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# FACILE FORMATION OF THE CYCLOHEPTATRIENYL TRIANION BY LANTHANIDE AND ACTINIDE IONS

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## Summary

The addition of lithium cycloheptadienide ($LiC_7H_8R$; R = hydrogen, methyl and n-butyl) to lanthanide and actinide chlorides results in the facile formation of the cycloheptatrienyl trianion complexed to the metal ion. Characterization of the ten-$\pi$-electron aromatic cycloheptatrienyl trianion ($C_7H_6R^{3-}$) was made by identification of the organic products resulting from chemical reaction of the coordinated ligand, for example, hydrolysis, deuterolysis and oxidation, as well as spectroscopic characterization ($^1H$ NMR) of paramagnetic uranium(IV) compounds. Formation of the cycloheptatrienyl trianion is believed to occur by the loss of two methylene protons from the metal-coordinated cycloheptadienide ion. The role of the lanthanide and actinide metal ions in cycloheptatrienyl trianion formation is briefly discussed.

## Introduction

Organolithium compounds are strongly basic and may be used to remove (metallate) allylic protons from olefinic compounds [1—5]. For olefins capable of forming anions with extensive charge delocalization or aromatic stabilization, olefinic dianion and trianion products may be prepared by multiple metallation reactions. Tetramethylethylenediamine (TMEDA) activated n-butyllithium [10] is an effective metallating agent for the preparation of delocalized dianion and trianion compounds from alkenes [7—10]. In addition to requiring strongly basic conditions, multiple metallation reactions often require long reaction times, typically four to ten days. For example, lithium cycloheptatrienide, $Li_3C_7H_7$, has been prepared by the double metallation of lithium cycloheptadienide, $LiC_7H_9$, by the addition of two equivalents of n-butyllithium (TMEDA) [9]. We have found that the cycloheptadienide anion, $C_7H_9^-$, is readily converted to the cycloheptatrienide trianion, $C_7H_7^{3-}$, in the presence of lanthanide or actinide ions. It should be emphasized that under our conditions no base, other than the cycloheptadienide anion, is present in the reaction solution.

## Results and discussion

Three equivalents of lithium cycloheptadienide react rapidly with one equivalent of uranium(IV) tetrachloride resulting in the formation of an unstable organo-uranium(IV) compound. Under oxygen- and water-free conditions, solutions of an initially formed red compound turn black with the precipitation of a black solid within approximately three hours. Although the cycloheptadienyl-uranium compound was not sufficiently stable to allow for complete compound characterization, i.e., composition and structure determination, the compound was sufficiently stable to permit the chemical and spectroscopic characterization of the coordinated ligand. A uranium-containing solid was obtained free from lithium cycloheptadienide reactant and other organic products by precipitation and washing with diethyl ether and pentane.

Chemical characterization, Fig. 1, of the coordinated ligand indicated that the ligand was not the added cycloheptadienyl anion, $C_7H_9^-$, but the ten-$\pi$-electron aromatic cycloheptatrienyl trianion, $C_7H_7^{3-}$. The $C_7H_7^{3-}$ ligand is hydrolytically unstable producing 1,3- and 1,4-cycloheptadiene as the only observed hydrolysis products. A complete mass spectroscopic analysis of the deuterolysis products of $C_7H_7^{3-}$ indicates that 1,3-cycloheptadiene-$d_3$ and 1,4-cycloheptadiene-$d_3$ are the exclusive products. From the mass spectra, no cycloheptadiene-$d_1$ isomers were observed. The latter are the expected deuterolysis products that would be obtained from the added $C_7H_9^-$ ion. Similar hydrolysis and deuterolysis results are obtained when one of the hydrogens in $C_7H_7^{3-}$ is replaced by an alkyl group, for example, methyl or n-butyl. In each case, the

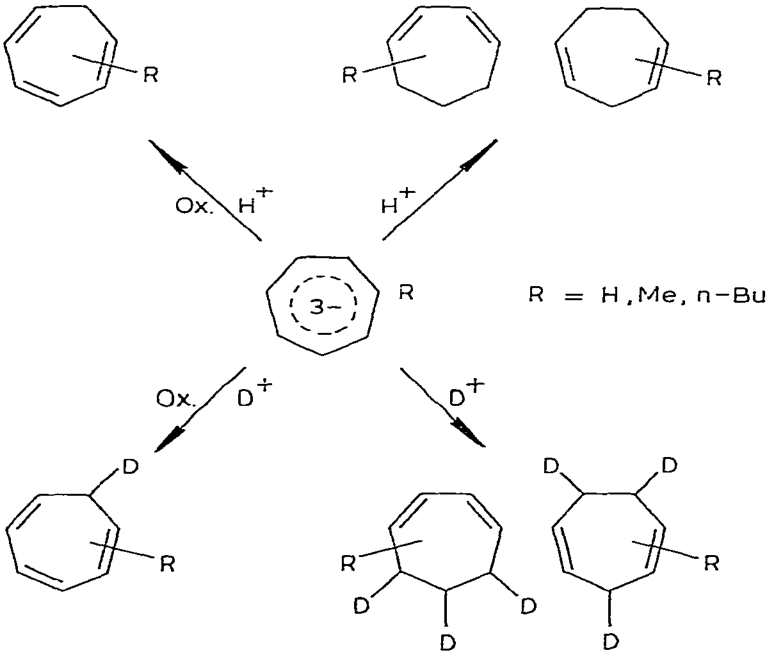
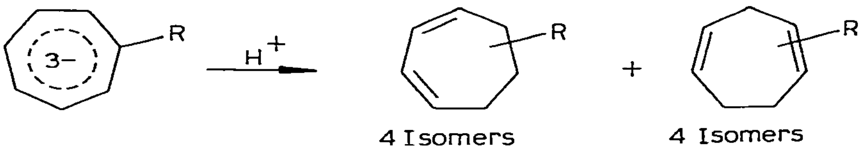


