring complexes **10** and **11** (1.66 and 1.67 Å), and in K-capped sandwich complexes **12** through **14** (1.48 - 1.51 Å). Greater variation is observed in the r_{COT} of mixed-ring sandwich complexes **16** through **19** (1.46 - 1.63 Å). Despite the increase in range of r_{COT} values for these complexes, the differences are not easily ascribable to greater or lesser degrees of covalent bonding. In fact, examination of these data leads one to concur with Raymond's conclusion that there is no structural evidence for covalent bonding in these compounds. Moreover, recognition of the importance of ligand-ligand interactions as well as long-range electrostatic repulsion allows rationalization of all significant variations in structural parameters for these compounds.

Steric and Electrostatic Repulsive Interactions

Closer examination of sets of structurally related compounds yields some interesting observations. First compare the bis([8]annulene) complexes **1** and **3** with their mono([8]annulene) derivatives **6**, **7** and **8**. The ionic radius of nine-coordinate U(IV) is approximately 0.04 Å smaller than that of ten-coordinate U(IV);[3] as the coordination number of the metal decreases from ten in the bis([8]annulene) complexes to nine in the mono([8]annulene) complexes, one would expect a shorter metal-carbon distance in the latter as a result of the smaller metal ionic radius. What is observed, however, is an increase in the metal-carbon distance on going from bis- to mono([8]annulene complexes.

Second, consider the K-C distances in compounds **12**, **13**, **14** and **24**. In each case the coordination environment of the potassium cation is identical; a cyclooctatetraene dianion coordinates one face of the potassium ion while a single diglyme molecule coordinates the other face. Given the identical nature of the coordination environment around potassium, one might expect the K-C distances to be approximately the same. However, in each of the sandwich complexes the K-C distance is significantly greater than that in **24**.

These observations can be rationalized by including effects of electrostatic interaction of more than just nearest neighbors. In an ionic model of **24** each potassium is attracted to the central dianion and is repelled by the other cation. In **12**, **13**, and **14**, however, the potassium is repelled by the more highly charged metal +3 cation, which also attracts the cyclooctatetraene-dianion more strongly. Accordingly, the K^+-ring distances are greater in the latter compounds. Similarly, in the half-sandwich compounds, **6**, **7** and **8** the metal-Cl and -O anion distances are less than the metal-ring distances and ring-ligand repulsions will be greater than the ring-ring repulsions in **1-4**. Additional repulsions in the half-sandwich compounds of **6** and **8** come from the dipoles of coordinated pyridine and THF, respectively.

Steric effects between ligands would not appear to be significant in the bis([8]annulene) metallocenes. Within experimental error the M-C distances in compounds

1, 2 and **3** are equal. The rings are approximately 4 Å apart and ring substituents can adopt staggered conformations if necessary to avoid unfavorable steric interactions. In more sterically congested systems, ring-ligand interactions may be more pronounced. Comparison of ten-coordinate **4** with **9** (whose coordination environment, while formally ten-coordinate, is significantly different from **4**) shows no significant difference in the cyclooctatetraene-dianion C-Th distances. However, comparison of ten-coordinate **9** with the related nine-coordinate compounds **10** and **11** indicates the likelihood of significant steric interactions when extremely bulky ligands such as bis(trimethylsilyl)amido and bis(trimethylsilyl)methyl are utilized. Steric factors aside, the Th-C distances in nine-coordinate **10** and **11** would be expected to be shorter than those in ten-coordinate **4** and **9**. That they are actually the same or slightly *longer* suggests that steric interactions are involved in **10** and **11**.

Other structural effects can be rationalized in the same manner. For the two eight-coordinate Lu^{3+} compounds **19** and **21**, **21** features a short bond to an aryl anion. The repulsion between this anion and the cyclooctatetraene-dianion ring results in a substantially longer Lu-ring distance than in **19**.

Conclusions

The analysis of the structural parameters of lanthanide and actinide [8]annulene metal complexes found in this Chapter extends both Raymond's original analysis, as well as the analysis of related cyclopentadienyl complexes by Stockwell and Hanusa. The central theses of both studies are affirmed herein: that there is no structural evidence for covalency in f-element [8]annulene complexes, and that ligand-ligand interactions play an important role in the structural parameters of these complexes. Moreover, this analysis concludes that all structural parameters in these complexes can be rationalized within a ionic model in which the disposition of ligands around a metal center is dictated by the total set of Coulombic interactions among ligands. Any evaluation of the structural parameters of such

complexes should bear in mind the importance of (a) the dependance of metal ionic radii on oxidation state and coordination number, (b) steric repulsion among ligands, particularly within high-valent metal complexes, and (c) potential through-space repulsive and attractive Coulombic interactions within the entire structural unit.

