AN ABSTRACT OF THE THESIS OF

Margaret A. Brault   for the degree of   Doctor of Philosophy

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Title: I. METAL ATOM SYNTHESIS, CHARACTERIZATION AND

PHYSICAL PROPERTIES OF Π-CYCLOOCTATETRAENE AND

SUBSTITUTED CYCLOOCTATETRAENE COMPLEXES OF

LANTHANIDE METALS. II. AN ATTEMPTED SYNTHESIS

OF HOMOCYCLOOCTATETRAENE DIANION COMPLEXES

WITH YTTERBIUM AND URANIUM

Abstract approved _ *Redacted for Privacy*

Dr. Carroll W. DeKock

A series of extremely air and moisture sensitive lanthanide

complexes of the formula $Ln_2(RC_8H_7)_3$ [R = H, CH_3, n-C_4H_9] were

prepared where Ln is Ce, Nd, Sm, Tb and Er. The complexes were

synthesized by allowing metal atoms to react with cyclooctatetraene

or alkyl substituted cyclooctatetraene at -196 °C and subsequently

extracting them with tetrahydrofuran. Reaction of COT with Yb metal

atoms yielded the known compound $Yb(C_8H_8)$. The infrared spectra of

these complexes strongly suggest the planarity of COT^{2-}. The mag-

netic susceptibility data of $Ln_2(C_8H_8)_3$ (Ln = Nd, Ce, Er, Sm)

are very close to the free ion term providing information that these

complexes are mostly ionic. The ^1H NMR spectra of all of these

paramagnetic complexes were obtained in pyridine-d_5. For all of the

complexes a single resonance was observed for the $C_8H_8^{2-}$ ring

protons. A single resonance was also observed due to the CH_3

substituents on the COT^{2-} rings. In addition, a single resonance

was observed for the CH_2 directly adjacent to the COT^{2-} ring in

$Nd_2(n-C_4H_9C_8H_7)_3$. These observations support the idea of ring

exchange for these complexes. Conductance studies showed that the

$Nd_2(C_8H_8)_3 \cdot 2C_4H_8O$ complex is partially ionized in pyridine to an

anion, $[Nd(C_8H_8)_2]^-$, and a cation, $[Nd(C_8H_8) \cdot 2C_4H_8O]^+$. Calcula-

tions from ^1H NMR data show that contact contributions, in addition

to dipolar contributions, are important in the isotropic shift for

$Nd_2(CH_3C_8H_7)_3$ and $Sm_2(CH_3C_8H_7)_3$. These observations support the

idea of ring exchange for these complexes.

Reaction of U and Yb atoms with cis-bicyclo[6.1.0]nona-2,4,6-

triene (1) and 9,9-dimethyl-cis-bicyclo[6.1.0]nona-2,4,6-triene (4)

provided evidence for the formation of a lanthanide or actinide homo-

aromatic species. The materials produced were extremely air and

moisture sensitive. Similar species were observed in the reaction of

n-butyllithium and UCl_4 with 4. Evidence for the formation of a di-

anion was provided by chemical reactions and ^1H NMR. Methanolysis

or deuterolysis of these materials gave cyclononatrienes (or $-d_2$).

However, the deuterolysis reaction showed, in addition to $-d_2$, con-

siderable amounts of $-d_1$ and $-d_0$. This indicates that protons were

picked up from the solvents. Oxidation of these materials or reaction

with CCl_4 yielded starting material and the appropriate dihydroindene.

The ^1H NMR of the U-4 species indicates the presence of a paramag-

netic center. These materials could not be purified and the reaction

with the solvent precluded isolation of a complex.

I. Metal Atom Synthesis, Characterization and Physical
Properties of Π-Cyclooctatetraene and Substituted
Cyclooctatetraene Complexes of Lanthanide
Metals. II. Attempted Synthesis of
Homocyclooctatetraene Dianion
Complexes with Ytterbium
and Uranium

by

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Typed by Opal Grossnicklaus for Margaret A. Brault

To the wolves

and

gentle people

ACKNOWLEDGEMENTS

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ABBREVIATIONS

CH_2Cl_2	dichloromethane
CH_3Li	methyllithium
C_4H_8O	tetrahydrofuran
$C_5H_5^-$	cyclopentadienide anion
C_6H_6	benzene
$C_8H_8^{2-}$	cyclooctatetraenide anion
$RC_8H_7^{2-}$	alkyl substituted cyclooctatetraenide anion
DME	dimethoxyethane
Na_2EDTA	ethylenediaminetetraacetic acid, disodium salt
THF	tetrahydrofuran
TMEDA	N, N, N', N'-tetramethylethylenediamine
TMS	tetramethylsilane
COT	cyclooctatetraene
HMPA	hexamethylphosphoramide

STRUCTURES LISTED IN TEXT
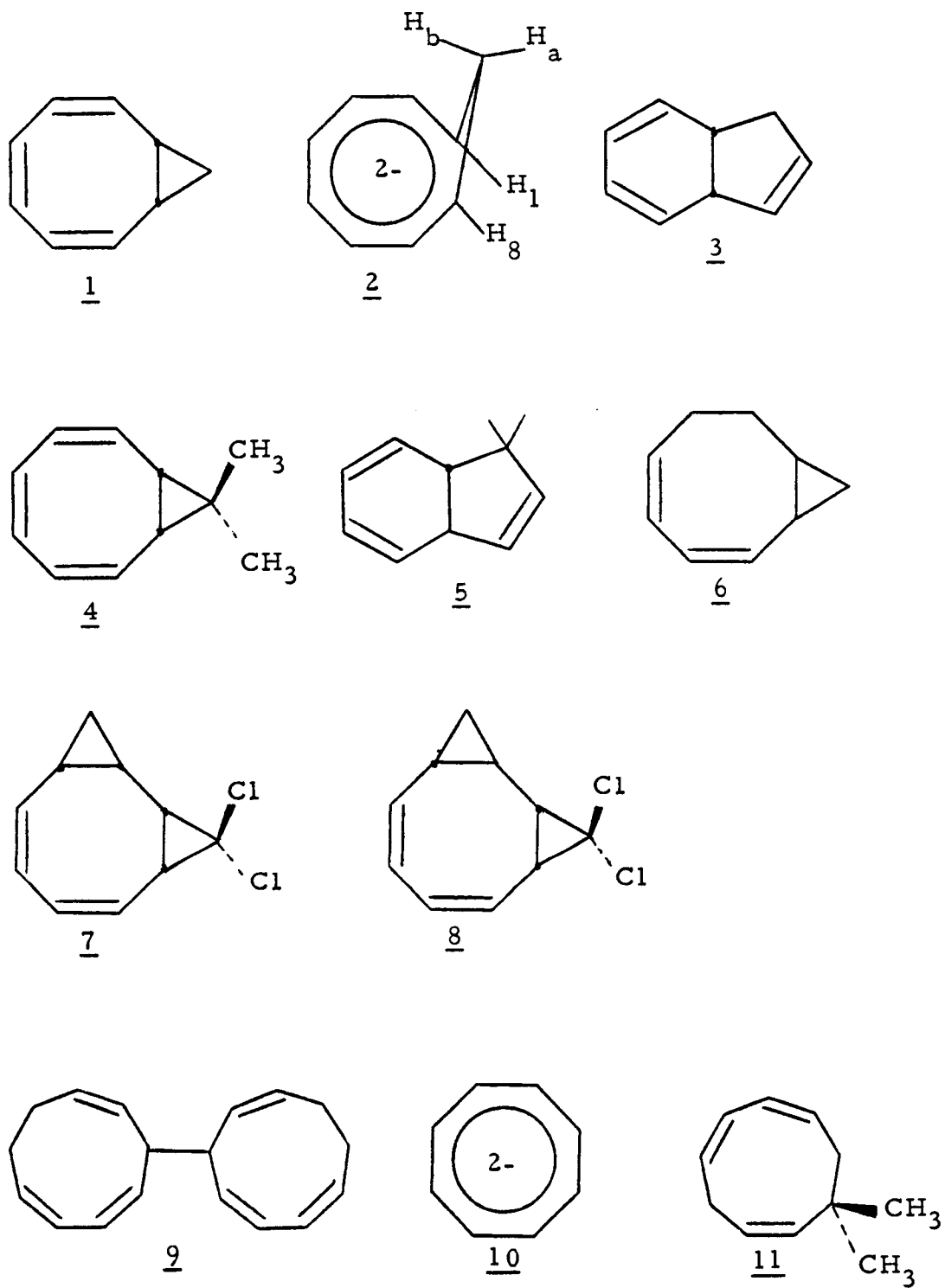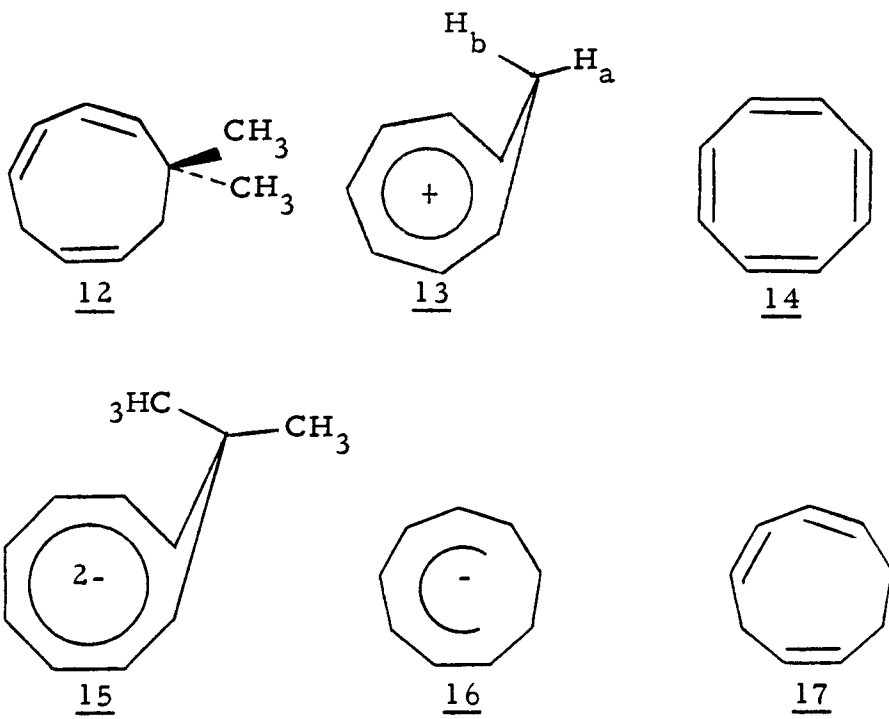
H_b H_a

H_1

H_8

2-

1

2

3

CH_3

CH_3

4

5

6

Cl

Cl

7

Cl

Cl

8

9

2-

10

CH_3

CH_3

11

$\underline{12}$

H_b H_a

$\underline{13}$

$\underline{14}$

$_3HC$ CH_3

2-

$\underline{15}$

$\underline{16}$

$\underline{17}$

I. METAL ATOM SYNTHESIS, CHARACTERIZATION AND
PHYSICAL PROPERTIES OF Π-CYCLOOCTATETRAENE
AND SUBSTITUTED CYCLOOCTATETRAENE
COMPLEXES OF LANTHANIDE METALS

INTRODUCTION

The first Π-carbocyclic rare-earth complexes were reported in the literature by Wilkinson and Birmingham (1) in 1954. A full report was published in 1956 (2). They synthesized the extremely air sensitive triscyclopentadienyls by the following method.

$$LnCl_3 + 3\ NaC_5H_5 \xrightarrow{\text{THF}} Ln\ (C_5H_5)_3 + 3\ NaCl$$
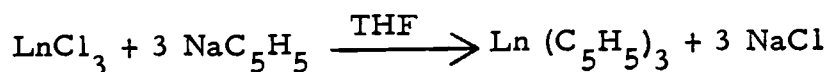
Ln = La, Ce, Pr, Nd, Sm, Gd, Dy, Er, Yb.

Infrared data (3, 4, 5) suggested pentahaptocyclopentadienyl bonding. In 1974, Burns et al. (6) published the single-crystal x-ray diffraction data on $Nd(CH_3C_5H_4)_3$. Each $CH_3C_5H_4^-$ ligand is bonded in a pentahapto fashion to Nd^{3+}. Each Nd^{3+} is additionally bonded in a monohapto manner to a ring carbon atom of one $CH_3C_5H_4^-$ on an adjacent molecule making the complex a tetramer.

Other pentahapto lanthanide Π-carbocyclic complexes have been reported. The most notable are the cyclopentadienyls and the indenyls. Several reviews (7, 8, 9, 10) have been published concerning these compounds and they will not be discussed in detail. These complexes have properties characteristic of organometallic lanthanide complexes. They are oxygen and moisture sensitive but

quite stable. Bonding is believed to be essentially ionic. ^{1}H NMR

data have broadened peaks due to paramagnetic centers. Magnetic

data give effective moments very near to that of the free ion again

indicative of ionic bonding using the 4f electron.

Streitwieser et al. (11) reported the first sandwich compound

between the cyclooctatetraenide dianion, depicted below, and U^{4+}.
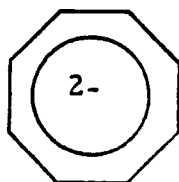
The complex was prepared in solution by the reaction of UCl_4 and $C_8H_8^{2-}$

or, more directly, from highly reactive uranium metal and cycloocta-

tetraene (12). Uranocene is insoluble and stable in water, although

wet organic solvents will cause decomposition of the complex over

extended periods of time. Strong acids instantly hydrolyze uranocene

liberating U^{4+} and cyclooctatrienes. Careful oxidation of uranocene

yields uranium oxide and a quantitative yield of cyclooctatetraene.

Solid uranocene ignites in the presence of pure oxygen. Substituted

uranocenes $(RC_8H_7)_2U$ (R = C_2H_5, n-C_4H_9, CH=CH$_2$, C_6H_5, cyclo-

C_3H_5) have been prepared (13). Octamethyl- and octaphenyluranocene

are also known (13, 14). Substitution on the C_8H_8 ring increases the

solubility of the complexes in organic solvents. Additionally, the substituents increase the stability of the complex towards oxygen indicating that decomposition occurs by initial attack on the metal center.

The crystal structure (15) of uranocene revealed D_{8h} symmetry of the molecule with planar $C_8H_8^{2-}$ rings Π-bonded to the uranium in an eclipsed fashion. X-ray data (16) of octaphenyluranocene reveals all of the phenyl groups tilted towards the uranium. Complexes of Th, Pa, Np, and Pu were also prepared (12, 17, 18).

The increased activity in the area of 5f-cyclooctatetraene organometallic chemistry inspired the synthesis of corresponding lanthanide systems. The lanthanide ions (Table 1) have their 4f electrons imperfectly shielded from the nuclear charge resulting in a contraction of the radius across the series. This lanthanide contraction makes the 4f electrons less available for covalent bonding than the electrons of the 5f elements. This is reflected in the marked difference in the reactivity of the cyclooctatetraene complexes of the lanthanides towards oxygen and water as compared with the actinides.

The first lanthanide-cyclooctatatetraene complexes were prepared by Hayes and Thomas (20) according to the following scheme.

$$Ln + COT \xrightarrow{NH_3} LnCOT$$

$$Ln = Eu, \ Yb$$
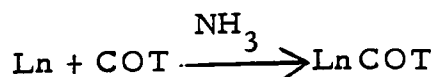
Table 1. Crystal radii, electronic configurations[a] and oxidation potentials[b] of the lanthanide ions.

| Name | Atomic no. | Symbol | Electronic-configurations | | | | Crystal radius, +3 | $Ln(c) = Ln^3(aq) + 3e$, V | $Ln^{2+}(aq) = Ln^{3+}(aq) + e^-$, V | $Ln^{3+}(aq) = Ln^{4+}(aq) + e^-$, V |
			Atom	M^{2+}	M^{3+}	M^{4+}				
Lanthanum	57	La	$5d6s^2$	$5d^1$	[Xe]	--	1.061	+2.522		
Cerium	58	Ce	$4f^1 5d^1 6s^2$	$4f^2$	$4f$	[Xe]	1.034	2.483		-1.74
Praseodymium	59	Pr	$4f^3 6s^2$	$4f^3$	$4f^2$	$4f^1$	1.013	2.462		About -2.86
Neodymium	60	Nd	$4f^4 6s^2$	$4f^4$	$4f^3$	$4f^2$	0.995	2.431		
Promethium	61	Pm	$4f^5 6s^2$	$4f^5$	$4f^4$	--	0.979	2.423		
Samarium	62	Sm	$4f^6 6s^2$	$4f^6$	$4f^5$	--	0.964	2.414	+1.55	
Europium	63	Eu	$4f^7 6s^2$	$4f^7$	$4f^6$	--	0.950	2.407	+0.43	
Gadolinium	64	Gd	$4f^7 5d6s^2$	$4f^7 5d^1$	$4f^7$	--	0.938	2.397		
Terbium	65	Tb	$4f^9 6s^2$	$4f^9$	$4f^8$	$4f^7$	0.923	2.391		
Dysprosium	66	Dy	$4f^{10} 6s^2$	$4f^{10}$	$4f^9$	$4f^8$	0.908	2.353		
Holmium	67	Ho	$4f^{11} 6s^2$	$4f^{11}$	$4f^{10}$	--	0.894	2.319		
Erbium	68	Er	$4f^{12} 6s^2$	$4f^{12}$	$4f^{11}$	--	0.881	2.296		
Thulium	69	Tm	$4f^{13} 6s^2$	$4f^{13}$	$4f^{12}$	--	0.869	2.278		
Ytterbium	70	Yb	$4f^{14} 6s^2$	$4f^{14}$	$4f^{13}$	--	0.858	2.267	+1.15	
Lutetium	71	Lu	$4f^{14} 5d^1 6s^2$	--	$4f^{14}$	--	0.848	2.255		
Yttrium[c]	39	Y	$4d^1 5s^2$		[Kr]		0.880			

a) Reference 19

b) Reference 7

c) Included for comparison

Divalent π-complexes with D_{8h} symmetry were produced, which,

unlike uranocene, are unstable to water and acetic acid.

The first lanthanide (III) cyclooctatetraene complexes were re-

ported by Mares et al. (21, 22). Two series of complexes were pre-

pared in tetrahydrofuran using the following scheme [equations (I), (II)].

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

$$Ln = La,\ Ce,\ Pr,\ Nd,\ Sm,\ Gd,\ Tb$$

$$2\,LnCl_3 + 2K_2C_8H_8 \xrightarrow{THF} [Ln(C_8H_8)Cl\cdot 2THF]_2 + 4KCl \quad (II)$$
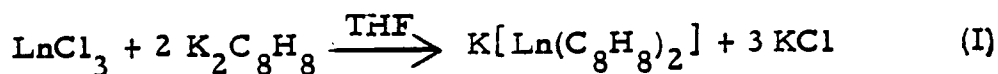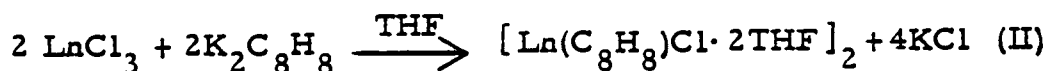
$$Ln = Ce,\ Pr,\ Nd,\ Sm$$

The crystal structures of both types of complexes showed the

formation of the planar $C_8H_8^{2-}$ π-bonded to the lanthanide ion (23,24).

The chemistry of $KLn(C_8H_8)_2$ and $[Ln(C_8H_8)Cl\cdot 2THF]_2$ displayed a

great deal more ionic character relative to their actinide counterparts

as evidenced by the following reactions (25).

$$KLn(C_8H_8)_2 + UCl_4 \xrightarrow{THF} (C_8H_8)_2U + KCl + LnCl_3 \qquad (III)$$

$$KLn(C_8H_8)_2 + LnCl_3 \xrightarrow{THF} [Ln(C_8H_8)Cl\cdot 2THF]_2 + KCl \qquad (IV)$$

$$[Ln(C_8H_8)Cl\cdot 2THF]_2 + 2K_2C_8H_8 \xrightarrow{THF} 2KLn(C_8H_8)_2 + 2KCl \quad (V)$$
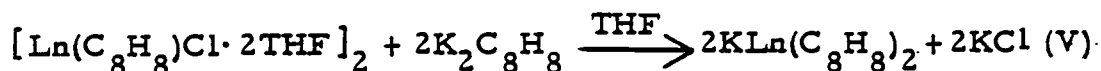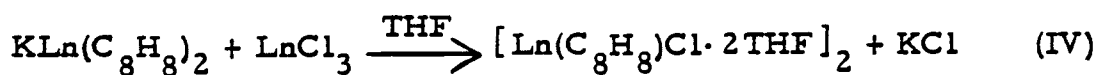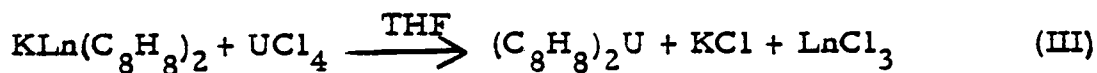
Apparently equation (III) would suggest that the 5f orbitals in uranium

are able to overlap better with the π-orbitals of $C_8H_8^{2-}$ than the 4f

orbitals of the lanthanides forming a more stable complex. The

reverse of equation (III) does not occur. In addition, ligand exchange

has not been observed for substituted uranocenes (13) although it is observed for both lanthanide species according to equations (IV) and (V). Hydrolysis and oxidation of both lanthanide species yields cyclooctatrienes and cyclooctatetraene, respectively. Magnetic data for these rare-earth complexes showed moments close to the moments of the free ions providing further evidence for ionic bonding.

