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Title: I. SYNTHESIS OF SUBSTITUTED CYCLOOCTATETRAENIDE

DIANIONS. II. CYCLOHEPTADIENYL COMPLEXES OF THE

d- AND f-TRANSITION ELEMENTS. III. REACTIONS OF

CYCLOHEXANONE WITH METAL VAPORS

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I. Lithium alkyl and aryl monosubstituted cyclooctatetraenide

dianions ($Li_2 C_8H_7$-R; R = methyl, n-butyl, sec-butyl, tert-butyl,

phenyl and benzyl) were synthesized by the reaction of the appropri-

ate organolithium reagent with cyclooctatetraene in diethyl ether or

tetrahydrofuran. The reaction occurred cleanly and with good yield

of lithium monosubstituted cyclooctatetraenide dianion at ambient or

lower temperature for all organolithium reagents studied except

tert-butyl-lithium. (TMEDA is needed as an activator for methyl-

lithium.) Substituted cyclooctatetraenide dianions were character-

ized by chemical reactions, i. e., oxidation, hydrolysis and deuter-

olysis, as well as, preparation of organometallic derivatives, sub-

stituted uranocenes. A two step mechanism for the reaction is pro-

posed which involves the addition of the organolithium reagent to

cyclooctatetraene followed by proton removal to yield the appropriate

ten-π electron aromatic dianion.

Several other alkyl organometallic compounds failed to produce

monosubstituted cyclooctatetraenide dianions on reacting with cyclo-

octatetraene. Lithium hexaalkyluranate(IV) complexes reacted with

cyclooctatetraene to give uranocene in good yield along with high

yields of coupled alkyl products.

II. The addition of lithium cycloheptadienide (LiC_7H_8-R;

R = hydrogen, methyl and n-butyl) to lanthanide and actinide chlorides

results in the facile formation of unstable cycloheptatrienyl trianion-

metal compounds. Characterization of the ten-π aromatic cyclohepta-

trienyl trianion (C_7H_6-R^{-3}) was made by identification of the organic

products resulting from chemical reactions of the coordinated ligand,

for example, hydrolysis, deuterolysis and oxidation, as well as,

spectroscopic characterization (^{1}H NMR) of paramagnetic uranium(IV)

compounds. Qualitative analysis of the paramagnetic ^{1}H NMR shifts

are discussed based on the assumption that metal-ligand bond dis-

tances and magnetic properties in cycloheptatrienyl-uranium(IV) com-

pounds are similar to those of uranocene. Formation of the cyclo-

heptatrienyl trianion is believed to occur by the loss of two methylene

protons from the metal coordinated cycloheptadienide ion. The role

of the lanthanide and acinide metal ions in cycloheptatrienyl trianion

formation is discussed.

III. Metal atom vapors of several d- and f-transition elements were cocondensed with cyclohexanone at -196 °C. Radical reduction of cyclohexanone to bicyclohexyl-1,1'diol, a pinacol, was observed for elements which are both highly electropositive and form strong metal oxygen bonds, for example, the early transition, lanthanide and actinide elements. High yields of aldol condensation products were produced along with a small amount of bicyclohexylidene. Metal atoms of the latter transition elements were much less reactive with cyclohexanone and did not yield a pinacol product.

Titanium clusters were prepared by codepositing titanium atoms with a large excess of solvent. Titanium clusters were less reactive than titanium atoms toward cyclohexanone radical reduction reactions. High surface area titanium powders produced by solution techniques, yield pinacols when cyclohexanone reacts in excess and further deoxygenate pinacolic dianions to olefins under conditions of limited stoichiometry.

Nitrobenzene was deoxygenatively coupled to azoxybenzene and azobenzene by lanthanide and actinide metal atoms.

I. Synthesis of Substituted Cyclooctatetraenide Dianions.
II. Cycloheptadienyl Complexes of the d- and
f-Transition Elements. III. Reactions of
Cyclohexanone with Metal Vapors.

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TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

I. SYNTHESIS OF SUBSTITUTED CYCLOOCTATETRAENIDE DIANIONS

INTRODUCTION

Many years ago Cope et al. reported that cyclooctatetraene reacts with organolithium compounds producing a complex mixture of products from which substituted cyclooctatetraenes may be isolated following hydrolysis.[1,2,3] Although this reaction has been used to prepare substituted cyclooctatetraenes, the usefulness of this reaction has been limited by the low yield of substituted cyclooctatetraene. In addition, other reaction products include an isomeric mixture of substituted cyclooctatrienes which must be separated by a time-consuming $AgNO_3$ extraction.

In our laboratory, 1,1'-di-n-butyluranocene[4] was isolated in good yield from a solution containing n-butyl-lithium, cyclooctatetraene and uranium(IV) tetrachloride. The dianion nature of the cyclooctatetraenyl ligand in the substituted uranocene suggested that the reaction between organolithium compounds and cyclooctatetraene proceeds to products different from those previously described. As a result, this reaction was reinvestigated.

Metallation of Olefinic Hydrocarbons by Organolithium Compounds

Organolithium compounds are strongly basic and may be used to remove (metallate) acidic protons from organic compounds.[5,6] Generally, olefinic hydrogen atoms are not sufficiently acidic to undergo metallation. Although hydrogen atoms adjacent to double bonds are more acidic than vinyl hydrogen atoms, allylic protons are not normally metallated by organolithium compounds. However, when a hydrogen atom is doubly allylic, simultaneously adjacent to two double bonds, organolithium compounds readily abstract the doubly allylic proton forming a delocalized carbanion,[6-10] for example, eq. 1-1.[7]

$$\text{(ring)} + \text{n-BuLi} \rightarrow \text{Li}^+ \text{(ring anion)} + \text{n BuH} \qquad (1\text{-}1)$$
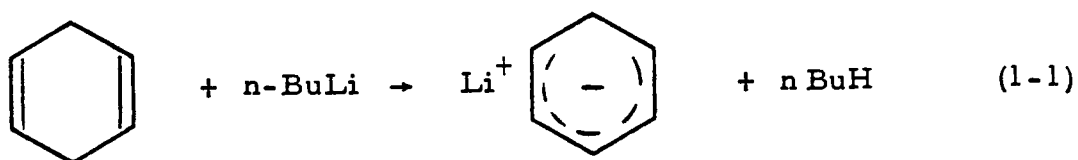
Carbon-hydrogen acidities are greatly increased when a methylene hydrogen atom is doubly allylic and the resulting anion is aromatic. Cyclopentadiene is easily deprotonated by organolithium compounds as well as many other bases, eq. 1-2.[6]

$$\text{(cyclopentadiene)} + \text{PhLi} \rightarrow \text{Li}^+ \text{(cyclopentadienyl anion)} + C_6H_6 \qquad (1\text{-}2)$$
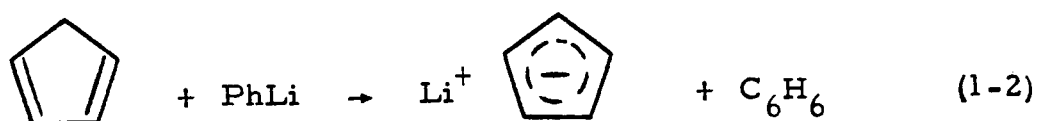
The metallation powers of organolithium reagents are greatly increased by the addition of coordinating tertiary amines.[5,6,11] For example, toluene and benzene are unreactive with n-butyl-lithium. However, in the presence of tetramethylethylenediamine (TMEDA), n-butyl-lithium rapidly and quantitatively metallates both toluene and benzene to benzyl-lithium and phenyl-lithium, respectively.[11]

The further removal of an allylic proton from a delocalized anion is an unfavorable reaction due to the increasingly negative π-orbital charge density in the resulting dianion. For olefins capable of forming anions with extensive charge delocalization or aromatic stabilization, however, olefinic dianion and trianion products may be prepared by multiple metallation reactions. TMEDA activated n-butyl-lithium is an effective metallating agent for the preparation of delocalized dianion and trianion compounds from alkenes.[12-15] In addition to requiring strongly basic conditions, multiple metallation reactions often require long reaction times, typically four to ten days, and proceed in low yield, approximately 40%. For olefins capable of forming aromatic anions, however, multiple metallation reactions are more facile.[14,15] Lithium cyclooctatetraenide dianion is produced in nearly quantitative yield by the multiple loss of protons from 1,3,6-cyclooctatriene or 1,5-cyclooctadiene to the base n-butyl-lithium and TMEDA, eq. 1-3.[15]

$$\text{(cyclooctatetraene)} + 2\ n\text{BuLi} \longrightarrow \text{Li}_2{}^+ \text{(cyclooctatetraene dianion, } -2\text{)} + 2\ n\text{BuH} \quad (1\text{-}3)$$
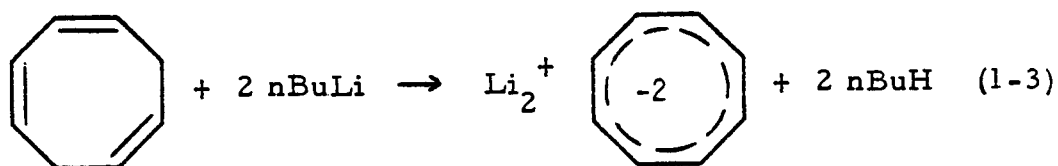
From these examples, it can be seen that although organolithium compounds are strong bases, proton removal from unsaturated hydrocarbons occurs with difficulty and only for the most acidic hydrogen atoms. In addition, reactive, acidic hydrogen atoms in alkenes are those which when lost result in the formation of highly delocalized or aromatic anions.

Addition of Organolithium Compounds to Carbon-Carbon Double Bonds

As discussed above, organolithium compounds are strongly basic; however, metallation is not the only reaction between organolithium compounds and unsaturated hydrocarbons. Alkenes undergo addition by organolithium reagents forming a new carbon-carbon bond and a new, more stable organolithium compound, eq. 1-4.[16]

$$H_2C{=}CH_2 + t\text{BuLi} \longrightarrow \text{LiCH}_2{-}CH_2{-}\underset{\underset{\textstyle CH_3}{|}}{\overset{\overset{\textstyle CH_3}{|}}{C}}{-}CH_3 \quad (1\text{-}4)$$
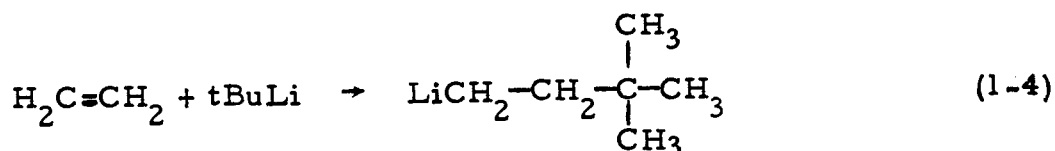
In the addition reaction, the localized carbon electron pair of the carbanion is a strong nucleophile attacking the unsaturated carbon of the alkene. The alkene, however, is not a good electrophile. As

a result, only the strongest nucleophiles attack the most reactive alkenes. For unconjugated alkenes, addition reactions are limited to attack of ethylene by tertiary and secondary alkyl lithium compounds.[16,17] The driving force for this reaction is the formation of the more stable primary alkyl lithium compound from the tertiary lithium compound. Alkyl substituents are electron donating and, thus, deactivate olefins toward nucleophilic attack. Ethylene is not only the most reactive unconjugated alkene, but it is the only isolated double bond, not activated by strain, which undergoes addition of organolithium compounds.[17]

Conjugated dienes and styrenes, on the other hand, are more reactive toward nucleophilic addition than unconjugated alkenes, although butadiene addition products are seldom isolated since butadiene is easily polymerized by organolithium compounds.[6] As with unconjugated alkenes, alkyl substitution decreases diene reactivity toward addition. Although nucleophilic addition by organolithium compounds is observed for monoalkylated butadiene derivatives, for example, isoprene, organolithium reagents fail to add to conjugated dienes with two or more alkyl substituents, for example, 1,3 cycloheptadiene.[7]

Addition reactions of highly conjugated olefins form extensively delocalized and often stable carbanions. For example, a phenyl

substituted cyclopentadienide derivative is produced from the reaction

between phenyl-lithium and dimethylfulvene, eq. 1-5.[18]

$$(1-5)$$
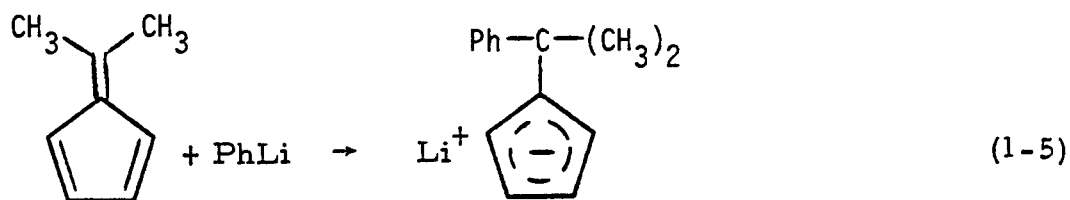
Also, nucleophilic addition of organolithium compounds to cyclo-

heptatriene forms lithium 6-substituted cycloheptadienide, eq. 1-6.[19]

$$(1-6)$$
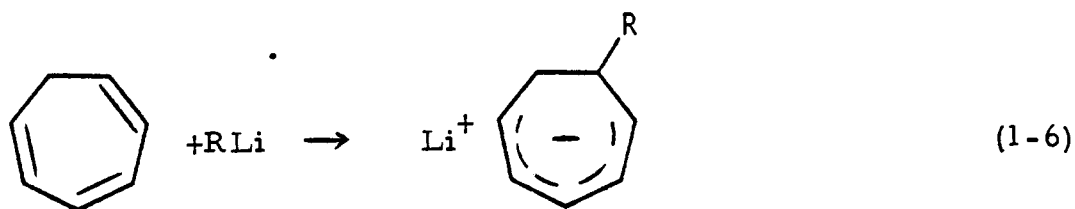
Finally, it should be noted that not all organolithium compounds

are equally good nucleophiles. For example, nucleophilic addition of

naphthalene is observed only for highly reactive alkyl organolithium

compounds, eq. 1-7. The rate of alkylation is a function of the alky-

lithium structure with tertiary alkyl > secondary alkyl > primary

alkyl.[20]

$$(1-7)$$
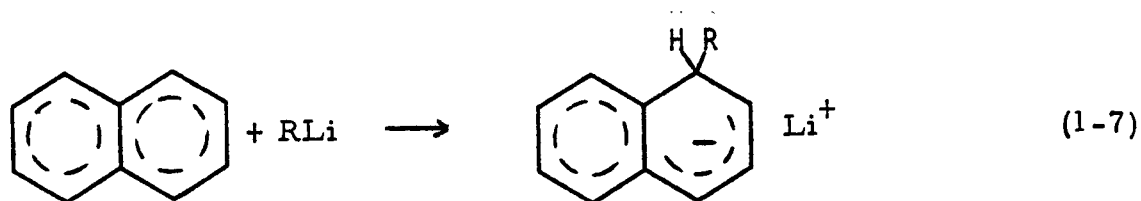
Kinetic rate measurements on 1, 1-diphenylethylene have been

used to determine the relative reactivities of organolithium compounds

toward styrene addition.[21, 22] Nucleophilic addition rates for diphenylethylene were benzyl > n-butyl > allyl > methyl > vinyl. From quantitative rate constant measurements, one estimates that n-butyl-lithium is three thousand times more reactive than methyl-lithium toward nucleophilic addition.[21]

Nucleophilic strengths of organolithium compounds have also been determined by equilibrium constant measurements for metal-halogen exchange reactions, eq. 1-8.[23]

$$RLi + R'I \longrightarrow RI + R'Li \qquad (1-8)$$
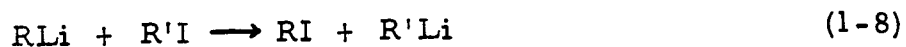
In the metal-halogen exchange equilibrium, the reaction occurs in the direction which forms the most stable, least reactive, organolithium compound. Organolithium reactivities are determined to be secondary alkyl > primary alkyl > cyclopropyl > phenyl > vinyl.

Organolithium nucleophilic reactivities are highly dependent on solvent conditions. Generally, nucleophilic addition rates are increased by strongly coordinating solvents according to the series TMEDA > THF > Et_2O > benzene > hexane. As a result, nucleophilic addition of an alkene by an organolithium compound may proceed in one solvent but not in another.

Previous Studies of Organolithium Compounds with Cyclooctatetraene

In 1950, aryl lithium compounds were first reported to react with cyclooctatetraene.[1] The reaction between two equivalents of cyclooctatetraene and one equivalent of phenyl-lithium in diethyl ether was believed to proceed by addition to yield lithium phenylcyclooctatrienide, eq. 1-9

$$(1-9)$$
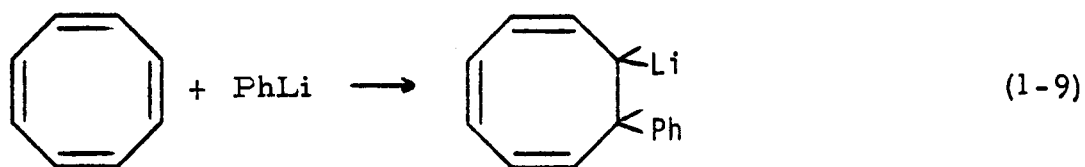
A mechanism was proposed in which the lithium phenylcyclooctatrienide was oxidized by the transfer of lithium hydride to a second equivalent of cyclooctatetraene, eq. 1-10.[2]

$$(1-10)$$
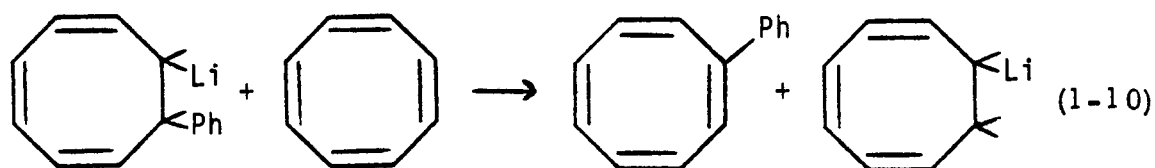
The products isolated from hydrolysis of the reaction mixture were phenylcyclooctatetraene, 27%, phenylcyclooctatriene, 9%, 1,3,5-cyclooctatriene and 1,3,6-cyclooctatriene, 36%, recovered cyclooctatetraene, 51%, and benzene. Similar reaction products have been observed for primary alkyl lithium compounds.[3]

Cyclooctatetraene and secondary alkyl lithium compounds, on the other hand, produced only substituted cyclooctatriene, rather than substituted cyclooctatetraene. In ether solution, methyl-lithium was unreactive with cyclooctatetraene.

From these examples, it is clear that many organolithium compounds add to cyclooctatetraene. In the following section, it will be shown that the proposed reaction intermediate is incorrect. In addition, the correct formulation of the reaction intermediate will make it possible to increase both product yields and selectivity.

RESULTS AND DISCUSSION

The Reaction of Cyclooctatetraene with Organolithium Compounds

When precautions are taken to rigorously exclude oxygen and water, alkyl and aryl lithium compounds react with cyclooctatetraene in ether solution to produce monosubstituted lithium cyclooctatetraenide dianions. The highest yields were obtained when two equivalents of organolithium compound were added to one equivalent of cyclooctatetraene. The substituted cyclooctatetraenide dianions were characterized by the chemical reactions in Figure 1-1.

For example, hydrolysis of lithium n-butylcyclooctatetraenide dianion gave an isomeric mixture of n-butylcyclooctatriene. No n-butylcyclooctatetraene was detected by either VPC or mass spectrometry. Mass spectral analysis of the deuterolysis products indicated that two deuterium atoms were present in the n-butylcyclooctatriene products, $C_8H_7D_2$-n-C_4H_9. In addition, singly deuterated n-butylcyclooctatriene, C_8H_8D-n-C_4H_9, accounted for less than one percent of the mass spectral ion intensity.

Oxidation of the lithium n-butylcyclooctatetraenide dianion with oxygen or air gave n-butylcyclooctatetraene as the only product. Formation of cyclooctatetraene by a two electron oxidation is highly characteristic of the ten-π aromatic cyclooctatetraenide dianion.[15,24]

R=methyl
R=n-butyl
R=sec-butyl
R=t-butyl
R=phenyl
R=benzyl
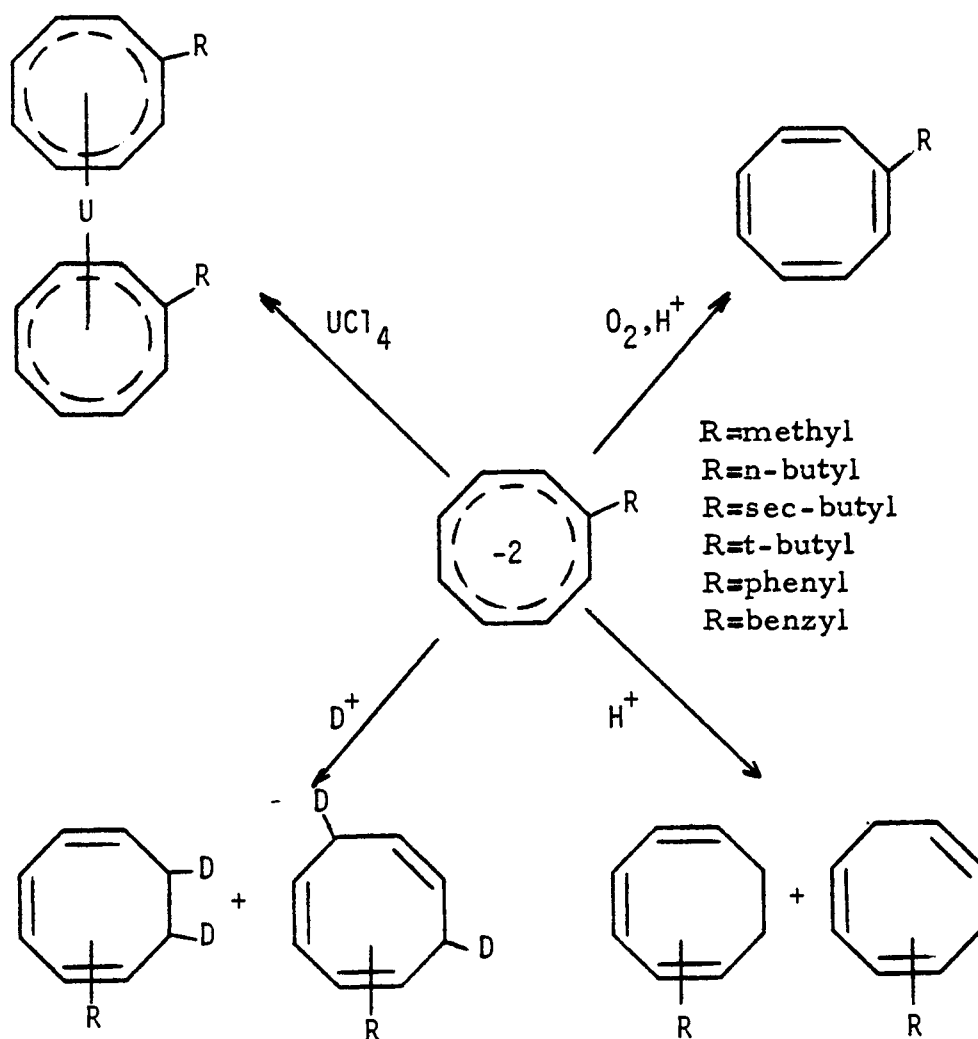
Figure 1-1.   Characterization of Substituted
Cyclooctatetraenide Dianions.