Table 1 Comparison of M-C Bond Lengths and r_{COT} for Several [8]annulene Complexes

Compound	M C.N.	M[a]	M-C Dist.	r_{metal}[b]	r_{COT}	Ref.
1. $U(C_8H_8)_2$	U^{4+}	10	2.647(4)	1.08	1.57	7
2. $U(Me_4C_8H_4)_2$	U^{4+}	10	2.658(4)	1.08	1.58	8
3. $U(C_8H_7SiMe_3)_2$	U^{4+}	10	2.659(13)	1.08	1.58(1)	9
4. $Th(C_8H_8)_2$	Th^{4+}	10	2.701(4)	1.13	1.57	10
5. $Ce(MeC_8H_7)_2$	Ce^{4+}	10	2.692(6)	1.07	1.62	11
6. $(C_8H_8)UCl_2(NC_5H_5)_2$	U^{4+}	9	2.683(6)	1.05	1.63	12
7. $(C_8H_8)U(acac)_2$	U^{4+}	9	2.694(4)	1.05	1.64	12
8. $(C_8H_8)ThCl_2(thf)_2$[c]	Th^{4+}	9	2.72(1) 2.71(2) 2.72(2)	1.09 1.09 1.09	1.63(1) 1.62(2) 1.63(2)	13
9. $(C_8H_8)(C_5Me_5)Th(\mu\text{-}Cl)_2$ $Mg(CH_2CMe_3)(thf)1/2(toluene)$[c]	Th^{4+}	10	2.739(33) 2.695(33)	1.13 1.13	1.61(3) 1.57(3)	14
10. $(C_8H_8)(C_5Me_5)Th[CH(SiMe_3)_2]$	Th^{4+}	9	2.746(10)	1.09	1.66(1)	14
11. $(C_8H_8)(C_5Me_5)Th[N(SiMe_3)_2]$	Th^{4+}	9	2.758(12)	1.09	1.67(1)	15
12. $[K(diglyme)][U(MeC_8H_7)_2]$[d]	U^{3+} U^{3+} K^{+}	10 10 8	2.732(8) 2.707(7) 3.263(14)	1.22 1.22 1.51	1.51 1.49 1.75(1)	11
13. $[K(diglyme)][Ce(C_8H_8)_2]$[d]	Ce^{3+} Ce^{3+} K^{+}	10 10 8	2.733(4) 2.746(6) 3.166(17)	1.25 1.25 1.51	1.48 1.50 1.66(2)	16
14. $[K(diglyme)][Yb(C_8H_8)_2]$[d]	Yb^{3+} Yb^{3+} K^{+}	10 10 8	2.610(8) 2.598(4) 3.191(14)	1.10 1.10 1.51	1.51 1.50 1.68(1)	11
15. $[K(glyme)]_2[Yb(C_8H_8)_2]$	Yb^{2+} K^{+}	10 7	2.741(10) 3.017(6)	1.26 1.46	1.48(1) 1.56	17
16. $(C_8H_8)Ti(C_5H_5)$	Ti^{3+}	8	2.323(4)	0.77	1.55	18

17. $(C_8H_8)Ti(C_5Me_5)$	Ti^{3+}	8	2.34(2)	0.77	1.57(2)	19
18. $(C_8H_8)Zr(C_5Me_5)$[c]	Zr^{3+}	8	2.42(2) 2.474(6)	0.84 0.84	1.58(2) 1.63	20
19. $(C_8H_8)Lu(C_5Me_5)$	Lu^{3+}	8	2.433(1)	0.977	1.46	21
20. $(C_8H_8)ZrCl_2(thf)$	Zr^{3+}	8	2.458(13)	0.84	1.62(1)	22
21. $(C_8H_8)Lu(o\text{-}C_6H_4CH_2NMe_2)\cdot(OC_4H_8)$	Lu^{3+}	8	2.549(15)	0.977	1.57(1)	23
22. $[(C_8H_8)CeCl(thf)_2]_2$	Ce^{3+}	9	2.710(2)	1.20	1.51	24
23. $(C_8H_8)Yb(C_5H_5N)_3\cdot 1/2(C_5H_5N)$	Yb^{2+}	8	2.64(3)	1.14	1.50	25
24. $[K(diglyme)]_2(Me_4C_8H_4)$	K^+	8	3.003(8)	1.51	1.49	26
25. $K_2C_8H_8\cdot(OC_4H_8)_3$	K^+	8	2.943(8)	1.51	1.43	27
26. $K_2C_8H_8\cdot(diglyme)$[d]	K^+	7 7	2.98(2) 3.05(2)	1.46 1.46	1.52(2) 1.59(2)	28

a) See text for discussion of coordination number calculation.
b) From the tables of Shannon.[3] For coordination numbers for which ionic radii are not known, values are obtained from second-order exponential interpolation from known coordination numbers.
c) The molecule adopts more than one conformation in the crystal.
d) The [8]annulene rings are in different coordination environments.

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