Ely et al. (26) and DeKock et al. (27) prepared a tris-π-cyclooctatetraene-lanthanide complex (Fig. 1) with the general formula $[(Ln(C_8H_8)(THF)_2][Ln(C_8H_8)_2]$ using metal atom techniques. The crystal structure showed an anion-cation pair. This complex can be viewed as a combination of $[KLn(C_8H_8)_2]$ and $[Ln(C_8H_8)Cl \cdot 2C_4H_8O]_2$ where the Ln of the cation can partially bond to the $C_8H_8^{2-}$ on the anion to complete its coordination sphere. Hydrolysis and oxidation yielded cyclooctatrienes and cyclooctatetraene, respectively. The extremely low solubility in THF precluded ^{1}H NMR and electronic absorption studies.

Greco et al. (28) reported the preparation of $Ce(C_8H_8)_2$. ^{1}H NMR and preliminary x-ray studies indicate this compound to be isomorphous with uranocene. This same author claims to have synthesized $Ce_2(C_8H_8)_3$ but was unable to obtain single crystal x-ray data or ^{1}H NMR data.

Extensive ^{1}H NMR studies (29, 30) were conducted on uranocene and octamethyluranocene to separate the contact and dipolar shifts.
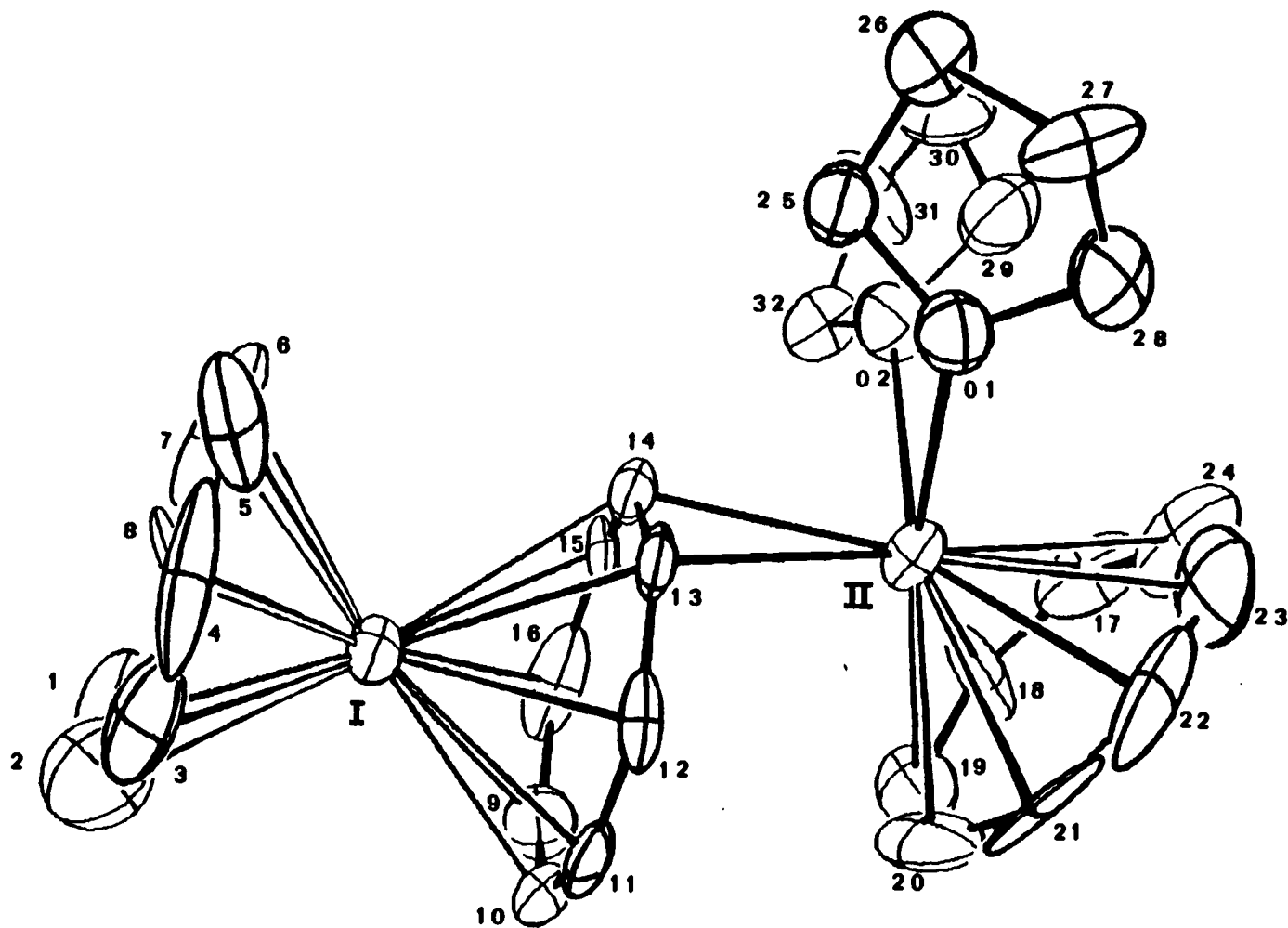
Figure 1. The [Nd $(C_8H_8) \cdot 2C_4H_8O$][Nd$(C_8H_8)_2$] molecule

The paramagnetic uranium centers caused a large upfield shift (41.3 ppm) indicative of some form of covalency. Hodgson et al. (25) has presented qualitative ^{1}H NMR data for $K[Ln(C_8H_8)_2]$ where Ln = Nd, Sm, La and Tb. La is diamagnetic and the n.m.r. of this complex showed a sharp singlet at 5.9 ppm relative to TMS. The remaining complexes are paramagnetic and display spectra with large upfield or downfield shifts and broadened peaks. No attempts were made to separate the contact and dipolar components.

Ely et al. and DeKock et al. (26, 27) used atoms of the lanthanides generated in a metal vaporization apparatus to prepare $Ln_2(C_8H_8)_3 \cdot 2C_4H_8O$. Several reviews have been published concerning metal vaporization techniques (31, 32, 33, 34, 35). This synthetic method is especially suitable for the preparation of the title compounds for several reasons.

First: the lanthanides are electropositive and have high oxidation potentials (Table 1)(7).

Second: the evaporation temperatures of the rare earths are well within the limits of metal vaporization techniques (Table 2)(35).

Third: Cyclooctatetraene readily accepts two electrons to achieve the π-aromatic dianion configuration.

Fourth: Atoms are endothermic, have no steric restrictions, possess readily available electrons and are overall more reactive than bulk metals.

Fifth: This technique allows for the study of the chemistry of the elements themselves in addition to the chemistry of their compounds.

Table 2. Evaporation temperatures of the lanthanides.

T [°C]	1000	1000-1400	1400-1700
	Sm	Pr, Nd, Gd	La, Ce, Lu
	Eu	Tb, Dy, Ho	
		Er, Tm	

This research was undertaken to provide more information on the chemistry of rare earth metal atoms. It was especially interesting to investigate Yb and Ce atoms and determine which valence state they would obtain under the experimental conditions. To date lanthanide-cyclooctatetraene complexes with hydrocarbon substituents are unreported. There are also no reported ^{1}H NMR data for any of the title compounds. During the course of this project π-cyclooctatetraene and substituted cyclooctatetraene complexes of Ce, Nd, Sm, Tb, Er and Yb were prepared and characterized and their ^{1}H NMR recorded.

EXPERIMENTAL

Materials

Ce, Nd, Sm, Tb, Er, and Yb, 99.9% were obtained from Michigan Chemical Corporation, St. Louis, MI, and Research Chemicals, Phoenix, AZ. $SmCl_3$ was purchased from Alfa Division, Danvers, MA, and $NdCl_3$ was purchased from Great Western Organics, Golden, CO. Small amounts of residual water were completely removed from the anhydrous trichlorides by heating at 300°C for several hours under high vacuum. Cyclooctatetraene (J. T. Baker Chemical Co., Phillipsburg, NJ) was distilled onto Linde 4A molecular sieve prior to use. Tetrahydrofuran (Mallinckrodt Analytical Reagent Grade) and ethyl ether were dried and stored under vacuum using sodium benzophenone. These solvents were vacuum transferred to dried glassware as needed. Tetramethylethylenediamine (Aldrich Chemical Company, Milwaukee, WI) was dried over activated Linde 4A molecular sieve and used without further purification. Methyllithium and n-butyllithium were purchased from Alfa Products, Danvers, MA. Pyridine-d_5 (Aldrich Chemical Company, Inc.) was dried over barium oxide and vacuum distilled preceding use. Deuterium oxide (Aldrich) was used as purchased. All of the solvents, as well as Nujol for IR, were degassed by use of repeated freezing-evacuation-thawing cycles. Prepurified nitrogen and argon (Air Reduction Company) were used as

obtained.   Eriochrome-T-black indicator was prepared by dissolving

0. 2 grams of solid Erio-T in 5 mL of ethanol and 15 mL of triethanol-

amine.   Potassium metal was purchased from Mallinckrodt Chemical

Works, St. Louis, MO.

All glassware was flamed under vacuum prior to use.

Synthetic Procedures

Metal Atom Synthesis

A schematic diagram of the apparatus used for the preparation

of the title compounds appears in Figure 2.   This was constructed by

glass-blowing a 3-inch glass pipe flange onto a Pyrex 2-L round-

bottom flask.   Three ports were added to facilitate the synthesis and

allow for isolation of a product.   The one inch port is used to maintain

a high vacuum on the system.   One 3/8 inch port serves as a means of

removal of volatile substances after the reaction is complete.   A sec-

ond 3/8 inch port is equipped with a high vacuum gauge and a nitrogen

inlet.   A high vacuum in the system is insured by Cajon ultra-torr

fittings for all connections.   The glass vessel is covered with a brass

plate which has a 1/8 inch copper tube and two water cooled electrodes

on it.   The copper tube is the means of entry into the vessel for the

potential ligand.   A Sylvania Type BC 10064 x 30 tungsten basket or an

aluminum oxide coated molybdenum boat, Sylvania MS003, is attached
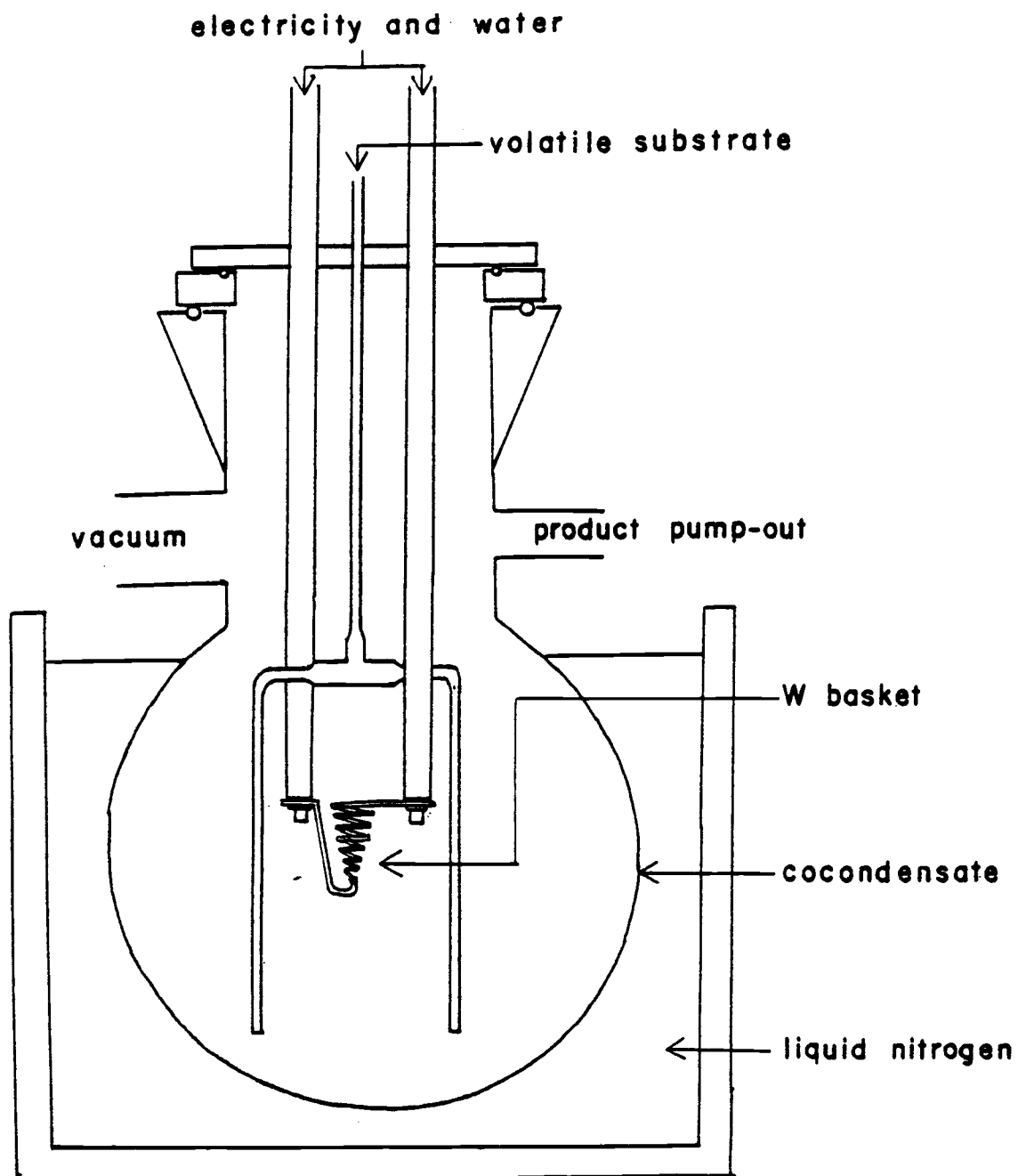
Figure 2. A schematic drawing of the metal atom apparatus

to the electrodes and the metal is placed in the basket or boat. The

metal atoms are produced by resistively heating the electrodes. The

vessel is cooled to -196 °C with liquid nitrogen during the codeposition

of the metal atoms and the organic substance. It is essential to main-

tain a pressure of less than 4×10^{-4} torr to prevent polymerization of

the cyclooctatetraene. After the reaction, the flask is warmed

to room temperature. Any volatile material is vacuum transferred

to a trap. The flask is filled with Pre-purified grade nitrogen, the ports

are capped and the flask is removed to a Vacuum Atmospheres Model

He-493-2 glove box with an anhydrous nitrogen recirculating atmos-

phere. The product is physically scraped from the walls of the flask

and transferred to a Soxhlet extractor (Figure 3). This extractor has

the same basic design as that of Streitwieser and coworkers (36) with

two salient differences. First, J. Young Acton Type POR/10 mm/RA

valves were used instead of vacuum stopcocks. Second, a Fischer-

Porter Solv-seal teflon joint connects the solvent bulbs to the extrac-

tor. Streitwieser's model has the bulbs glass-blown onto the extractor

body which necessitates breaking the seal to isolate the purified prod-

uct. THF is vacuum transferred into the solvent bulb. Continuous

extraction is done on $Ln_2(RC_8H_7)_3$. Crystalline material forms in the

bulb directly beneath the glass frit. When extraction is complete, the

solvent is poured into the second bulb. The solid is washed by dis-

tilling small portions of THF into the first bulb. This removes all
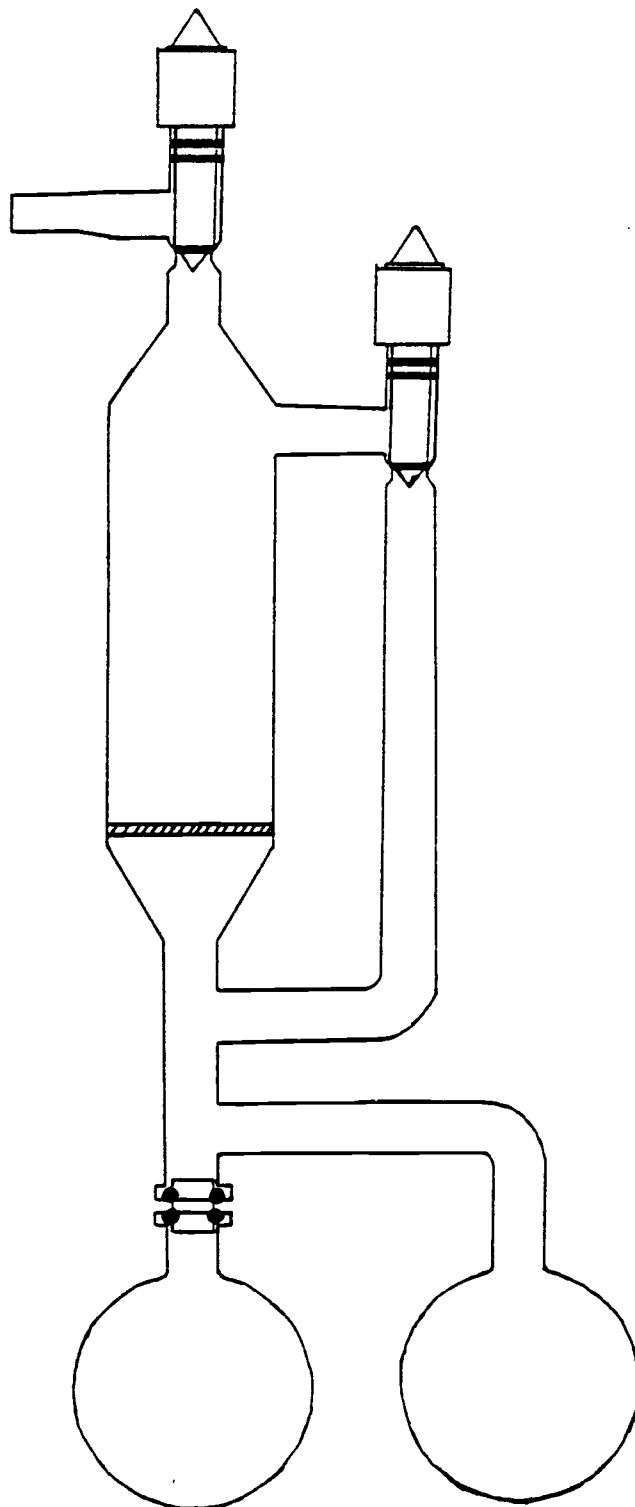
Figure 3. A schematic drawing of the Soxhlet extractor used to purify the title compounds.

organic impurities and provides a very pure compound.

Reaction of Ln Metals with Cyclooctatetraene, Methylcyclooctatetraene and n-Butylcyclooctatetraene

This preparative work was conducted by cocondensing 1.0-2.0 grams of metal vapor and 10-15 mL (89-133 mmol) of COT (or substituted COT) on the walls of a liquid nitrogen cooled flask under high vacuum. A typical reaction time was from 1.0-1.5 hours. Nd, Er, Ce and Yb deposited easily whereas Sm and Tb were considerably more difficult. After the reaction was complete, unreacted organic substrate was pumped into the vacuum line as the vessel was warmed. The flask was then filled with pre-purified nitrogen, the ports capped and the flask was transferred to the glove box where the crude product was placed into the Soxhlet extractor for purification. Nd, Er, and Ce yielded 0.5 grams of $Ln_2(RC_8H_7)_3$ for every 1.0 gram of metal deposited whereas Yb metal yielded 0.5 gram of $Yb(C_8H_8)$. The yields for the Sm and Tb complexes of COT were on the order of milligrams. Difficulty was observed in depositing the Sm and Tb metals which may have been the reason for the low yields.

Reaction of $Ln_2(RC_8H_7)_3$ with $H^+(D^+)$

A THF solution (2.0 mL) containing 50 mg of the complex was prepared in the inert atmosphere box, placed in a test tube and capped.

The unsubstituted complexes did not completely dissolve. The tempera-
ture was reduced to -10°C after which 0.5 mL of CH_3OH (or CH_3OD)
was added. After methanolysis, the solution was extracted with hexane
(3 x 2 mL) and the extract dried over Na_2SO_4. The products were
identified by gc/ms. Mass spectrum (70 eV) m/e: cyclooctatrienes

C_8H_{10} 106(M^+), 105(M-H), 91(M-CH$_3$), 78(M-C$_2$H$_4$); $C_8H_8D_2$ 108(M^+),
107(M-H), 93(M-CH$_3$), 79(M-C$_2$H$_3$D); methylcyclooctatrienes,

$CH_3C_8H_9$ 120(M^+), 119(M-H), 105(M-CH$_3$); $CH_3C_8H_7D_2$ 122(M^+),
121(M-H), 107(M-CH$_3$); n-butylcyclooctatrienes, n-$C_4H_9C_8H_9$ 162(M^+),
134(M-C$_2$H$_4$), 119(M-C$_3$H$_7$), 105(M-C$_4$H$_9$); n-$C_4H_9C_8H_7D_2$ 164(M^+),
135(M-C$_2$H$_3$D), 134(M-C$_2$H$_2$D$_2$) 121(M-C$_3$H$_7$), 107(M-C$_4$H$_9$).