Substituted cyclooctatetraenide dianion complexes of uranium(IV), uranocenes, have been previously synthesized.[4,25] In addition, substituted uranocenes are stable, when protected from oxygen, and display highly unique, characteristic spectra and chemical reactions. The addition of one equivalent of uranium(IV) tetrachloride to two equivalents of lithium n-butylcyclooctatetraenide dianion produced 1,1'-di-n-butyluranocene in good yield which was identified by ^{1}HNMR, infrared, visible and mass spectrometry, as well as by its reaction with nitrobenzene. Uranocene is the only organometallic compound known to react with nitrobenzene yielding azobenzene and cyclooctatetraene.[26]

Reaction times and yields, based on oxidation products of the corresponding dianion, are listed in Table 1-1. Reaction rates for the formation of lithium substituted cyclooctatetraenide dianions were in the order tert-butyl > benzyl(TMEDA) > sec-butyl > n-butyl > methyl(TMEDA) > phenyl ≫ methyl. Methyl lithium reacted in trace amounts without activation by TMEDA. The order of reactivity is similar to that determined for nucleophilic addition of organolithium compounds discussed above. Several other nucleophiles were tested for reactivity with cyclooctatetraene. No reaction was observed for lithium cyclopentadienide, lithium phenyl acetylide, vinyl-lithium, lithium ethoxide or lithium dimethylamide.

For most of the reactions studied, little side product formation

Table 1-1. REACTION DATA FOR MONOSUBSTITUTED CYCLOOCTATETRAENIDE DIANIONS

Compound	Temperature	Solvent	Time for Complete Reaction	Yield[a]
methylcyclooctatetraene[b]	25 °C	Et_2O	18 hours	60%
n-butylcyclooctatetraene	25 °C	Et_2O	45 min	70%
sec-butycyclooctatetraene	0 °C	Et_2O	30 min	51%
t-butylcyclooctatetraene	-78 °C	Et_2O/pentane	5 min	45%
phenylcyclooctatetraene	25 °C	Et_2O	36 hours	76%
benzylcyclooctatetraene	0 °C	THF	5 min	60%

[a] Based on O_2 oxidation to the monosubstituted cyclooctatetraene followed by hydrolysis. All yields are based on VPC data.

[b] 1.2 mole ratio $TMEDA/CH_3Li$.

accompanied substituted dianion formation. No disubstituted products

were observed for any of the organolithium compounds with the excep-

tion of t-butyl-lithium. In the case of t-butyl-lithium, two, disubsti-

tuted, non-lithium containing isomers were produced, as well as,

lithium t-butylcyclooctatetraenide dianion (see Experimental). With

the exception of methyl-lithium, all reactions produced approximately

one to two percent unsubstituted lithium cyclooctatetraenide dianion.

For methyl-lithium, thirty percent of the cyclooctatetraene was con-

verted to lithium cyclooctatetraenide dianion.

A possible mechanism for the formation of substituted cyclo-

octatetraenide dianions by the reaction of cyclooctatetraene with

organolithium compounds is given in equations 1-11 and 1-12.

$$\text{COT} + RLi \longrightarrow Li^+ \text{[C}_8\text{H}_8\text{R]}^- \qquad (1\text{-}11)$$

$$Li^+ \text{[C}_8\text{H}_8\text{R]}^- + RLi \longrightarrow Li^+_2 \text{[C}_8\text{H}_7\text{R]}^{-2} + RH \qquad (1\text{-}12)$$
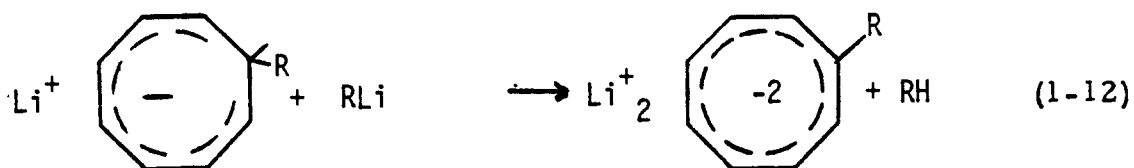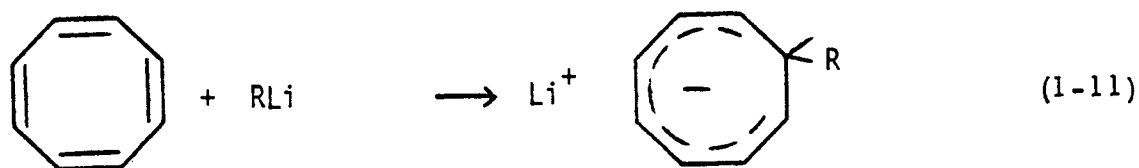
The first step of the mechanism, eq. 1-11, proceeds as a

nucleophilic attack of the organolithium compound on a cyclooctatetra-

ene double bond forming the delocalized lithium 8-substituted

cyclooctatrienide. The second step of the mechanism, eq. 1-12, requires a second equivalent of organolithium compound to abstract a proton from the cyclooctatrienide intermediate to yield the ten-π electron substituted cyclooctatetraenide dianion.

The overall stoichiometry for the proposed mechanism requires two equivalents of organolithium compound to react with one equivalent of cyclooctatetraene forming one equivalent of substituted cyclooctatetraenide dianion. Experimentally, 1.7 equivalents of n-butyllithium is required to completely react with one equivalent of cyclooctatetraene. In addition, the reaction between 1.7 equivalents of n-butyl-lithium and 1.0 equivalents of cyclooctatetraene yields 0.85 equivalents of n-butylcyclooctatetraenide dianion, based on the hydrolysis products. The experimental stoichiometry is in good agreement with the stoichiometry for the proposed mechanism.

In the second step of the reaction mechanism, eq. 1-12, one equivalent of protonated organolithium compound is formed during the metallation of the lithium 8-substituted cyclooctatrienide intermediate. During the formation of lithium n-butylcyclooctatetraenide dianion, n-butane evolution was detected in the vapors above the reaction solution prior to hydrolysis.

All attempts to isolate the lithium 8-substituted cyclooctatrienide intermediate were unsuccessful. The addition of a large excess of cyclooctatetraene to a limited quantity of organolithium compound

resulted in the formation of substituted cyclooctatetraenide dianion

and unreacted cyclooctatetraene. The substituted dianions were

characterized by oxidation and deuterolysis reactions. Oxidation of

the reaction products yielded substituted cyclooctatetraene, and a

mass spectroscopic determination of the deuterolysis products

resulted, exclusively, in dideuterated substituted cyclooctatriene.

Metallation of lithium 8-substituted cyclooctatrienide, therefore, is

both quantitative and rapid. The facile removal of a proton from the

cyclooctatrienide intermediate, eq. 1-12, is remarkable. It is the

aromatic stabilization of the cyclooctatetraenide dianion which

accounts for the unusual acidity of the methylene hydrogen atom in

substituted lithium cyclooctatrienide.[15,27]

Unlike organolithium compounds, Grignard reagents, diisopropyl

aluminum hydride and lithium dialkyl cuprate(I) compounds were

unreactive with cyclooctatetraene. Lithium hexaalkyluranate(IV)[28]

complexes, on the other hand, reacted with cyclooctatetraene; how-

ever, unsubstituted uranocene was the only product.[24] No alkyl

substituted uranocenes were formed. Since unsubstituted cycloocta-

tetraenide dianion formation had not previously been observed for

other organometallic alkyl compounds, this reaction was more closely

examined.

The Reaction of Cyclooctatetraene with Lithium
Hexaalkyl Uranate(IV) Complexes

It has been reported that lithium hexaalkyl uranate(IV) com-

pounds thermally decompose by β-hydrogen elimination to reactive

uranium metal. No coupled alkyl products were observed.[29] Addi-

tion of cyclooctatetraene to the uranium metal produces uranocene,

$(C_8H_8)_2U$, in good yield,[30-32] eqs. 1-13 and 1-14.

$$Li_2 R_6U(IV) \xrightarrow{\Delta} RH + R(-H) + U^0 \qquad (1-13)$$

$$U^0 + 2 C_8H_8 \longrightarrow (C_8H_8)_2U \qquad (1-14)$$
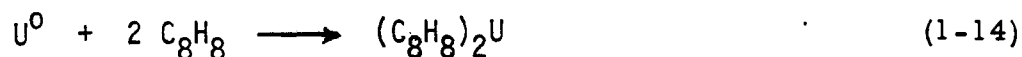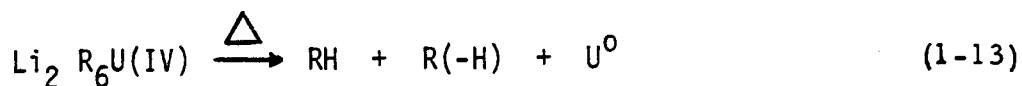
The thermal decomposition of lithium hexa-n-butyluranate(IV) is

complete within six days forming equal quantities of n-butane and

1-butene, eq. 1-13.[29] After six days, cyclooctatetraene was added

to the reaction solution. Uranocene formation was complete in

approximately five to seven days, eq. 1-14.[30] The entire reaction is

complete in two weeks at room temperature. The above experiments

were repeated and the results were verified.

When cyclooctatetraene is added immediately to freshly pre-

pared lithium hexa-n-butyluranate(IV), however, uranocene forma-

tion is complete within 24 hours at room temperature. In addition,

octane is isolated from the reaction solution in yields 78% of theo-

retical, based on added n-butyl-lithium. Similar results are obtained

for lithium hexaphenyluranate(IV). Biphenyl was isolated in 80%

theoretical yield, and uranocene was prepared in 60% theoretical

yield. The high yields of coupled alkyl and aryl reaction products

and the drastically different reaction rates establish that cycloocta-

tetraenide dianion formation from the reaction of cyclooctatetraene

with lithium hexaalkyluranate(IV) complexes does not occur by the

reduction of cyclooctatetraene by uranium metal. The coupled alkyl

and aryl reaction products strongly suggests that alkyl free radicals

are present in the solution[33] even when the alkyl group contains a

β-hydrogen. From the reaction conditions it could not be determined

whether cyclooctatetraene was reduced by low valent uranium com-

pounds or whether electron transfer to cyclooctatetraene occurred

directly from the alkyl ligand. Since uranium(IV) is readily reduced

to uranium(III), the former is more likely.

CONCLUSIONS

It has been demonstrated that cyclooctatetraene reacts with many organolithium compounds to form monosubstituted ten-π aromatic cyclooctatetraenide dianions. The reaction is, however, limited to the most reactive carbon nucleophiles. Although alkoxides and amides are good nucleophiles, they do not add to cyclooctatetraene. Some organolithium compounds which fail to react with cyclooctatetraene, for example, methyl-lithium, may undergo addition following activation by TMEDA.

By proper control of the reactant stoichiometry, two equivalents of organolithium reagent to one equivalent of cyclooctatetraene, lithium substituted cyclooctatetraenide dianions are prepared in high yield with little side product formation. By taking advantage of the chemistry of the cyclooctatetraenide dianion, organic or organometallic derivatives of the substituted cyclooctatetraenide dianion are readily prepared in high yield and purity. For example, n-butyl-cyclooctatetraene is prepared in approximately 70% yield, free from troublesome n-butylcyclooctatriene, by the oxidation of lithium n-butylcyclooctatetraenide dianion. Solutions of substituted cyclooctatetraenide dianions have been used to prepare monosubstituted uranocenes in good yield.[34] The procedure is both simple and rapid making substituted uranocenes available from commercial

reagents in a minimum of time.

In the discussion of the proposed mechanism for the formation of substituted cyclooctatetraenide dianions, eqs. 1-11 and 1-12, no mention was made as to the role of the metal cation in the reaction. It is important to note that the cation is more than a simple counter ion. Copper(I), magnesium(II), aluminum(III) and uranium(IV) ions are well suited to serve as counter ions for the substituted cyclo-octatetraenide dianion; however, alkyl compounds of each of these ions failed to undergo addition with cyclooctatetraene. The importance of the nucleophilic carbanion has been emphasized. The failure of organometallic alkyl groups, for example, in Grignard reagents, to add to cyclooctatetraene results from the decreased nucleophilicity of the magnesium alkyl bond. Metal coordination may be expected to reduce carbanion reactivity in two ways. For alkyl groups bonded to highly positive metal ions, the alkyl carbon will interact with the metal ion forming strong ionic bonds. Because of the strong ionic interaction, the alkyl carbanion is less available for nucleophilic addition. For example, organometallic bonding in uranium(IV) com- pounds is considered to be highly ionic.[35] Alkyl groups ionically bonded to uranium(IV) in lithium hexaalkyluranate(IV) complexes fail to add to cyclooctatetraene. In some cases, alkyl carbanion groups bonded to metal ions which are not highly charged are also unreactive to cyclooctatetraene addition, for example, lithium dialkylcuprate(I).

For these compounds, covalent bonding reduces carbanion reactivity

by the sharing of the carbon atom's electron pair with the metal ion.

Although these arguments are too simple to be complete, they serve

as a useful guide for predicting which organometallic alkyl compounds

might react with cyclooctatetraene forming substituted cyclooctatetra-

enide dianions.

Since addition reactions of cyclooctatetraene are limited to

strong nucleophiles, it is likely that future research will focus on

ways to activate cyclooctatetraene toward addition by weak nucleo-

philes. The chemical properties of an organic group are often signifi-

cantly modified on coordination to a transition metal. For example,

cycloheptatriene undergoes addition reactions by organolithium com-

pounds forming lithium 6-alkylcycloheptadienide, eq. 1-6.[19] Sodium

methoxide is unreactive under the same conditions. In tetraphenyl-

cyclobutadienecycloheptatriene cobalt(I) hexafluorophosphate,

$[(\phi_4 C_4)Co(C_7 H_8)]PF_6$, cobalt-coordinated cycloheptatriene readily

adds sodium methoxide forming the 6-methoxycycloheptadienyl

ligand.[36] Similar activation is observed for many transition metal-

coordinated olefins, and it is likely that coordinated cyclooctatetraene

will exhibit an increased susceptibility toward nucleophilic addition.

It will be of interest to see if addition reactions of coordinated cyclo-

octatetraene will lead to the formation of substituted cyclooctatetra-

enide dianion-transition metal complexes or whether other reactions

will occur. For example, other reactions include isomerization of cyclooctatetraene,[37] reduction of the metal ion, formation of unsubstituted cyclooctatetraenide dianion or, perhaps, the isolation of the substituted cyclooctatrienide intermediate.

EXPERIMENTAL

General Considerations

All manipulations were carried out using either high vacuum line or glove box techniques. Solvents were purified by vacuum transfer from $LiAlH_4$ or Na/benzophenone. Commercial alkyl- or aryl-lithium reagents were purchased from Alpha Products. Benzyl-lithium[11], lithium phenylacetylide[38] and vinyl-lithium[39] were prepared by published procedures. Cyclooctatetraene (J. T. Baker Co.) was distilled onto Linde 4A Molecular Sieves and stored under nitrogen. N, N, N', N'-tetramethylethylenediamine, TMEDA, (Aldrich) was dried over molecular sieves, stored under nitrogen and used without further purification. Uranium(IV) tetrachloride (Great Western Inorganics) was used without purification.

Isolation and calibration of organic products were performed on Varian 920 and HP 5720A gas chromatographs respectively. ^{1}H NMR spectra were recorded using Varian HA-100 or Varian CFT-80A spectrometers. ^{13}C NMR spectra were obtained on the Varian CFT-80A spectrometer. All organic NMR spectra were refer-enced to internal Me_4Si. GC-mass spectral data were obtained using a Varian MAT GmbH CH7 Massenspectrometer at an ionization poten-tial of 70 eV interfaced with a Varian 1200 gas chromatograph.

Synthetic Procedures

The general procedures for the formation of each of the substi-
tuted cyclooctatetraenide dianions was the same. Formation of lithium
methycyclooctatetraenide dianion also requires the addition of two
equivalents of TMEDA per equivalent of methyl-lithium to the reaction
solution. Scale-up procedures present no additional problems.
Organic products may be isolated by standard vacuum distillation
techniques. As an example, preparation and reactions of lithium
n-butylcyclooctatetraenide dianion will be presented.

Preparation of n-Butylcyclooctatetraenide Dianion

In an atmosphere of prepurified nitrogen 0.50 ml (4.4 mmol) of
cyclooctatetraene was added to 25 ml of dry Et_2O. A solution of 4.4
ml (2.0 M, 8.8 mmol) of n-butyl-lithium was added to this solution
with rapid stirring which was continued for 1 hr. Aliquots of the
resulting red solution were taken for oxidation, hydrolysis, deuter-
olysis and yield data.

n-Butylcyclooctatetraene

At room temperature air or oxygen was bubbled through an
aliquot of the n-butylcyclooctatetraenide dianion solution yielding an
orange solid which was treated with 1 M HCl. Extraction of the

organic products with hexane (3 x 2 ml) and drying with $MgSO_4$, followed by evaporation of the hexane, yielded a bright yellow liquid which was isolated by preparative VPC and identified as n-butylcyclooctatetraene by ^{1}H NMR and mass spectrometry. Spectral data for all compounds have been reported.[40] The yield of n-butylcyclooctatetraene was 505 mg (70%) by VPC (18" x 0.125", 10% UCW 982 on AW-DMCS Chromosorb W) using an external standard.

n-Butylcyclooctatriene and n-Butylcyclooctatriene-d$_2$

To an aliquot of the n-butylcyclooctatetraenide dianion solution 1 M HCl or D_2O was added. Work-up, as above, gave a pale yellow liquid consisting of a mixture of isomers of n-butylcyclooctatrienes or n-butylcyclooctatriene-d$_2$, respectively. The mass spectra of the individual isomers differ slightly from one another in intensity only. For all dianions, deuterolysis gave n-butylcyclooctatriene-d$_2$ in excess of 98% by mass spectrometry. No evidence of monodeuteration was observed. The yield of n-butylcyclooctatriene was 605 mg (85%) by VPC using an external standard.

1,1'-Di-n-Butyluranocene

To a solution of lithium n-butylcyclooctatetraenide dianion prepared from 1.0 ml (8.9 mmol) cyclooctatetraene and 8.9 ml (2.0 M,

17. 8 mmol) of n-butyl-lithium in Et_2O, UCl_4 (1.75 g, 4.5 mmol)

dissolved in 25 ml of THF was added dropwise at 0°C with stirring.

After the solution was stirred for 1 hr, solvents were removed under

vacuum, and the green solid was transferred to a Soxhlet extractor.

Extraction with hexane was complete in 4 days yielding 1.23 g (2.2

mmol, 50% based on added cyclooctatetraene) n-butyluranocene.

Identification was made by an identical match of its infrared, ^{1}H NMR,

mass and visible spectra with the literature.[4,25]

Stoichiometry

The general procedure is the same as that described in the

preparation of lithium n-butylcyclooctatetraenide dianion using freshly

distilled cyclooctatetraene and titrated n-butyl-lithium (1.64 M).[41]

The amount of cyclooctatetraene was fixed at 0.5 ml (4.4 mmol). Ini-

tially, 4.00 ml (5.5 mmol) of n-butyl-lithium was added to the cyclo-

octatetraene and allowed to react for 12 hr. An aliquot of the reac-

tion solution was hydrolyzed with 1 M HCl and residual cyclooctatetra-

ene was determined by VPC (8' x 0.125, 10% Carbowax 20 M on

Chromosorb P). At this time, additional n-butyl-lithium (0.30 ml,

0.50 mmol) was introduced, and after 2.5 hr a second aliquot of the

reaction mixture was removed and residual cyclooctatetraene was

determined as before. Additions of 0.10 ml (.16 mmol) of n-butyl-

lithium were continued at 2.5 hr intervals until no cyclooctatetraene

remained. At this point, 4.6 ml (7.5 mmol) of n-butyl-lithium had been added. Reaction stoichiometry, based on the consumption of cyclooctatetraene, is determined to be 1.7 equivalents of n-butyl-lithium to 1.0 equivalent of cyclooctatetraene.

Tert-Butyl-Lithium and Cyclooctatetraene

To a solution of 50% pentane and 50% Et_2O, 0.50 ml (4.5 mmol) of cyclooctatetraene was added at -78°C. 5.0 ml (1.8 M, 9.0 mmol) of t-butyl-lithium was added. The reaction immediately turned violet, and after 5 min., 1 ml aliquots were taken for hydrolysis, deuterolysis or oxidation samples. Following oxidation, the yield of t-butyl-cyclooctatetraene by VPC was 325 mg (45%) using an external standard. In addition, a second compound was isolated from oxidation or hyrdolysis reactions which showed no deuterium incorporation on deuterolysis. The reaction product was partially identified as an isomer of 2,7-di-t-butyl-$[4, 2, 0^{1.6}]$-bicyclo-octa-2,4 diene, Fig. 1-2. The exact position of t-butyl substitutions were not specifically determined. The yield of 2,7-di-t-butyl-$[4, 2, 0^{1.6}]$-bicyclo-octa 2,4 diene by VPC was 423 mg (43%) using an external standard.
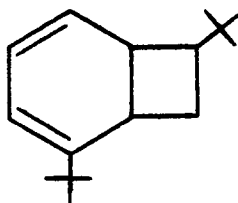
Fig. 1-2. 2,7-Di-t-butyl-$[4, 2, 0^{1.6}]$-bicyclo-octa-2,4 diene

Elemental Analysis (Schwartzkoff): $C_{16}H_{26}$, Calc. C = 88.07,

H = 11.92, exp. C = 88.38, H = 11.92. ^{1}H NMR (CCl_4): δ 0.84

(s, 9H), δ 1.03 (s, 9H), δ 2.68 (m, 4.75H), δ 5.2-5.9 (5 peaks,

2.87H). ^{13}C NMR (CCl_3D): δ = 29.4, 30.9, 31.4, 34.2, 36.3,

37.1, 37.6, 59.0, 121.2, 125.1, 131.9, 142.9. Mass spectrum

(70 eV) m/e: 218 (M), 203 $(M-CH_3)$, 161 $(M-C_4H_9)$,

134 $[C_6H_5-C(CH_3)_3]$, 119 $[C_6H_5-C(CH_3)_2]$, 69 $[H_2C=C-(CH_3)_3]$.