Fig. 1. Chemical characterization of the cycloheptatrienyl trianion.

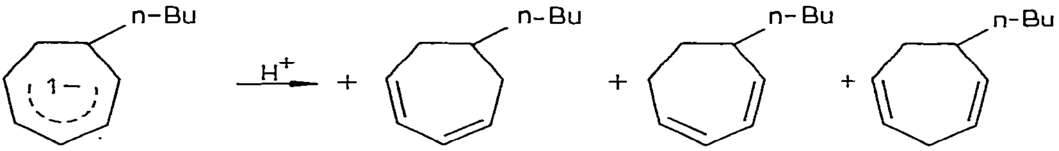
degree of deuterium labeling in the cycloheptadiene deuterolysis products is consistent with the addition of three and only three deuteriums (see Table 2).

Further evidence for the formation of ten-π-electron aromatic cycloheptatrienyl trianions, may be inferred from the number of hydrolysis isomers of monosubstituted cycloheptyl anions. From the hydrolysis of the alkyl-substituted cycloheptatrienyl trianion, $C_7H_6R^{3-}$, a mixture of eight isomers of 1,3- and 1,4-cycloheptadiene are possible, eq. 1.



(1)

Hydrolysis of 6-substituted cycloheptadienyl ions, on the other hand, produces only three cycloheptadiene isomers. For example, hydrolysis of lithium 6-n-butylcycloheptadienide produces 5-n-butyl-1,3-cycloheptadiene, 6-n-butyl-1,3-cycloheptadiene and 6-n-butyl-1,4-cycloheptadiene, eq. 2.



(2)

Experimentally, hydrolysis of alkyl-substituted cycloheptatrienyl-uranium compounds gives a mixture of, at least, six isomers of substituted cycloheptadiene. Although not all of the eight possible substituted cycloheptadiene hydrolysis isomers are detected by VPC, the presence of more than three isomeric hydrolysis products indicates that the uranium coordinated ligand is not simply the added $C_7H_9^-$ ion. In addition, hydrolysis of $Li_3C_7H_6$-n-Bu, prepared according to the literature [9], also produces only six detectable substituted cycloheptadiene isomers. The hydrolysis and deuterolysis products of $Li_3C_7H_6$-n-Bu were identical (by VPC retention times, mass spectral and $^1H$ NMR analysis) to the hydrolysis and deuterolysis products obtained from the uranium-coordinated cycloheptatrienyl trianion.

If the $C_7H_7^{3-}$ ion is a ten-π-electron aromatic anion, $C_7H_7^{3-}$ would be expected to display many of the same chemical reactions that are known for $C_8H_8^{2-}$ [11]. Specifically, $C_8H_8^{2-}$ may be oxidized by a number of oxidizing agents, for example, cadmium(II) chloride [10] or oxygen [12], to cyclooctatetrene, $C_8H_8$. A two-electron oxidation of $C_7H_7^{3-}$ would, correspondingly, lead to the formation of the cycloheptatrienyl monoanion, $C_7H_7^-$. Solutions of uranium cycloheptatrienyl trianion compounds are observed to undergo slow internal redox reactions resulting in the formation of $C_7H_7^-$ and reduced uranium. The reduced uranium probably exists as a mixture of uranium(III) and uranium metal. Solutions of cycloheptatrienyl trianion-uranium compounds are initially red. After a few hours, at either room temperature or −78°C, the red solutions turn black. Black solids are also formed. The hydrolysis of the resulting black mixture yields cycloheptatriene as well as 1,3- and 1,4-cycloheptadiene. Significantly, cycloheptatriene-$d_1$ is obtained on deuterolysis. It should be emphasized that cyclo-

TABLE 1

$^1$H NMR DATA FOR RING PROTONS AT 20°C IN PYRIDINE-$d_5$ ($U^{4+}$ COMPLEXES)[a]