Reaction of $Ln_2(RC_8H_7)_3$ with O_2

The sample was prepared in a manner similar to that for the
hydrolysis. Oxygen was slowly bubbled through the solution at 0°C
until the solution was clear. Workup was the same as that for
hydrolysis. Samples for ^1H NMR and mass spectra were isolated
using vpc (8 ft. x 0.250 in. on 10% Carbowax 4000, AW-DMCS Chro-
mosorb P, cyclooctatetraene, C_8H_8, 80°C; methylcyclooctatetraene,

$CH_3C_8H_7$, 100°C; n-butylcyclooctatetraene, n-$C_4H_9C_8H_7$, 120°C)

C_8H_8 ^1H NMR $\delta_{TMS}^{CCl_4}$ 5.70 (s, 8H); mass spectrum (70 eV) m/e

$104(M^+)$, $103(M-H)$, $78(M-C_2H_2)$; $CH_3C_8H_7$ ^{1}H NMR $\delta \, \frac{CCl_4}{TMS}$

$1.72(s, 3H, CH_3)$, 5.68 (s, 7H, C_8H_7 - with small shoulder

at 5.50); mass spectrum (70 eV) m/e $118(M^+)$, $117(M-H)$, $103(M-CH_3)$;

$n-C_4H_9C_8H_7$ ^{1}H NMR $\delta \, \frac{CCl_4}{TMS}$ $0.87-0.98$ (m, 3H, $-CH_3$), $1.32-1.45$

(m, 4H, $-CH_2CH_2$), 2.02 (t, 2H, $> CH_2$), 5.71 (s, 7H, $-C_8H_7$ with small

shoulder at 5.50); mass spectrum (70 eV) m/e $160(M^+)$, $145(M-CH_3)$,

$131(M-CH_2CH_3)$, $117(M-CH_2CH_2CH_3)$.

Attempted Preparation of $Nd_2(n-C_4H_9C_8H_7)_3$ by the Reaction n-Buytylcyclooctatetraenide Dianion with $NdCl_3$

The complex, $K_2(n-C_4H_9C_8H_7)$ was prepared in a method simi-

lar to that of Streitwieser et al. (36).

Into a 100 mL Schlenk flask equipped with a reflux condenser and

containing 30 mL of refluxing THF was placed 0.94 g (24 mmol) of

potassium metal. A potassium sand was prepared after which time

the mixture was cooled to -25°C. To this stirring THF-K mixture was

added 1.92 g (12 mmol) of n-butylcyclooctatetraene. The solution

turned yellow-brown after two hours. This solution was quickly added

at -25°C to two grams (8 mmol) of anhydrous $NdCl_3$ which was in 30

mL of THF in a 100 mL Schlenk flask. The solution immediately

turned brown and upon warmup to room temperature, the solution

turned dark green. Attempts to isolate a pure product proved fruit-

less and this method of synthesis for the compounds of interest was

abandoned.

Solution Syntheses

Solution syntheses were performed in an atmosphere of Pre-purified grade nitrogen. All reagents were introduced into the system from syringes through septum capped joints.

Methylcyclooctatetraene

Into a 500-mL round-bottom 3-neck flask were placed 260 mL of freshly distilled ethyl ether, 170 mL (1.6M, 272 mmol) of CH_3Li and 55 mL (366 mmol) of TMEDA. A white precipitate appeared. The mixture was stirred for 15 minutes and 15 mL (13.9 g, 134 mmol) of COT was added. A brown color slowly developed. The reaction was complete after 18 hours. Oxygen was then slowly bubbled through the solution which had been cooled to 0 °C. Oxidation was followed by hydrolysis with 1 M HCl. The layers were separated and the aqueous layer was washed with ether (2 x 100 mL). The combined organic layers were washed with 5M HCl until all traces of TMEDA were removed. The organic phase was neutralized with saturated Na_2CO_3 (2 x 100 ml), extracted with saturated NaCl (2 x 150 mL) and then dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue distilled. Final purification was done by vpc (8 ft x 0.250 in. in 10% Carbowax 4000 on AW-DMCS Chromosorb P, 80°C), yielding 8.6 g (55%) of methylcyclooctatetraene

$(CH_3C_8H_7)$, ^1H NMR $\delta^{CCl_4}_{TMS}$: 1.72 (s, 3H), 5.68 (s, 7H, with shoulder at 5.50); mass spectrum (70 eV) m/e 118 (M^+), 117 (M-H), 103 (M-CH_3); and 3.1 g (22%) of cyclooctatetraene, ^1H NMR $\delta^{CCl_4}_{TMS}$ 5.70 (s, 8H); mass spectrum (70 eV) m/e 104 (M^+), 103 (M-H), 78 (M-C_2H_2)(64).

n-Butylcyclooctatetraene

This compound was prepared according to the procedure of J. Miller (37).

n-Butyllithium (80 mL, 2M, 160 mmol) was added to a 500-mL round-bottom flask containing 250 mL of ethyl ether. The temperature of the solution was lowered to 0°C. Cyclooctatetraene, (8.32 g) (9.0 mL, 80 mmol) was added to the flask resulting in a red solution within minutes. After 45 minutes, the solution was allowed to warm to room temperature and the reaction continued for two hours. The reaction was quenched with oxygen at 0°C. Workup is the same as that described for methylcyclooctatetraene. Pure n-butylcyclooctatetraene, 7.9 g (62%) was obtained by distillation: bp 68°C (5.0 torr) ^1H NMR $\delta^{CCl_4}_{TMS}$ 0.87-0.98 (m, 3H), 1.32-1.45 (m, 4H), 2.02 (t, 2H), 5.71 (s, 7H with shoulder at 5.50); mass spectrum (70 eV) m/e 160 (M^+), 145 (M-CH_3), 131 (M-CH_3CH_2), 117 (M-$CH_3CH_2CH_2$)(64).

Preparation of KNd(C_8H_8)$_2$

This compound was prepared by the literature method of Hodgson et al. (25).

A THF solution (150 mL) containing 30.1 mmol of K_2COT in a

three neck flask was prepared as previously described. This solution

was at -15 °C when 3.5 g (14 mmol) of $NdCl_3$ in 50 mL of THF was

quickly added to the solution containing the dianion of COT. The solu-

tion immediately turned brownish-green. This was allowed to slowly

warm to ambient temperature after which time the THF was removed

and the solid transferred to the Soxhlet extractor. Purification

required two independent extractions with THF. The compound was

identified as $KNd(C_8H_8)_2$ by its visible and infrared spectrum; λ_{max},

nm, 486; $\nu(cm^{-1})$ 882(s), 806(s), 790(s) 765(m), 720(ms) 670(s) (25).

Metal Analyses

Approximately 100 mg of the lanthanide complex was placed into

a preweighed tube which was then capped with a rubber septum. The

tube and its contents were weighed after which the moisture sensitive

rare-earth complex was hydrolyzed with 5 mL of degassed distilled

water. The contents of the tube were transferred to a beaker and

digested with hot concentrated HNO_3. The solution was then diluted

to 100.0 mL. An aliquot of the above solution and a measured

excess of 0.01 M Na_2EDTA was transferred to a beaker. The pH

of the solution was adjusted to 8-8.5 with NaOH. The solution

was then buffered with NH_4Cl/NH_3, pH = 8.9. Two drops of

Erio-T indicator was added and the solution was back-titrated with a 0.1 M $ZnSO_4$ solution standardized with Na_2EDTA until the color of the solution turned from blue to pink. Titrations are accurate to ±0.5%. Precision is 2 ppt.

Thermal Studies

Thermal stability of the $Ln_2(C_8H_8)_3$ complexes was determined by attaching sealed capillary tubes containing the compounds of interest to a thermometer. The tubes and the thermometer were placed in a sand bath which could be heated slowly to 250°C.

Conductance Measurements

The conductance measurement was obtained from a saturated solution of $Nd_2(C_8H_8)_3 \cdot 2C_4H_8O$ in pyridine using an Industrial Instruments Model RC16B2 conductivity cell with a cell constant of 0.102.

Physical Measurements

The ^1H NMR spectra of the title compounds were recorded with a Varian HA-100 Spectrometer or a Varian FT-80 A Spectrometer in pyridine-d_5. The shifts are given with respect to the proton resonance of COT^{2-} at 5.9 ppm with reference to TMS. The initial measurements on the spectra were referenced to the upfield pyridine resonance which was used as an internal reference. These measurements were then corrected to the COT^{2-} resonance. Decomposition

was precluded by sealing the n.m.r. tubes under vacuum or by capping the tubes with rubber septums.

The IR spectra were obtained using Nujol mulls on a Perkin-Elmer 621 Grating Spectrophotometer. The samples, prepared in the dry box and placed between NaCl plates, could be exposed to the atmosphere for several hours without decomposition.

A Varian-MAT GmbH CH7 Massenspektrometer at an ionization potential of 70 eV interfaced with a Varian 1200 gas chromatograph was used to obtain the vpc-mass spectral data.

A Cary 82 Spectrophotometer using the 6471-Å exciting line of a Spectra Physics Model 164 Krypton ion laser operating at 100 mW was used in the attempts to obtain Raman spectra. The samples were sealed in glass capillary tubes.

Magnetic susceptibility studies at ambient temperature were conducted by Dr. John Gardner of the Physics Department of Oregon State University using an automatic Faraday susceptibility apparatus of his own design and construction. The tube was loaded in the dry box, and sealed which insured the integrity of the sample and that the tube would remain intact. Curie behavior was assumed. Diamagnetic and temperature independent paramagnetic corrections were not made. The magnetic moments were calculated according to the method described by Figgis and Lewis (63).

RESULTS AND DISCUSSION

Analytical Results

The metal analyses for the lanthanide-tris(cyclooctatetraene)

complexes were done by using back complexometric titration with

$ZnSO_4$ as described in the Experimental Section. Back titration was

necessary because the rare-earth ions react slowly with $EDTA^{2-}$

resulting in an endpoint difficult to detect. Uranocenes and rare-

earth COT^{2-} complexes (25, 27) do not give satisfactory C, H analyses

because of the extreme oxygen sensitivity of these complexes. All the

complexes, except Er and Tb, readily lost THF of solvation making it

necessary to remove all solvent under high vacuum prior to analysis.

The results are presented in Table 3.

Table 3. Metal analysis and color of $Ln_2(RC_8H_7)_3$.[a]

| | | % Ln | |
Complex	Color	Found	Calcd
$Ce_2 (C_8H_8)_3$	green	47.25	47.28
$Nd_2 (CH_3C_8H_7)_3$	gold	44.73	44.90
$Nd_2 (n\text{-}C_4H_9C_8H_7)_3$	deep gold	40.37	39.54
$Sm_2 (C_8H_8)_3$	black	48.75	49.08
$Sm_2 (CH_3C_8H_7)_3$	black	43.23	45.87
$[Tb_2 (C_8H_8)_3] \cdot 2C_4H_8O$[b]	gold	41.24	41.05
$[Er_2 (C_8H_8)_3] \cdot 2C_4H_8O$[b]	brown	42.58	42.28
$Yb (C_8H_8)$	pink	64.08	62.43

[a]R = H, CH_3, n - C_4H_9
[b]THF adduct

Physical Properties

The colors of the $Ln_2(RC_8H_7)_3$ complexes, reported in Table 3, vary with solvation. $Ce_2(C_8H_8)_3 \cdot 2C_4H_8O$ is brown, whereas the unsolvated complex is green. Exposure of this unsolvated green complex to THF causes the color to return to brown. The ease with which THF can be lost can be observed by the color change from brown to green while the complex is exposed to the dry nitrogen atmosphere of the box. Both $Nd_2(CH_3C_8H_7)_3$ and $Nd_2(n-C_4H_9C_8H_7)_3$ complexes are green in THF but turn golden brown upon solvent removal. The THF coordinated to $Nd_2(C_8H_8)_3 \cdot 2C_4H_8O$ can be removed by heating the complex under vacuum whereas the alkyl substituted complexes of Nd readily lose THF at room temperature. Similar results have been observed by Hodgson et al. (25) for $[Ln(C_8H_8)Cl \cdot 2C_4H_8O]_2$ where Ln is Sm and Pr. The Sm complexes are different from the above in that no THF of solvation is present. Color changes were not observed during removal of THF following extraction. In addition, no THF resonances were observed in the ^{1}H NMR indicating that the Sm complexes are not solvated.

The unsubstituted complexes are moderately soluble in pyridine, sparingly soluble in THF and insoluble in diethyl ether, benzene and hexane. Alkyl substitution on the COT ring increases the solubility of the Nd complexes giving green THF solutions. The

$Nd_2(n-C_4H_9C_8H_7)_3$ complex was extracted with hexane. All of the

lanthanide complexes gave deep brown solutions in pyridine. Extrac-

tion of these complexes took from two days for the substituted

$Nd_2(CH_3C_8H_7)_3$ complex in THF to two weeks for $Er_2(C_8H_8)_3 \cdot 2C_4H_8O$

in THF. $Yb(C_8H_8)$ was extracted with pyridine.

The Ce and Er complexes are thermally stable under nitrogen at

temperatures up to 250°C. They do not sublime in vacuo. All of the

complexes in Table 3 can be stored under vacuum with no signs of

decomposition.

Chemical Properties

All of the lanthanide (III) complexes in this study are extremely

oxygen sensitive and will decompose to free cyclooctatetraene or

substituted cyclooctatetraene in the presence of trace amounts of

oxygen. The unsubstituted complexes ignite when they are exposed

to the atmosphere. Substitution on the cyclooctatetraene ring appears

to increase the stability of these compounds towards oxygen because

they do not ignite upon exposure to the atmosphere. Streitwieser

and Harmon (13) observed the same behavior towards oxygen for

1,1-disubstituted uranocenes in which the substituents are electron

donating. The effects of these substituents is to increase the energy

of the π-orbitals on the ring providing better overlap between the

metal orbitals and the $C_8H_8^{2-}$ anion. The complexes react with

protic solvents giving cyclooctatrienes or substituted cycloocta-
trienes. They also react with halogenated solvents, acetone and
alcohols.

Raman Spectra

The Raman spectra of the title complexes could not be recorded
because the frequency of the absorption band is close to the incident
radiation frequency resulting in fluorescence.

Magnetic Moments

The magnetic moments of $Ln_2(C_8H_8)_3 \cdot 2C_4H_8O$ are presented
in Table 4. The values are close in comparison to the magnetic
moments of the free ion terms providing further evidence for the
ionicity of these compounds. The moments are also similar to those
of the complexes prepared by Hodgson et al. (25) indicating that the
electronic configurations of these three types of lanthanide complexes
are not markedly different.

Table 4. Magnetic moments of rare earth-cyclooctatetraene complexes.

	μ, BM[a]	μ, BM[b]	μ, BM[c]	μ, BM[d]
Ln				
Nd[e]	3.20[e]	3.37	2.98	3.5
Ce	1.86	1.79	1.88	2.4
Er	9.31			9.5
Sm[f]	1.46[f]	1.36	1.42	1.5

[a]$Ln_2(C_8H_8)_3 \cdot 2C_4H_8O$

[b]$[Ln(C_8H_8)Cl \cdot 2C_4H_8O]_2$; Ref. 23

[c]$K[Ln(C_8H_8)_2]$; Ref. 23

[d]Free ion terms; Ref. 38

[e]$Nd_2(C_8H_8)_3 \cdot 2C_4H_8O$; Ref. 25

[f]THF absent

Infrared Spectra

The infrared spectra for the $Ln_2(RC_8H_7)_3$ complexes in the 600-1000 cm^{-1} region are all similar (Table 5). This indicates that the planar nature of the $C_8H_8^{2-}$ ring is still intact. The distinctive bands attributed to the C-H(11) and C-H ($\perp$) bending fundamentals of $C_8H_8^{2-}$ (i.e. for $Ce_2(C_8H_8)_3$, 890 (s) and 690 (vs) are clearly present in the spectra of all the complexes. Additional bands in the infrared are attributed to a change from D_{8h} in the effective site symmetry of the ligand. The 1010 cm^{-1} band (i.e. $Ce_2(C_8H_8)_3 \cdot 2C_4H_8O$) is due to co-ordinated THF (C-O stretch) which disappears upon removal of the solvent. A typical infrared spectrum, that of $Ce_2(C_8H_8)_3$, is presented in Figure 4.

Table 5. $Ln_2(RC_8H_7)_3$[e] infrared spectrum (cm^{-1})[a, b]

Ce[c]	Ce	Nd	Nd[f]	Nd[g]	Sm	Sm[f]	Er[c]	Yb[h]	$K_2C_8H_8$[d]
1012 (m)			1005 (wb)	1020 (m)	1013 (wb)		1007 (s)		
893 (s)	890 (s)	894 (s)	900 (m)	890 (s)	898 (s)	880 (s)	894 (s)	888 (s)	880 (s)
859 (m)	855 (m)		848 (m)		840 (w)		855 (s)		
	800 (m)			800 (w)		810 (m)	830 (m)		
	765 (m)	798 (m)			788 (w)	790 (m)	775 (m)		
		771 (m)				772 (m)			
739 (m)	740 (m)	744 (s)		740 (w)	745 (m)		742 (m)		
724 (m)	728 (m)		730 (w, sh)						
				696 (w, sh)			723 (m)		
681 (vs)	690 (vs)	685 (vs)	690 (vs)	680 (vs)	690 (vs)	672 (vs)	670 (vs)	678 (s)	684 (s)

[a] As Nujol mulls

[b] vs = very strong, s = strong, m = medium, w = weak, wb = weak broad, sh = shoulder

[c] THF adduct

[d] Reference 39

[e] R = H, CH_3, $n\text{-}C_4H_9$
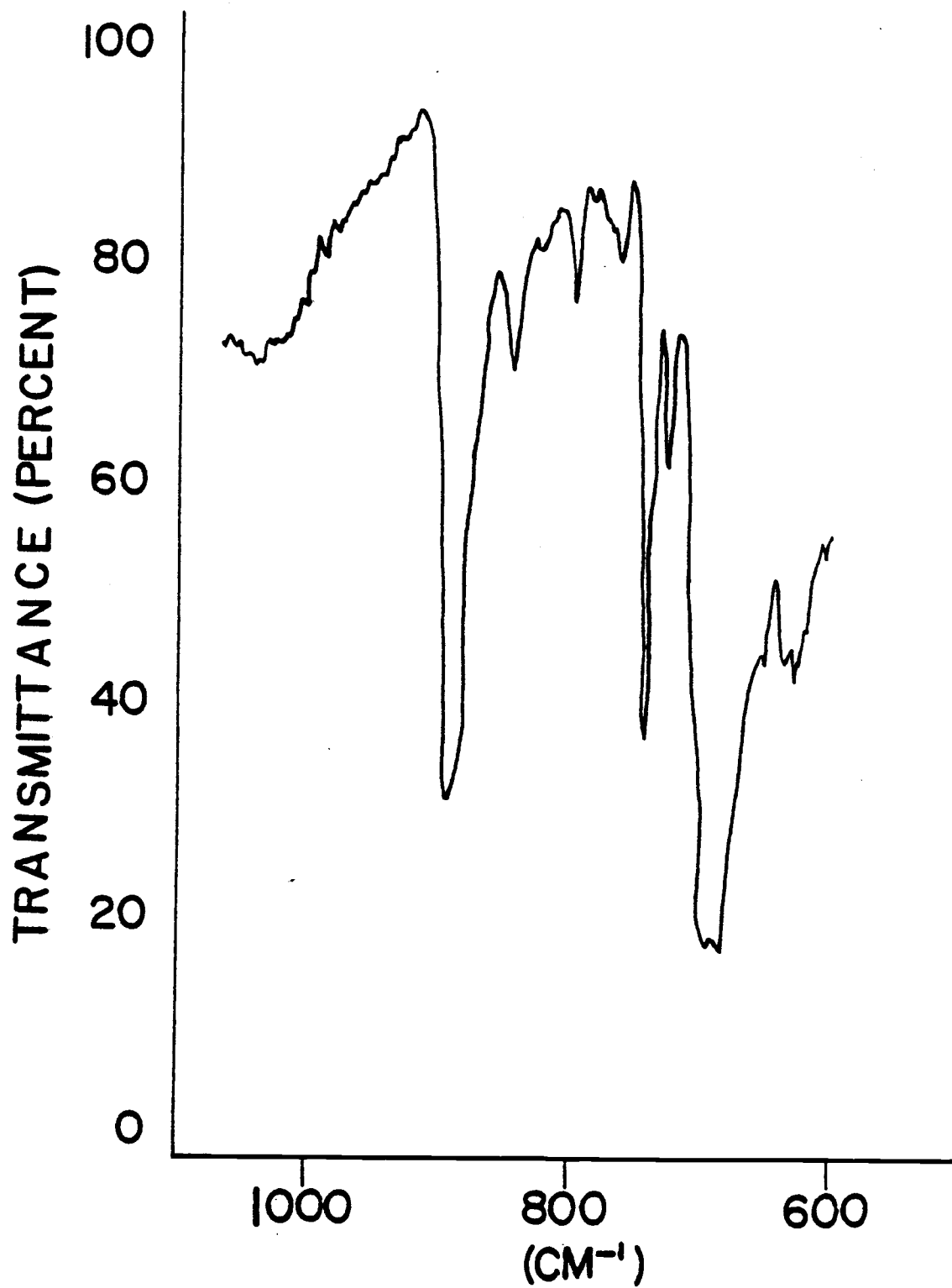
[f] R = CH_3

[g] R = $n\text{-}C_4H_9$

[h] $Yb(C_8H_8)$

Figure 4. Infrared spectrum of $Ce_2(C_8H_8)_3$

Paramagnetic ^{1}H Nuclear Magnetic Resonance

Diamagnetic n. m. r. arises from the interaction of a nucleus

precessing in an applied magnetic field, H_o, with an alternating field,

H_1. For a nuclear spin, I, there are 2I+1 possible orientations of the

nucleus precessing in the uniform magnetic field with the values I, I-1,

I-2, ..., -I. This Zeeman splitting of nuclear energy levels allows

for the observation of spectra in ^{1}H NMR from the transitions between

these levels when the nucleus is placed in an alternating field, H_1.