Under different reaction conditions, other reaction products may be

obtained. For example, at room temperature 15.0 ml (136 mmol)

of cyclooctatetraene was added to 50 ml of Et_2O. 150 ml (1.8 M,

271 mmol) of t-butyl-lithium was added to the cyclooctatetraene and

stirred for 15 min. The entire reaction solution was oxidized with

oxygen and acidified with HCl. The organic layer was dried over

$MgSO_4$ and distilled under reduced pressure. The yield of t-butyl-

cyclooctatetraene was 3.68 g (17%). A second reaction product was

isolated and partially identified as an isomer of 6,7-di-t-butyl-1,3,5-

cyclooctatriene, Fig. 1-3.
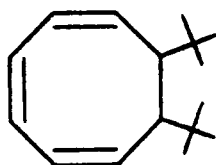
Fig. 1-3. 6,7-Di-t-butyl-1,3,5-cyclooctatriene

The yield of 6, 7-di-t-butyl-1, 3, 5-cyclooctatriene was 20.2 g (69%).

Elemental Analysis (Schwartzkoff): $C_{16}H_{26}$, Calc. C = 88.07,

H = 11.92, exp. C = 87.79, H = 11.82. ^{1}H NMR (CCl_4): δ 0.93

(s, 18H), δ 2.62 (s, 1.06H), δ 5.2-6.3 (6 peaks, H = 4.95).

^{13}C NMR (CCl_3O): δ = 27.1, 27.4, 31.8, 32.3, 47.2, 47.3, 123.6,

125.0, 127.0, 127.7, 129.1, 135.9. Mass spectrum (70 eV) m/e:

218 (M), 203 (M-CH_3), 161 (M-C_4H_9), 119 [C_6H_5-$C(CH_3)_2$],

91 (C_7H_7), 57 (C_4H_9). Infrared spectra (neat): 658 (m), 740 (s),

779 (s), 860 (w), 944 (w), 1178 (w), 1200 (m), 1220 (m), 1240 (m),

1361 (s), 1392 (m) 1464 (s), 1603 (w), 2855 (vs), 2948 (vs), 3010 (s).

NMR: s = singlet, d = doublet, etc., m = multiplet.

IR: w = weak, m = medium, s = strong, vs = very strong.

Lithium Hexabutyluranate(IV) plus Cyclooctatetraene

A suspension of 1.0 g of UCl_4 (2.6 mmol) in 35 ml of Et_2O was

cooled to -78 °C. n-Butyl-lithium, 9.7 ml (1.6 M, 15.5 mmol), was

added with rapid stirring. The mixture turned brown and was allowed

to stir for 1 hr. At -78°C, 0.59 ml (5.3 mmol) of cyclooctatetraene

was added. The reaction temperature was slowly raised, over

approximately 4 hrs, to room temperature and stirred overnight at

which time a green solid precipitated. The solution was filtered and

the green solid was placed in a Soxhlet extractor for three days with

benzene. The solid was identified as uranocene, $(C_8H_8)_2U$, by an

identical match of its visible, infrared, and mass spectra with the literature.[24] The yield of uranocene was 0.731 g (1.6 mmol, 61%). From the filtered solution, octane, was isolated and identified by an identical match of its ^{1}H NMR and mass spectra with an authentic sample. The yield of octane by VPC using an external standard was 689 mg (6.0 mmol, 78%).

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II. CYCLOHEPTADIENYL COMPLEXES OF THE d- AND f-TRANSITION ELEMENTS

INTRODUCTION

During the past twenty-five years, cyclopentadienyl compounds

of the d- and f-transition elements have received intensive study. Far

less attention has been given to other polyolefin anion ligands which

coordinate to the metal in the h^5-dienyl manner. One of the simplest

ligands in this category is the cycloheptadienide anion, $C_7H_8R^-$,

Fig. 2-1.
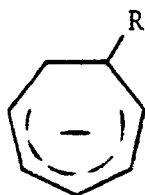
R = H

R = Me

R = n-Bu

Figure 2-1. Cycloheptadienide Ion

Comparison of the Cycloheptadienide and Cyclopentadienide Anions

In many ways the cycloheptadienide ion and the cyclopentadienide

ion are very similar. Both ions are delocalized, singly charged

anions with delocalization occurring over a planar five carbon frame-

work. Both anions form ionic compounds with group IA counter

cations, requiring coordinating solvents, primarily ethers or amines,

to solvate the cation. Solutions of cycloheptadienide and

cyclopentadienide ions exhibit moderate thermal stability and are not subject to isomerization reactions or spontaneous loss of hydride ion.[2,3] Bonding to transition metal ions occurs primarily in the π-bonding geometry and each anion contributes six electrons to the metal coordination sphere during bond formation.

In a closer comparison of the cycloheptadienide ion and the cyclopentadienide ion, one finds that there are, however, several important differences in properties between the two. Although both anions are delocalized, anion geometries of the two ions are different.[4] Because of the differing anion structures, molecular orbital energies and electron distributions for the two ions are significantly different. As a result of the cyclic structure of the cyclopentadienide anion, electron delocalization extends evenly over the five carbon-carbon bonds; whereas, in the cycloheptadienide anion, the electron distribution extends over only four carbon-carbon bonds.

By the use of simple Hückel molecular orbital theory, it is possible to calculate π-molecular orbital energies and π-electron densities for delocalized ions.[5,6] Orbital energies for the cycloheptadienide ion and the cyclopentadienide ion are presented in Fig. 2-2. Symmetry labels for the molecular orbitals have also been included.[7]

$e_2, e_3 = \alpha - 1.618\beta$ —— —— E_2'' 　　　B_1 —— 　$e_5 = \alpha - 1.732\beta$

　　　　　　　　　　　　　　　　　　　　A_2 —— 　$e_4 = \alpha - \beta$

　　　　　　　　　　　　　　　　　　　　B_1 ⥯ 　$e_3 = 0$

$e_1, e_4 = \alpha + .618\beta$ ⥯ ⥯ E_1''

　　　　　　　　　　　　　　　　　　　　A_2 ⥯ 　$e_2 = \alpha + \beta$

　　　　　　　　　　　　　　　　　　　　B_1 ⥯ 　$e_1 = \alpha + 1.732\beta$

$e_0 = \alpha + 2\beta$ 　　　⥯ 　A_2''

—————————————————————

$C_5H_5^- \ (D_{5h})$ 　　　$C_7H_9^- \ (C_{2v})$

$e_j = \alpha + 2\beta \cos (2\pi j/n_c)$ 　　　$e_j = \alpha + 2\beta \cos [2\pi j/(n_c-1)]$

$[j = 0, 1 \ldots (n_c-1)]$ 　　　$(j = 1, 2 \ldots n_c)$
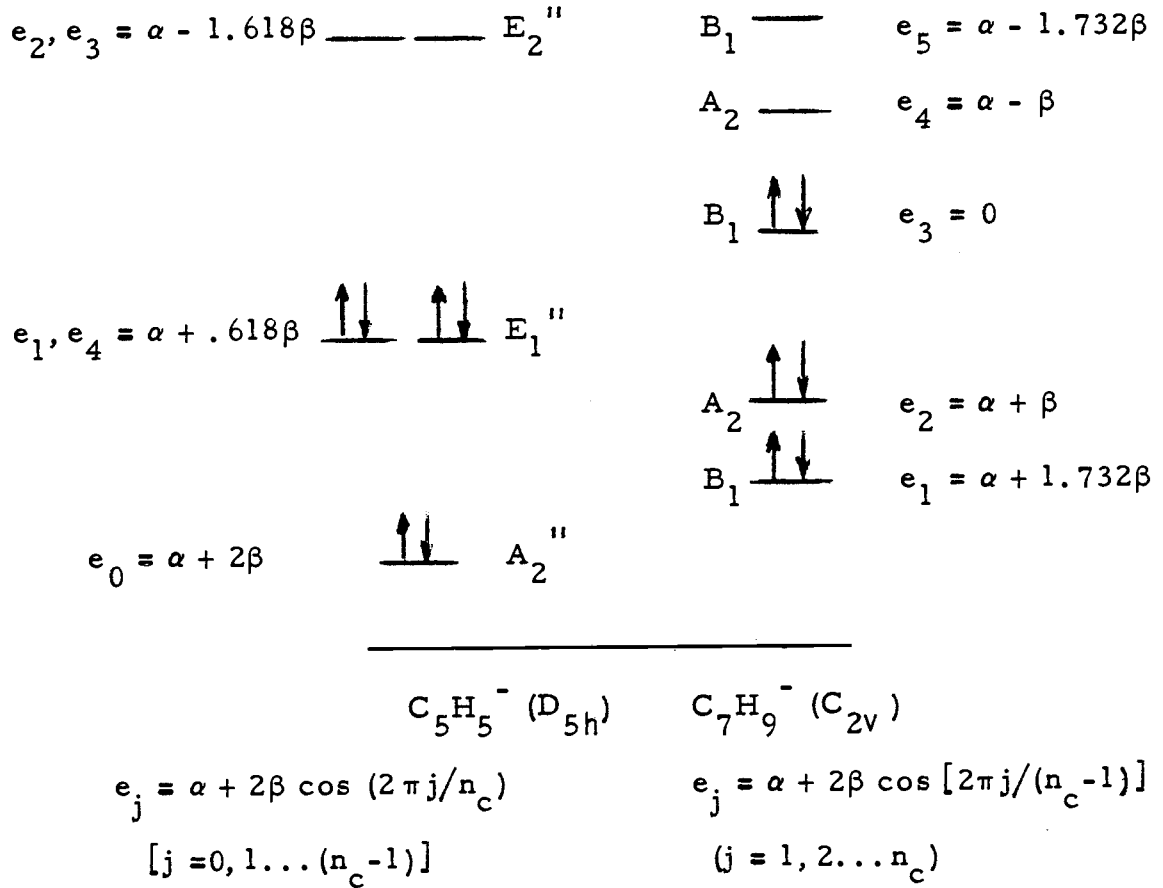
Figure 2-2.　Hückel Molecular Orbital Energies for
　　　　　　Cyclopentadienide and Cycloheptadienide.

In the Hückel molecular orbital approach, α represents the energy of an electron located on a carbon 2p orbital and is usually, arbitrarily, set to zero energy. β represents a bonding contribution to the energy, and 2β is the energy associated with a carbon-carbon double bond. From Fig. 2-2, several conclusions can be drawn. By lowering the symmetry of the delocalized anion from D_{5h} to C_{2v}, the energy of the degenerate E orbitals are split. This has two effects. For the bonding orbitals, the highest occupied molecular orbital is now at the non-bonding level. As a result the cycloheptadienide anion may be more easily oxidized relative to the cyclopentadienide anion, or, conversely, the cycloheptadienide ion may be a better reducing agent than the cyclopentadienide ion. A reduction in symmetry also raises the total energy of the cycloheptadienide ion. By summing the energy of all of the electrons in a particular ion, one may calculate the total bonding energy, in β units, for that ion. From a calculation of the bonding energies, the cycloheptadienide ion is expected to be less stable than the cyclopentadienide ion by 1.008 β.

Because of the reduction in molecular symmetry, not only are the energies of the molecular orbitals altered, but the nodal properties of the molecular orbital wave functions are also changed. The wave function nodal properties of the occupied molecular orbitals controls π-electron distribution and, therefore, determines the charge distribution of the anion. Calculated Hückel electron

densities[5] for cycloheptadienide and cyclopentadienide anions are given in Fig. 2-3.

$$C_7H_9^- \qquad\qquad C_5H_5^-$$
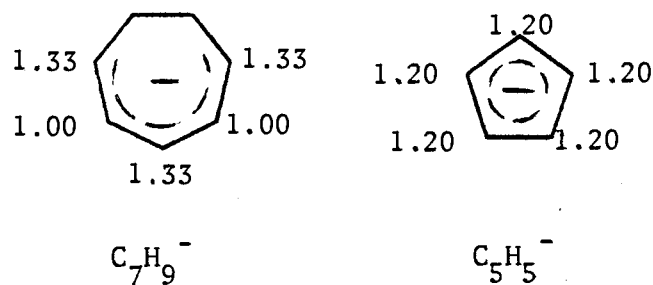
Fig. 2-3. Calculated Hückel Electron Densities for the Cycloheptadienide and Cyclopentadienide Anions.

The electron density calculations for cyclopentadienide indicate that the negative charge is evenly distributed over each carbon in the anion. The charge on each carbon is -0.20 e.s.u.

Electron distribution calculations for the cycloheptadienide ion indicate that the negative charge is evenly distributed over only the odd carbon atoms of the anion, with a charge of -0.33 e.s.u. per carbon. The even carbon atoms are expected to be uncharged.

^{13}C NMR shifts have been used to experimentally determine π-electron densities in planar sp^2 hybridized conjugated systems.[4,8,9] An empirical relationship between ^{13}C NMR shifts and π-electron density distributions has been derived,[8] eq. 2-1.

$$\delta = 289.5 - 156.3\,\rho \qquad\qquad (2\text{-}1)$$

ρ is the π-electron density, and δ is the ^{13}C NMR shift measured in ppm, TMS = 0. Experimentally determined π-electron densities and distributions are nearly identical to those calculated by Hückel molecular orbital theory,[4, 9] Fig. 2-4.

93.0 (1.257)

133.8 (0.996)

77.3 (1.357)

103.1 (1.19)

$C_7H_9^-$

$C_5H_5^-$
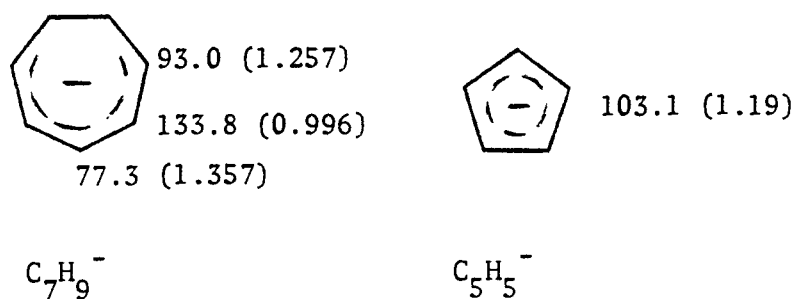
Fig. 2-4. ^{13}C NMR (π-Electron Densities) for Cyclohepta-
dienide and Cyclopentadienide Anions.

Finally, in addition to their electronic differences, cyclohepta-dienide and cyclopentadienide ions display different steric requirements. Not only is the seven membered ring larger than the five membered ring, but the ethylene bridge of the cycloheptadienide anion is not coplanar with the five carbons of the pentadienyl anion.

Because of their general similarities, the cycloheptadienide ion might be expected to form transition metal compounds of similar stability and composition to those known for the cyclopentadienide ion. In addition, because of their differing electronic and steric requirements, cycloheptadienyl metal complexes might be expected to display metal redox potentials, ligand reactivities or other molecular

properties different from those of the corresponding cyclopentadienyl compound.

Cycloheptadienyl Compounds of the Transition Metals

A brief review of some of the presently known cycloheptadienyl transition metal compounds will be made. In addition to indicating which metals and oxidation states form cycloheptadienyl complexes, special attention will be made to synthetic methods, in cases where the mechanism for the synthesis is known.

Transition metal cycloheptadienyl complexes $[M(C_7H_7)(C_7H_9)]$ (M = Ti, Fe, Mo, or W) have been synthesized by the reaction of metal atoms with cycloheptatriene.[10,11] The Fe and Ti compounds have also been prepared by solution techniques where metal chlorides were reduced by Grignard reagents in the presence of cyclohepta-triene.[12] Other cycloheptadienyl iron compounds are known, for example, $[(C_7H_9)Fe(CO)_3]BF_4$,[13] $[Fe(C_6H_8)(C_7H_9)CO]BF_4$,[14] and $[Fe(C_7H_9)_2]$.[15] The latter compound is the cycloheptadienyl analog of ferrocene. $[Fe(C_7H_9)_2]$ displays moderate thermal stability, de-composing between 80° and 90°C to a metallic iron mirror. $[Fe(C_7H_9)_2]$ is also reactive to oxygen, resulting in the oxidation of Fe^{+2} to Fe^{+3}. Ferrocene, on the other hand, is thermally stable to over 500°C and is unreactive toward oxygen.[16] Substitution of the cycloheptadienyl ion for the cyclopentadienyl ion results in the

formation of an iron compound which is both more easily reduced (thermally) and more easily oxidized (oxygen).

Other transition metal cycloheptadienyl compounds include $[(Ph_4C_4)Co(C_7H_8-Y)]$[17] (Y = H, OH, OCH_3), $[Ru(SiMe_3)(CO)_2(C_7H_9)]$[18] and $[Rh(C_5Me_5)(C_7H_8-OCH_3)]$ PF_6.[19] For each of these compounds, synthetic routes to cycloheptadienyl formation were achieved by indirect methods. The most commonly observed route to cycloheptadienyl formation occurs by nucleophilic attack on coordinated cycloheptatriene. For example, coordinated cycloheptatriene in $[(Ph_4C_4)Co(C_7H_8)]Br$[17] forms a 6-substituted cycloheptadienyl ligand on addition of H^-, HO^-, or CH_3O^-, eq. 2-2.

$$(Y = H^-,\ HO^-,\ CH_3O^-)$$

(2-2)
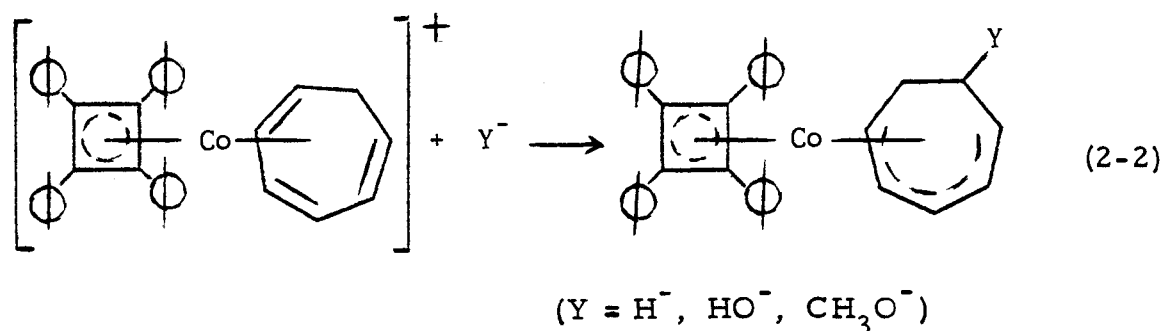
It is important to note that free cycloheptatriene is unreactive with each of these nucleophiles under the same reaction conditions. Coordinated cycloheptatriene in $[(C_5Me_5)Rh(C_7H_8)][PF_6]_2$ is also subject to nucleophilic attack.[19] In this case, the solvent, e.g. MeOH, is the nucleophile resulting in the formation of the 6-methoxycycloheptadienyl ligand, eq. 2-3.

$$(2-3)$$
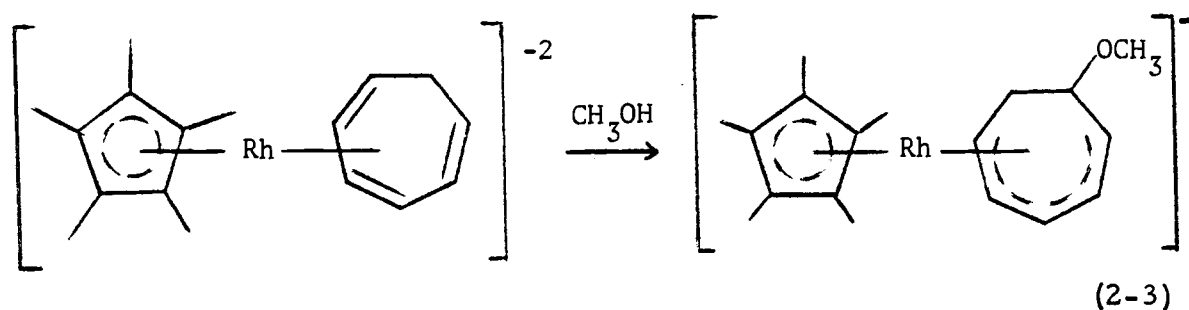
These two examples indicate the degree to which metal coordination can increase ligand reactivity, i.e., susceptibility to nucleophilic attack. Other examples of cycloheptadienyl formation by nucleophilic attack of coordinated cycloheptatriene are known.[20-22]

Another synthetic route to cycloheptadienyl compound formation, one which is less often observed, is available because of an increased reactivity of coordinated 1,3-cycloheptadiene to proton removal. Addition of 1,3-cycloheptadiene, C_7H_{10}, to $[Ru(CO)_4(SiMe_3)_2]$ results in the formation of $[Ru(CO)_2(SiMe_3)(C_7H_9)]$ and $HSiMe_3$.[18] It is believed that the dienyl product is produced from the $[Ru(CO)_2(SiMe_3)_2(C_7H_{10})]$ intermediate, followed by an intramolecular proton abstraction from 1,3-cycloheptadiene by the trimethylsilyl anion, with subsequent elimination of trimethylsilane, eq. 2-4.

$$Ru(CO)_4(SiMe_3)_2 + C_7H_{10} \longrightarrow \left[\begin{array}{c} \text{CO} \\ \text{CO} \\ \text{Ru} - \text{SiMe}_3 \\ \text{SiMe}_3 \end{array} \right] \longrightarrow$$

$$\begin{array}{c} \text{Ru} \\ \text{CO} \quad \text{CO} \quad \text{SiMe}_3 \end{array} + HSiMe_3 \tag{2-4}$$
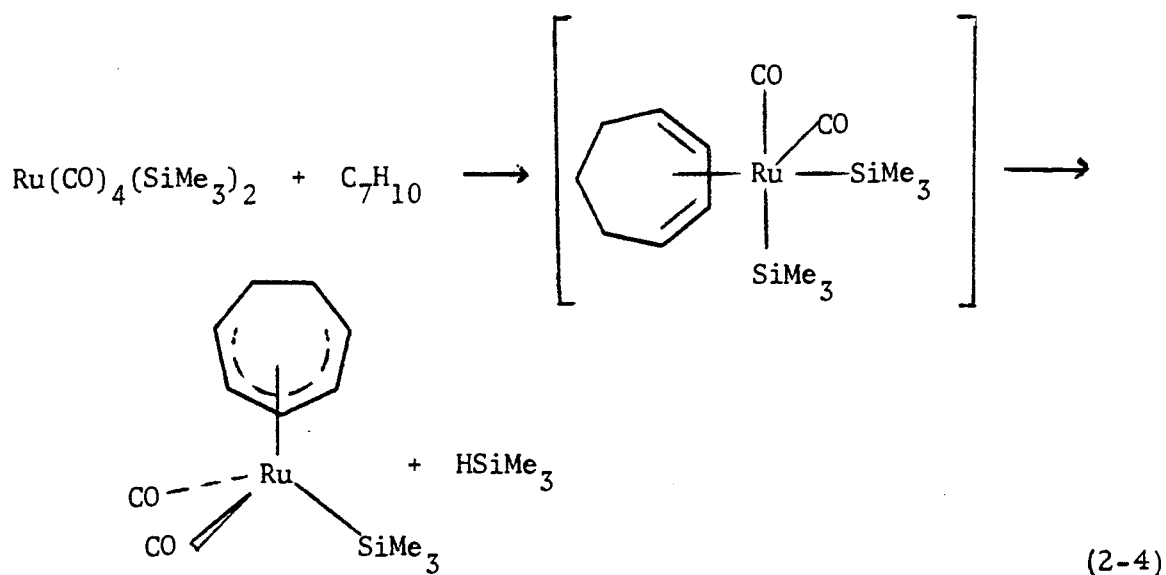
Pentadienyl carbanion formation by α-metallation of uncomplexed 1,3-dienes by strong bases has been repeatedly unsuccessful.[23] The ability of trimethylsilyl anion to metallate 1,3-cycloheptadiene is most unexpected since silyl anions are poor metallating agents.