Once the transition from the lower Zeeman levels has occurred,

there exist relaxation mechanisms by which the nucleus can return

to its lower spin state. Spin-spin relaxation allows for energy trans-

fer between two nuclei by an exchange in spin states of each nucleus

with relaxation time T_2. Spin-spin relaxation does not restore the

Boltzmann distribution of spin states. Spin-lattice relaxation occurs

by the transfer of energy from the excited nuclear spin state into

thermal energy of the molecular surroundings. The time required

for this transition, T_1, determines the breadth of the absorption

resonance in solutions. Extremely short T_1 relaxation times give

rise to broad resonances. The spin-lattice relaxation time can be

shortened by the introduction of a paramagnetic species to an other-
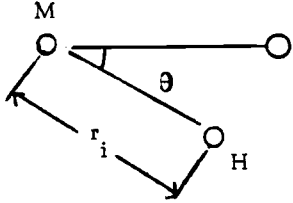
wise diamagnetic system.

Paramagnetic centers present in samples often give rise to

^{1}H NMR resonances which are characteristically broad and may be shifted either upfield or downfield with respect to the diamagnetic species. These shifts are referred to as isotropic shifts. Resonances broadened by paramagnetic interactions will, at times, vanish completely.

These broad shifted resonances are a direct result of the interaction of the unpaired electron spin with the excited nucleus allowing this nucleus to return to the ground state. If an electron has a long relaxation time, the nuclear relaxation time is short which results in the observation of a broad ^{1}H NMR signal. Referring to the Heisenberg uncertainty principle ($\Delta E \Delta t \geq \hbar$) decreasing Δt increases ΔE or the energy of the excited states becomes more uncertain. Broad-line n.m.r. are observed when protons with relaxation times up to 10^{-9} seconds are present compared to sharp resonances which are observed for diamagnetic complexes with relaxation times up to several seconds.

The isotropic shift is the result of two separate electron-nuclear spin interactions. The Fermi contact shift is a measure of the unpaired spin density which is delocalized onto the n.m.r. nucleus. This term decreases very rapidly as the distance between the paramagnetic center and the n.m.r. nuclide increases. The pseudocontact or dipolar shift is a through space effect and is dependent on the position of the proton in the molecule relative to the paramagnetic center.

The difficulty in the interpretation of paramagnetic n.m.r.
spectra arises in the separation of these two components. For the
dipolar component in systems with axial symmetry, relationship (VI)
(40) for the induced chemical shift for $\Delta\nu^{dip}$ holds. The shift is

$$\frac{\Delta\nu_i^{dip}}{\nu} = \frac{K(3\cos^2\theta - 1)}{r_i^3}(\chi_{11} - \chi_{\perp}) \qquad (VI)$$

dependent on the distance, r_i, from the nucleus to the para-
magnetic center, θ, the angle between the principle magnetic
axis and MH, χ_{11} the magnetic susceptibility parallel to the
molecular axis and $\chi_{\perp}$ the magnetic susceptibility perpendicular to the
molecular axis. K is a constant. This equation is applicable for
systems with axial symmetry for which the structure is known from
single crystal x-ray studies and the solid state geometry is retained
in solution.

The Fermi contact term (40) is usually expressed as

$$\frac{\Delta\nu_i^{con}}{\nu} = \frac{A_i g_{av}\beta S(S+1)}{g_N \beta_N 3kT} \qquad (VII)$$

where A_i is the hyperfine coupling constant, g_{av} is the average g

value, β is the value of the Bohr magneton, g_N is the nuclear g factor,

β_N = eh/2Mc [e=charge of proton; M=mass of proton; c=speed of light],

k is Boltzmann's constant, T is the absolute temperature and S is the

spin quantum number. Unfortunately equations (VI) and (VII) are use-

ful only in limited cases. Extensive ^{1}H NMR studies have been done

on uranocene which have resulted in the separation of the contact and

dipolar components of the observed shifts (29, 30). Similar studies

have not been reported for Ln-COT complexes.

Hodgson et al. (25) has presented the only Ln-COT ^{1}H NMR data

in THF-d_8 by using the complex $KLn(C_8H_8)_2$ for Ln = La, Nd, Sm, and

Tb. Diamagnetic La^{3+} showed a resonance at 5.9 ppm downfield from

external TMS, which was identical to that observed for $K_2C_8H_8$ at

5.9 ppm. However, the paramagnetic centers broadened and shifted

the $C_8H_8^{2-}$ proton resonances as exhibited by the shifts of -14.0,

7.4 and 113.4 for Nd^{3+}, Sm^{3+} and Tb^{3+}, respectively. These shifts

are reported with respect to COT^{2-}. These values give an indication

of the types of shifts that can be expected from the interaction of

unpaired spin density on the rare-earths with the protons on the

$C_8H_8^{2-}$ ring. The ^{1}H NMR of $KNd(C_8H_8)_2$ in pyridine-d_5 is presented

in Figure 12. The broad singlet for the $C_8H_8^{2-}$ protons is observed at

-13.0 with respect to COT^{2-}. The difference between the resonance

observed in this laboratory (-13.0) and that observed by Hodgson

et al. (25) (-14.0) for $KNd(C_8H_8)_2$ can be attributed to solvent

effects.

The single-crystal structure of $Nd_2(C_8H_8)_3 \cdot 2C_4H_8O$ presented

in Figure 1 (26, 27) reveals three different COT^{2-} entities. If this

solid state geometry is retained in solution, ideally, two resonances

would be observed for the terminal COT^{2-} rings and a complex multi-

plet for the central dianion. The possibility exists that the terminal

COT^{2-} rings are so similar that they will appear as a single reso-

nance. In addition, the protons on the central $C_8H_8^{2-}$ will exhibit

a single resonance if the molecule is fluxional and free rotation of

this ring occurs.

Fluxional molecules have intramolecular exchange of the same

atoms which, if rapid enough, makes these otherwise non-equivalent

atoms equivalent. For example, a fluxional $C_5H_5^-$ anion σ-bonded

to a Fe^{2+} center, as depicted below, shows a sharp singlet in an

^1H NMR spectrum at 30°C (41). At -60°C there is the first indica-

tion of three different protons in the σ-bonded species and at -100°C

a singlet is observed for H_1 and two complex doublets are observed

for H_2 and H_5 and for H_3 and H_4. Reduction of the temperature

"freezes" the σ-bonded $C_5H_5^-$ anion into position long enough for

the n.m.r. spectrometer to detect the different protons. Low
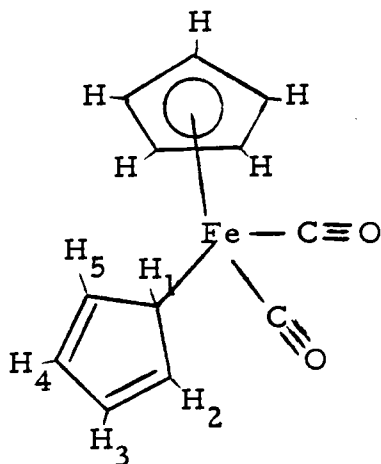
temperature studies may be able to give some insight into the fluxional

nature of these rare-earth COT^{2-} complexes.

An alternative way of viewing $Nd_2(C_8H_8)_3 \cdot 2C_4H_8O$ is as an infin-

itely separated anion-cation pair. In this case a single resonance due to

the anion, $[Nd(C_8H_8)_2]^-$, and a single resonance due to the cation,

$[Nd(C_8H_8) \cdot 2C_4H_8O]^+$, would be expected. This latter view is

attractive because it allows the comparison of the spectrum of

$Nd_2(C_8H_8)_3 \cdot 2C_4H_8O$ with that of $KNd(C_8H_8)_2$. The shift in reso-

nance of the anion signal from that of $KNd(C_8H_8)_2$ is a measure of

the anion-cation interaction in solution. It may be in fact that the

$Nd_2(C_8H_8)_3 \cdot 2C_4H_8O$ molecule dissociates in solution into a cation-

anion pair according to the following equation.

$$[Nd(C_8H_8) \cdot 2C_4H_8O][Nd(C_8H_8)_2] \rightleftarrows [Nd(C_8H_8) \cdot 2C_4H_8O]^+$$
$$+ [Nd(C_8H_8)_2]^- \qquad \text{(VIII)}$$
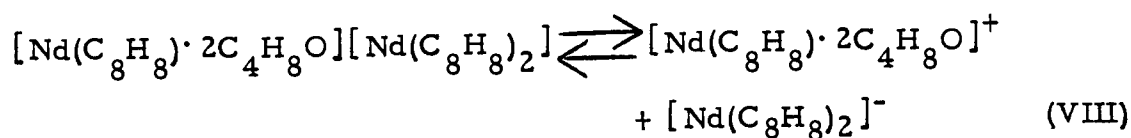
Several possibilities occur from equation (VIII). Complete dissocia-

tion gives rise to the infinitely separated cation-anion pair discussed

previously which will result in two resonances in the ^1H NMR spec-

trum. If exchange of the $C_8H_8^{2-}$ rings occurs between these two

species all $C_8H_8^{2-}$ rings become equivalent and the two resonances

may appear as a single resonance. If dissociation is very small, the

concentration of cation and anion will be low probably precluding

observation of their resonances. As the equilibrium shifts to the

right, it would be expected that three resonances due to the cation,

the anion and the undissociated complex might be observed. However,

if exchange occurs, a single resonance may be observed even though

all three species are present.

The assumption is often made that the shifts observed for

lanthanide complexes are due exclusively to pseudocontact interac-

tions because of the fact that the f-electrons are so well shielded.

However, a small contact contribution does arise from the direct

delocalization of unpaired spin density from the metal onto the n.m.r.

nucleus. For example, Donato and Martin (42), in studies with

lanthanide shift reagents, observed small contact shifts for the pro-

tons nearest to the paramagnetic center. The presence of contact

shifts indicates at least some covalency is present within a molecule.

In our Ln-COT complexes, contact shifts can be investigated

by the addition of methyl substituents on the aromatic

$C_8H_8^{2-}$ ring. In paramagnetic complexes which exhibit some co-

valency methyl groups attached to π-bonded aromatic species exhibit

contact shifts opposite in sign to that of the ring protons (29). This is

due to the correlation of the spin of the unpaired e^- in the carbon

π-orbital with the spin of the electrons in the sp^2 orbitals. A diagram
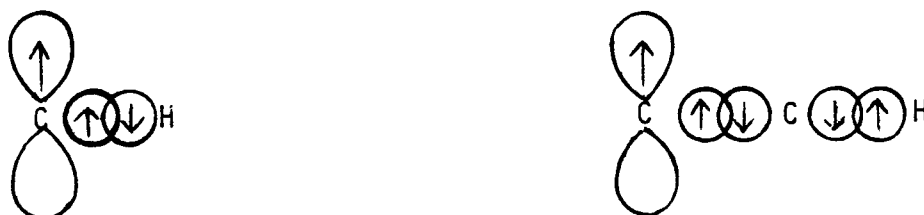
is presented to clarify this phenomenon. If this phenomenon is

observed in the ^1H NMR spectrum for the title compounds a certain

amount of covalency exists.

The preceding discussion now allows for the examination of the

^1H NMR spectra of the $Ln_2(RC_8H_7)_3$ complexes. All of the complexes

studied contain Ln^{3+} ions with incomplete 4f shells. The presence

of the paramagnetic centers in the complexes produced spectra with

broadened solvent and COT^{2-} resonances. The ^1H NMR data recorded

in pyridine-d_5 are presented in Table 6. All shifts are referenced to

$K_2C_8H_8$ at 5.9 ppm. The purpose of this reference is to give directly

the isotropic shift of the $C_8H_8^{2-}$ rings in the complexes under study.

The spectra of the $Ln_2(RC_8H_7)_3$ are displayed in figures 5-12. These

complexes are extremely oxygen and moisture sensitive. This sensi-

tivity often causes slight decomposition of the complexes resulting in

the observation of free COT and cyclooctatrienes in the ^1H NMR. In

addition resonances were often observed at -3.2, -3.5, -4.6 and

-4.9 ppm (referenced to COT^{2-}) and are assigned to impurities in

the system. Resonances due to the ligand protons were not observed

for the $Er_2(C_8H_8)_3 \cdot 2C_4H_8O$ complex. The fact that the Er^{3+} com-

plex produced no observable resonance is not unusual. In neither

case was a $C_5H_5^-$ proton resonance recorded for $Er(C_5H_5)_3$ or

$(C_5H_5)_3ErCNC_6H_{11}$. This was attributed to unusual line broadening

(38).

Examination of the $Nd_2(RC_8H_7)_3$ spectra (Figures 5, 6, 7)

reveals a broad single resonance upfield from COT^{2-} which is

assigned to the ring protons (vide infra). (R=H, δ -14.5; R =CH_3,

δ -15.4; R = n-C_4H_9, δ -14.8). This resonance is in the area and

direction for that observed for $KNd(C_8H_8)_2$ (δ -13.0). Ring substitu-

tion appears to have little effect on the location of the ring proton

resonance for these Nd^{3+} complexes.

Ionic dissociation of $Nd_2(C_8H_8)_3 \cdot 2C_4H_8O$ may be expected to

occur in solution according to equation (VIII).

Table 6. ^{1}H NMR spectrum of the title compounds.[a]

Compound	δ[b] Ring Protons	Substituent Protons
$Nd_2(C_8H_8)_3 \cdot 2C_4H_8O$[d]	-14.5	
$Nd_2(CH_3C_8H_7)_3$[c]	-15.4	4.3 (CH_3)
$Nd_2(n\text{-}C_4H_9C_8H_7)_3$[d]	-14.8	0.5 ($>CH_2$), -4.3 (CH_2), -4.8 (CH_2), -5.2 (CH)$_3$
$KNd(C_8H_8)_2$[d]	-13.0	
$Ce_2(C_8H_8)_3$[c]	-3.5	
$Sm_2(C_8H_8)_3$[d]	7.8	
$Sm_2(CH_3C_8H_7)_3$[d]	6.4 , 7.5 , 8.0 , 8.5	-0.9 (CH_3)
$Tb_2(C_8H_8)_3 \cdot 2C_4H_8O$[c]	125	

[a] The spectra were recorded in pyridine-d_5

[b] Minus sign indicates upfield referenced to COT^{2-} at 5.9 ppm

[c] Recorded with a Varian HA-100 spectrometer at 28°C

[d] Recorded with a Varian FT-80A spectrometer at 33°C

* pyridine

impurities

+ THF

ξ $C_8H_8{}^{2-}$ (-14.5 ppm)
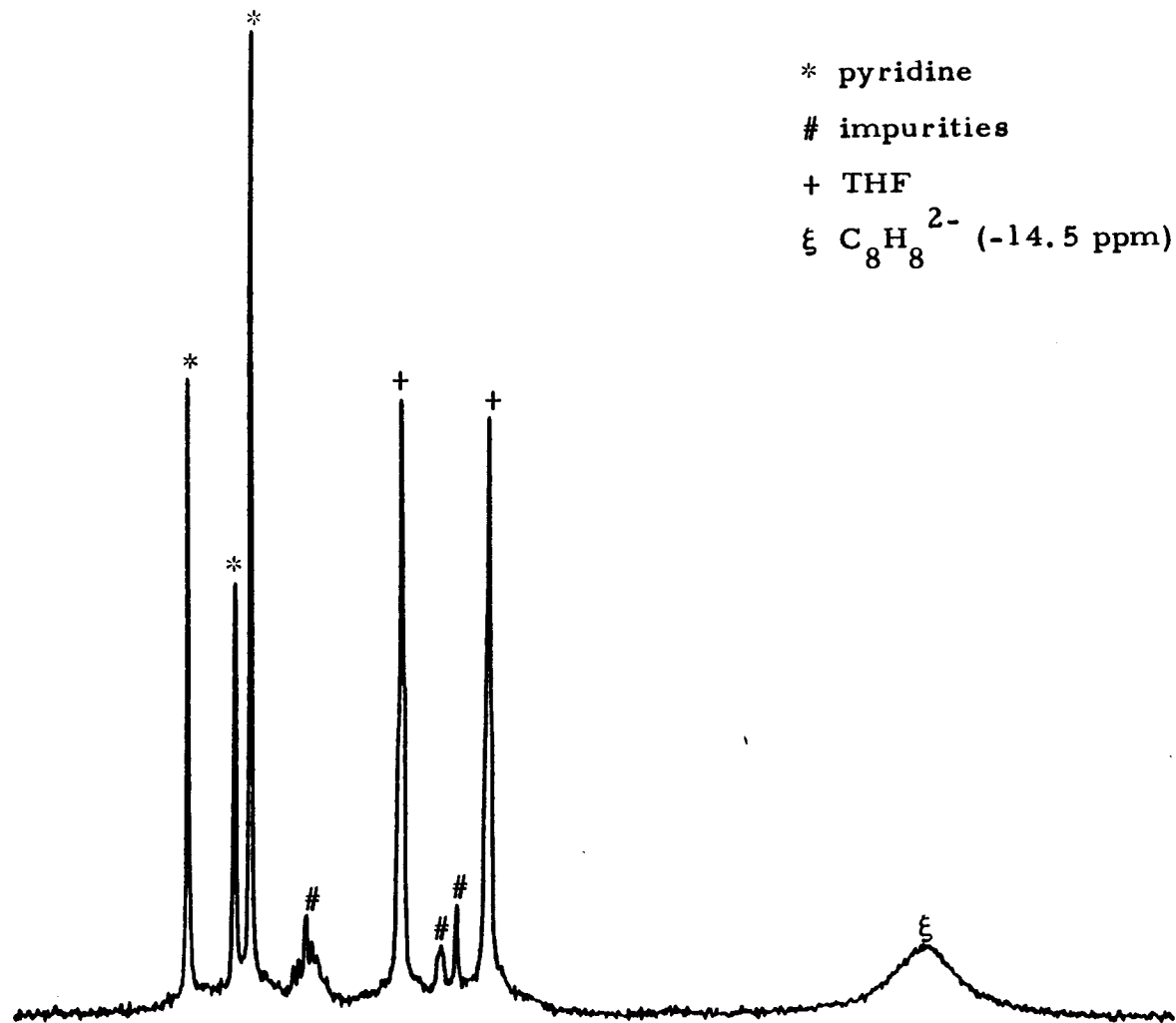
Figure 5. ^{1}H NMR spectrum of $Nd_2(C_8H_8)_3 \cdot 2C_4H_8O$ in pyridine-d_5 at 80 MHz

* pyridine

impurities

@ CH_3 (4.3 ppm)

δ $C_8H_7^{2-}$ (-15.4 ppm)
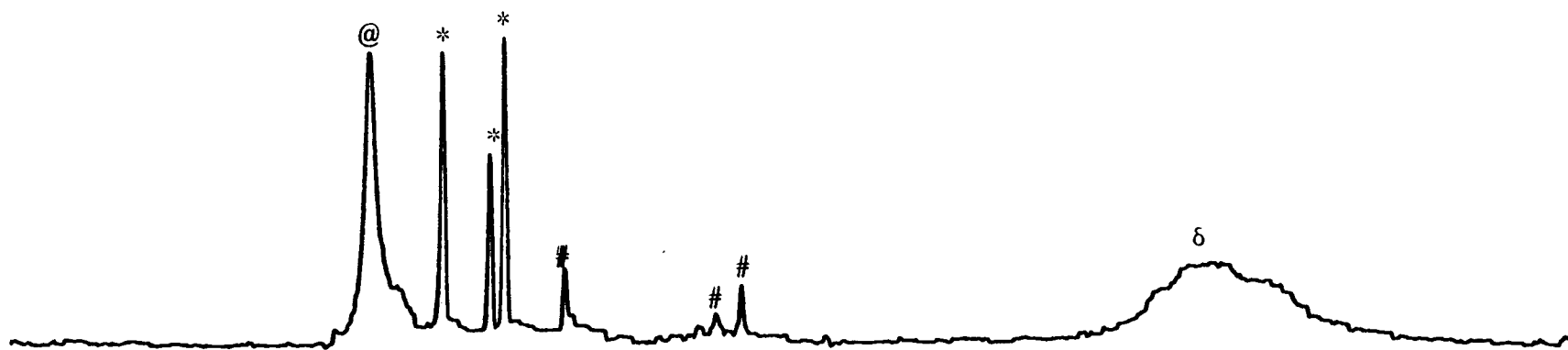
Figure 6. ^{1}H NMR spectrum of $Nd_2(CH_3C_8H_7)_3$ in pyridine-d_5 at 100 MHz

* pyridine

\# impurities

ξ $C_8H_7^{2-}$ (-14.8)

@ n-C_4H_9(0.5, > CH_2; -4.3, CH_2;