The increased reactivity of metal coordinated olefins may be understood in terms of an increased acidity of that olefin. For cyclo-heptatriene, the olefin acts as a Lewis acid, electron pair accpetor, and readily undergoes nucleophilic attack. 1,3-cycloheptadiene, on the other hand, is subject to α-metallation, acting as a Brønsted acid, a proton donor. For both reactions, metal coordination has increased reaction rates by, at least, several orders of magnitude.

From this brief review, it can be seen that cycloheptadienyl compounds are known for many of the d-transition metals. Stable cycloheptadienyl compounds are known for both large and small metal ions, as well as, with elements of both the early and later transition

metals. Presently there are no cycloheptadienyl compounds known

for any of the lanthanide or actinide elements. In part, this results

from the inability of either the lanthanide or actinide elements to inter-

act strongly with neutral olefins. Without metal-olefin bond forma-

tion, cycloheptadienyl formation is prevented.

In this study attempts were made to prepare cycloheptadienyl

d- and f-transition metal compounds by the direct addition of pre-

formed lithium cycloheptadienide to solutions of the d- and f-transition

metal chlorides. The purpose of this study is two-fold. First, does

the addition of lithium cycloheptadienide to transition metal chlorides

result in the formation of cycloheptadienyl compounds? Second, can

this general synthetic approach be used to synthesize new cyclohepta-

dienyl compounds which are direct analogs of the well-known and more

thoroughly studied d and f-transition metal-cyclopentadienyl com-

pounds?

RESULTS AND DISCUSSION

Preparation of Lithium Cycloheptadienide

The preparation of 6-alkylsubstituted lithium cycloheptadienide has previously been reported. Prior to the synthesis of organo-metallic cycloheptadienyl compounds, preparative methods for lithium cycloheptadienide compounds used in this study were examined in order to determine the necessary experimental conditions for obtaining high anion yields and to limit side-reaction product formation. In addition, solutions of lithium cycloheptadienide served as a convenient source for authentic samples of 1, 3- and 1, 4-cycloheptadiene isomer hydroly-sis (deuterolysis) products.

Unsubstituted lithium cycloheptadienide may be prepared in high yield by metallation of 1, 3, 6-heptatriene in THF solution by n-butyl-lithium.[2] Proton abstraction occurs at low temperature and cycliza-tion to the cycloheptadienide anion is quantitative above -30°, eq. 2-5.

(2-5)
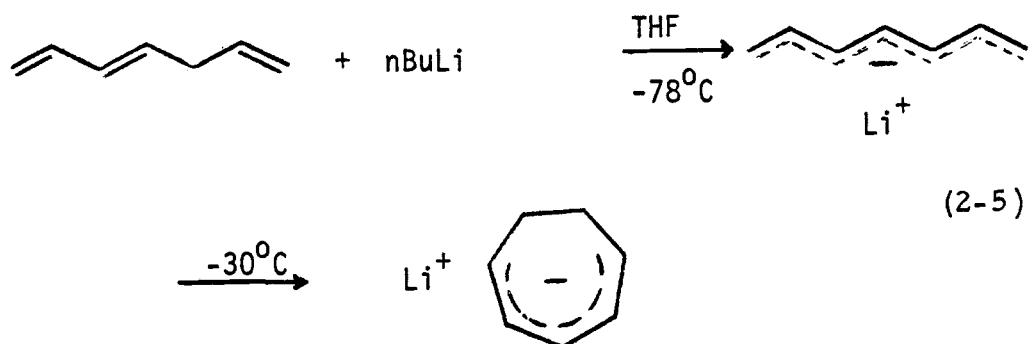
Low temperature hydrolysis (deuterolysis) of lithium cyclo-
heptadienide produces 1,3- and 1,4-cycloheptadiene in a 68:32 mix-
ture eq. 2-6.

$$Li^{+} \quad \text{(anion)} \quad \xrightarrow{H^{+}(D^{+})} \quad \text{(product + H(D))} \quad + \quad \text{(product H(D))} \quad (2\text{-}6)$$
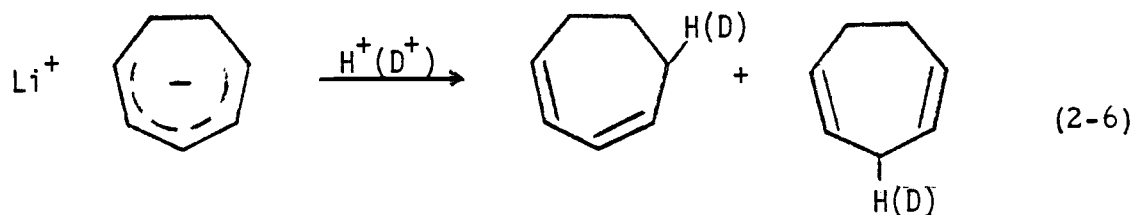
These experiments were repeated, and the results were verified
by isolation and identification (^{1}H NMR)[24] of hydrolysis products. The
number of deuteriums incorporated into the deuterolysis products were
determined by mass spectrometry. Lower yields of the cyclohepta-
dienide anion were obtained in Et_2O solution. In addition, extensive
side product formation, which were not identified, was observed in
Et_2O.

High yields of 6-alkyl or 6-aryl substituted lithium cyclohepta-
dienide may be obtained in Et_2O solution by the addition of organo-
lithium reagents to cycloheptatriene.[3] Nucleophilic attack of cyclo-
heptatriene simultaneously leads to carbon-carbon bond formation and
to the formation of a delocalized anion adjacent to the new carbon-
carbon bond, eq. 2-7.

$$(2-7)$$
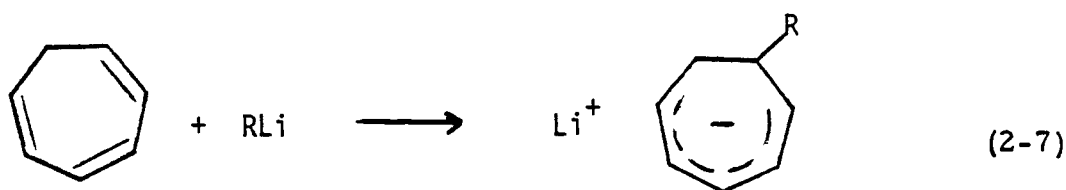
The reaction of n-butyl-lithium with cycloheptatriene is complete in approximately two to three hours at room temperature. Methyl-lithium is unreactive under the same conditions. Addition of tetramethylethylenediamine (TMEDA) to methyl-lithium, however, increases the nucleophilicity of methyl-lithium. In the presence of TMEDA, methyl-lithium reacts with cycloheptatriene to form lithium 6-methycycloheptadienide. The reaction between methyl-lithium (TMEDA) and cycloheptatriene is complete in approximately twenty-four hours at room temperature.

On hydrolysis (deuterolysis or alkylation) of lithium 6-substituted cycloheptadienide, a mixture of three isomers of 1,3- and 1,4-cycloheptadiene is obtained. For example, hydrolysis of lithium 6-n-butyl-cycloheptadienide produces 5-n-butyl-1,3-cycloheptadiene, 6-n-butyl-1,3-cycloheptadiene and 6-n-butyl-1,4-cycloheptadiene, eq. 2-8.

$$(2-8)$$
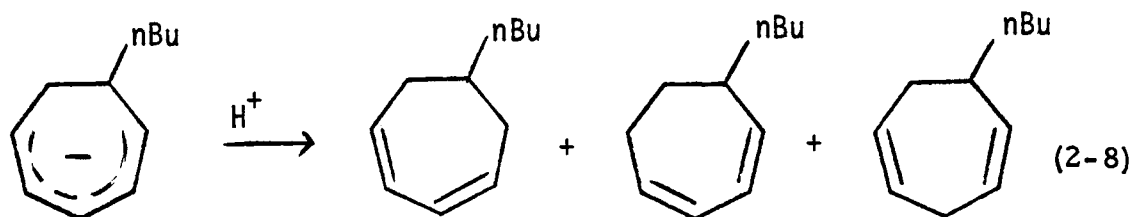
The charge of the cycloheptadienide ion may be confirmed on deuterolysis or alkylation. The addition of one deuterium or alkyl group may be determined by mass spectrometry.

Bis(6-Methylcycloheptadienyl) Iron(II)

Before preparing any new cycloheptadienyl compounds, it was necessary to demonstrate the viability of the proposed synthetic approach. That is, can a known cycloheptadienyl compound be prepared by the direct reaction of lithium cycloheptadienide with a metal halide.

Bis(6-methylcycloheptadienyl) iron(II), $(C_7H_8\text{-Me})_2$ Fe, can be isolated in approximately 60% yield by the addition of two equivalents of lithium 6-methylcycloheptadienide to one equivalent of iron(II) bromide. $(C_7H_8\text{-Me})_2$Fe was identified by its physical, chemical and spectroscopic properties and by an elemental analysis (high resolution mass determination of the molecular ion). Each of the determined molecular properties for the compound isolated in this synthesis (see Experimental) was identical to the corresponding molecular properties reported for $(C_7H_9)_2$Fe in the literature.[14] A 60% yield in product formation represents a 30% increase over the previously reported synthesis for this iron(II) compound.

Reaction of Lithium Cycloheptadienide with Dichlorobiscyclopentadienyl Titanium(IV)

The synthetic potential of the cycloheptadienyl anion was further investigated by attempts to prepare mixed cyclopentadienyl and cycloheptadienyl derivatives of titanium(IV).

The addition of one equivalent of lithium n-butylcycloheptadienide LiC_7H_8-nBu, to one equivalent of dichlorobiscyclopentadienyl titanium(IV), $(C_5H_5)_2TiCl_2$, results in the nearly quantitative reduction of titanium(IV) to titanium(III). Chlorobiscyclopentadienyl titanium(III), $[(C_5H_5)_2TiCl]_2$, is isolated in nearly 90% of the theoretical value. $[(C_5H_5)_2TiCl]_2$ was identified spectroscopically[25, 26] and by elemental analysis.

Under similar reaction conditions NaC_5H_5 reacts with $(C_5H_5)_2TiCl_2$ to produce $(C_5H_5)_4Ti$ in yields of 80%[2]. In part, the reduction potential of the cycloheptadienyl anion is responsible for the extreme differences in reactivities observed for LiC_7H_9 and NaC_5H_5. Furthermore, based on the yields of $[(C_5H_5)_2TiCl]_2$, the cycloheptadienyl anion is a better reducing agent for this reaction than many conventional reductants, for example, zinc dust, lithium aluminum hydride, sodium amalgam and others.[26]

It has also been observed in our laboratory that lithium cycloheptadienide has caused the reduction, in some cases, of other

titanium(IV), zirconium(IV) and halfnium(IV) compounds to undetermined oxidation states.

Reaction of Lithium Cycloheptadienide
with Lanthanide and Actinide Chlorides

Although the cycloheptadienide anion has been shown to be a strong reducing agent, the synthesis of cycloheptadienyl lanthanide and actinide compounds was attempted since most lanthanide and actinide ions are extremely resistant toward reduction.

Since chlorotriscyclopentadienyl uranium(IV) [28] is one of the most stable organouranium compounds known, chlorotriscycloheptadienyl uranium(IV) might, similarly, be expected to be the most stable cycloheptadienyl-uranium(IV) compound which could be synthesized. Unfortunately, three equivalents of lithium cycloheptadienide react completely with one equivalent of uranium(IV) tetrachloride resulting in the formation of an unstable organouranium(IV) compound. Although the cycloheptadienyl-uranium compound was not sufficiently stable to allow for complete compound characterization, i. e. composition and structure determination, the compound was sufficiently stable to permit the chemical and spectroscopic characterization of the coordinated ligand.

Chemical characterization, Fig. 2-5, of the "cycloheptadienyl-uranium(IV)" complex indicated that the coordinated ligand was not the

R= Hydrogen
R= Methyl
R= n-Butyl
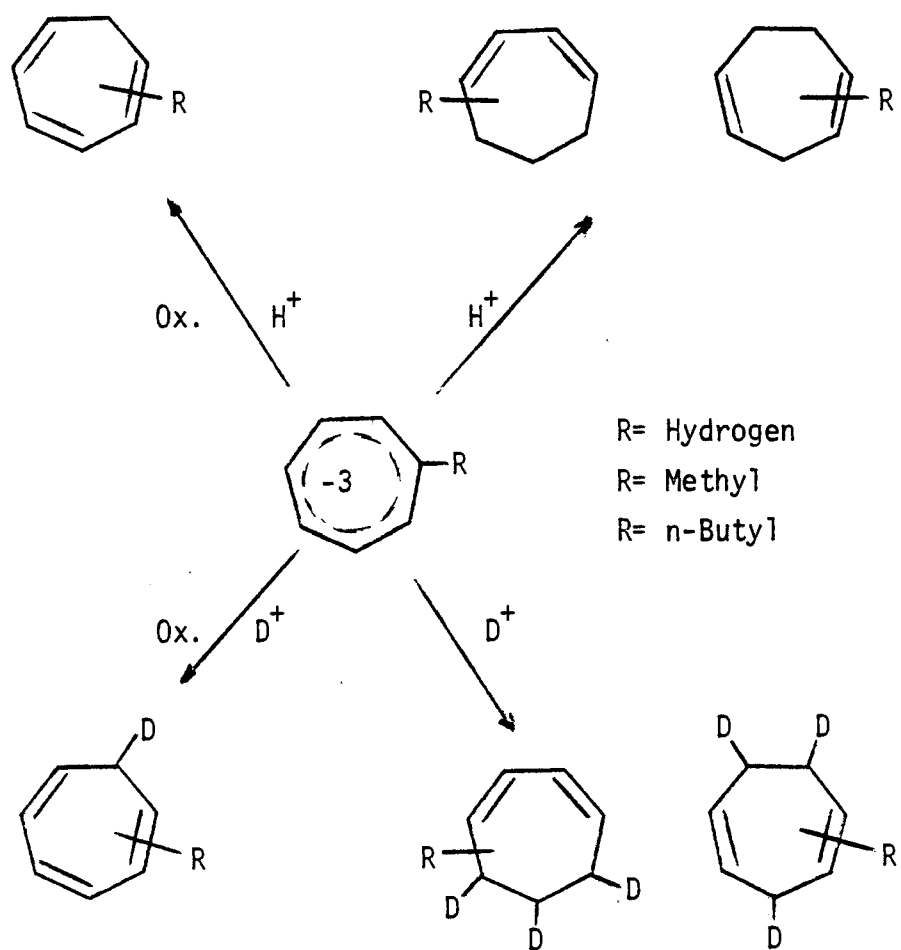
Figure 2-5. Chemical Characterization of Lanthanide and
Actinide Cycloheptatrienyl Trianion Complexes.

added cycloheptadienyl anion, $C_7H_9^-$, but a ten-π electron aromatic

cycloheptatrienyltrianion, $C_7H_7^{-3}$. The $C_7H_7^{-3}$ ligand is hydro-

lytically unstable producing 1,3- and 1,4-cycloheptadiene as the only

observed hydrolysis products. A complete mass spectroscopic analy-

sis of the deuterolysis products of $C_7H_7^{-3}$ indicates that d_3-1,3-cyclo-

heptadiene and d_3-1,4-cycloheptadiene are the exclusive products.

From the mass spectra, no d_1-cycloheptadiene isomers were

observed. The latter are the expected deuterolysis products that

would be obtained from the added $C_7H_9^-$ ion. Similar hydrolysis and

deuterolysis results are obtained when one of the hydrogens in $C_7H_7^{-3}$

is replaced by an alkyl group, for example, methyl or n-butyl. In

each case, the degree of deuterium labeling in the cycloheptadiene

deuterolysis products is consistent with the addition of three and only

three deuteriums.

Further evidence for the formation of cyclic, ten-π electron

aromatic cycloheptatrienyl trianions, may be inferred from the

number of hydrolysis isomers of monosubstituted cycloheptyl anions.

From the hydrolysis of the alkylsubstituted cycloheptatrienyl tri-

anion, $C_7H_6R^{-3}$, a mixture of eight isomers of 1,3- and 1,4-cyclo-

heptadiene, eq. 2-9, are possible.

$$\text{(2-9)}$$
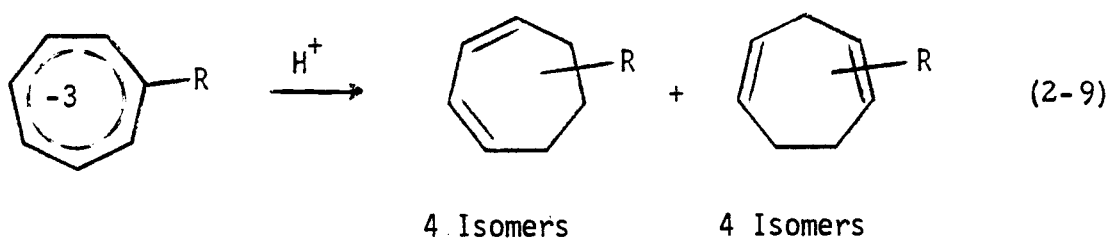
4 Isomers   4 Isomers

Hydrolysis of 6-substituted cycloheptadienyl ions, on the other hand, produces only three cycloheptadiene isomers, eq. 2-8.

Experimentally, hydrolysis of alkyl substituted cycloheptatrienyl-uranium(IV) compounds gives a mixture of, at least, six isomers of substituted cycloheptadiene. Although not all of the eight possible substituted cycloheptadiene hydrolysis isomers are detected by VPC, the presence of more than three isomeric hydrolysis products indicates that the uranium coordinated ligand is not simply the added $C_7H_9^-$ ion.

Formation of lithium n-butylcycloheptatrienyl trianion, $Li_3C_7H_6$-nBu, has been reported.[29] Hydrolysis of $Li_3C_7H_6$-nBu also produces only six detectable cycloheptadiene isomers. In addition, the hydrolysis and deuterolysis products of $Li_3C_7H_6$-nBu are identical (by VPC retention times, mass spectral and ^{1}H NMR analysis) to the hydrolysis and deuterolysis products obtained from the uranium(IV)-cycloheptatrienyl trianion complex.

Since the $C_7H_7^{-3}$ ion and the cyclooctatetraenide dianion, $C_8H_8^{-2}$, are both ten-π electron aromatic anions, $C_7H_7^{-3}$ would be

expected to display many of the same chemical reactions that are

known for $C_8H_8^{-2}$.[30] Specifically, $C_8H_8^{-2}$ may be oxidized by a

number of oxidizing agents, for example, cadmium(II) chloride[31] or

oxygen,[32] to cyclooctatetraene, C_8H_8. A two electron oxidation of

$C_7H_7^{-3}$ would, correspondingly, lead to the formation of the cyclo-

heptatrienyl monoanion, $C_7H_7^-$. Solutions of uranium(IV) cyclohepta-

trienyl trianion compounds are observed to undergo slow internal

redox reactions resulting in the formation of $C_7H_7^-$ and reduced

uranium. The reduced uranium probably exists as a mixture of

uranium(III) and uranium metal. Solutions of cycloheptatrienyl

trianion-uranium(IV) compounds are initially red. After approxi-

mately eight hours, at either room temperature or -78°C, red solu-

tions turn black. Black solids are also formed. The hydrolysis of

the resulting black mixture yields cycloheptatriene, as well as,

1,3- and 1,4-cycloheptadiene. Significantly, d_1-cycloheptatriene is

obtained on deuterolysis. It should be emphasized that cyclohepta-

triene is not a hydrolysis product of the initial red uranium-trianion

solutions. Furthermore, yields of cycloheptatriene obtained from

the hydrolysis of the black uranium mixture increase directly with

the length of time that the uranium(IV)-cycloheptatrienyl trianion

complex remains in solution. Similar ligand-metal slow internal

redox reactions occur for alkyl substituted cycloheptatrienyl trianion-

uranium(IV) compounds.

Spectroscopic properties, i.e. ^{1}H NMR,[33,34] magnetic suscep-

tibilities[35,36] and electronic spectra,[37] of uranocene,[32] $(C_8H_8)_2U$,

have been carefully investigated and interpreted in terms of metal-

ligand molecular orbital interactions.[32-38] Because of the similari-

ties between $C_7H_7^{-3}$ and $C_8H_8^{-2}$, spectroscopic properties of the

cycloheptatrienyl trianion-uranium(IV) complexes should be empiri-

cally similar and dominated by the same molecular controls as

uranocene.

^{1}H NMR spectroscopy has proven most useful for the confirma-

tion of the aromatic, symmetrically π-bonded $C_7H_7^{-3}$ ligand.