-4.8, CH_2; -5.2, CH_3)
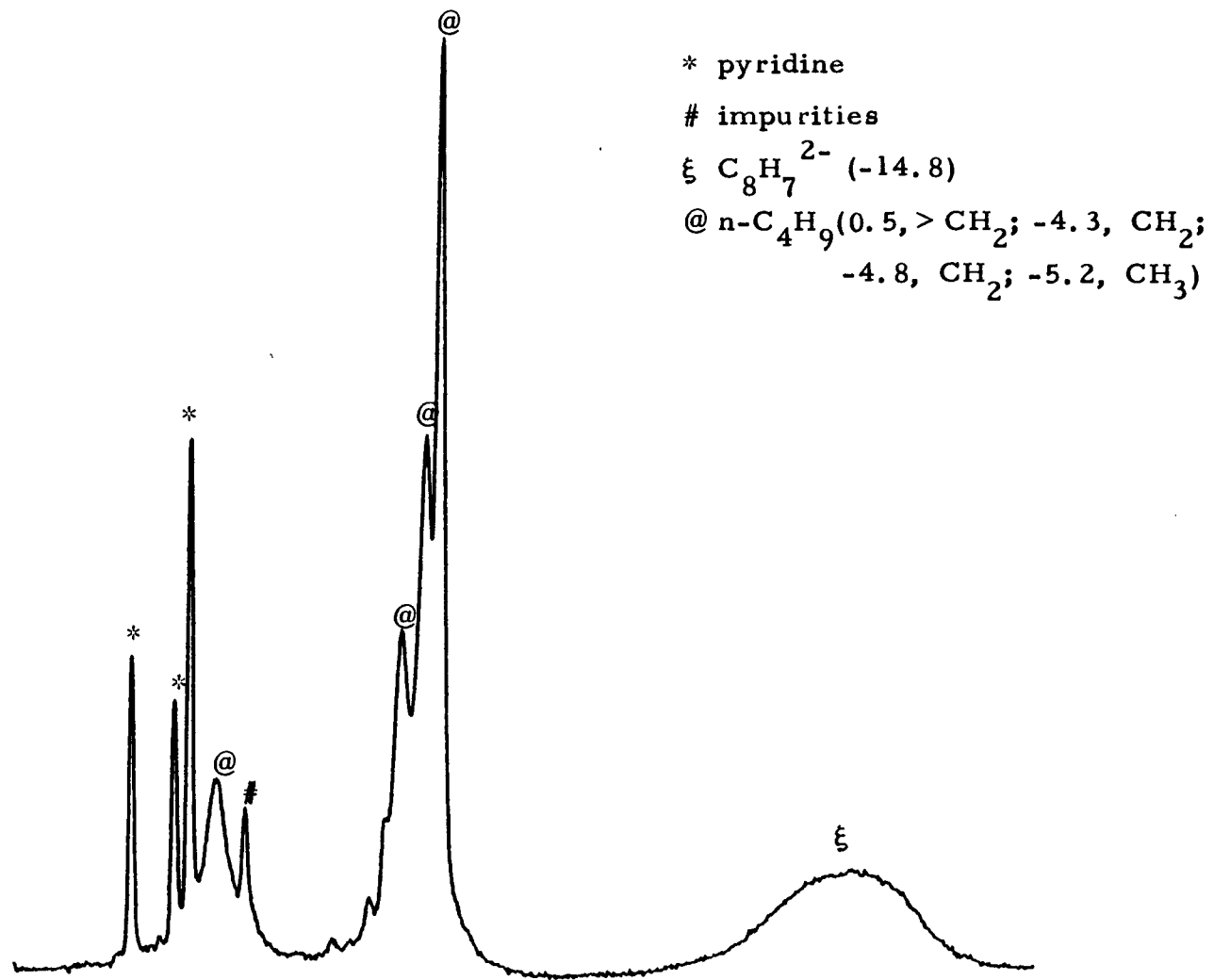
Figure 7. ^{1}H NMR spectrum of $Nd_2(n-C_4H_9C_8H_7)_3$ in pyridine-d_5 at 80 MHz

* Lower side band of pyridine

+ Lower side band of THF

ξ $C_8H_8{}^{2-}$ (125 ppm)
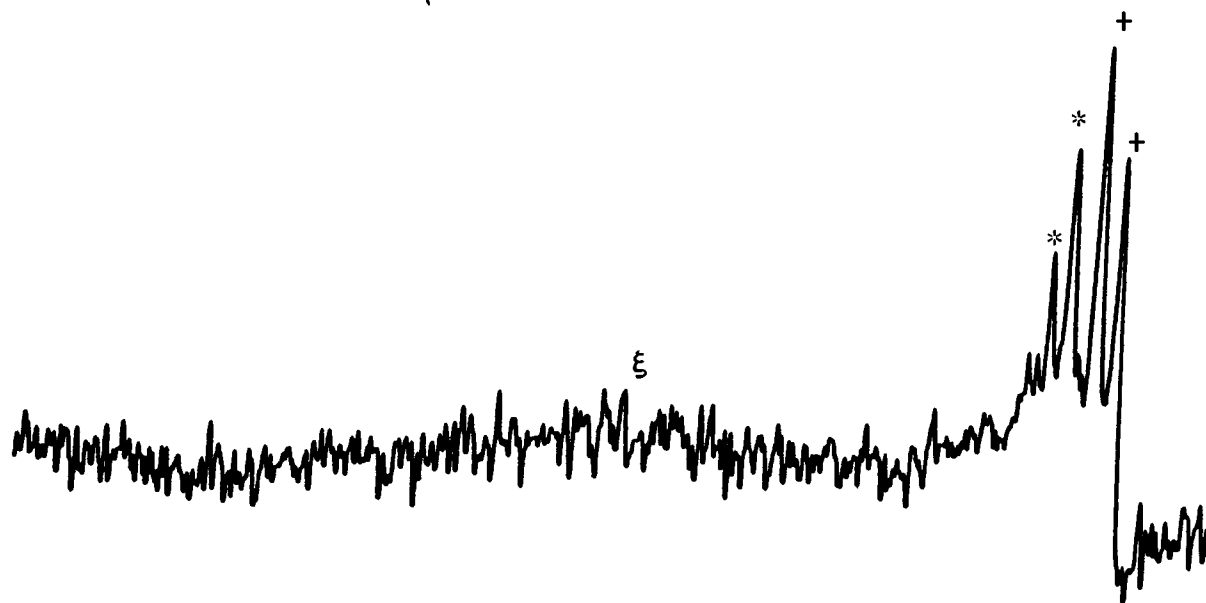
Figure 8. ^{1}H NMR spectrum of $Tb_2(C_8H_8)_3$ in pyridine-d_5 at 100 MHz
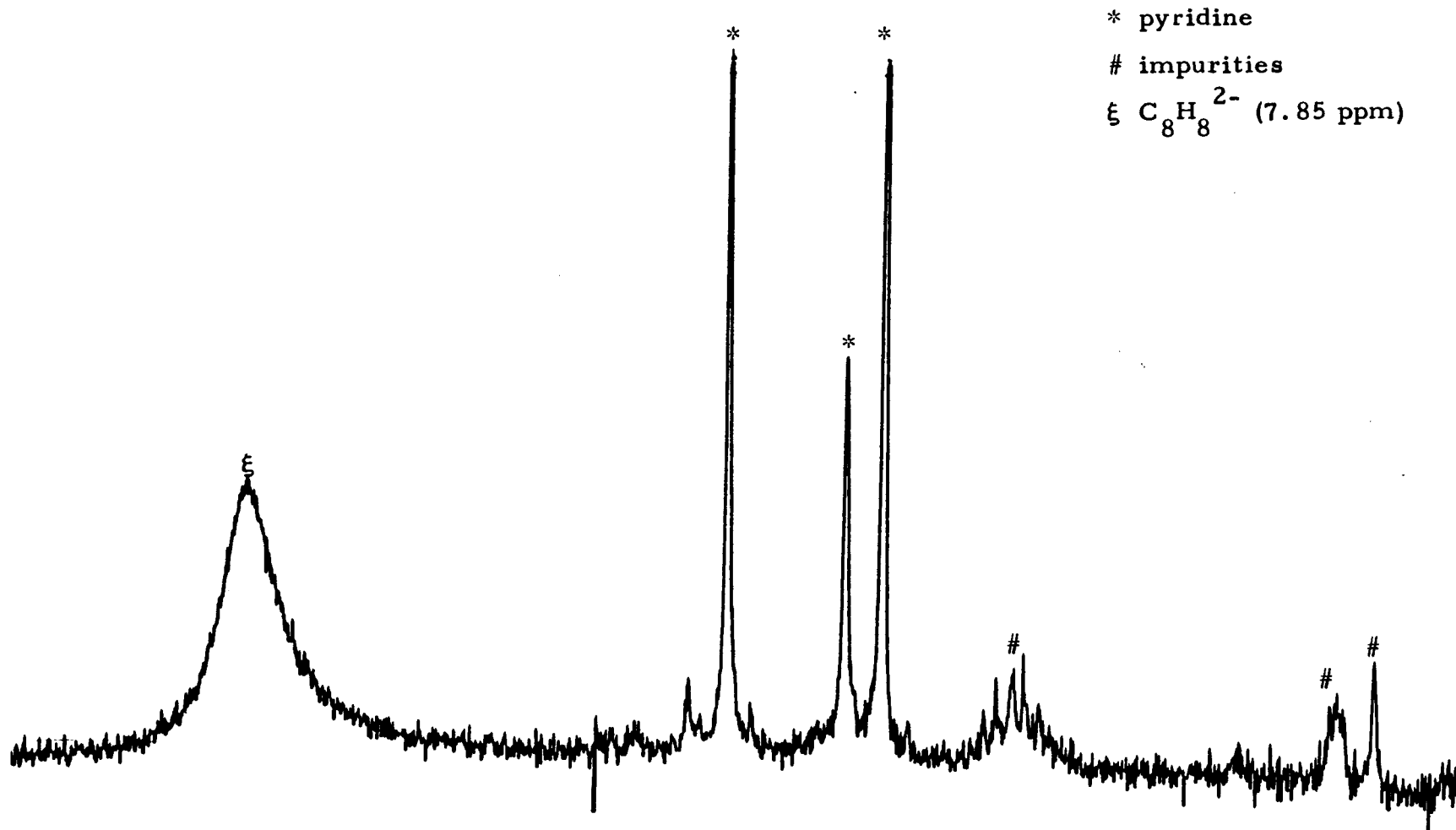
Figure 9. ^{1}H NMR spectrum of $Sm_2(C_8H_8)_3$ in pyridine-d_5 at 80 MHz

Legend:
* pyridine
# impurities
ξ $C_8H_8^{2-}$ (7.85 ppm)

* pyridine

impurities

@ CH_3 (-0.9 ppm)

ξ $C_8H_7^{2-}$ (6.4, 7.5, 8.0, 8.5 ppm)
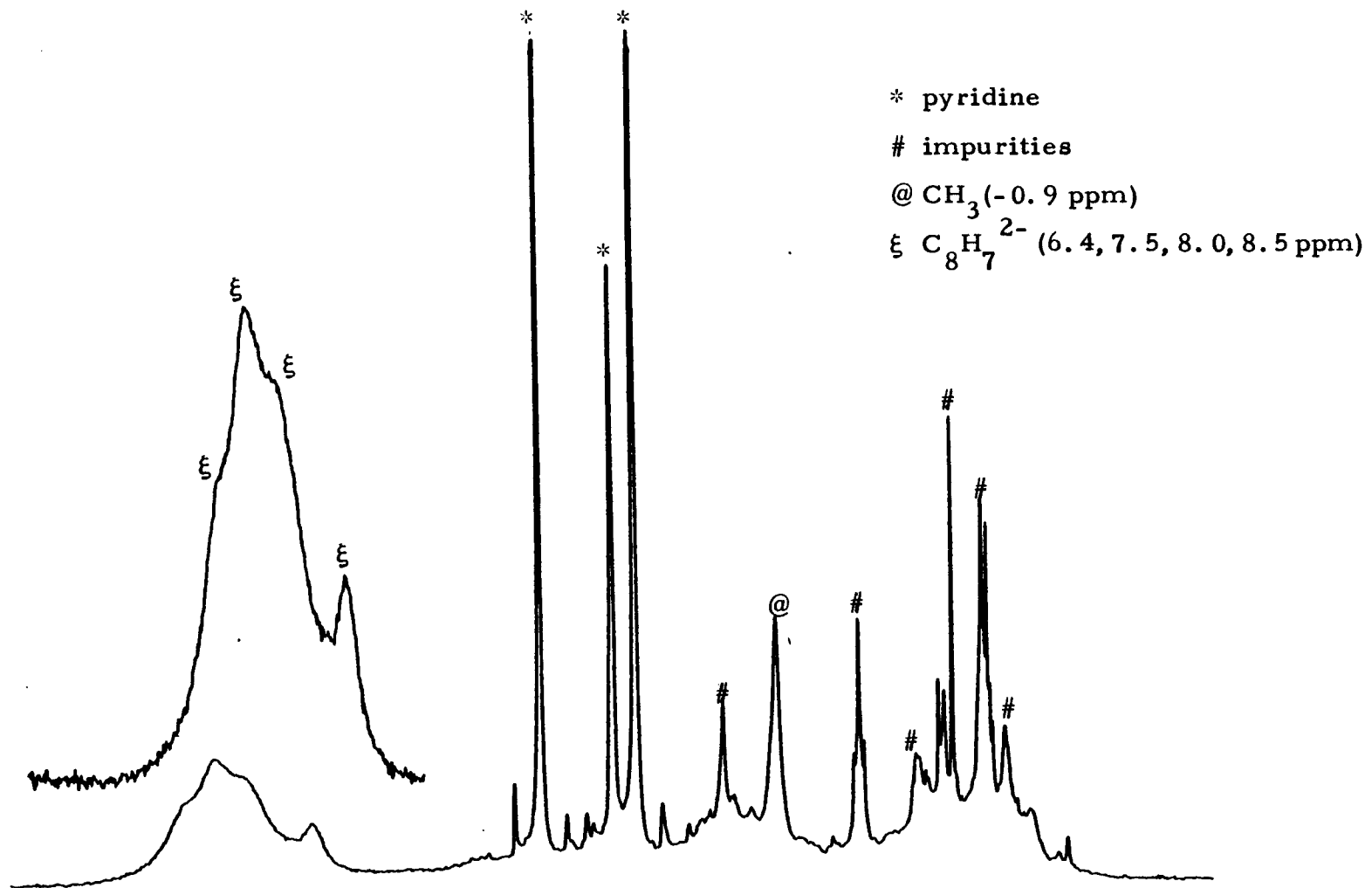
Figure 10. ^{1}H NMR spectrum of $Sm_2(CH_3C_8H_7)_3$ in pyridine-d_5 at 80 MHz

* pyridine

impurities

ξ $C_8H_8{}^{2-}$ (-3.5 ppm)
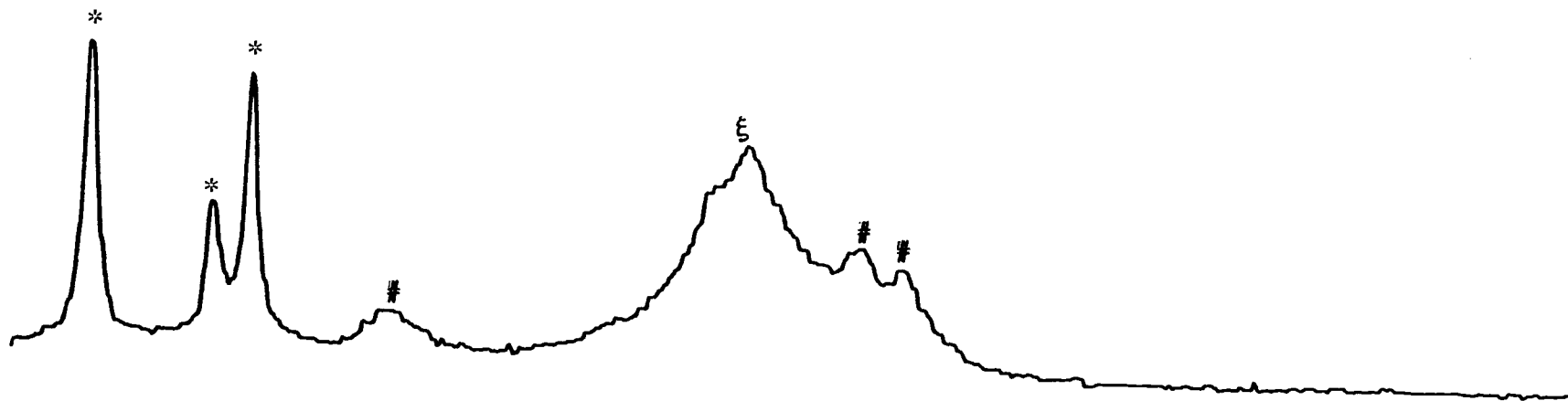
Figure 11. ^{1}H NMR spectrum of $Ce_2(C_8H_8)_3$ in pyridine-d_5 at 100 MHz

* pyridine

impurities

+ THF

ξ $C_8H_8{}^{2-}$ (-13.0)
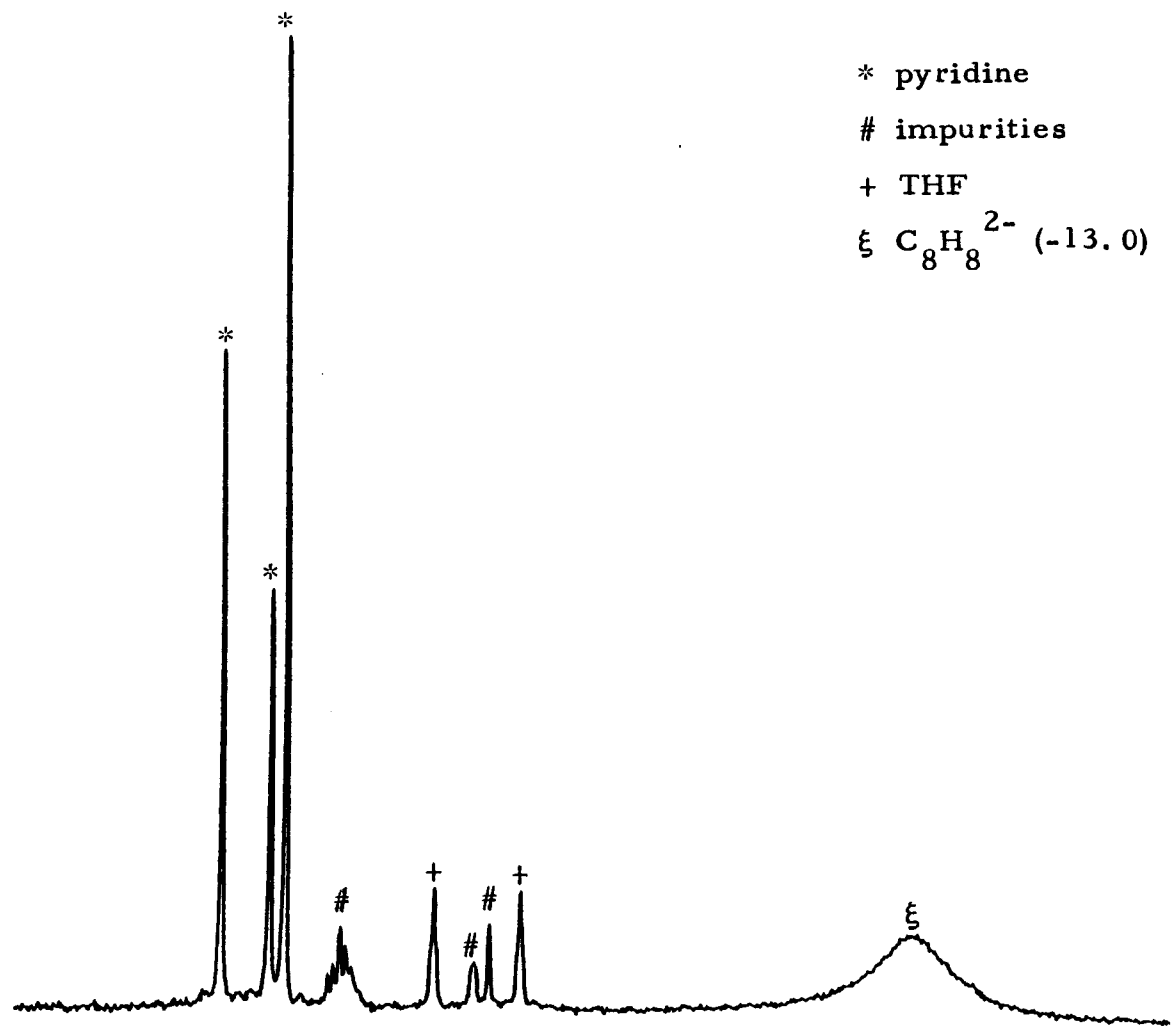
Figure 12. ^{1}H NMR spectrum of KNd(C_8H_8)$_2$ in pyridine-d$_5$ at 80 MHz

$$[Nd(C_8H_8)\cdot 2C_4H_8O][Nd(C_8H_8)_2] \rightleftharpoons [Nd(C_8H_8)\cdot 2C_4H_8O]^+$$

$$+ [Nd(C_8H_8)_2]^- \qquad (VIII)$$
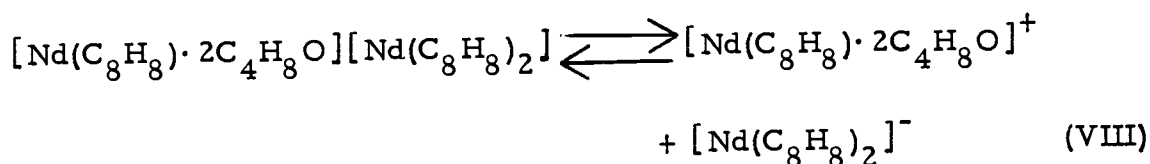
In order to answer this question $KNd(C_8H_8)_2$ was prepared (25) and its ^1H NMR spectrum (Figure 12) was compared with that of $Nd_2(C_8H_8)_3\cdot 2C_4H_8O$ (Figure 5). Using the Varian FT-80A spectrometer and pyridine-d_5 as a lock, the ring protons of the potassium complex exhibit a single resonance at -13.0 ppm compared to a single resonance at -14.5 ppm for the $C_8H_8^{2-}$ protons of $Nd_2(C_8H_8)_3\cdot 2C_4H_8O$. This observation, together with a single proton resonance appears to rule out the possibility of complete dissociation according to equation (VIII) in the limit of no exchange of $C_8H_8^{2-}$ units. Rapid exchange of the $C_8H_8^{2-}$ rings via a mechanism as shown by equation (VIII) would lead to a single resonance near that of $KNd(C_8H_8)_2$ as observed.

Attempts were made to study the fluxional nature of the title compounds by using $Nd_2(RC_8H_7)_3$ (R = H, CH$_3$). Unfortunately, low solubilities of the complexes precluded ^1H NMR studies at temperatures below -20°C. As expected the resonances of the $C_8H_8^{2-}$ protons are observed to shift with a decrease in temperature (i.e. R = H -20°C, δ -18.7 ppm; 0°C, δ -17.3 ppm; 28°C, δ -15.4 ppm). The $C_8H_8^{2-}$ peak was not observed to sharpen with a decrease in temperature nor did any other resonances appear. In addition,

resonances of $Nd_2(CH_3C_8H_7)_3$ show the same behavior with no new resonances appearing as the temperature was lowered.

The unsubstituted $Sm_2(C_8H_8)_3$ complex has a single resonance at 7.8 ppm (Figure 9) which is assigned to the $C_8H_8^{2-}$ protons. Again, this is near that of $KSm(C_8H_8)_2$ which is at 7.4 ppm [25]. Rapid exchange of the $C_8H_8^{2-}$ rings appears to be occurring in this system as well. The Tb^{3+} complex (Figure 8) displayed an extremely broad downfield resonance for the ring protons at 125 ppm. Hodgson et al. [25] observed proton resonances for $KTb(C_8H_8)_2$ at 113.4 Apparently Tb^{3+} has a very long electron relaxation time which broadens the resonance more than the other rare earth ions. The spectrum of the $Ce_2(C_8H_8)_3$ complex (Figure 11) shows three resonances at -3.5, -4.6, and -4.9 ppm with respect to COT^{2-}. The resonances at -4.6 and -4.9 ppm are due to impurities because these remained when the sample was oxidized. The observation of a resonance at 0.0 ppm shows evidence of a small amount of free COT in the sample. The resonance at -3.5 ppm is assigned to the $C_8H_8^{2-}$ rings of the Ce^{3+} complex and, again, rapid exchange of the rings is occurring.

Perusal of the substituted $Nd_2(CH_3C_8H_7)_2$ spectrum (Figure 6) reveals a resonance at 4.3 ppm in addition to the ring proton resonance at -15.4. This resonance is assigned to the CH_3 protons of

$CH_3C_8H_7^{2-}$. The $Nd_2(n-C_4H_9C_8H_7)_3$ complex (Figure 7) has a resonance at 0.5 ppm (ring protons at -14.8 ppm) in its ^{1}H NMR spectrum which is assigned to the CH_2 group directly adjacent to the $C_8H_7^{2-}$ ring. The remaining resonances of the butyl group located at -4.3, -4.8 and -5.2 ppm do not show significant shifts from the uncomplexed species. Similar results were observed for $(n-C_4H_9C_8H_7)_2U$ (13). Both of these $Nd_2(RC_8H_7)_3$ systems provide evidence of ligand exchange from their ^{1}H NMR spectra. If exchange were not occurring more than one resonance would be expected to be observed in the ^{1}H NMR spectrum for the non-equivalent CH_3 and CH_2 protons.

The spectrum of $Sm_2(CH_3C_8H_7)_3$ (Figure 10) appears to be complex. Yields were very low for this system and the product was difficult to purify. However, after oxidation of a sample in pyridine-d_5, the ^{1}H NMR showed the presence of all resonances except the resonance at -0.9 ppm and the resonance due to the ring protons centered at 7.8 ppm. The resonance at -0.9 is assigned to the CH_3 protons. Again, this datum supports the idea of exchange of the $C_8H_8^{2-}$ rings because only one CH_3 resonance is observed. Addition of a CH_3 group to the COT^{2-} ring causes the ring proton resonances in the $Sm_2(CH_3C_8H_7)_3$ system to give rise to a partial first order spectrum. Definite structure can be observed for the nonequivalent ring protons. Sm^{3+} has a highly populated first excited state, shortening T_{1e} and

giving rise to spectra which are well resolved. Other Sm^{3+} systems

also give rise to first order spectra (43).

These methyl substituted systems can be used to determine if

contact contributions are present in the complexes under study. A

measure of the contact contribution can be estimated from a ratio of

experimentally observed CH_3/H shifts to that same ratio calculated

for a purely dipolar contribution using the equation (VI). The calcu-

lated factor from the dipolar equation (Figure 13) for the methyl

protons of the $Nd_2(CH_3C_8H_7)_3$ complex is $-0.00457 Å^{-3}$ and that for H

is $-0.00132 Å^{-3}$. The CH_3/H ratio from this calculation is 3.46. The

observed CH_3/H ratio obtained from experimentally determined reso-

nances is 0.545. This was calculated by using a shift of -15.4 for the

ring protons referenced to COT^{2-} and a shift of 8.4 referenced to a

CH_3 resonance of $CH_3C_8H_7^{2-}$ at -4.1 ppm $[(8.4/-15.4) = -0.545]$.

These ratios are significantly different indicating that the observed

^{1}H NMR shifts are not exclusively dipolar in origin but that a signifi-

cant contact contribution exists in this molecule. The corresponding

calculation for the $Sm_2(CH_3C_8H_7)_3$ complex gives a calculated CH_3/H

ratio of 2.16 $(-0.00520/-0.00240)$ and an experimentally observed

ratio of 0.41 $(3.2/7.8)$. Again this large difference between the

calculated and experimentally observed ratios can be assigned to

contact contributions. The data for the structure of

Nd-H 3.51 Å
ND-C 2.69 Å
C-H   1.09 Å
θ 55.9°

Nd-H 4.20 Å
Nd-C_1 2.69 Å
C-C   1.54 Å
C-H   0.35 A
θ 62.0°

$$\frac{3\cos^2(55.9) - 1}{(3.51\ \text{Å})^3} = -0.00132\ \text{Å}^{-3}$$

$$\frac{3\cos^2(62.0) - 1}{(4.20\ \text{Å})^3} = -0.00457\ \text{Å}^{-3}$$

$Nd_2(C_8H_8)_3$

$Nd_2(CH_3C_8H_7)_3$

Sm-H 3.47 Å
Sm-C 2.63 Å
C-H   1.09 Å
θ 56.8°

Sm-H 4.17 Å
Sm-C_1 2.63 Å
C-C   1.54 Å
C-H   0.35 Å
θ 62.9°

$$\frac{3\cos^2(56.8) - 1}{(3.47\ \text{Å})^3} = -0.00240\ \text{Å}^{-3}$$

$$\frac{3\cos^2(62.9) - 1}{(4.17\ \text{Å})^3} = -0.00520\ \text{Å}^{-3}$$

$Sm_2(C_8H_8)_3$

$Sm_2(CH_3C_8H_7)_3$
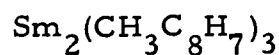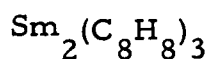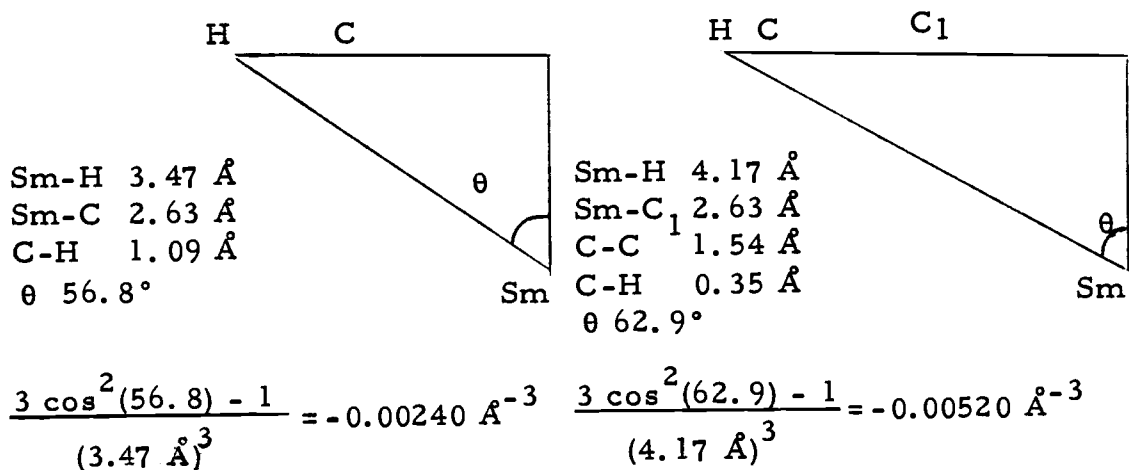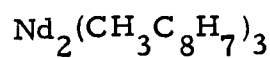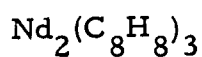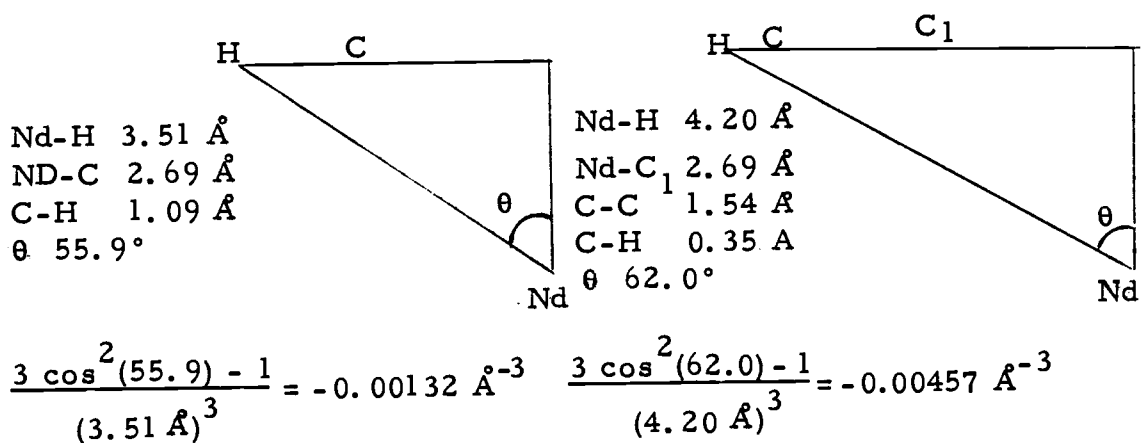
Figure 13. Dipolar factor for $Ln_2(RC_8H_7)_3$

$Nd(C_8H_8) \cdot 2C_4H_8O$ (27) and extrapolated data based on ionic radii for

$Sm_2(C_8H_8)_3$ were used to calculate the geometric factors for these

two complexes. In addition, a freely rotating methyl group was

assumed for the calculation of the geometric factors for the

$Nd_2(CH_3C_8H_7)_3$ and $Sm_2(CH_3C_8H_7)_3$ systems.

Conductance Study

The specific conductance of a saturated solution of

$Nd_2(C_8H_8)_3 \cdot 2C_4H_8O$ in pyridine is 2.78×10^{-6} ohm^{-1} cm^{-1}. In

contrast, the specific conductance of pyridine is 0.1×10^{-8} ohm^{-1}

cm^{-1}. This shows the complex to be a conductor. The magnitude

of the equivalent conductance of the complex can be obtained by

assuming a solubility of 0.5 mmol/L (27). The ability to obtain

^1H NMR of $Nd_2(C_8H_8)_3 \cdot 2C_4H_8O$ insures that this complex is at least

as soluble in pyridine as it is in THF. The upper limit of the equiva-

lent conductance of a saturated solution of $Nd_2(C_8H_8)_3 \cdot 2C_4H_8O$ is

5 ohm^{-1} cm^2 eq^{-1} in pyridine indicating the complex to be a poor

conductor (44, 45).

CONCLUSIONS

Metal atom synthesis can be used to prepare $Ln_2(RC_8H_7)_3$

(R = H, CH_3, n-C_4H_9) for Ce, Nd, Sm, Tb and Er lanthanide metals.

However, Yb could not be oxidized to Yb^{3+} using this technique and

only $Yb(C_8H_8)$ was produced. All of these rare-earth COT complexes

are unstable with respect to oxygen and proton sources. Addition of

alkyl groups to the cyclooctatetraene ring appears to increase the

stability of the complexes towards oxygen. However, the alkyl substi-

tuted complexes are still sensitive towards oxygen and proton sources

indicating they are essentially ionic. The magnetic susceptibility

data of $Ln_2(C_8H_8)_3$ (Ln = Nd, Ce, Er, Sm) are very close to the free ion

term providing additional information that these complexes are mostly

ionic. The conductance data confirm that $Nd_2(C_8H_8)_3 \cdot 2C_4H_8O$ is at

least partially ionized in pyridine. The ionized species are assumed

to be the anion $[Nd(C_8H_8)_2]^-$ and the cation $[Nd(C_8H_8) \cdot 2C_4H_8O]^+$.

This formulation is supported by the ^{1}H NMR data which show a single

resonance for $Nd_2(C_8H_8)_3 \cdot 2C_4H_8O$ in the region of that found for

$Nd(C_8H_8)_2^-$. This single resonance is also indicative of exchange of

$C_8H_8^{2-}$ ligands between the anion and the cation. Additional evidence

of exchange of $C_8H_8^{2-}$ ligands arises from the observation that a

single resonance is observed for the CH_3 group in $Ln_2(CH_3C_8H_7)_3$ for

Ln being Nd and Sm and a single resonance for the CH_2 group adjacent to

the ring in $Nd_2(n-C_4H_9C_8H_7)_3$. The presence of paramagnetic cen-
ters in these complexes broadens the ^{1}H NMR resonances and the

ring proton resonances are found to be upfield for the Nd and Ce

complexes and downfield for the Sm and Tb complexes. No reso-

nance was observed for the Er complex. The ^{1}H NMR spectra also

show that contact contributions are important and that isotropic

shifts are not due exclusively to dipolar contributions.

II. ATTEMPTED SYNTHESIS OF HOMOCYCLOOCTATETRAENE
DIANION COMPLEXES WITH YTTERBIUM
AND URANIUM

INTRODUCTION

The monohomocyclooctatetraene dianion, 2, is structurally very

similar to the cyclooctatetraene dianion, 10. Dianion 2 has an eight-

carbon ten π electron aromatic base very much like dianion 10. In

10   2
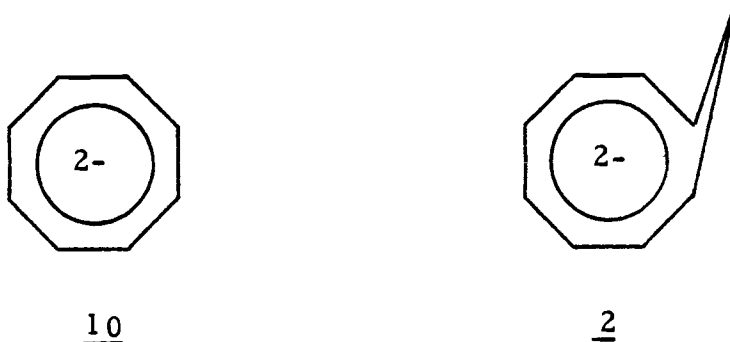
view of the stability of uranocene and the rare-earth COT complexes

discussed in Part I and the similarities between 10 and 2, an attempt

was made to prepare uranium and ytterbium complexes of dianion 2

using both metal atom and solution techniques. Both of these methods

of syntheses provide a means by which stable complexes of

dianion 2 may be prepared. The distinguishing structural difference

between these two dianions is the presence of an additional out of plane

CH_2 group in dianion 2 resulting in a homoaromatic structure.

Homoaromaticity may be thought of as an interruption of an

aromatic π-network by one or more sp^3 centers. Homoaromatic

species, as their aromatic counterparts, have cyclic electron

delocalization and an induced ring current. For example, the homo-

tropylium ion, 13, can be prepared by the protonation of cycloocta-

tetraene, 14, in concentrated H_2SO_4 (46). In order for 13 to attain
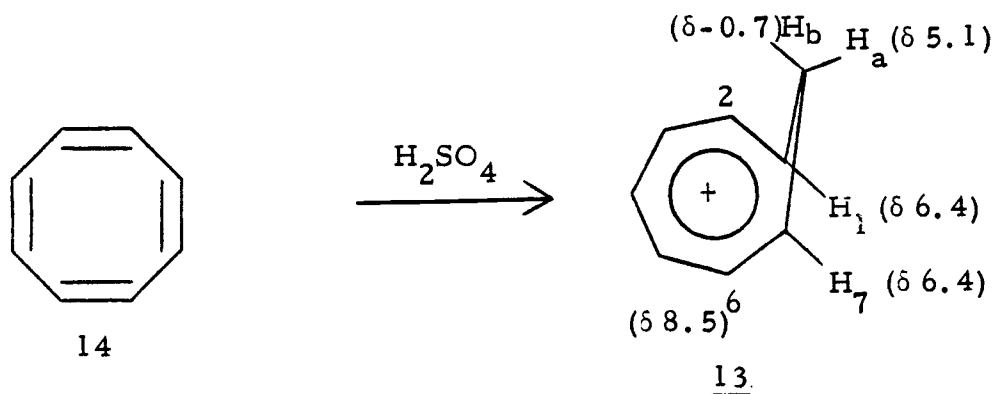
and maintain homoaromaticity, C_8 must be almost perpendicular to

the aromatic plane. This allows the aromatic sextet to delocalize

over the seven planar carbons which puts H_a and H_b in a position to

feel the effects of induced ring currents from the aromatic ring. The

^{1}H NMR provides evidence for the aromatic structure as can be

observed by the shifts presented above. The large upfield shift for

H_b is due to the fact that H_b lies above the ring and is shielded by the

induced ring current of the delocalized aromatic electrons resulting

in an upfield shift. The shifts of protons H_a, H_1, and H_7 are down-

field because of deshielding by ring currents. The homotropyllium

cation, 13, is a stable species for which an Fe complex has been

isolated and its ^{1}H NMR studied (47). This homoaromatic cation

can also be isolated as $C_8H_9^+SbCl_6$ (47).

The homoaromatic species in this study is the monohomocyclo-octatetraene dianion 2. This dianion can be prepared by the two electron reduction of 1 with potassium metal which generates the homoaromatic species 2 as first reported in 1966 by Ogliaruso and coworkers (48) according to scheme 1. The structure of dianion 2

Scheme 1
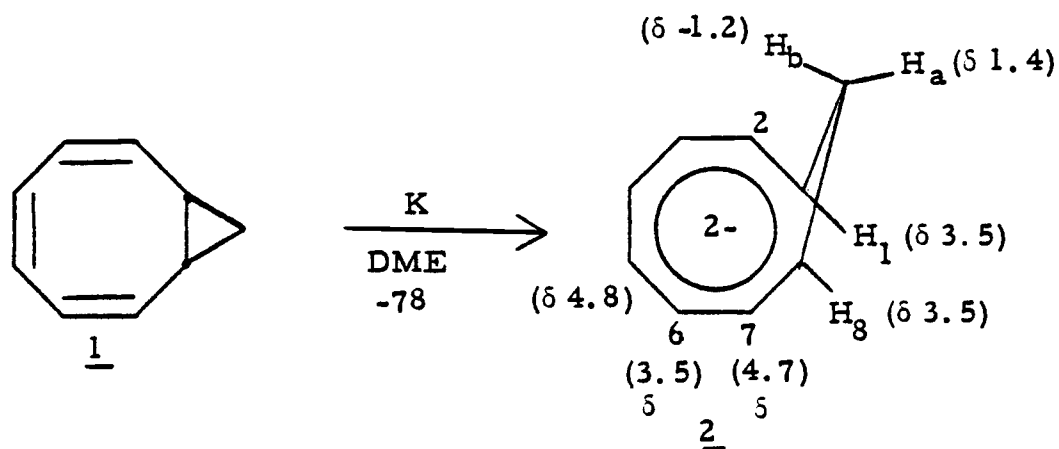
was elucidated by ^{1}H NMR spectroscopy by Barfield et al. (49) for the dilithium salt of 1. Ring currents, present in dianion 2, shift H_b upfield due to increased shielding and H_a downfield because of de-shielding. Decoupling experiments on the Li$^+$ salt of 1 provided evidence that the C_8 ring is not planar but that there is some twist about the ring bonds.

Okamura and coworkers (50) and Ley and Paquette (51) attempt-ed to prepare 2 in liquid ammonia (or HMPA-THF) and ND_3 respec-tively. Unfortunately, the dianion produced was quickly protonated by the solvent at -60°C forming a monoanion. The dimethyl anion

of 2, 15, was successfully prepared in ND_3 by Ley and Paquette (51)

from 9, 9-dimethyl-cis-bicyclo[6.1.0]nona-2,4,6-triene, 4, accord-

ing to scheme 2. However at -65 °C, dianion 15 was partially
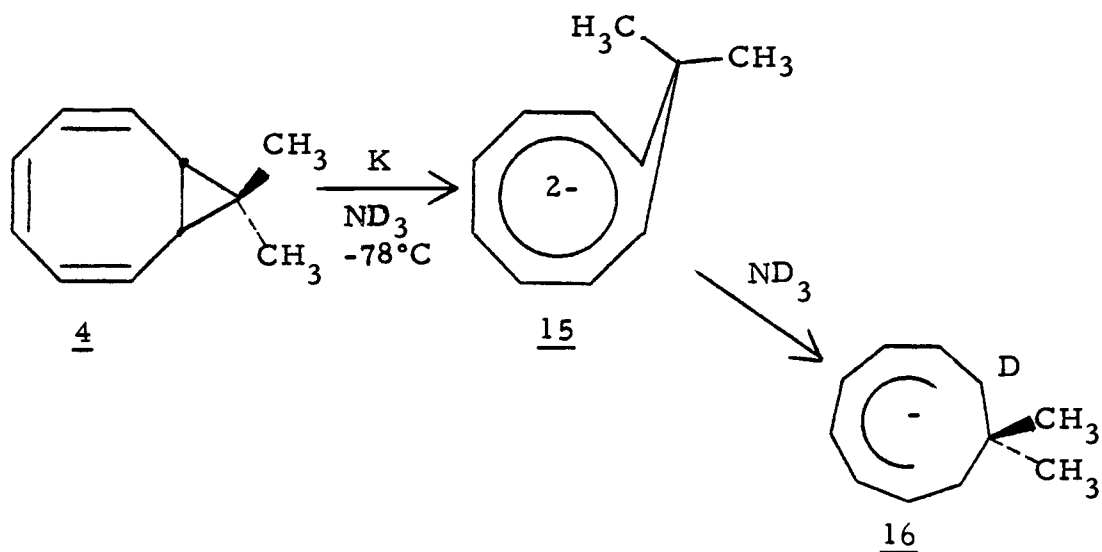
Scheme 2

converted to monoanion 16 in 45 minutes. Complete conversion was

observed in four minutes at room temperature. This behavior of 15

in $NH_3(ND_3)$ is in contrast to the behavior of the cyclooctatetraenide

dianion 10 which is stable at -33 °C in liquid ammonia. This indicates

that dianion 15 is more basic than dianion 10. Compound 4 is pre-

pared in NH_3 by the addition of 2, 2-dichloropropane to $K_2C_8H_8$ (52).