^{1}H NMR specra of the ring protons for both uranocene[38] and

uranium(IV) cycloheptatrienyl trianion are given in Table 2-1. The

uranium(IV) ion has an f^2 electronic configuration and is paramag-

netic. Aromatic ring protons for both the cycloheptatrienyl and

cyclooctatetraenyl rings are shifted far upfield. From the appear-

ance of only one proton resonance in the ^{1}H NMR spectrum for

$C_7H_7^{-3}$, one may conclude that all ring protons are magnetically

equivalent. In other words, the C_7 ring is planar, each carbon has

the identical number of hydrogens, one, and the C_7 ring is sym-

metrically bonded to the uranium ion, that is π-bonded. These

conclusions are confirmed by both the intensity and number of ring

proton resonances which occur in the n-butyl cycloheptatrienyl

trianion, C_7H_6-nBu. Three equal intensity peaks are observed for the ring protons in C_7H_6-nBu^{-3}.

TABLE 2-1. ^{1}H NMR FOR RING PROTONS (U^{+4} COMPLEXES)*

$C_7H_7^{-3}$	46.5			
$C_8H_8^{-2}$	35.2			
C_7H_6-nBu^{-3}	40.6	48.6	53.0	
C_8H_7-nBu^{-2}	32.0	33.5	35.6	39.2

*All values in ppm upfield from TMS = 0.

^{1}H NMR paramagnetic shifts for uranocene have been interpreted in terms of dipolar and contact shifts.[33, 34] Ring proton shifts are dominated by positive, upfield, contact shifts. Based on the assumption that the magnetic susceptibility[35, 36] and metal-ligand bond distance[39] for "U(IV)-$C_7H_7^{-3}$" are identical to those of uranocene, Fig. 2-6, one can calculate the dipolar contribution[33] of the paramagnetic shift for $C_7H_7^{-3}$, Fig. 2-7. Because the quantity $(3 \cos^2\theta - 1)$ is close to the zero in $C_7H_7^{-3}$, the dipolar shift is only a minor contribution to the total paramagnetic shift. The Fermi contact contribution to the paramagnetic shift, therefore, is the major component of the large, observed upfield ring-proton resonance shift.
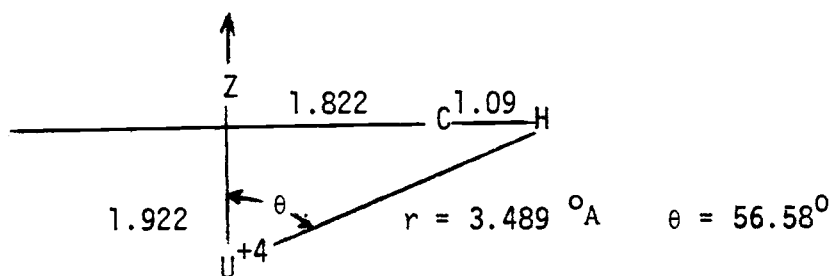
$$\frac{\Delta H^{dip}}{H} = -\frac{1}{3N} [\ \chi_{\parallel} - \chi_{\perp}] \ [\frac{3\cos^2\theta - 1}{r^3}] = + 8.6 \text{ ppm}$$

Figure 2-6. Dipolar Contribution to ^{1}H NMR Shift for $C_8H_8^{-2}$.
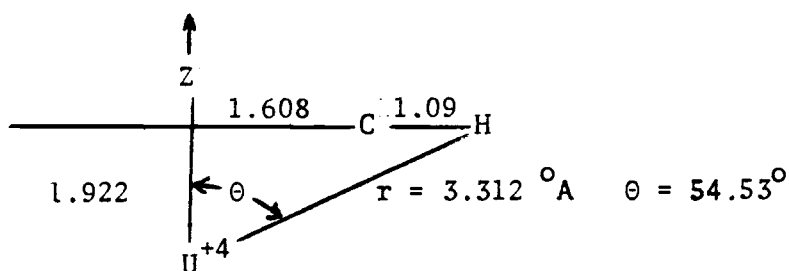
$$\frac{\Delta H^{dip}}{H} = -\frac{1}{3N} [\ \chi_{\parallel} - \chi_{\perp}] \ [\frac{3\cos^2\theta - 1}{r^3}] = -1.1 \text{ ppm}$$

Figure 2-7. Dipolar Contribution to ^{1}H NMR Shift for $C_7H_7^{-3}$.

The origin of the large, upfield contact shift in uranocene was attributed to the transfer of ligand π-orbital electron density to the vacant metal 5$\underline{f}$ orbitals.[33, 34] From a simple molecular orbital model,[32, 38] Fig. 2-8, the energy of the filled E_{2u} π-orbitals of the cycloheptatrienyl trianion should be closer in energy to the uranium 5$\underline{f}$ E_{2u} molecular orbitals than is predicted for uranocene. As a result, stronger π-bonding is expected for $C_7H_7^{-3}$ than for $C_8H_8^{-2}$ leading to larger observed contact shifts for $C_7H_7^{-3}$. For uranocene, contact shifts have been estimated between 30 and 40 ppm. Contact shifts were estimated by subtracting the calculated dipolar shift from the experimentally observed ^{1}H NMR shift.[33] By the same method, contact shifts for cycloheptatrienyl tiranion-uranium(IV) complexes are approximately 40 to 50 ppm upfield. (The diamagnetic proton resonance for $C_7H_7^{-3}$ was taken as 4.6 ppm downfield of TMS.[29])

In addition to the formation of the cycloheptatrienyl trianion, the reaction between uranium(IV) tetrachloride and lithium cyclohepta-dienide produces large amounts of free cycloheptadiene. Approximately 20% of the cycloheptadienide ion is converted to the aromatic trianion while the remaining 80% of the cycloheptadienide anion is converted to a mixture of isomers of cycloheptadiene. Cyclohepta-diene is isolated from the reaction solution prior to hydrolysis. The mixture of cycloheptadiene isomers isolated from the reaction of
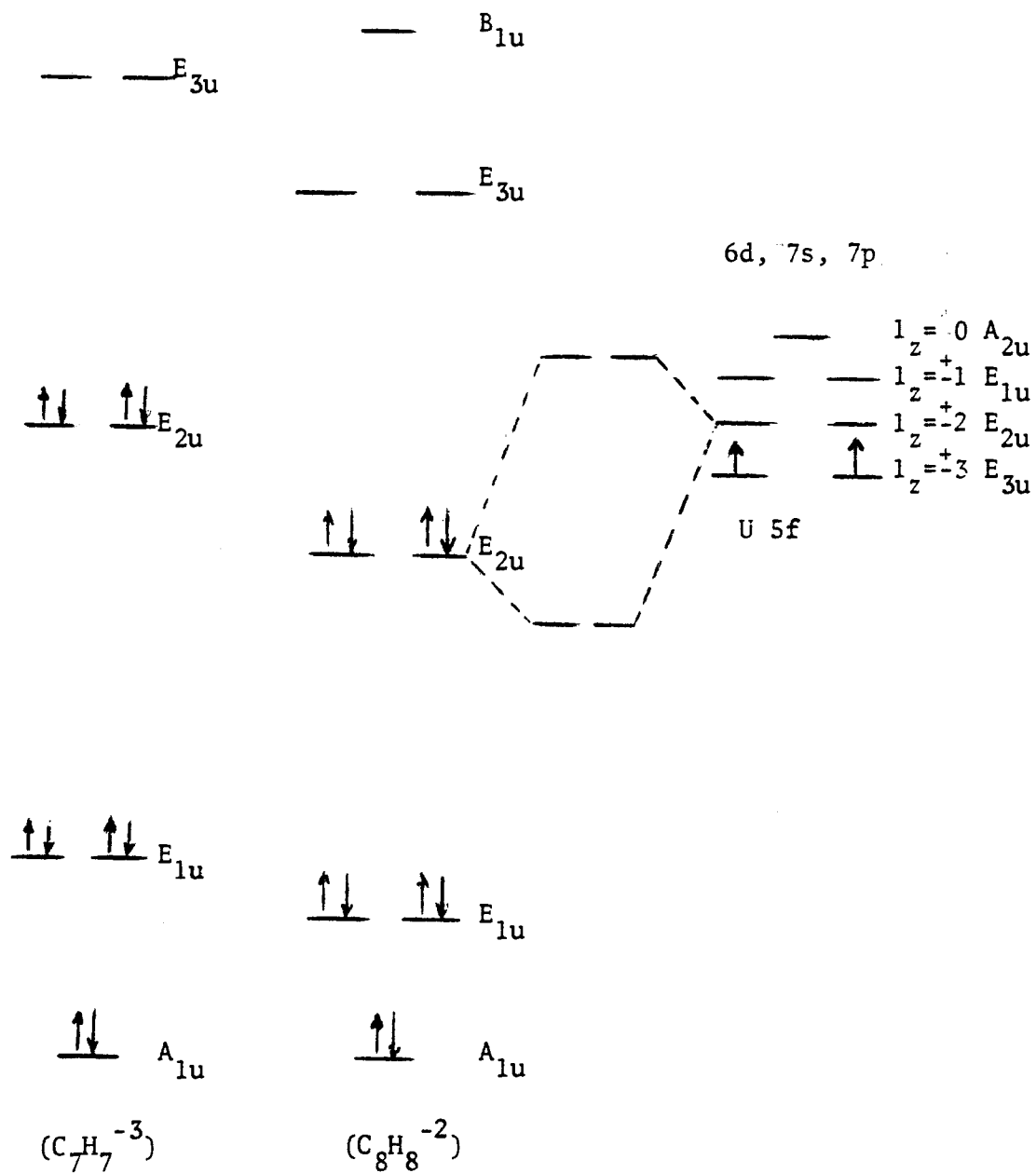
Figure 2-8.   Molecular Orbital Model of the Electronic Structure for
10-π Aromatic-Uranium(IV) Compounds.

uranium(IV) tetrachloride with 6-alkyl substituted cycloheptadienide are the identical isomers which are obtained from the direct hydrolysis of lithium 6-alkyl substituted cycloheptadienide (see eq. 2-8), eq. 2-10.

$$UCl_4 \;+\; 3\; LiC_7H_8\text{-}R \xrightarrow[-20\ ^\circ C]{20\ min} \text{'' } U^{+4} \text{---} \left(\text{-3}\right)\text{-}R \text{ ''}$$

$$+ \qquad (2\text{-}10)$$

$$2\left(\quad \text{-R} + \quad \text{-R} + \quad \text{-R}\right) \quad .$$
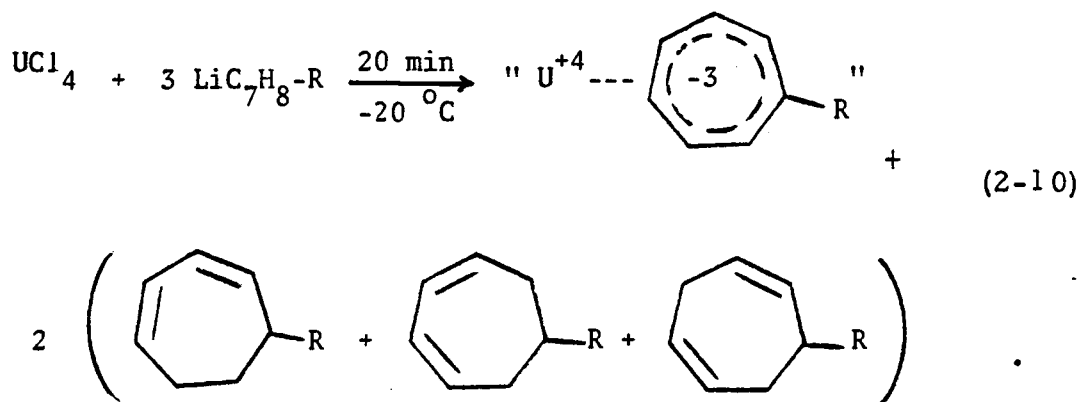
Chloride salts of thorium(IV), erbium(III) and gadolinium(III) have also been used to prepare the cycloheptatrienyl trianion from lithium cycloheptadienide. These compounds are unstable and undergo redox reactions in solution similar to those described for uranium(IV). No stoichiometric compounds, therefore, were isolated.

Cycloheptatrienyl Trianion Compounds of Zirconium

From an examination of cycloheptatrienyl trianion-lanthanide and actinide compounds, it would appear that $C_7H_7^{-3}$ is a powerful reducing agent and does not form stable metal-coordinated compounds. The following preliminary work will show that this is not the case. Reduction of cycloheptatriene by potassium napthalide

in the presence of zirconium(IV) tetrachloride and triphenylphosphine lead to the formation of a brown zirconium compound which contains the coordinated cycloheptatrienyl trianion. This result is especially interesting since attempts to reduce cycloheptatriene by potassium napthalide do not lead to the formation of either $C_7H_7^-$ or $C_7H_7^{-3}$. Although the presence of the ten-π electron aromatic cycloheptatrienyl trianion has been confirmed, the composition and structure of the organozirconium compound have not yet been determined.

CONCLUSIONS

The synthetic approach to preparing cycloheptadienyl transition metal compounds by the reaction of transition metal halides with lithium cycloheptadienide met with limited success. In those cases where metal reduction was not a major side reaction, however, compound yields were superior to those of other synthetic alternatives. It would appear that this synthetic approach should be useful when restricted to the preparation of low valent, cycloheptadienyl transition metal compounds.

In addition to metal reduction reactions, the cycloheptadienyl-anion was found to be readily converted to the cycloheptatrienyl trianion in the presence of chloride salts of the lanthanide and actinide elements. The mechanism for this unusual transformation may be inferred from both the yield of the trianion and from the presence and type of cycloheptadiene isomers which are isolated from the reaction solution, eq. 2-10. Apparently, metal coordination of $C_7H_9^-$ increases the acidity of the methylene hydrogens of the cyclohepta-dienyl ligand. By acting as a base, a second $C_7H_9^-$ abstracts a methylene proton from the coordinated cycloheptadienyl ligand in an acid-base reaction. This is followed by an additional proton abstraction from the remaining methylene carbon by a third $C_7H_9^-$ resulting in the formation of $C_7H_7^{-3}$ and two equivalents of cycloheptadiene. The

ease with which these acid-base reactions occur is remarkable. Solutions of LiC_7H_9 show no tendency to disproportionate into $Li_3C_7H_7$ and two C_7H_{10}. In addition, although metallation of LiC_7H_9 by strong bases has been reported, it is extremely difficult. For example, $Li_3C_7H_7$ has been formed by the double metallation of LiC_7H_9 by the very powerful base n-butyl-lithium (TMEDA),[29] eqs. 2-11 and 2-12.

(2-11)

$$+ \quad 3 \text{ BuH}$$

(2-12)

$$+ \quad 2 \text{ BuH}$$
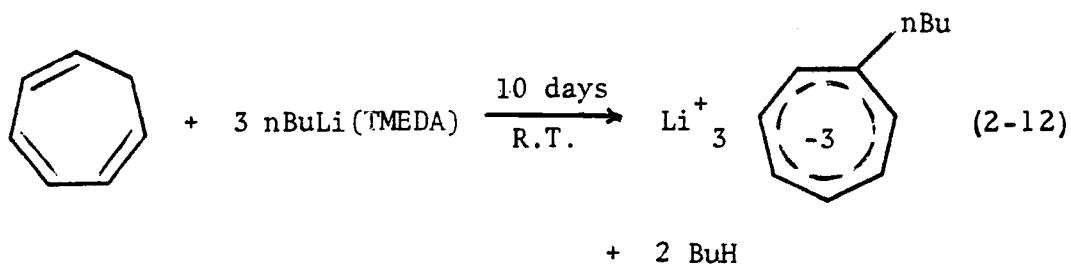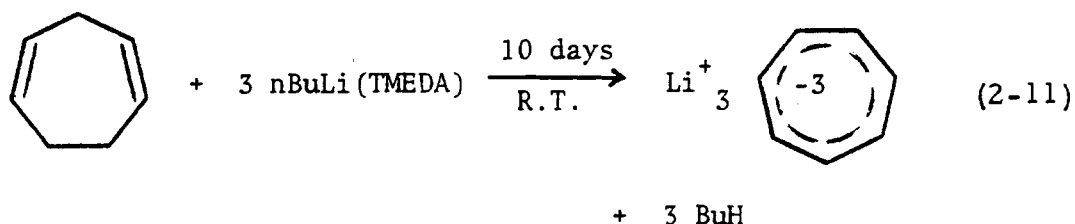
After reaction times from three to ten days, reactions were 70% complete. In the presence of lanthanide and actinide ions, on the other hand, $C_7H_9^-$ is readily deprotonated. Reaction times have been reduced to approximately 30 min, and the strongest base in the solution is the cycloheptadienide anion.

Metal ions may be thought of as functioning in two ways to increase the methylene carbon-hydrogen acidities in the cyclohepta-dienyl ligand. The first function of the metal ion is to act as a strong electron withdrawing group polarizing ligand π-electron density toward the metal ion. The bonding in this model is predominantly ionic. As the methylene proton is lost, the resulting negative charge on the methylene carbon is stabilized by distributing that charge throughout the delocalized π-orbital system. The electron withdrawing effect of the metal ion decreases the electron density on the carbon atoms with the greatest negative charge, the odd dienyl carbon atoms. As a result of the decreased electron density on the carbon atom adjacent to the methylene carbon, the conjugate base of the cyclohepta-dienyl ligand is stabilized relative to the conjugate base of the free cycloheptadienide ion. In addition, the electron withdrawing effects of the metal ion also remove electron density from the cycloheptatri-enyl trianion π-orbitals. The reduction in ligand electron density (negative charge) lowers the energy of the metal coordinated cyclo-heptatrienyl trianion. Since the primary increase in acidity of the cycloheptadienyl anion is attributed to the stabilization of the con-jugate base by the metal ion, either of the two methylene hydrogens may be abstracted. If the incoming base directly removes the proton from the coordinated ligand, the exo-methylene proton will be lost. If, on the other hand, the base coordinates to the metal ion prior to

proton abstraction, the endo hydrogen is likely to be removed. There are many examples in organic chemistry of an electron withdrawing group increasing the acidity of an adjacent carbon-hydrogen bond. The primary acid-strengthening effect of the electron withdrawing group is attributed to the stabilization of negative charge of the conjugate base.[40]

The second way which metal ions may function to increase methylene acidity may result from the formation of strong covalent π-bonds. Strong π-bond formation between the filled ligand π-orbitals and the empty metal orbitals, transfers π-ligand electron density to the metal ion. Because of the spacial proximity of the σ-bonding electron pair of the exo-methylene carbon-hydrogen bond, electron density from the exo-sigma-bonding orbital is transferred to the π-bonding orbitals of $C_7H_9^-$, Fig. 2-9. This is a hyperconjugation effect. The reduction of electron density in the exo-methylene carbon-hydrogen bond leaves that hydrogen more acidic. The central role of the metal ion, for both the ionic and covalent model, is to remove electron density out of the cycloheptadienyl π-orbitals.

From a consideration of the known organolanthanide and organoactinide chemistry, the ionic bonding, polarization model is more likely responsible for the observed increase in acidity. Although weak covalency resulting from π-bond formation has been attributed to many organoactinide compounds,[28,32] π-bonding in

organolanthanide compounds is not chemically significant.[41]

Although increased ligand acidity resulting from π-bonding effects

is not indicated for organolanthanide and actinide compounds, the

influence of π-bond formation should become increasingly important

for ligands coordinated to metals of the d-transition elements.
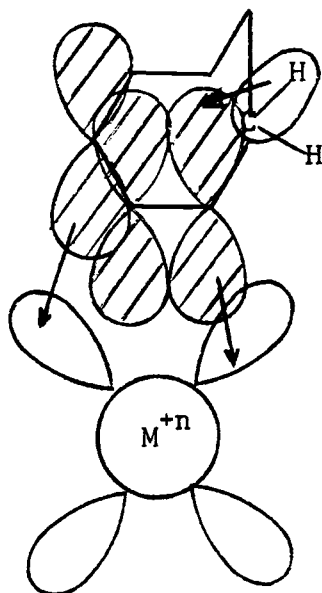
Figure 2-9. Activation of Carbon-Hydrogen Acidity by
π-Bond Overlap.

In this study lanthanide and actinide ions have been observed to

increase cycloheptadienyl reactivity following coordination to the

metal ion. Specifically, the cycloheptadienyl ligand displays

increased methylene carbon-hydrogen acidity leading to the facile

formation of the cycloheptatrienyl trianion. In the presence of either lanthanide or actinide ions, reaction times for the formation of the cycloheptatrienyl trianion have been reduced from approximately ten days to 30 min. In addition, the base strength required to remove the methylene hydrogen atoms has been reduced from the very powerful base n-butyl-lithium (TMEDA) to the weakly basic cycloheptadienyl anion. The ability of a metal ion to activate organic molecules and increase reaction rates (lower activation energies) is one of the most important molecular properties of an organometallic catalyst. In the future it is likely that lanthanide and actinide ions will function in stoichiometric and catalytic reactions as polarization centers activating organic molecules by inductive effects.[28, 42]

EXPERIMENTAL

General Considerations

All of the manipulations were carried out using either high vacuum line or glove box techniques. Solvents were purified by vacuum transfer from $LiAlH_4$ or Na/benzophenone. NMR solvents, benzene-d_6 and pyridine-d_5 (Aldrich), were dried over barium oxide and vacuum transferred prior to use. All materials are commercially available. Cycloheptatriene was distilled under N_2 and stored over Linde 4A molecular sieves. All other materials were used without further purification. Isolation and calibration of organic products were performed on Varian 920 and HP 5720A gas chromatographs, respectively.

^{1}H NMR spectra were recorded using Varian HA-100 or Varian CFT-80A spectrometers. IR spectra were obtained on a Perkin-Elmer 727B spectrometer. Mass spectral data was obtained using a Varian MAT GmbH CH7 Massenspectrometer at an ionization potential of 70 eV, interfaced with a Varian 1200 gas chromatograph.

Preparation of Cycloheptadienide Anions

The preparation of lithium cycloheptadienide[2] and lithium 6-n-butylcycloheptadienide[3] have been previously described. Lithium 6-methylcycloheptadienide may be prepared in the following manner. In 40 ml of Et_2O, 0.91 ml (0.93 mmol) of freshly distilled cyclohepta-triene was added to 6.62 ml (0.93 mmol) of 1.4 M MeLi and 1.40 ml

of TMEDA. After stirring for 24 hrs at room temperature all of the cycloheptatriene had reacted producing a dark red solution of lithium 6-methylcycloheptadienide. Aliquots (1.0 ml) of the resulting red solution were taken for hydrolysis, deuterolysis and alkylation reactions. The substituted cycloheptadiene isomers may be isolated by VPC (1/8" x 8', 15% Carbowax 20 M). Results obtained for lithium 6-methycycloheptadienide were identical with those obtained from other cycloheptadienide anions. Average yields were 80% based on added cycloheptatriene.