Reactions of dianion 2 prepared in THF or DME with proton

sources gave as the major product (85%), bicyclo[6.1.0]nona-2,4-

diene, 6, presented in scheme 3 (53).
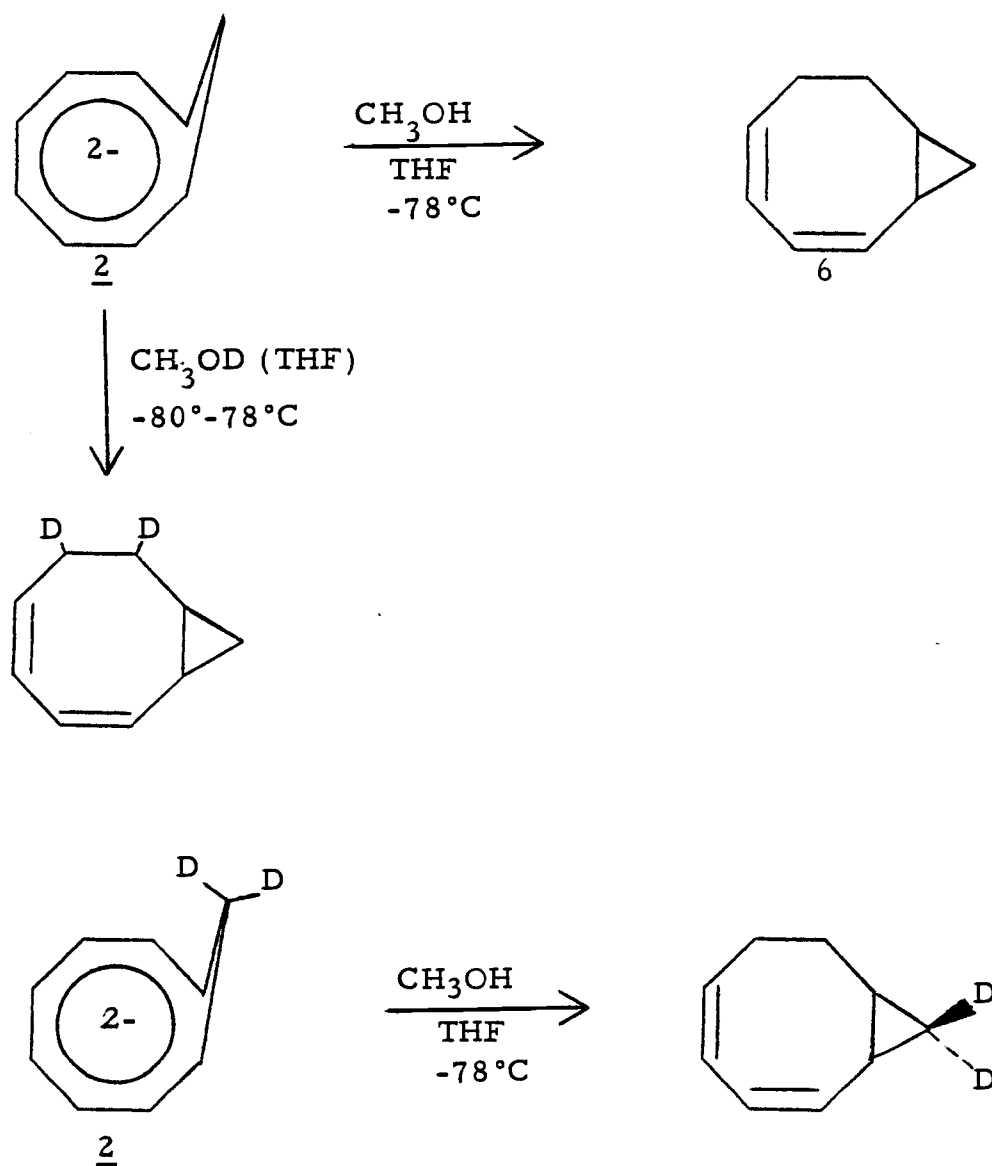
Scheme 3

In contrast, reaction of dianion 15 prepared in $NH_3(ND_3)$ yields 8, 8-

and 9, 9-dimethylcyclonona-1, 3, 6-triene, 11 and 12 (51) as depicted

in scheme 4 when 15 is reacted with proton sources. The difference

Scheme 4
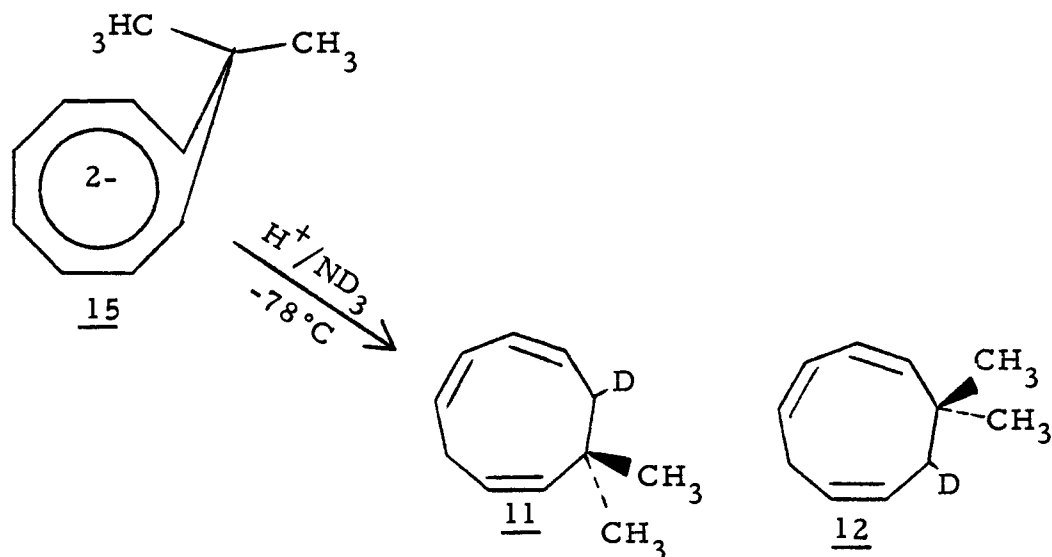
between these hydrolysis results observed by Ogliaruso et al. (53)

and Ley and Pacquette (51) is attributed to the fact that dianion 15 is

protonated (deuterated) by the solvent to monoanion 16. Subsequent

protonation results in 11 and 12. Another documented reaction of

dianion 2 was reported by Ogliaruso et al. (54) which yielded two

products upon reaction of 2 with CCl_4; 3, 3-dichloro-cis- and trans-

tricyclo$[7.1.0.0^{2,4}]$deca-5, 7-dienes, 7 and 8 (scheme 5). This

reaction is similar to that observed for the reaction of 10 with

CCl_2X_2 (X = H, Cl, CH_3) molecules in which the CX_2 species adds

across the double bond. This reaction is used in the preparation of

1 (55) and 4 (52). Oxidation (O_2) of a concentrated solution of

dianion 2 prepared in liquid ammonia followed by the addition of
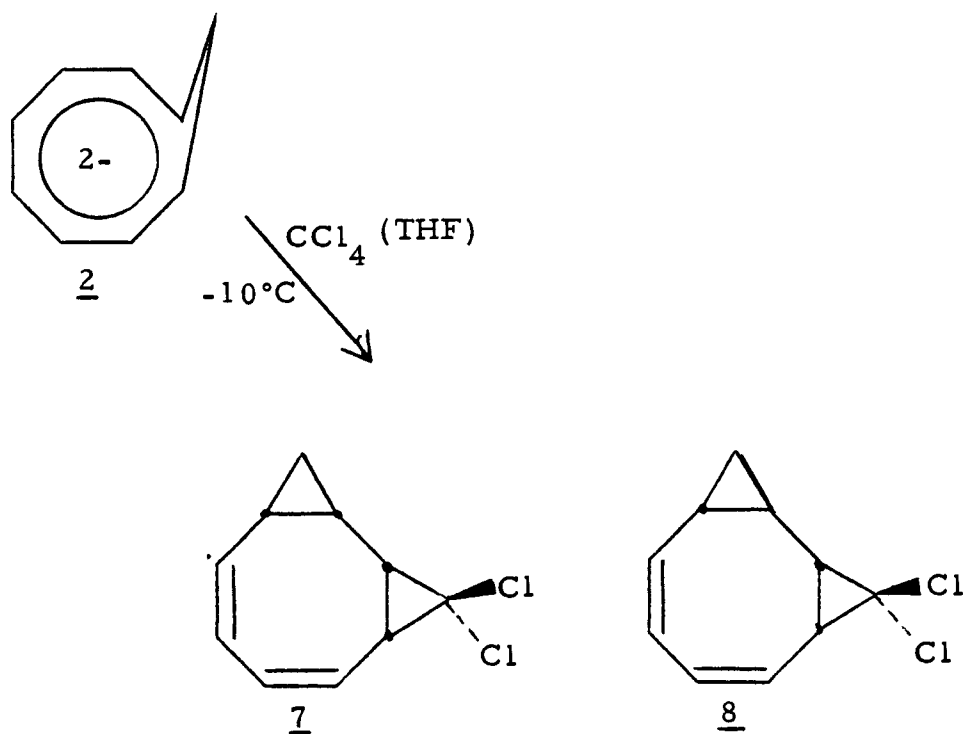
Scheme 5

methanol yields triene <u>17</u> and ditriene <u>9</u> (scheme 6). Slow oxidation

(1 hour) of dilithium <u>2</u> prepared in liquid ammonia, yields starting

material <u>1</u> (85%) (56). However, slow oxidation of disodium <u>2</u>

gives <u>9</u> (67%). Oxidation of the dianion prepared in THF or DME

has not been reported in the literature.
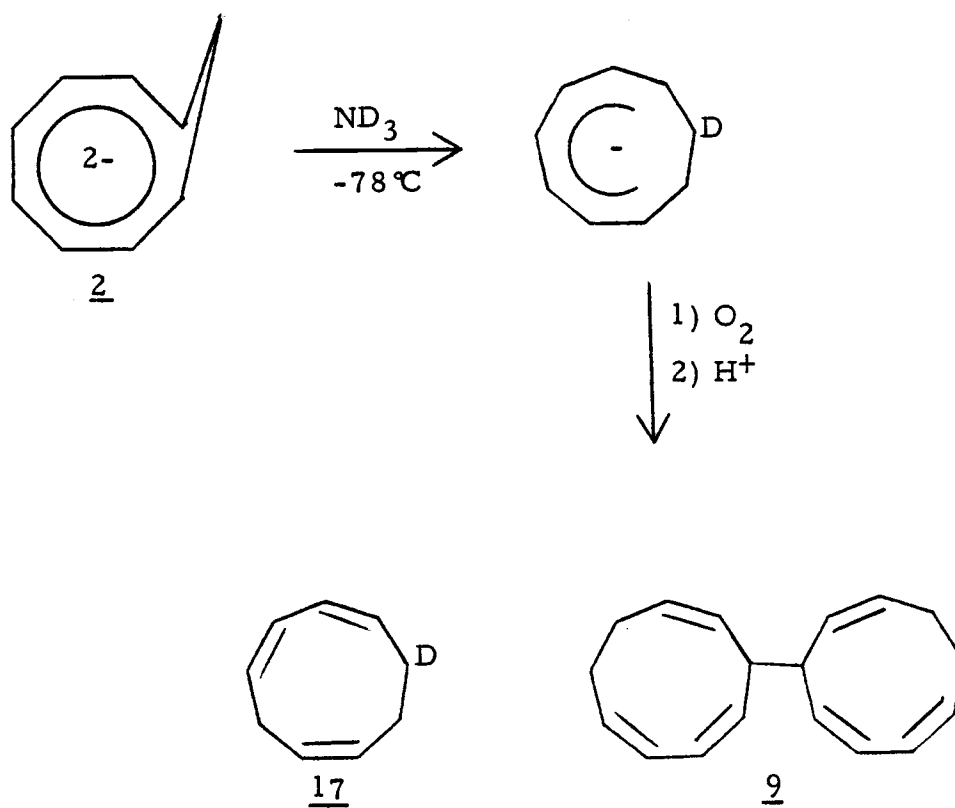
Scheme 6

One additional reaction of importance is that of the neutral compounds

1 and 4. Compound 1 is known to rearrange to cis-8, 9-dihydroindene

with 90% conversion observed in 27 minutes at 120°C with the
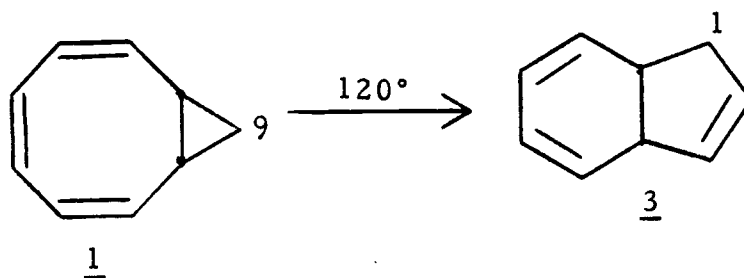
Scheme 7

substituents on C_9 going to the C_1 position (scheme 7). The proposed intermediate is cis, cis, cis, cis-1, 3, 5, 7-cyclononatetraene (57). The major product of the rearrangement of the 9, 9-dimethyl-derivative of 1 is 1, 1-dimethyl-trans-8, 9-dihydroindene, 5 (58) (scheme 8). The conversion of 4 is only 12% complete after 15 minutes at 151 °C. Addition of the two methyl groups at the C_9 position of 1 stabilizes the bicyclic material 4. Also, as discussed earlier, dianion 15 is more stable than dianion 2 in liquid ammonia.
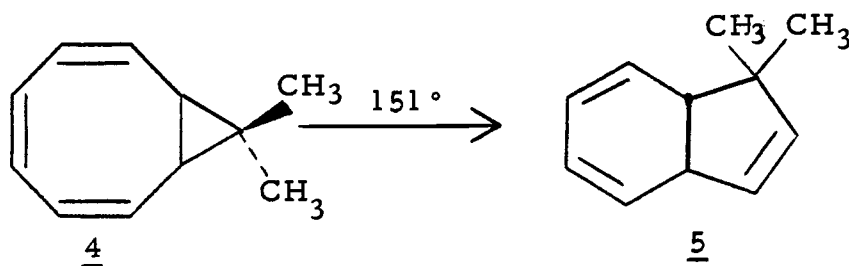
Scheme 8

To date there have been no transition metal, lanthanide or actinide complexes of 2 or 15 reported. As a further extension of 10π-carbocyclic lanthanide and actinide chemistry, metal atom and solution methods were used in an attempt to stabilize this elusive dianion. Uranocene (12) and $Yb(C_8H_8)$ complexes can be prepared from the reaction of metal atoms and C_8H_8. Therefore, 1 and 4 were codeposited with uranium and ytterbium atoms. Uranocene can also be prepared by the solution reaction of $K_2C_8H_8$ with UCl_4 (11)

and from the reaction of UCl_4 and n-butyllithium with C_8H_8 (59).
Thus, literature preparations for uranocene from solution were per-
formed with the substitution of 15 for 10 in the synthesis. The com-
plex $Yb(C_8H_8)$ can be prepared in liquid ammonia (20) making this
method of preparation an additional means by which a stable product
of dianion 2 or 15 might be isolated and characterized.

EXPERIMENTAL

Materials

The Yb metal, 99.9%, was obtained from Michigan Chemical Corporation, St. Louis, MI. The uranium metal came from Batelle Northwest Laboratory, Richland, WA. Lithium, potassium and sodium metals were purchased from Mallinckrodt Chemical Works, St. Louis, MO. Uranium tetrachloride, 99%, was manufactured by Great Western Inorganics, Golden, CO. Carbon tetrachloride (Mallinckrodt) was washed with concentrated H_2SO_4, 10% Na_2CO_3 and water. It was then dried over $CaCl_2$ and distilled from P_2O_5. 2,2-dichloropropane (Fairfield Chemical Company, Blythewood, S.D.) was distilled onto molecular sieve under argon and used without further purification. Dimethoxyethane, (Mallinckrodt) was

purified with sodium benzophenone and vacuum distilled immediately prior to use. Methanol (Matheson, Coleman and Bell, Norwood, OH) was dried over molecular sieve. Benzene was dried over $LiAlH_4$ and distilled under vacuum. Liquid ammonia (Air Reduction Company) was dried with sodium metal and distilled immediately prior to use. The sources and treatment of cyclooctatetraene, tetrahydrofuran and n-butyllithium are described in Part I of this thesis.

Spectral Analyses

The ^{1}H NMR were obtained with a Varian HA-100 spectrometer

in C_6H_6. The n.m.r. tubes were capped with rubber septums to pre-

vent atmospheric decomposition.

The vpc-ms data were obtained from a Varian-MAT GmbH

CH7 Massenspektrometer at an ionization potential of 70 eV inter-

faced with a Varian 1200 gas chromatograph.

Preparative vpc samples were isolated with a Varian 920 gas

chromatograph.

Synthetic Procedures

The method employed for the metal atom reactions is the same

as that described in Part I of this thesis. Metal atoms of U and Yb

were allowed to react with cis-bicyclo[6.1.0]nona-2,4,6-triene.

Uranium atoms were allowed to react with 9,9-dimethyl-cis-bicyclo-

[6.1.0]nona-2,4,6-triene and cis-8,9-dihydroindene. No reaction

occurred between the U atoms and cis-8,9-dihydroindene. The mater-

ial produced during the metal atom reaction was washed several times

with hexane in an attempt to remove all excess starting material which

had not been pumped off following the reaction.

All solution syntheses were performed in an atmosphere of

prepurified argon using Schlenk line and syringe techniques.

Potassium Cyclooctatetranide (K$_2$C$_8$H$_8$)

This synthesis was performed according to the directions of Streitwieser and coworkers (36).

Potassium metal, 12 g (307 mmol) was added to 250 mL of THF which had been freshly distilled into a 500 mL triple-neck round bottom flask. A potassium sand was prepared by vigorously stirring the metal in refluxing THF followed by cooling the unstirred mixture to -30°C. Cyclooctatetraene (16 mL, 142 mmol) was added. After four hours, the resulting brown solution was filtered and transferred to a Schlenk addition funnel.

cis-Bicyclo[6.1.0]nona-2,4,6-triene, 1

This compound was prepared by the procedure of Katz and Garratt (55).

The K$_2$C$_8$H$_8$ in THF was added dropwise to 357 mL of CH$_2$Cl$_2$ over a one hour period at room temperature. The resulting yellowish-brown solution was stirred an additional eight hours after which time 20 mL of ethanol were added. This was followed by enough water to dissolve the precipitated KCl. The layers were separated and the aqueous layer was washed with ether (2 x 75 mL). The combined organic phases were washed with water (3 x 200) and saturated NaCl

(3 x 100 mL). Final drying was done over Na_2SO_4. The solvents were removed under reduced pressure. Final purification of the cis-bicyclo[6.1.0]nona-2,4,6-triene was done by vpc (8 ft x 0.250 in. in 6% Carbowax 4000 on AW-DMCS Chromosorb P, 80°C). The compound (5.9 g, 35%) was identified by ^{1}H NMR $\delta_{TMS}^{CCl_4}$ 5.85 (m, 6H), 1.4 (m, 3H), 0.2 (m, 1H), mass spectrum (70 eV) m/e 118 (M$^+$) parent ion peak (55).

9,9-Dimethyl-cis-bicyclo[6.1.0]nona-2,4,6-triene 4

The procedure of Staley and Henry (52) was used to prepare this material.

Several grams of Na metal was added to liquid ammonia (400 mL) which had been transferred to a 500 mL triple-neck round bottom flask. An immediate deep blue color resulted. The ammonia was then distilled into a 1000 mL insulated three-neck round bottom flask equipped with a Dewar condenser, a mechanical stirrer and an addition funnel containing 150 mmol of 2,2-dichloropropane in 125 mL of anhydrous diethyl ether. Li metal (2.07 g, 300 mmol) was added to the dry ammonia yielding a blue solution. The solution was stirred and 150 mmol of COT was added. Within minutes, a color change to yellow-brown was observed. The stopcock of the addition funnel was opened and the 2,2-dichloropropane/ether mixture was added dropwise to the

$Li_2C_8H_8$ over a period of two hours. The dark brown solution was

stirred for an additional three hours at which time NH_4Cl (220 mmol)

was added resulting in a light yellow solution. The flask was opened

to the atmosphere and the ammonia was allowed to evaporate over-

night. The cream colored solid remaining was dissolved in water and

diethyl ether. The aqueous layer was washed with diethyl ether

(2 x 50 mL). The combined organic phases were washed with satu-

rated NaCl and dried over Na_2SO_4. The ether was removed under

reduced pressure. Final purification was done by distillation (b. p.