1,3- and 1,4-Cycloheptadiene

Authentic samples of 1,3- and 1,4-cycloheptadiene were prepared by the reduction of cycloheptatriene by sodium metal in liquid ammonia.[3,43] At -60°C, 10 ml of liquid ammonia was added to 0.22 g (0.96 mmol) Na. The metal dissolved, resulting in a blue solution. Cycloheptatriene (0.50 ml) was added at -60°C, and the solution carefully hydrolyzed with ethanol. Approximately 15 ml of Et_2O was added and the temperature was raised to 0°C. The NH_3 was removed under vacuum and 1,3- and 1,4-cycloheptadiene were obtained by preparative VPC (1/4" x 8', 10% Carbowax 4000). ^{1}H NMR spectra were identical to those reported in the literature.[43]

Lithium n-Butylcycloheptatrienyl Trianion, $Li_3C_7H_6$-nBu

Authentic samples of the deuterolysis products from the n-butyl-cycloheptatrienyl trianion were obtained by D_2O addition to $Li_3C_7H_6$-nBu. In 35 ml of hexane, $Li_3C_7H_6$-nBu was prepared, according to the literature,[29] by the addition of 0.30 ml (3.06 mmol) of cycloheptatriene and 1.5 ml (9.96 mmol) TMEDA to 5.75 ml of 1.6 M (9.2 mmol) n-BuLi. After approximately 4 hr, the solution turned green. Lithium 6-n-butylcycloheptadienide is rapidly formed. After stirring the green solution for 11 days, a black solid had precipitated. Deuterolysis of the entire reaction mixture, resulted in the 35% formation of six d_3-n-butylcycloheptadiene isomers. The degree of deuterium labeling was determined by VPC mass spectrometry.

Bis(6-Methyl h^5-Cycloheptadienyl) Iron(II)

1.0 g (4.6 mmol) of $FeBr_2$ in 40 ml Et_2O was cooled to -78 °C. A solution of lithium 6-methyl cycloheptadienide (9.3 mmol), prepared separately, was added to the $FeBr_2$ over 15 min. The color of the solution changed immediately to dark brown. Stirring was continued for 8 hrs while warming to room temperature. The solvent was removed under vacuum and the compound was extracted with hexane. The filtered hexane solution was concentrated and cooled to -78 °C. Brown air sensitive crystals were isolated by low

temperature filtration, yield 0.71 g (57%).

Analysis (high resolution mass spectrum): $C_{16}H_{22}Fe$, Theo. m/e

270.106; exp. 270.107.

Mass Spectrum (70 eV): 270 (M^+), 214 ($C_{16}H_{22}$), 162 ($M-C_7H_8CH_3-H$),

107 ($C_7H_8CH_3$).

IR (neat): 814 (w), 1025 (w), 1370 (w), 1449 (m), 1585 (w), 2819 (m),

2860 (s), 2915 (s), 2950 (s), 3005 (s).

^{1}H NMR (benzene-d_6): δ .95 (t), δ 1.3 (m), δ 1.5-2.1 (m),

δ 3.78 (m), δ 4.4 (m), δ 4.8 (m), δ 5.6 (t). ^{1}H NMR was

extremely complex although proton resonances for the dienyl

anion were clearly present (δ = 3.6 to 5.8).

Biscyclopentadienyl Titanium(III) Chloride

A solution of lithium 6-n-butylcycloheptadienide (8.1 mmol) was

prepared by adding 5.10 ml (8.1 mmol) of 1.6 M n-BuLi to 0.79 ml

(8.1 mmol) of cycloheptatriene in 25 ml Et_2O. After stirring for four

hours at room temperature, lithium 6-n-butylcycloheptadienide was

added slowly to a cooled, -78 °C, suspension of dichlorobiscyclo-

pentadienyl titanium(IV) in Et_2O. The mixture was slowly warmed

to room temperature and stirred for two hours. A green solid was

present. The solid was filtered and placed in a Soxhlet extractor.

Extraction with pentane or benzene resulted in the isolation of violet

or green crystals, respectively, identified as biscyclopentadienyl

titanium(III) chloride,[25, 26] yield 1.50 g, 87%.

Analysis (Schwartzkoff): $C_{10}H_{10}ClTi$, Theo. C = 56.23; H = 4.72; exp. C = 57.61, H = 5.07.

IR (Nujol): 724 (m), 782 (s), 819 (s), 849 (m), 900 (m), 1017 (s), 1069 (w).

^{1}H NMR (pyridine-d_5): δ 5.0 (weak, broad). Solvent peaks are broadened and shifted, characteristic of a Ti^{+3} paramagnetic sample.

Formation and Characterization of the Cycloheptatrienyl Trianion

A solution of lithium 6-n-butylcycloheptadienide was prepared from 7.4 ml (11.8 mmol) of 1.6 M n-BuLi and 1.16 ml (11.8 mmol) of cycloheptatriene in 35 ml Et_2O. A suspension of 1.5 g (3.95 mmol) of UCl_4 in 35 ml Et_2O was cooled to -20°C. The solution of lithium 6-n-butylcycloheptadienide was added to the UCl_4 over approximately 10 min. After 15 min, the temperature was rapidly brought to room temperature. After an additional 30 min of stirring, the solution was pale yellow, and a dark red, insoluble uranium-containing cycloheptatrienyl trianion compound had been formed. The solid was filtered and washed with 3 x 15 ml of Et_2O. The reaction solution and washings were combined and analyzed by VPC. 6-n-butyl-1,3-cycloheptadiene, 5-n-butyl-1,4-cycloheptadiene and

5-n-butyl-1,3-cycloheptadiene were identified by a comparison of VPC retention times with authentic samples. Calibration was made using an external standard, yield 1.39 g (4.3 mmol, 78%). Mass spectral analysis of the reaction solution treated with D_2O gave no evidence of deuterium incorporation into the cycloheptadiene products.

The cycloheptatrienyl trianion-uranium(IV) complex was dissolved in THF and filtered. Addition of pentane to the filtered THF solution precipitated the red uranium complex. The precipitate was filtered and washed with 3 x 15 ml of pentane and dried under vacuum (10^{-3} mm Hg) for no more than 30 min. Prolonged vacuum drying causes extensive decomposition. The solids obtained by this procedure were stable, when stored under N_2, for periods up to approximately one week. Other cycloheptadienide anions react similarly with UCl_4.

The yield of cycloheptatrienyl trianion formation was determined by hydrolyzing a THF solution containing all of the isolated product with 1 M HCl. The isomeric mixture of cycloheptadiene hydrolysis products was extracted with pentane and dried over Na_2SO_4. Six isomers of n-butylcycloheptadiene were analyzed by VPC, yield 355 mg (2.4 mmol, 20% yield based on starting cycloheptatriene).

Hydrolysis. THF solutions of the isolated cycloheptatrienyl trianion-uranium(IV) compound were hydrolyzed (deuterolyzed) with

H_2O (D_2O). The resulting mixture was acidified with 1 M HCl.

Organic products were isolated as described above. Hydrolysis

products were identified by identical comparisons with authentic

samples by VPC retention times, ^{1}H NMR and mass spectra. The

degree of deuterium labeling was determined by VPC mass spec-

trometry, Table 2-2.

Oxidation. Solutions of the uranium(IV)-cycloheptatrienyl tri-

anion compound were observed to irreversibly change from red to

black in approximately 8 hrs at room temperature. This reaction

occurred at nearly the same rate at -78°C. Hydrolysis (deuterolysis)

of the resulting black mixture, followed by previously described

work-up procedures, indicated the presence of cycloheptatriene

(d_1-cycloheptatriene). The degree of deuterium labeling was deter-

mined by VPC mass spectrometry, Table 2-2.

Attempts to oxidize the cycloheptatrienyl trianion by air, O_2

or nitrobenzene were unsuccessful, causing complete decomposition

of the uranium-trianion compound. No cycloheptatriene was observed.

Alkylation. All attempts to alkylate the cycloheptatrienyl tri-

anion were unsuccessful. THF solutions of the uranium-bound tri-

anion were decomposed by MeI, EtBr, CCl_4, $(EtO)_2SO_2$ and FSO_3Me.

The only identifiable products isolated from these reactions were non-

alkylated isomers of cycloheptadiene.

Other lanthanide, erbium(III) and gadolinium(III), and actinide,

TABLE 2-2. MASS SPECTRAL PARENT ION FRAGMENTATION PATTERN OF DEUTEROLYSIS PRODUCTS OF C_7H_8-R^-, C_7H_6-R^{-3}, and C_7H_6-R^- (R=H, n-Bu, Me).

Hydrolysis Product	M(m/e)	Ion Intensity (%)			
		(M-2)	(M-1)	M	(M+1)
C_7H_{10}	94	3.9	14.0	36.7	3.4
C_7H_9D	95	4.7	18.9	66.0	5.4
$C_7H_7D_3$	97	6.1	18.0	68.0	5.2
C_7H_8	92	- .8	100.0	47.5	3.2
C_7H_7D	93	100.0	91.9	30.4	1.4
C_7H_9-nBu	150	.3	.2	34.5	4.1
C_7H_8D-nBu	151	1.8	1.7	43.8	5.8
$C_7H_6D_3$-nBu	153	.5	1.4	64.1	9.0
C_7H_7-nBu	148		1.4	19.1	2.1
C_7H_6D-nBu	149		8.9	19.3	2.6

Table 2-2. (Continued)

Hydrolysis Product	M(m/e)	Ion Intensity (%)			
		(M-2)	(M-1)	M	(M+1)
C_7H_9-Me	108	1.4	8.6	80.9	7.5
$C_7H_6D_3$-Me	111	4.3	17.8	96.9	11.6
C_7H_7-Me	106	2.2	21.9	47.6	3.4
C_7H_6D-Me	107	10.7	35.5	63.6	6.1

thorium(IV), chlorides were found to convert solutions of lithium cycloheptadienide to the cycloheptatrienyl trianion under the same reaction conditions described for uranium(IV) tetrachloride.

NOTE: For the lanthanide elements one equivalent of lithium cyclo-heptadienide per equivalent of lanthanide chloride was used.

Preparation of a Zirconium Cycloheptatrienyl Trianion Compound

The synthetic route to formation of cycloheptatrienyl trianion zirconium compounds differs from the previously described synthesis for the lanthanide and actinide elements. In 40 ml THF, 1.50 g (6.4 mmol) $ZrCl_4$ was dissolved and added to 1.68 g (6.4 mmol) $(C_6H_5)_3P$. The resulting yellow solution was cooled to -78°, followed by the addition of 1.25 ml (12.8 mmol) of cycloheptatriene, 1.00 g (25.6 mmol) K and approximately 0.10 g of napthalene. The temperature was slowly raised, over 5 hrs, to room temperature and stirred overnight. The THF was removed under vacuum leaving a brown oil. Addition of 30 ml of hexane produced a brown solid and red solution. The solid was filtered and washed with 3 x 10 ml of hexane and 3 x 15 ml of Et_2O. The brown solid is not soluble in either Et_2O or hexane. The brown solid is soluble in THF and is reactive to both oxygen and H_2O.

The isolation of d_3-1,3-cycloheptadiene and d_3-1,4-cyclohepta-diene following D_2O addition to THF solutions of this zirconium compound confirm the formation the $C_7H_7^{-3}$ ligand. When stored under N_2, solid samples of the cycloheptatrienyl trianion zirconium compound appear to remain unchanged for, at least, several weeks. Further compound characterization of this new zirconium compound is in progress.

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III. REACTIONS OF CYCLOHEXANONE
WITH METAL VAPORS

INTRODUCTION

Within the past few years, there have been a number of investigations which have used transition metal compounds to affect the reduction of aldehydes and ketones. These reduction reactions lead, depending upon the exact reducing agent, to either dimeric pinacol products or dimeric olefin products. Yields are often excellent, and the method is quite general toward carbonyl reduction. A brief review of the known reduction reactions will be given in order to determine the general characteristics of the known reducing agents and to determine what properties are responsible for general reactivity and product selectivity.

Reductive Coupling of Carbonyl Compounds to Pinacols

A number of titanium based compounds have been used to affect the reduction of carbonyl compounds to pinacols, Table 3-1. Generally, these reactions begin with titanium(III) chloride followed by the reduction of the Ti^{+3} ion by some reducing agent. Often the exact nature of the final titanium compound is in doubt. Most investigators have assumed that the Ti^{+3} ion is reduced to Ti(II). Ti(II) is a strong reducing agent $(Ti^{+2} \rightarrow Ti^{+3} + e^-; E^o = 0.37 \text{ v})$ and is believed to

Table 3-1. MATERIALS FOR REDUCTIVE COUPLING OF
           CYCLOHEXANONE

Materials	% Yield	Ref
$Mg(Hg)/TiCl_3$	93	1
$6(C_5H_5)TiCl_2/4.5 \ LiAlH_4$	89	1
$(C_6H_6)TiCl_2 \cdot 2AlCl_3$	90	1
$Mg/TiCl_3$	45	2
$Zn/TiCl_3$	24	1
$Al(Hg)$	55	3
$TiCl_3/nBuLi$	n/a (poor)	1
$TiCl_3/DIBAL$	n/a (poor)	1

*n/a Not Available

transfer an electron to the carbonyl group forming a radical-anion

intermediate,[1,4] eq. 3-1.

$$R_2C=O \;+\; Ti^{+2} \;\rightarrow\; Ti^{+3} \left[R_2\dot{C}-O^- \right] \tag{3-1}$$
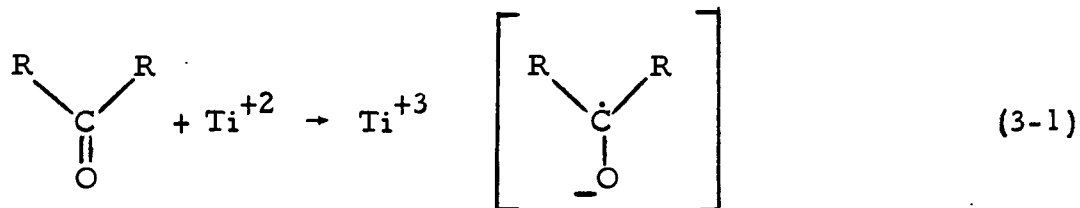
Product formation may proceed by a number of reaction paths to

the pinacolic dianion,[1] Fig. 3-1.

$$R_2C=O + Ti(II) \rightarrow R_2\text{-}\dot{C}\text{-}O\text{-}Ti(III) \tag{a}$$

$$R_2\dot{C}\text{-}O\text{-}Ti(III) + R_2C=O \rightarrow R_2C\diagup\diagdown Ti(IV) \tag{b}$$

$$R_2C \diagup\diagdown Ti(IV) + Ti(II) \rightarrow R_2C \diagup\diagdown Ti(III) + Ti(III) \tag{c}$$

$$\text{or} \quad 2R_2\dot{C}\text{-}O\text{-}Ti(III) \rightarrow R_2C\text{-}O\text{-}Ti(III) \;\; R_2C\text{-}O\text{—}Ti(III) \tag{d}$$
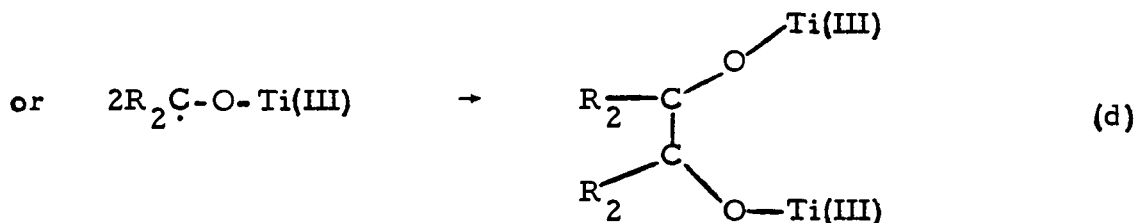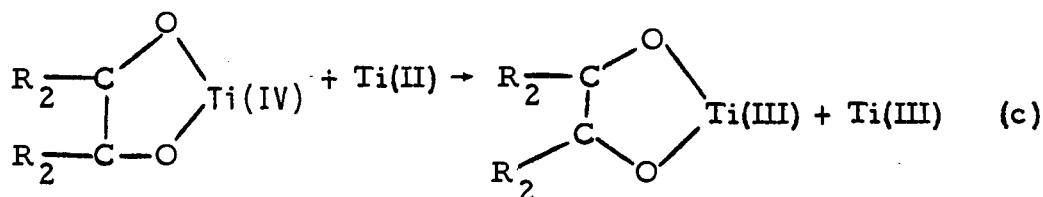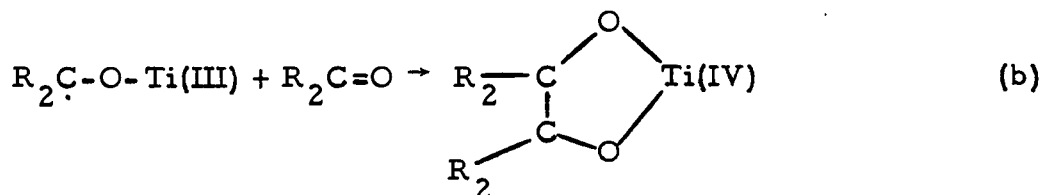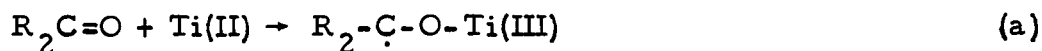
Figure 3-1. Mechanism for Pinacolic Dianion Formation.

Strong support for the importance of the Ti(II) oxidation state

comes from the observation that well characterized Ti(II) arene

complexes effectively couple both alkyl and aryl ketones to pinacols.[1]

Although the importance of the Ti(II) oxidation state for pinacol

production is clearly indicated, Table 3-1 shows that not all Ti(II)

compounds are equally effective reducing agents. Although aryl

ketones are easily coupled to pinacols by many reducing agents, only

the most reactive reagents are capable of coupling aliphatic ketones

to pinacols. In addition to the selectivity differences displayed by

various reducing agents, product yields also vary among the reducing

agents. Reactivity and selectivity are sensitive functions of the exact

method of Ti(III) reduction.

Reductive Deoxygenation of Carbonyl Compounds to Dimeric Olefins

In addition to the reduction of carbonyl compounds to pinacols,

carbonyl compounds have been deoxygenatively coupled to olefins. A

number of compounds capable of olefin production are listed in Table

3-2. Deoxygenative coupling of ketones to olefins is a slower reac-

tion than the corresponding pinacol coupling reaction, requiring

stronger reducing agents.

TABLE 3-2. MATERIALS FOR CARBONYL REDUCTION TO
OLEFINS

Material	% Yield Alkyl	% Yield Aryl	Ref
$2TiCl_3/LiAlH_4$	95	95	5
$TiCl_3/3K$	85	n/a	6
$WCl_6/LiAlH_4$	43	55	7
$W(CO)_6$	--	21	7
$W(CO)_5PPh_3$	--	9	7
$W(CO)_5 = C \diagup^{OCH_3}_{\diagdown Ph}$	--	13	7
$WCl_6/1.6nBuLi$	10	76	8
$WCl_6/2Li$	n/a		8
K_2WCl_6	n/a		8

* n/a Not Available

For reductions which use low valent titanium compounds, olefin production is believed to proceed by a two step mechanism,[5,6] eqs. 3-2 and 3-3.

$$(3\text{-}2)$$

$$+ \; TiO_2 \quad (3\text{-}3)$$
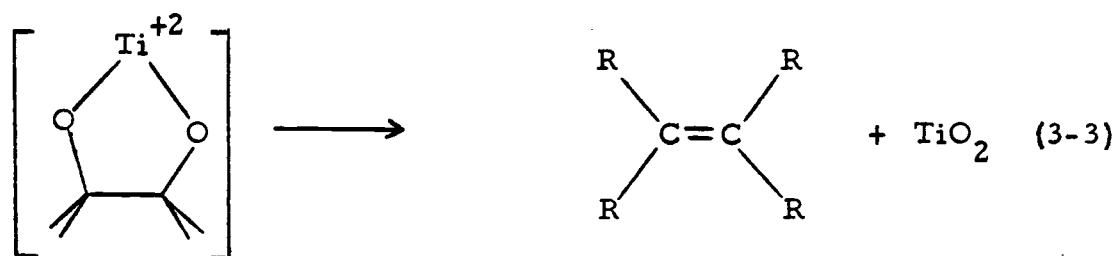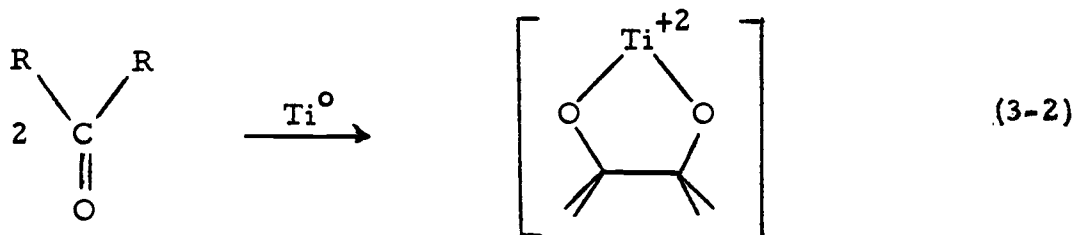
The first step of olefin production is identical to the process for pinacol production described above. Active titanium metal produces radical-ion intermediates, eq. 3-1, which couple to pinacol dianions. The pinacolic dianion is further reduced by the Ti^{+2} ion to olefin and TiO_2. It is not known whether eq. 3-3 proceeds in a sequential or in a concerted manner, but it is believed that the carbon-oxygen bond cleavage proceeds through a radical intermediate.

Tungsten and molybdenum compounds have also been used to deoxygenatively couple ketones. For all systems which have been studied, tungsten induced couplings give fair to poor yields and are restricted to aryl ketones and aldehydes. Tungsten compounds are

believed to produce a tungsten-carbene complex which leads to product

formation,[7] Fig. 3-2. Evidence for tungsten carbenes comes pri-

marily from three sources: (i) When benzaldehyde and 1-(2-methyl-

propenyl)pyrrolidine are treated with WCl_6-$LiAlH_4$ in THF a cyclo-

propane product is obtained in 6.2% yield along with the expected

stilbene, yield 1.1%, eq. 3-4.

$$Ph-C=O + \quad CH_3, CH_3 \; C=C \; H, N \quad \xrightarrow[\text{THF}]{WCl_6/LiACH_4} \quad CH_3, CH_3 \; H, Ph, H, N \; + PhHC=CHPh \qquad (3-4)$$

$$WCl_6 + Reductant \rightarrow WX \text{ (lower valent)} \qquad (a)$$

$$Ph-C=O + WX \rightarrow XW=C(H)(Ph) \text{ with } O \qquad (b)$$

$$XW=C(O)(Ph) + Ph-C=O \longrightarrow XW(O) ... Ph, Ph \qquad (c)$$

$$XW—C(Ph)(O-C(Ph)) \longrightarrow PhHC=CHPh + XWO_2 \qquad (d)$$

Figure 3-2. Mechanism for Tungsten Reduction of Carbonyls
to Olefins.

(ii) Reduction of p-methoxybenzyaldehyde and phenyldiazomethane with WCl_6-$LiAlH_4$ results in a 12% production of p-methoxystilbene.

(iii) Well-characterized tungsten-carbene complexes affect carbonyl coupling. Although tungsten-carbene complexes do couple carbonyl compounds, no products are dérived from the carbene attached to the metal.

In a separate study of tungsten(IV) compounds, it was found that many of the same compounds which reduce ketones and aldehydes to olefins, reduce 1,2-diols to olefins.[9] Tungsten reduction of pinacols to olefins was found to be very active, reducing alkyl diols in high yield. Pinacolic dianions treated with tungsten(IV) compounds eliminate the olefin while forming two metal-oxygen bonds, eq. 3-5.

$$(3-5)$$
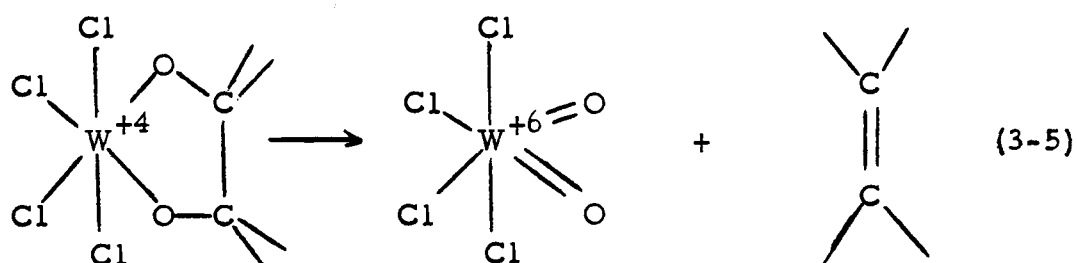
Active intermediates are believed to be radical species. The similarities between tungsten and molybdenum reduction of pinacols with the titanium reductive deoxygenative coupling of ketones is unmistakable. The only differences are the particular metals which are used and the oxidation states of those metals.

From the previous review, several questions come to mind. Are there other transition metal compounds which will reduce ketones and aldehydes to pinacols or olefins? If there are other compounds, which compounds would be expected to produce pinacol products and which would be expected to produce olefin products? Finally, what molecular properties are most responsible for the preparation of effective carbonyl reducing agents?

Transition metal atom vapors are extremely reactive and can be prepared under conditions suitable for study with organic molecules.[10,11] In addition, very reactive metal slurries can be prepared by codepositing metal atoms in a solvent matrix. The reactivity of these metal species is highly dependent on the choice of solvent.[12] Since a large number of metals may be vaporized and a number of zero valent reactive species may be prepared for each metal, a study of cyclohexanone reductions, as a typical alkyl ketone, with d- and f-transition metals was undertaken. It was hoped that a study of many different metals would allow the previously posed questions to be answered.

Finally, one brief report exists on the reduction of cycloheptanone by magnesium metal atoms.[13] In that study, magnesium atoms deoxygenated cycloheptanone to produce cycloheptene (46%), norcarane (2%), cycloheptane (2%)(bicycloheptyl)-1, 1'diol (19%) and aldol condensation products (31%). Carbene intermediates were proposed to account for

the presence of seven membered deoxygenated hydrocarbon products.

High surface area clean magnesium powders, however, were found to

be unreactive toward ketones.

Reduction of Nitro Compounds by Transition Metal Compounds

Although a number of transition metal compounds have been used

to reduce carbonyl and pinacol compounds, relatively little is known

about the reduction of other functional groups by transition metal com-

pounds.[4] While nitro compounds may be reduced by many reducing

agents, relatively few transition metal compounds have been used to

affect nitro reduction. The reduction of nitro compounds by the action

of metal (Zn, Sn, Fe and others) and mineral acids, generally,

results in the formation of amines.[14] In some cases, it has been

possible to stop nitro reduction at an intermediate stage, yielding

hydroxyl amines, azo, azoxy or hydrazo compounds. In those few

cases where transition metal compounds have been used to reduce

nitro compounds, reduction products usually differ from the products

obtained from conventional reducing agents. For example, aqueous

solutions of the Ti^{+3} ion have been used to convert nitro compounds

into carbonyl compounds,[15] eq. 3-6.

$$(3\text{-}6)$$
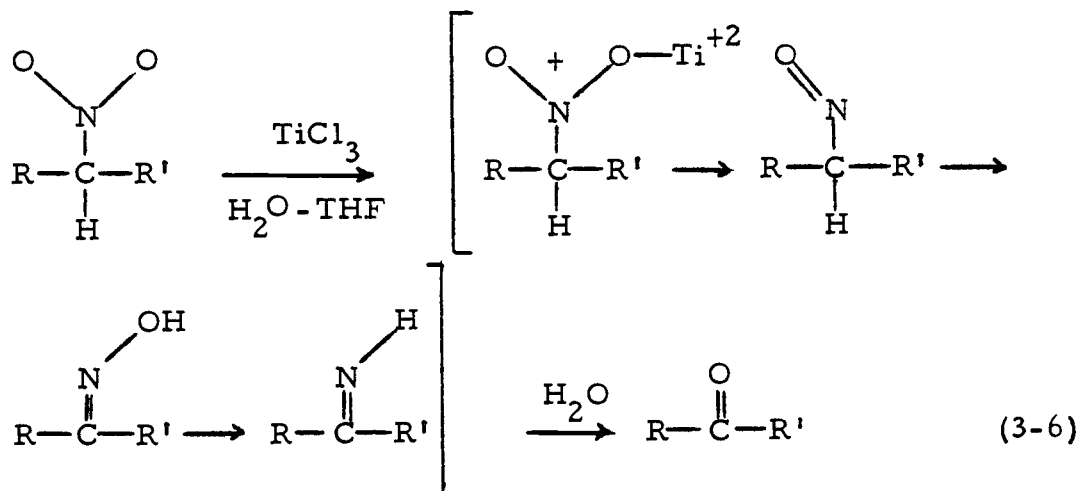
The addition of $LiAlH_4$ and $TiCl_3$ to nitro compounds, on the other hand, yields hydrazo compounds.[16] Also uranocene has recently been reported to reduce nitro compounds to the corresponding azo compounds,[17] eq. 3-7.

$$2(C_8H_8)_2U + 2\ R\text{-}NO_2 \qquad R\text{-}N{=}N\text{-}R + 2UO_2 + 4\ C_8H_8 \qquad (3\text{-}7)$$
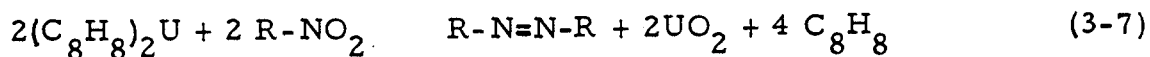
Since there are only a limited number of d- or f-transition metal compounds to have been reported to reduce nitro compounds, it was of interest to see if transition metal atom vapors could be used as reducing agents for nitro compounds and to identify the corresponding reduction products. In addition, it is of interest to compare the metal atom reduction methods to those of the solution techniques.

RESULTS AND DISCUSSION

Metal Atom Cocondensation with Cyclohexanone
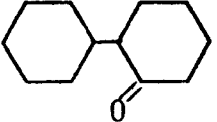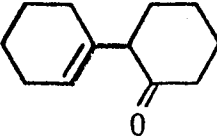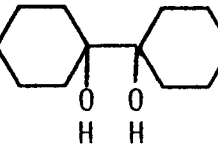
In an attempt to produce reactive materials which would reduc-
tively couple cyclohexanone, metal atoms of the d- and f-transition
elements were cocondensed at -196 °C with cyclohexanone. The metals
which were selected for this study represent a wide range of metallic
properties and are given in Table 3-3. The metals in Table 3-3 vary
in size, electronic configuration, ionization potential, oxidation poten-
tial, stability of oxidation states, heats of vaporization, tendency to
form ionic or covalent bonds, and metal-oxygen bond strengths. In
addition, each metal has a sufficiently low boiling point under the
experimental conditions to allow a suitable quantity of metal to be
deposited, at least 0.10 g.

Metal atom vapors were reactive toward cyclohexanone, and the
organic products are given in Table 3-4. On the basis of Table 3-4,
metal atom reactions with cyclohexanone may be divided into two
groups. All group I metals reductively couple cyclohexanone to
(bicyclohexyl)-1,1'diol, a pinacol, with little formation of bicyclo-
hexylidene. In addition, for most group I metals, aldol derived com-
pounds were the major product. Group II metals show much less
reactivity toward cyclohexanone reduction than do group I metals, and

TABLE 3-3. METAL PROPERTIES

Metal	Heat of[18] Vap. (Kcal/mole)	Electronic Configuration	Oxidation States	Ion[19] Size Å	Oxidation[18,20] Potential E^O (volts)	Metal-oxygen[18,21] bond energies (Kcal)
K	21.5	$[Ar]\,4s^1$	K^+	1.38	K/K^+ 2.93	-43.2
Ti	112.6	$[Ar]\,4s^2 3d^2$	Ti^{+3} Ti^{+4}	.67 .61	Ti/Ti^{+2} 1.6 Ti^{+2}/Ti^{+3} .37	-112.9
Cr	94	$[Ar]\,4s^2 3d^4$	Cr^{+2} Cr^{+3}	.89 .63	Cr/Cr^{+2} .91 Cr^{+2}/Cr^{+3} .41	-90.9
Co	102	$[Ar]\,4s^2 3d^7$	Co^{+2} Co^{+3}	.72 .63	Co/Co^{+2} .28	-57.1
Ni	101	$[Ar]\,4s^2 3d^8$	Ni^{+2}	.69	Ni/Ni^{+2} .23	-57.3
Nd	69	$[Xe]\,6s^2 4f^4$	Nd^{+3}	1.12	Nd/Nd^{+3} 2.25	-147.3
U	120	$[Rn]\,7s^2 5f^4$	U^{+3} U^{+4}	1.06 1.00	U/U^{+3} 1.80 U^{+3}/U^{+4} .63	-129.6

TABLE 3-4. REACTION PRODUCTS OF CYCLOHEXANONE AND METAL ATOM VAPORS.

Metal	(olefin)	(ketone, O)	(enone, O)	(pinacol, OH OH)	Mole Ratio $\frac{Aldol}{Pinacol}$	Mole Ratio $\frac{Pinacol}{Metal}$
Ti .120 g	8.0% (10 mg)	--	21% (27 mg)	71% (100 mg)	.29	.21
Cr .366 g	2.0% (23 mg)	--	70% (620 mg)	27% (270 mg)	2.5	.19
Nd .184 g	--	--	76% (380 mg)	24% (130 mg)	2.1	.50
U .378 g	3.0% (6.5 mg)	--	71% (150 mg)	26% (60 mg)	2.8	.19
Co .825 g	--	8.6% (8.4 mg)	91% (89 mg)	--	--	--
Ni .657 g	--	69% (52 mg)	31% (23 mg)	--	--	--

group II metals show no tendency to reductively couple alkyl ketones
to pinacols or olefins.

Despite the wide range of metallic properties of the metals of
group I (Ti, Cr, Nd and U), the product selectivity and general reac-
tivity of each metal is remarkably similar. With the exception of Nd,
the yields of pinacol were nearly constant, approximately 20% based
on the amount of metal deposited. Nd atoms, however, show far
greater reactivity than all other metals towards pinacolic coupling of
cyclohexanone. One equivalent of Nd yields 0.50 equivalents of
(bicyclohexyl)-1,1' diol. The higher yield of pinacol coupling for Nd
relative to the other group I metals may be explained, in part, by
higher oxidation potentials of Nd metal as compared with the oxidation
potentials of the other metals (see Table 3-3). If the reduction of
ketones to pinacols proceeds by a radical-ion intermediate, then the
ease with which metal atoms lose electrons should affect product
yields. This is what is observed. Unlike magnesium metal atom
reactions, d- and f-transition metal vapors produce no volatile deoxy-
genated carbene derived products.

Unlike any of the previously reported reduction materials,
Tables 3-1 and 3-2, metal atoms produce high yields of aldol conden-
sation products. With the exception of titanium, aldol condensation
products were the major product. Even for titanium, aldol condensa-
tion products account for 20% of the total product. It is significant

that mole ratios of aldol to pinacol products are nearly two to one.

Aldol condensation reactions can, and most often do, result from the

addition of a strong base to an alkyl ketone.[22] The pinacolic dianion,

which is the actual reduction product prior to hydrolysis, is a suffici-

ently strong base to attack cyclohexanone, eqs. 3-8 and 3-9, leading

to 2-(1-cyclohexene-1-yl)-cyclohexanone, an aldol derived product.[13]

(3-8)

(3-9)
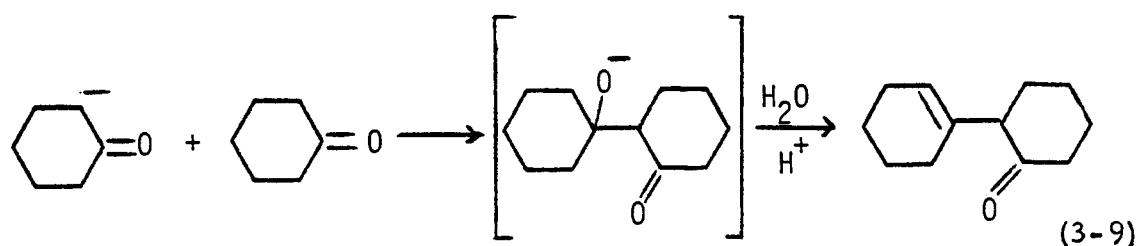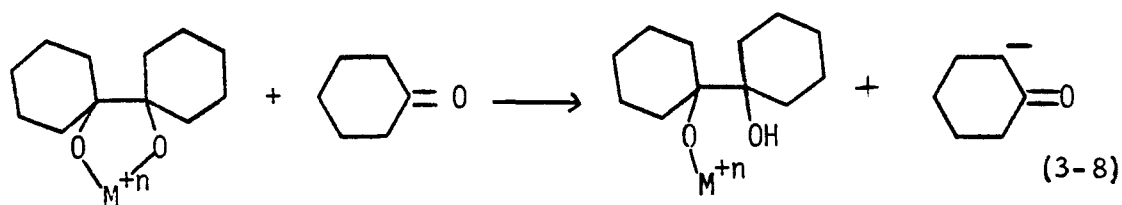
Although aldol to pinacol ratios are close to two, they are,

actually, greater than two to one in most cases. The hydrogen atom

on the hydroxyl intermediate, eq. 3-10, is acidic and readily reduced

by reactive, low valent, electropositive metal ions reforming the

pinacolic dianion, eq. 3-9.

(3-10)
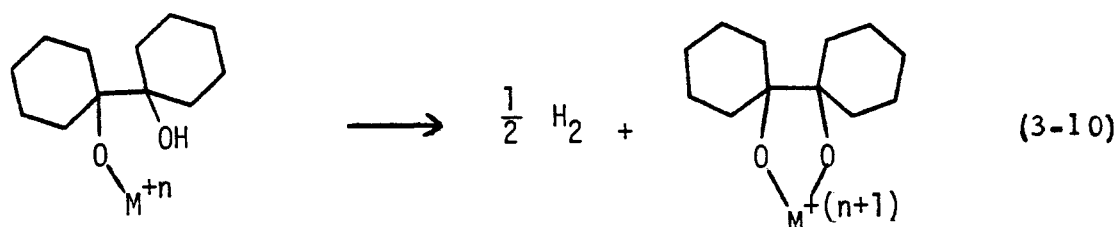
In this way, metals may be oxidized without producing additional pina-

colic dianions and, at the same time, produce greater amounts of

aldol product than is expected from the amount of alkoxide ion present.

For example, the reaction between potassium metal and cyclohexanone

in THF is rapid, producing a gas and high yields of 2-(1-cyclohexene-1-

yl)-cyclohexanone with only traces of (bicyclohexyl)-1, 1'diol.

It is somewhat surprising that titanium atoms cocondensed with

cyclohexanone lead to low yields of bicyclohexylidene. From predic-

tions based on cyclohexanone reductions by known titanium reducing

agents,[5,6] one would have expected that titanium atoms would not only

produce bicyclohexylidene in high yield, but that bicyclohexylidene

would have been the only product. Since carbonyl reduction has been

shown to be highly dependent on the nature of the reducing agent, sev-

eral additional attempts were made to produce titanium compounds by

the metal atom vaporization technique which would reduce cyclohexan-

one to bicyclohexylidene.

Cyclohexanone Reduction with Titanium Atom/Solvent Clusters

Titanium clusters prepared from the deposition of titanium atoms

with a large excess of solvent were found to be reactive toward cyclo-

hexanone reduction. These clusters were maintained at -196 °C while

a layer of cyclohexanone was added to the suface of the matrix.
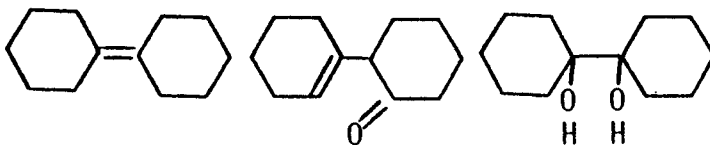
Cyclohexanone reduction occurred on matrix warm-up. Although Klabunde has characterized several distinct phases for nickel atom-solvent clusters,[12] no other titanium atom phases were tested for reactivity in this study. Cyclohexanone reduction products for titanium atom/solvent clusters are presented in Table 3-5.

From Table 3-5 it can be seen that titanium atoms condensed with saturated solvents, hexane and tetrahydrofuran, are less reactive towards cyclohexanone radical reduction processes than are titanium atoms in a matrix of cyclohexanone. In addition, titanium-hexane and titanium-THF reactions produce high yields of aldol condensation product, 2-(1-cyclohexenyl-1-yl)-cyclohexanone.

Metal atom reactions of neopentane have recently been studied.[23] Titanium atoms were found to be highly reactive toward oxidative addition of carbon-hydrogen and carbon-carbon bonds. Oxidative addition reactions are believed to occur immediately upon titanium atom impact with the alkane at -196 °C. Although the final metal oxidation states were not determined, the presence of reactive metal alkyl fragments and metal hydrides was established. Other metals have been shown to behave similarly although are less reactive than titanium.[23, 24]

Titanium atom-solvent reactions can be seen to affect carbonyl reductive coupling reactions in two ways. First, zero valent species are partially oxidized through solvent reactions, prior to reaction with cyclohexanone. Yields of the corresponding pinacol are lower. Secondly,

TABLE 3-5. REACTION PRODUCTS OF TITANIUM ATOM VAPOR/SOLVENT PLUS CYCLOHEXANONE.

Metal	Solvent				Mole Ratio $\frac{\text{Aldol}}{\text{Pinacol}}$	Mole Ratio $\frac{\text{Pinacol}}{\text{Metal}}$
Ti .100 g	C_6H_{14} (hexane)	1.5% (2.4 mg)	81% (150 mg)	18% (37 mg)	4.4	.09
Ti .110 g	C_4H_8O (THF)	4.7% (11 mg)	81% (200 mg)	14% (39 mg)	5.6	.09
*Ti .151 g	C_7H_8 (toluene)	--	24% (68 mg)	76% (240 mg)	.31	.39
Ti .120 g	$C_6H_{10}O$ (Cyclohexanone)	8.3% (10 mg)	21% (27 mg)	71% (100 mg)	.29	.21

*Some Solvent Products were Observed.

reactive metal alkyl and hydride fragments attack carbonyl compounds leading to non-radical routes of carbonyl reduction. The primary reduction route leads to aldol condensation reactions.

The reaction of titanium atoms with arene solvents produces high yields of bisarene titanium (0) compounds.[25] These sandwich compounds are reactive toward cyclohexanone, reacting immediately on matrix warm-up. Bistoluene titanium (0) is effective at reductively coupling alkyl ketones to pinacols. Bisarene titanium (0) compounds are the most reactive titanium species produced by the metal atom technique, studied thus far. Reactivities are twice as high as even metal atom reactions with cyclohexanone and are only slightly less reactive than the neodymium atom cyclohexanone reaction.

A number of titanium species have been produced and have been used as reducing agents with cyclohexanone. These titanium species may be expected, and do, exhibit a wide range of reducing properties. At one extreme, zero valent "bare" titanium atoms were reacted directly with the pure ketone. At the other extreme, discrete zero valent bisarene titanium (0) compounds have been prepared and used to reduce a dilute solution of cyclohexanone. Under yet different conditions, titanium species of intermediate oxidation state containing bound reactive ligands have been used to reduce dilute solutions of cyclohexanone. Despite the vastly differing properties of the various titanium metal-cyclohexanone systems, none of these titanium species

have been an effective reducing agent for the transformation of cyclo-
hexanone to bicyclohexylidene.

Titanium Tetrachloride-Potassium
Reduction of Cyclohexanone

From the above studies it seemed evident that reduction of cyclo-
hexanone to bicyclohexylidene requires more than the presence of high
surface area zero valent titanium metal. Titanium species produced
by the use of the metal atom technique have consistently failed to pro-
duce olefins from carbonyl compounds. On the other hand, titanium
powders prepared by the reduction of titanium tetrachloride have
consistently coupled alkyl ketones to olefins.[5] Because of these
differences in reduction properties, reduction of cyclohexanone with
titanium tetrachloride-potassium metal, which has been the most
effective reductant reported, was reinvestigated.

Reduction of titanium tetrachloride with four equivalents of
potassium metal in refluxing THF produces a highly reactive black
solid. No excess potassium metal can be seen. From the proposed
mechanism, two equivalents of ketone should be reduced to one equiva-
lent of olefin and one equivalent of titanium dioxide,[5,6] eq. 3-11.