64 °C (8 torr) yielding 16. 4 g (75%). The compound was identified by

^{1}H NMR $\delta \, ^{CCl_4}_{TMS}$ 5.8 (m, 6H), 1.2 (s, 5H), 0.96 (s, 3H) and mass

spectrum (70 eV) m/e 146 (M^+), 131 ($M-CH_3$), 116 ($M-C_2H_6$),

91 ($M-C_4H_7$)(52).

cis-8, 9-Dihydroindene, $\underline{3}$

This compound was prepared according to the procedure of

Staley and Henry (52).

cis-Bicyclo[6. 1. 0]nona-2, 4, 6-triene was heated at 90 °C for

three hours. Vpc chromatograms showed three components present

with the desired material as the major component. The product was

purified using vpc (8 ft x 0. 25 in. on 10% Carbowax 4000 on AW-DMCS

Chromosorb P, 80 °C). Identification was made by a match of the

literature ^{1}H NMR, $\delta\,^{CCl_4}_{TMS}$ 2.0-3.8 (m, 4H), 5.2-5.9 (m, 6H) (51)

and mass spectrum (70 eV) m/e 118 (M^+) (52).

Reaction of UCl_4 with Potassium Dianion 15

The potassium dianion 15 was prepared in a method similar to

that of Streitwieser et al. (36) for $K_2C_8H_8$.

Potassium metal (0.12 g, 3.0 mmol) in 25 mL of THF was

dispersed into a fine sand in a 100 mL Schlenk flask equipped with

a reflux condenser. The temperature was reduced to -78°C. The

bicyclic material, 4, (1.5 mmol) was added resulting in a deep red

solution. A mixture of THF and UCl_4 (0.28 g, 0.75 mmol) was added

rapidly to the potassium salt of 4 at which time a color change to

brown was observed. The material was precipitated at -78°C with

diethyl ether and redissolved in THF giving a muddy green-brown

solution which eventually turned clear green. There was no change

in color upon exposure to oxygen or a proton source. The solution

was extracted with hexane and only starting material 4 was recovered

by vpc (8 ft x 0.25 in. on 6% Carbowax 4000 on AW-DMCS Chromosorb

P, 92°C). Identification was made by ^{1}H NMR and mass spectrum.

No further work was done on the system.

Reaction of the Products of Yb Atoms and 1 with H$^+$
_____

A saturated THF solution containing the above product was

placed in a test tube which was then sealed with a rubber septum.

Approximately 0.5 mL of CH$_3$OH was added at -10°C. Immediate

discoloration of the solution occurred along with the formation of a

red precipitate which turned to white upon exposure to the atmosphere.

The solution was extracted with hexane and the major product isolated

by vpc (8 ft x 0.25 in. on 6% Carbowax 4000 on AW-DMCS Chromosorb

P, 93°C) and identified as 1,3,6-cyclononatriene by ^{1}H NMR

$\delta_{TMS}^{CCl_4}$ 5.3-6.0 (m, 6H, olefinic) 2.72 [t, J = 7 Hz, 2H, bisallylic],

1.8-2.25 (m, 4H, allylic) and mass spectrum (70 eV) m/e 120 (M$^+$).

Reaction of the Products of Yb Atoms and 1 with CCl$_4$
_____

The sample was prepared in the same manner as for hydrolysis.

Addition of CCl$_4$ at -78°C resulted in a color change from green to

yellow. A white precipitate was formed upon exposure of this solu-

tion to the atmosphere. The products were identified as starting

material 1 and rearranged 3 by ^{1}H NMR and mass spectrum.

Reaction of the Product of U Atoms and 4 with H$^+$(D$^+$)
_____

A saturated THF solution of the material synthesized from the

reaction between uranium metal atoms and 4 was prepared in the inert

atmosphere box. This resulting amber solution was placed in a test

tube and protected from the atmosphere by sealing the test tube with a

rubber septum. The temperature of the solution was reduced to -10 °C

after which 0.5 mL of CH_3OH (or CH_3OD) was added. A reaction

occurred immediately. The solution was extracted with hexane. The

products were isolated by vpc (8 ft x 0.25 in. on 6% Carbowax 4000 on

AW-DMCS Chromosorb P, 85 °C) and identified by ^{1}H NMR as 8,8-di-

methylcyclonona-1,3,6-triene $\delta_{TMS}^{CCl_4}$ 5.9-5.15 (m, 6H, olefinic), 2.9

(dd, 2H, bisallylic), 2.27 (d, 2H, allylic), 1.18 (s, 6H, CH_3) and the

starting material $\underline{4}$. Minor products (< 10%) were identified as 9,9-

dimethylcyclonona-1,3,6-triene $\delta_{TMS}^{CCl_4}$ 6.0-5.2 (m, 6H, olefinic),

2.7 (t, 2H, bisallylic) 2.28 (d, 2H, allylic), 1.0 (s, 6H, CH_3) and

1,1-dimethyl-trans-8,9-dihydroindene $\underline{5}$ $\delta_{TMS}^{CCl_4}$ 6.0-5.26 (m, 6H,

olefinic), 3.60 (m, 1H, bisallylic), 2.60 (dd, 1H, allylic) 1.1 (s, 3H,

CH_3), 0.94 (s, 3H, CH_3). Mass spectrum of dimethylcyclonona-1,3,6-

trienes-d_2 (70 eV) m/e 150 (M^+), 135 (M-CH_3), 107 (M-C_3H_7).

Quenching with CH_3OD gave by mass spectrometry 45.6% d_2, 28.0%

d_1, 26.4% d_0. Mass spectrum of dimethylcyclonona-1,3,6-trienes

(70 eV) m/e 148 (M^+), 133 (M-CH_3), 105 (M-C_3H_7).

Reaction of the Product of U Atoms and $\underline{4}$ with CCl_4

The saturated THF solution was prepared in the same manner as

the immediately preceding solution for hydrolysis. CCl_4 was added to

the amber solution at -10 °C until discoloration was complete and a

whitish precipitate was observed. The solution was extracted with hexane, the products were separated by vpc (8 ft x 0.25 in. in 6% Carbowax 4000 on AW-DMCS Chromosorb P, 90°C). The major component (50%) was identified as 4 and the minor component (35%) was identified as 5 by ^{1}H NMR and mass spectrum.

Reaction of n-butyllithium, UCl_4 and 4
_____

This reaction is patterned after the procedure of Cernia and Mazzei (59) for the preparation of uranocene.

To a 100 mL Schlenk flask containing 2.7 g UCl_4 (7.1 mmol) in 60 mL of diethyl ether at -78°C was added 19.2 mL of n-butyllithium (2.2 M, 42 mmol). The material was stirred for two hours during which time the color turned to a dark green-brown. The bicyclic material, 4, was then added (2.6 cc, 14.2 mmol). There was no noticeable immediate color change. After warm-up to 10°C the color of the solution became red-brown. The mixture was cooled and filtered at -10°C. The reaction product was precipitated and washed with hexane at -10°C. Addition of diethyl ether to the oily material resulted in a brown solution. Diethyl ether was added until it remained colorless. The remaining material was dissolved in THF. Both the diethyl ether and THF soluble material were stored at -78°C.

Reaction of the Product of n-Butyllithium, UCl$_4$ and 4 with H$^+$(D$^+$)

An aliquot (5 mL) of the THF fraction was transferred to a capped test tube. To this solution, 0.5 mL of CH$_3$OH(CH$_3$OD) was added at -10°C causing an immediate color change from deep brown to clear amber. Workup with hexane gave the two isomers of dimethylcyclonona-1,3,6-triene (-d$_2$) 11 and 12 as isolated by vpc (8 ft x 0.25 in in 10% Carbowax 4000, AW-DMCS Chromosorb P, 92°C) 40% and 39% respectively. The trienes 11 and 12 were identified by mass spectrum and ^{1}H NMR.

Reaction of the Product of n-Butyllithium, UCl$_4$ and 4 with CCl$_4$ and O$_2$

To 5 mL of the THF fraction under a nitrogen atmosphere at 0°C was added 0.5 mL of CCl$_4$. Oxygen was bubbled through another 0.5 mL aliquot. In both cases, several hours were required for a color change from a red-brown to a clear gold-yellow to take place. Each solution was extracted with hexane and the products isolated by vpc (8 ft x 0.25 in. in 10% Carbowax 4000, AW-DMCS Chromosorb P, 88°C) and identified by ^{1}H NMR and vpc-ms as 4 (70%) and 5 (15%). Each of the above quenches gave the same yield.

Reaction of Yb Metal and 4 in Liquid Ammonia

Some ammonia (50 mL) was dried with sodium metal in a 100 mL triple-neck Schlenk flask and distilled to another similar flask equipped with a Dewar condenser. Yb metal (1.3 g, 7.5 mmol) was added to the dry NH_3 resulting in a bluish colored solution. To this blue solution, 4 (1.1 g, 7.8 mmol) was added. The first run of this experiment resulted in a green coloration of the previously blue solution within five minutes and retention of this green color for 60 minutes. Unfortunately, attempts to repeat this experiment were unsuccessful resulting in foaming and bubbling of the Yb/NH_3 solution upon addition of 4. At first the liquid turned red but within ten minutes a cream colored solid appeared which was air stable. Extraction with hexane provided starting material, 4, as identified by vpc and ^1H NMR and mass spectrum.

RESULTS

The materials formed during the reactions of Yb and U atoms

with 1 and U atoms with 4 were extremely unstable. Repeated

attempts were made to purify the materials by precipitating and

washing it with hexane or diethyl ether. This washed material

would not completely redissolve in THF, DME, or C_6H_6, solvents

in which, originally, it was completely soluble. A serious effort

was made to crystallize the material prepared from the reaction of

U atoms and 4 from various solvent mixtures (i.e. THF/hexane,

C_6H_6/hexane) but the material, again, would not go back into solu-

tion. Others have found this type of system difficult to characterize.

For example, Evans et al. (60, 61) have obtained products difficult to

characterize from the rare-earth metal atom reactions with 1, 3-buta-

dienes and hex-3-yne, respectively. They also studied the chemistry

of their complexes to reveal the nature of the species present. Be-

cause attempts to isolate a pure complex of U atoms and 4 were not

successful, the chemistry of the system was studied to determine the

species present by using known reactions of dianions 2, 10, and 15,

depicted below. For example, hydrolysis and deuterolysis of

dianions 2 and 15 according to schemes 3 and 4 could yield com-

pounds 6 or 11 and 12. Addition of two deuteriums would indicate

that the dianion had been formed and that proton abstraction from
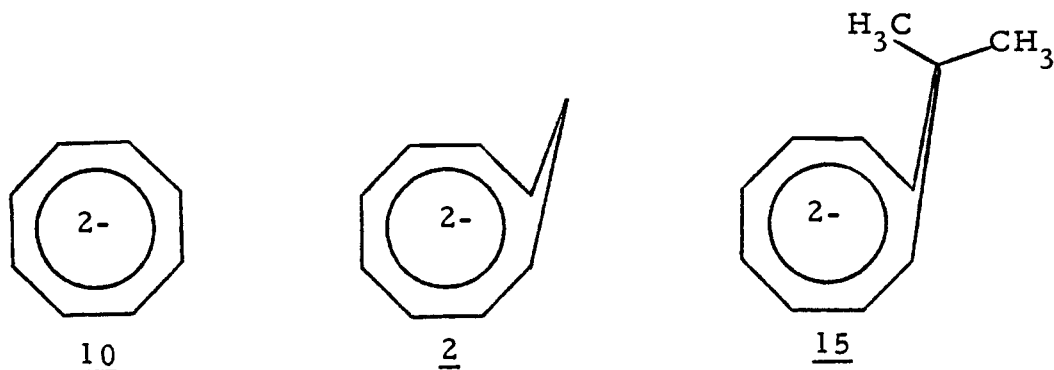
the solvent had not occurred. Oxidation of the U atom-4 material

could be expected to give starting material 4 and, possibly, the

rearranged dihydroindene 5. If dianions 2 or 15 are present, the

reaction of these dianions with CCl_4 are expected to give 7 and 8

based on scheme 5. Starting material 4 and the rearranged 5 could

also be expected from the "reaction" of the U atom-4-material with

CCl_4 based on the observation of Grant and Streitwieser (62) that

$(n-C_4H_9C_8H_7)_2U$ decomposes to free $n-C_4H_9C_8H_7$ and UCl_4 in the

presence of CCl_4. This brief review of the chemistry of dianions 2,

10 and 15 now allows for a closer examination of the results obtained

in this study.

The initial reactions of U and Yb metal atoms with 1 provided

evidence for the formation of dianion 2. Reaction of Yb atoms with 1

resulted in an air and moisture sensitive brown material which was

moderately soluble in DME. The brown air and moisture sensitive

material of U atoms and 1 was soluble in DME and THF. Hydrolysis

of the Yb complex of 1 yielded 1,3,6-cyclononatriene, 17, whereas

reaction with CCl_4 gave starting material 1 and 3.

Unfortunately, during the metal atom reaction with both Yb and U atoms, rearrangement of unreacted starting material 1 to cis-8, 9-dihydroindene was observed. Because of its increased stability over the starting material, 9, 9-dimethyl-cis-bicyclo[6.1.0]nona-2, 4, 6-triene, 4 was substituted for 1 and subsequent rearrangement of excess 4 during the metal atom reactions with Yb and U was not observed.

Reaction of U atoms with 4 gave a product which was soluble in THF, DME and C_6H_6. The complex was air and moisture sensitive. Reaction of the material formed from U metal atoms and 4 with $H^+(D^+)$ gave 8, 8- and 9, 9-dimethylcyclonona-1, 3, 6-triene (or -d_2) 11 and 12 as identified by literature ^{1}H NMR and vpc-mass spectral data. The parent ions had a mass of 148 upon protonation and 150 upon deuteration of dianion 15. Hydrolysis products 11 and 12 are expected from dianion 15. This chemical evidence is reinforced by addition of two deuteriums to dianion 15 which increases the mass of starting material 4 by four units. Mass spectrometry showed 45.6% d_2, 28.0% d_1 and 26.4% d_0. The M-1 and M-2 mass spectral peaks for protonation were insignificant (0.5%) or nonexistent with reference to the parent ion of 148. This indicates that protons were abstracted from the solvents which, again, provides additional information that not only was dianion 15 formed but that U is unable to stabilize this dianion

with respect to proton abstraction reactions. Similar deuterolysis

results were obtained for the material prepared from the reaction of

n-butyllithium and UCl_4 with 4. In addition, starting material 4 and

dihydroindene 5 were observed in the hydrolysis products of the mater-

ial produced in the reaction of U atoms and 4. Even though several

washings were done with hexane, it was impossible to remove com-

pletely all of the excess materials, 4 and 5. ^{1}H NMR spectra showed

the presence of starting material 4 and the rearranged 5 after the

material had been washed.

Reaction of the material formed between U atoms and 4 with

oxygen or CCl_4 gave starting material 4 and rearranged 5. Grant

and Streitwieser (62) observed the complete decomposition of

$(n-C_4H_9C_8H_7)_2U$ in CCl_4 to $n-C_4H_9C_8H_7$ and UCl_4 in 12 hours.

CCl_4 behaves in the same manner as oxygen in the presence of the

uranium material in this study.

The material prepared from U atoms and 4 reacts slowly with

CH_3OH. After 24 hours at -78°C there was no observable color

change in the brown solution upon addition of CH_3OH. After warm-up

to -10°C, the mixture turned to the bright green color of the U^{4+} ion.

Uranocene itself reacts slowly with H_2O and acetic acid (36). This

slow hydrolysis of the product of U metal atoms and 4 suggests that

basicity of dianion 15 has been sharply reduced when complexed to

uranium. Slow reactivity of this material was also observed for

CCl_4 quenches.

The ^1H NMR of the complex formed between U metal atoms and

4 in C_6H_6 revealed two large broad resonances 18 and 26 ppm down-

field from external TMS and a sharp single resonance -7.7 ppm upfield

with reference to TMS. The region between 0-10 ppm showed the

presence of starting material 4 and rearranged dihydroindene 5.

Assignment of these resonances cannot definitely be made, but large

upfield and downfield shifts clearly indicate the presence of a para-

magnetic species.

The visible spectrum of a THF solution provides additional evi-

dence that a complex between U and 15 was formed. Absorbances

are observed at 600, 615 and 757 nm which are similar to the absorb-

ances of uranocene which are located at 616, 643, 661 and 671 nm

(34). Substituted uranocenes also absorb in the same region. In

contrast, UCl_4 in THF has absorptions at 670, 652, 566, 498 and

483.

One last attempt to isolate the elusive dianion 15 with U^{4+} was

made by the method of Cernia and Mazzi (54); these authors claimed

to have prepared uranocene from the reaction of a mixture of UCl_4

and n-butyllithium with COT. Solubilities of the isolated reaction

product formed from UCl_4, n-butyllithium and 4 in diethyl ether and

THF indicated the presence of at least two brown complexes. Reac-

tion of both complexes with $H^+(D^+)$ gave two isomers of

dimethylcyclonona-1, 3, 6-triene $\underline{11}$ and $\underline{12}$. Again this substantiates

the formation of the dianion $\underline{15}$. Oxidation of this product yielded

starting material $\underline{4}$ and $\underline{5}$. It appeared to be impossible to remove

completely the LiCl. Atomic absorption indicated the presence of

Li^+ in the THF soluble fraction, which may have been from LiCl, a

lithium salt of $\underline{4}$ or some sort of Li-U-$\underline{4}$ complex.

DISCUSSION AND CONCLUSIONS

The dianion of cis-bicyclo[6.1.0]nona-2,4,6-triene 1 and the

9,9-dimethyl-derivative 4 were definitely formed. Hydrolysis of the

material formed by the reaction between Yb atoms and 1 resulted in

the formation of 1,3,6-cyclononatriene. Hydrolysis and deuterolysis

of the material formed during the reaction of U^{4+} with 15 and also U

metal atoms and 4 yielded the dimethylcyclononatrienes 11 and 12

and the dideuterio trienes. This is different from the results observed

by Ogliaruso and Winstein (54) in which they obtained 6 upon hydrolysis

of 2. However, the trienes indicate that the dianion was stabilized as

a U or Yb complex enabling a two-step attack to occur. This is con-

sistent with scheme 9 proposed by Ley and Paquette (51) for the

formation of dianion 4 in ND_3 which was subsequently protonated by the

solvent to give the monoanion 16.
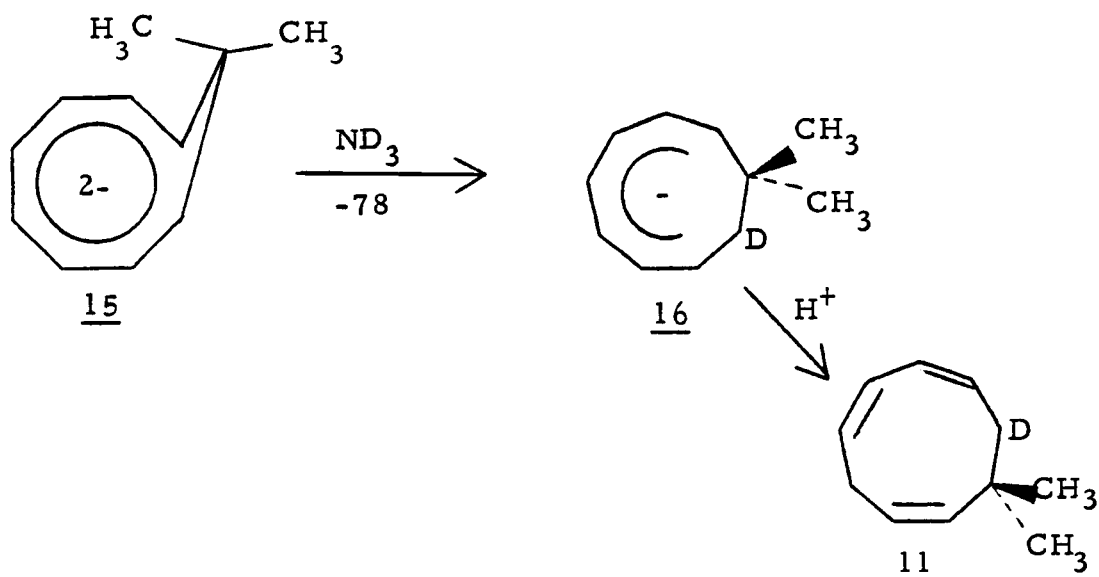
Scheme 9

Hydrolysis of the monoanion yields cyclononatrienes. Deuterolysis,

however, provides evidence for proton abstraction by the dianion

from the solvents. The cyclononatrienes-d_2 are not the exclusive

trienes formed. Mass spectrometry also shows the presence of

d_1 (28.0%) and d_0 (26.4%).

Oxidation of the U species formed from U atoms and $\underline{4}$ yielded

starting material and rearranged product $\underline{5}$. Reaction of this same

complex with CCl_4 also gave starting material $\underline{4}$ and rearranged $\underline{5}$.

Ogliaruso's (54) findings led to the expectation that the reaction

products could be the 1, 1-dimethyl-derivative of $\underline{7}$ and $\underline{8}$. However,

$\underline{4}$ and $\underline{5}$ were the only products recovered indicating that CCl_4 is

behaving as an oxidizing agent. Grant and Streitwieser (62) observed

similar results in the decomposition of $(n\text{-}C_4H_9C_8H_7)_2U$ in the pres-

ence of CCl_4.

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