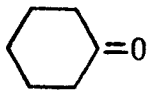$$2 \underset{\underset{O}{\|}}{RCR} + Ti^{o}(4KCl) \longrightarrow R_2C{=}CR_2 + TiO_2 \qquad (3\text{-}11)$$
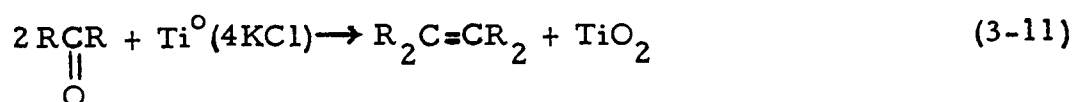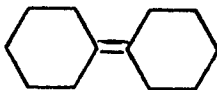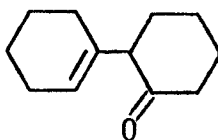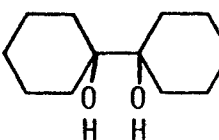
Surprisingly, cyclohexanone fails to be reduced to bicyclohexylidene

under these conditions, even after THF reflux overnight. The ob-
served products are given in Table 3-6. It can be seen from Table
3-6 that, when cyclohexanone is in excess, product yield and distribu-
tion are similar to products produced by the metal atom technique,
Table 3-5. In the presence of excess ketone, pinacols are the pre-
ferred radical reductive coupling product and aldol condensation
products are the major product. It should be emphasized that experi-
mentally, two equivalents of ketone is an excess for the titanium reduc-
tion of carbonyl compounds to olefins.

In the literature preparation of bicyclohexylidene from cyclo-
hexanone, McMurry and Flemming used one equivalent of ketone per
equivalent of titanium metal.[5] When as little as one-fourth equivalent
of cyclohexanone per equivalent of metal is used bicyclohexylidene is,
indeed, the only observed organic product. Because of the high reac-
tivity of the titanium metal, and the large excess of metal present, a
great many solvent derived products were also observed. Some of the
solvent products incorporated cyclohexanone into the product as well
as THF. This, in part, accounts for the overall low yield of bicyclo-
hexylidene based on added cyclohexanone, 14%. None of the solvent
products were specifically identified.

Reduction of ketones to pinacols by potassium reduced titanium
tetrachloride has not been previously reported; however, pinacolic

TABLE 3-6. REACTION PRODUCTS OF CYCLOHEXANONE BY $TiCl_4$/4K POWDERS.

Metal Chloride	Solvent	Equivalents	$\bigcirc$=O			
$TiCl_4$	THF	2.00	.8%		81%	18%
(2.42 g)			(12 mg)		(1300 mg)	(330 mg)
*$TiCl_4$	THF	.25	100%		--	--
(2.35 g)			(69 mg)			

*Extensive Solvent Decomposition was observed.

dianions have been proposed as intermediates in the reductive coupling of ketones to olefins, eq. 3-2 and 3-3. Reductive coupling of two carbonyl groups to the pinacolic dianion, eq. 3-2, is a two electron reduction. Further reduction of the dianion to olefin, eq. 3-3, is a two electron reduction as well. In the presence of excess ketone, there is a competition between the two reduction processes. From these results, it may be concluded that the rate of formation of the pinacolic dianion is, at least, several times faster than reduction of the coordinated dianion to olefin. In addition, it is clear that stoichiometric control of the reactants is critical to the product distribution for reduction of carbonyl compounds by titanium metal. It is likely that stoichiometric control of the carbonyl compound is important in reduction reactions induced by other transition metal compounds as well. For each of the reactions using the metal atom technique, cyclohexanone was always present in great excess, relative to the amount of metal deposited. The observed products were (bicyclohexyl)-1, 1'-diol, a pinacol, and 2-(cyclohexene-1-yl) cyclohexanone, an aldol. Under the conditions of the metal atom technique neodymium, uranium and chromium metal atoms displayed the same general reduction characteristics as titanium metal atoms. In addition, titanium atoms display reduction properties identical to conventional solution techniques when subjected to the same stoichiometric conditions.

Nitrobenzene Reduction by Metal Atoms

Nitrobenzene codeposited with neodymium or uranium atoms was found to be highly reactive, leading to coupled and deoxygenated reduction products. Neodymium atoms produced azoxybenzene as the sole product in 95% overall yield based on deposited metal, eq. 3-12.

$$2Nd + 2C_6H_5-NO_2 \longrightarrow C_6H_5-N\overset{\overset{\displaystyle O}{\|}}{=}N-C_6H_5 + Nd_2O_3 \qquad (3-12)$$
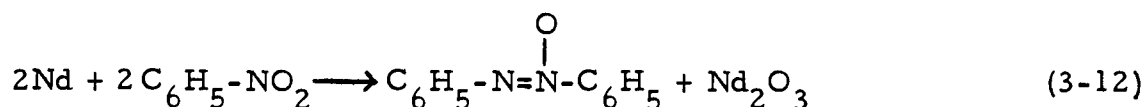
In addition to azoxybenzene, uranium atoms reduced nitrobenzene to azobenzene. Based on deposited metal, yields of azobenzene and azoxybenzene were 24% and 11% respectively, eqs. 3-13 and 3-14.

$$2U + 2C_6H_5NO_2 \longrightarrow C_6H_5-N\underset{\underset{\displaystyle O}{\backslash}}{=}N-C_6H_5 + 2UO_2 \qquad (3-13)$$

$$3U + 4C_6H_5NO_2 \longrightarrow C_6H_5N=N-C_6H_5 + 3UO_2 \qquad (3-14)$$
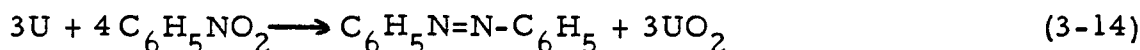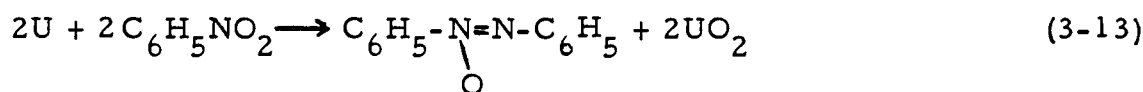
The ratio of azobenzene to azoxybenzene was 1.67 to 1.00.

Although the full scope of the nitro reduction reaction has not been studied, it has been demonstrated that transition metal induced reductions are not limited to the carbonyl functional group. Transition metal reductions are often highly selective with product distribution dependent on the particular reducing metal, metal oxidation state, functional group and stoichiometry.

CONCLUSIONS

The results of this work demonstrate several important features

about the reductive coupling of carbonyl compounds to pinacolic dian-

ions and the further reduction of pinacols to olefins. First, the reduc-

tion of alkyl ketones to pinacols is a general reaction brought about by

many metals in addition to the titanium compounds which are pres-

ently known. Materials capable of pinacol formation possess two

important properties. All compounds or metals which are effective

coupling reagents are highly electropositive while non-pinacol pro-

ducing metals, on the other hand, are only slightly electropositive.

From a comparison of the 3d-transition metal oxidation potentials,

one might expect that manganese metal $(Mn^{o} \longrightarrow Mn^{+2} + 2e^{-}, V = +1.18)$

would effectively couple ketones to pinacols, whereas iron metal

$(Fe^{o} \longrightarrow Fe^{+2} + 2e^{-}, V = +.44)$ would be ineffective or, at best, couple

carbonyl compounds in low yield. Also, those metals to the left of

manganese in the periodic table would be expected to be coupling

reagents, while those metals to the right of iron in the periodic table

would be unreactive toward pinacol formation. Although oxidation-

reduction potentials are an important consideration, in carbonyl

coupling reactions, high oxidation potentials are, however, not a

sufficient condition to insure pinacol product formation. For example,

potassium metal $(K \longrightarrow K^{+} + e^{-}, V = +3.045)$ has a higher oxidation

potential than any transition metal, yet cyclohexanone reduction by potassium produces only traces of (bicyclohexyl)-1, 1'diol.

In addition to favorable oxidation potentials, uranium, neodymium, titanium and chromium form strong metal-oxygen bonds (see Table 3-3). Nickel, cobalt and potassium, on the other hand, form relatively weak metal-oxygen bonds. Successful coupling of carbonyl compounds requires a strong metal-oxygen interaction. As the metal atom transfers an electron to the carbonyl function, a very reactive radical-anion intermediate is formed, eq. 3-1. Because of the strong metal ion-oxygen interaction, the metal ion stabilizes the highly reactive radical intermediate. Metal stabilized radicals then proceed in high yields to pinacolic dianions, Fig. 3-1.

From a comparison of the 3$\underline{d}$-transition element metal-oxygen bond energies, one can make qualitative predictions as to which metals would best be able to stabilize the oxygen bonded carbonyl radical intermediate. Generally, metal-oxygen bond energies decrease from left to right across the periodic table for the 3$\underline{d}$-transition elements, Table 3-7.

TABLE 3-7. METAL-OXYGEN BOND ENERGIES (KCAL/MOLE)[21] (FROM HEAT OF FORMATION OF THE METAL OXIDE.)

Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
-112.9	-98.7	-90.9	-92.1	-65.6	-57.1	-57.3	-37.6	-83.3

For the early transition elements up to and including manganese, metal oxygen bonds are strong. Bond energies are approximately -90 to -100 Kcal/mole. The early transition elements would be expected to stabilize carbonyl radicals and favor pinacolic reduction of ketones. Metal-oxygen bonds for the elements to the right of manganese in the periodic table, however, are much weaker than those of the early transition elements. The latter metals would be expected to be ineffective at radical coupling reactions of carbonyl compounds.

Deoxygenative coupling of ketones to olefins was not a high yield reaction under the conditions of the metal atom reaction. Low olefinic yields have been shown to be due to the large excess of ketone required in such reactions. The presence of bicyclohexylidene in cyclohexanone/metal atom reductions is significant, even though the yields are low. Under the conditions of limited stoichiometry, uranium, chromium, and neodynium metal powders would be expected to deoxygenate pinacolic dianions to alkenes similar to the previously reported compounds of titanium, molybdenum and tungsten. Recently, uranium metal prepared by potassium reduction of uranium tetrachloride reduced benzophenone to tetraphenylethylene in 50% yield.[26] This result demonstrates that the deoxygenative reduction of carbonyl compounds is a general reaction and may occur for many low valent transition metal compounds and metals not yet reported.

Two mechanisms have been reported for the reduction of carbonyl

compounds to olefins.[5,7] The results of this study are in agreement

with the mechanism proposed by McMurry and Flemming,[5] eq. 3-2

and 3-3. Ketone reduction is a two step radical reduction, proceed-

ing, first, to a pinacolic dianion which may further be reduced to

dimeric alkene products in a radical-deoxygenation step under condi-

tions of limited stoichiometry. Under favorable conditions (excess

ketone) high yields of pinacol may be isolated. In addition, reaction

rates for pinacolic reduction are faster than reaction rates for alkene

formation. The generalized mechanism for ketone reduction does not

specifically require titanium as the reducing agent. Any low valent

compound or metal of an electropositive d- or f-transition metal

which forms strong metal-oxygen bonds should participate, in princi-

ple, in radical-type ketone reduction reactions.

Although metal species served as the primary reducing agents

throughout this study, zero valent compounds may be excellent reduc-

ing agents as well. For titanium, bisarene titanium (0) compounds

proved to be the most effective reducing agent prepared. The in-

creased reactivity for zero valent titanium compounds may be attribut-

ed primarily to the increase in surface area afforded by the solubility

of the compound. Even for the most reactive high surface area metal

powders, much of the metal remains non-oxidized after carbonyl reduc-

tion is complete.[27] Although soluble compounds increase reactive

metal surface areas, metal-ligand bonding reduces metal reactivity

relative to metal atom vapors. As a result, increased molecular stability limits unwanted side reactions, for example, solvent attack. However, if ligand-metal bonding forces become too strong, molecular reducing agents may become partially or totally unreactive. In the future, by careful control of the metal coordination sphere as well as control of the metal and metal oxidation state, one may be able to design highly reactive and highly selective carbonyl reducing agents which will effect reductions in the presence of other reactive functional groups.

The use of d- and f-transition elements for reducing agents is not limited to the carbonyl group or its closely related derivatives.[28,29] Nitrobenzene reduction by lanthanide and actinide metal atoms is highly metal selective. Nitro reductive coupling appears to require electropositive metals which, in addition, form strong metal-oxygen bonds although this has not been studied for a large number of elements or nitro compounds. Transition metal induced nitro reductions are likely to be of continued synthetic interest because of their high reactivity and product selectivity. It seems likely that nitro reduction reactions will be reported for many low or zero valent species of the lanthanide, actinide and early transition elements in the future.

EXPERIMENTAL

Several excellent reviews are available which discuss equipment
and general experimental requirements for the metal atom vaporiza-
tion technique.[10,30] The most important equipment requirements are
a need for a reaction chamber capable of sustaining a high vacuum,
a high-vacuum diffusion pump ($< 10^{-5}$ mm Hg), and a suitable metal
vaporization source. The experimental apparatus used in this study
is similar to other metal atom reactors with metal atoms being gener-
ated by resistive heating methods. A complete description of this
equipment has been reported.[31]

Materials

Ti, Cr, Co, Ni, Nd and U were obtained from Research Chemi-
cals or MC/B and were better than 99.5% pure. $TiCl_4$ was purchased
from Alfa Div, Ventron Corp. and was used without purification.
Cyclohexanone (Analytical Reagent Grade), hexane (Spectrograde)
and toluene (Spectrograde) were obtained from Mallinckrodt Chemical
Works and were dried over molecular sieves and were degassed by
successive freeze-thaw cycles under reduced pressure ($< 10^{-3}$ mm Hg).
Nitrobenzene (Purified) was obtained from J. T. Baker and was dried
and degassed as above.

Tetrohydrofuran, THF, (Mallinckrodt, Analytical Reagent Grade)

was dried over Na/benzophenone or $LiAlH_4$ and distilled under N_2

prior to use. Authentic samples of azobenzene were obtained from

MC/B.

General Procedure for Metal Atom Vapor
Plus Cyclohexanone Cocondensation

At 40 °C approximately 15 ml of cyclohexanone (145 mmol) was

condensed with from 0.1 to 0.7 g (2 mmol-15 mmol) of metal at

-196 °C over 45-60 min. The pressure inside the reaction vessel was

kept below 2×10^{-4} mm Hg. For most metals used, a reaction could

be seen to take place at -196 °C with matrices turning orange to gold in

color. After deposition was complete, the liq. N_2 bath was removed

and the matrix was allowed to warm to room temperature. Volatile

products were pumped-off and collected in a liq. N_2 trap. VPC

analysis showed only cyclohexanone present. The reaction vessel was

filled with N_2 and dry Et_2O was added. The reaction mixture was

hydrolyzed slowly, dropwise, with H_2O. CAUTION: Highly divided

metal powders are often pyrophoric and may react vigorously on

hydrolysis with gas evolution. Hydrogen evolution was not observed

for any of the metals studied. After 15 ml H_2O had been added, the

mixture was acidified with 1 M HCl. Organic products were extracted

with 3×50 ml Et_2O or pentane. The combined extracts were dried

over Na_2SO_4 and reduced to two to three ml volume. Solutions were

diluted to exactly 5 ml, and yields were determined by VPC (1/4" x 20", 10% UCW 982) using benzophenone as an external standard. Products were collected by preparative VPC (3/8" x 8', 20% OV 101) and identified spectroscopically by standard IR, ^{1}H NMR, and g.c.-mass spectrometric techniques. Spectra were compared with the literature.

General Procedure for Titanium Atom Vapor/Solvent Plus Cyclohexanone Cocondensation

Approximately 50 ml of dry, degassed solvent, hexane (380 mmol) was condensed with approximately 0.10 g of titanium metal (2.1 mmol) at -196 °C over 45 min. The pressure was maintained below 4 x 10^{-4} mm Hg. At the completion of metal deposition an additional 5 to 10 ml of hexane was condensed over the metal/solvent matrix. While still at -196 °C, approximately 5 ml of cyclohexanone (48 mmol) was condensed on top of the reaction matrix. The liq. N$_2$ bath was removed and the temperature was raised to room temperature. The reaction vessel was filled with N$_2$ and a magnetic stir bar was added. The vessel was partially evacuated (approximately 350 mm Hg), and the mixture was heated to reflux with stirring. The water cooled electrodes served as the condenser. Refluxing continued for two hours. After cooling to room temperature, the mixture was hydrolyzed, and the products were isolated and identified as before.

Cyclohexanone Reduction by Potassium Reduced
Titanium Tetrachloride Metal Powders

1.99 g (50.9 mmol) of freshly cut K metal was added to approximately 60 ml of dry THF in a Schlenk flask under a N_2 atmosphere. The Schlenk flask was fitted with a reflux condenser, and the THF was heated with rapid stirring. Under THF reflux, the K melted producing many small spherical globules. To this K sand, 1.40 ml (12.7 mmol) $TiCl_4$ was added dropwise by syringe. Addition of $TiCl_4$ to K-THF was followed by a vigorous reaction producing a great deal of heat and an insoluble violet solid. The mixture was refluxed for an additional 3 hrs resulting in an insoluble black solid. No excess K could be seen. 2.65 ml of cyclohexanone (25.4 mmol) in 10 ml THF was added dropwise over 5 min to the Ti metal powder. The reaction mixture was refluxed overnight (18 hrs). Unlike metal atom reactions, hydrolysis was vigorous with a great deal of heat being produced. Products were obtained as described.

Nitrobenzene-Metal Atom Reactions

At 60°C approximately 15 ml of nitrobenzene (146 mmol) was condensed with between 0.3 g and 0.8 g of uranium (12.6 mmol) or neodymium (5.55 mmol) metal at -196°C over 45-75 min. The pressure during the reaction was maintained below 2×10^{-4} mm Hg. An immediate reaction occurred at -196°C as observed by the formation

of a gold to orange colored matrix. On warming to room temperature,
the matrix turned to a dark red-orange with some black solid present.
The reaction vessel was filled with N_2 and Et_2O was added. The
reaction mixture was worked up as before. Yields were determined
by VPC using an external azobenzene standard. Under preparative
VPC conditions, 20 min retention time at 200°C, azoxybenzene was
found to be converted to azobenzene by Al_2O_3 supported columns.
With shorter retention times, 6 min, and lower temperatures, 160°,
azoxybenzene to azobenzene reactions were not observed.

Spectral Data

PMR data were recorded on either a Varian HA-100 or a Varian
CFT-80A spectrophotometer with Me_4Si as an internal standard. ^{13}C
NMR spectra were recorded on the Varian CFT-80A spectrometer with
Me_4Si as an internal standard. IR spectra were obtained on a Perkin-
Elmer 727 B spectrometer and peaks were calibrated using the
1601 cm^{-1} absorption of polystyrene as a standard. GC-mass spec-
tral data were obtained using a Varian MAT Gmb H CH7 Massen-
spectrometer at an ionization potential of 70 eV interfaced with a
Varian 1200 gas chromatograph.

Bicyclohexylidene, $C_{12}H_{20}$: ^1H NMR[32c] (CCl_4): δ 1.51 (s, 3 H)
δ 2.13 (s, 2 H). IR (CCl_4): 855 (m), 895 (w), 1015 (m), 1105 (s), 1239
(m), 1268 (m), 1370 (w), 1452 (s), 2855 (vs), 2944 (vs). Mass

spectrum (70 eV) m/e: 164 (M^+), 135 ($M-C_2H_5$), 122 ($M-C_3H_6$),

107 ($M-C_4H_9$), 93 ($M-C_5H_{11}$), 91 (C_7H_7), 82 (C_6H_{10}), 81 (C_6H_9),

79 (C_6H_7), 67 (C_5H_7), 55 (C_4H_7), 53 (C_4H_5), 41 (C_3H_5).

2-(1-cyclohexene-1-yl) cyclohexanone, $C_{12}H_{18}O$: ^{1}H NMR:[33a] δ 1.60

(m), δ 1.90 (m) δ 2.31 (m) δ 2.74 (m) δ 5.32 (s). IR (neat):[34a]

816 (w), 840 (w), 934 (m), 1038 (w) 1079 (m) 1138 (s), 1212 (m),

1198 (w), 1523 (m), 1260 (m) 1460 (s), 1720 (vs), 2872 (vs), 2948 (vs).

Mass spectrum (70 eV) m/e: 178 (M^+), 149 ($M-C_2H_5$), 135 ($M-C_3H_7$),

121 ($M-C_4H_9$), 107 (C_8H_{11}) 93 (C_7H_9), 91 (C_7H_7), 79 (C_6H_7).

2-cyclohexylcyclohexanone, $C_{12}H_{20}O$: ^{1}H NMR[33b] (CCl_4) δ 1.19 (d),

δ 1.64 (m), δ 1.96 (t), δ 2.22 (d). ^{13}C NMR δ 55.4, 40.76, 35.6,

30.4, 28.2, 26.8, 25.4, 25.3, 22.9 (carbonyl carbon absent). IR

(neat):[34b] 837 (w), 882 (w), 1020 (w), 1063 (m), 1131 (m), 1237 (w),

1298 (w), 1318 (w), 1454 (s), 1716 (vs), 2857 (vs), 2935 (vs). Mass

spectrum (70 eV) m/e: 180 (M^+), 98 ($C_6H_{10}O$), 83 (C_6H_{11}),

70 (C_5H_{10}), 67 (C_5H_7), 55 (C_4H_7, C_3H_3O).

(Bicyclohexyl)-1,1'-diol, $C_{12}H_{22}O_2$: ^{1}H NMR[33c] (CCl_3D) δ 1.5, 1.55,

1.60, 1.78 (10 H), δ 2.15 (1 H). IR[34c] (CCl_4) 925 (m), 1263 (m),

1480 (s), 1560 (s), 2875 (s), 2955 (vs) 3450 (vs, br). Mass spectrum

(70 eV) m/e: 180 ($M-H_2O$), 178 ($M-H_2O-H_2$), 99 ($C_6H_{11}O$), 98

($C_6H_{10}O$), 81 (C_6H_9), 55 (C_4H_7, C_3H_3O).

Azobenzene, $C_{12}H_{10}N_2$: ^{1}H NMR[32a] (CCl_4) δ 7.44 (m, 3 H), δ 7.91

(m, 2 H). IR[35a] (CCl_4): 437 (m), 1026 (m), 1079 (m), 1160 (m),

1128 (m), 1310 (w), 1461 (s), 1472 (s), 1594 (w), 3082 (m).

Azoxybenzene, $C_{12}H_{10}N_2O$: ^{1}H NMR (CCl_4)[32b] δ 7.42 (m, 3H),

δ 8.24 (m, 2H). IR[35b] (CCl_4): 686 (s), 912 (w), 934 (w), 1029 (m),

1077 (m), 1169 (m), 1281 (m), 1304 (m), 1338 (m), 1461 (s), 1489 (s),

3085 (m).

^{1}H NMR: s = singlet, d = doublet, m = multiplet, IR: w =

weak, m = medium, s = strong, vs = very strong, br = broad.

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