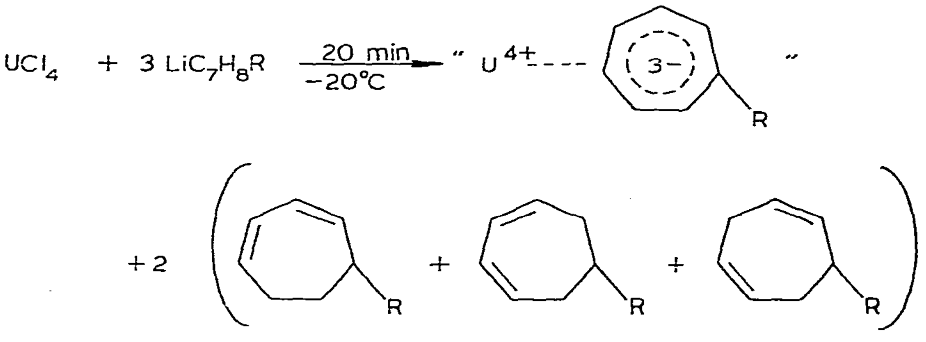
| | | | | |
|---|---|---|---|---|
| $C_8H_8^{2-}$ | 35.2 | | | |
| $C_7H_7^{3-}$ | 46.5 | | | |
| $C_7H_6$n-Bu$^{3-}$ | 40.6 | 48.6 | 53.0 | |
| $C_8H_7$n-Bu$^{2-}$ | 32.0 | 33.5 | 35.6 | 39.2 |

[a] All values in ppm upfield from TMS = 0.

heptatriene is not a hydrolysis product of the initial red uranium-trianion solutions. Furthermore, yields of cycloheptatriene obtained from the hydrolysis of the black uranium mixture increase directly with the length of time that the uranium-cycloheptatrienyl trianion compound remains in the solution. Similar ligand—metal internal redox reactions occur for alkyl-substituted cycloheptatrienyl trianion-uranium compounds.

$^1$H NMR spectroscopy has proven most useful for the confirmation of the aromaticity of the $C_7H_7^{3-}$ ligand. $^1$H NMR spectra of the ring protons for both uranocene [13—15] and uranium cycloheptatrienyl trianion are given in Table 1. Aromatic ring protons for both the cycloheptatrienyl and cyclooctatetraenyl rings are shifted far upfield. From the appearance of only one proton resonance in the $^1$H NMR spectrum for $C_7H_7^{3-}$, one may conclude that all ring protons are magnetically equivalent. In other words, the $C_7$ ring is planar, each carbon has the identical number of hydrogens, one. These conclusions are confirmed by both the intensity and number of ring proton resonances which occur in the n-butyl cycloheptatrienyl trianion, $C_7H_6$-n-Bu$^{3-}$. Three equal intensity peaks are observed for the ring protons in $C_7H_6$-n-Bu$^{3-}$.

In addition to the formation of the cycloheptatrienyl trianion, the reaction between uranium(IV) tetrachloride and lithium cycloheptadienide produces large amounts of free cycloheptadiene which must be washed free from the uranium cycloheptatrienyl trianion compounds, eq. 3. Approximately 20% of the cycloheptadienide ion is converted to the aromatic trianion while the remaining 80% of the cycloheptadienide anion is converted to a mixture of isomers of cycloheptadiene. Free cycloheptadiene is isolated from the reaction solution prior to cycloheptatrienyl trianion hydrolysis reactions. The mixture of cycloheptadiene isomers isolated from the reaction of uranium(IV) tetrachloride with 6-alkyl-substituted cycloheptadienide are the identical isomers which are obtained from the direct hydrolysis of lithium 6-alkyl-substituted cycloheptadienide (see eq. 2, eq. 3).

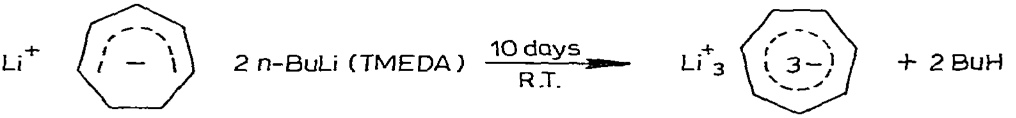


(3)

Chloride salts of thorium(IV), erbium(III) and gadolinium(III) have also been used to prepare the cycloheptatrienyl trianion from lithium cycloheptadienide with similar results to those of uranium(IV).

## Conclusions

In the presence of chloride salts of the lanthanide and actinide elements, the cycloheptadienyl anion was found to be readily converted to the cycloheptatrienyl trianion. The mechanism for this unusual transformation may be inferred from both the yield of the trianion and from the presence and type of cycloheptadiene isomers which are isolated from the reaction solution, eq. 3. Apparently, metal coordination of $C_7H_9^-$ increases the acidity of the methylene hydrogens of the cycloheptadienyl ligand. By acting as a base, a second $C_7H_9^-$ abstracts a methylene proton from the coordinated cycloheptadienyl ligand in an acid—base reaction. This is followed by an additional proton abstraction from the remaining methylene carbon by a third $C_7H_9^-$ resulting in the formation of $C_7H_7^{3-}$ and two equivalents of free cycloheptadiene. The ease with which these acid—base reactions occur is remarkable. Solutions of $LiC_7H_9$ show no tendency to disproportionate into $Li_3C_7H_7$ and two $C_7H_{10}$. In addition, although metallation of $LiC_7H_9$ by strong bases has been reported, it is extremely difficult. For example, $Li_3C_7H_7$ has been formed by the double metallation of $LiC_7H_9$ by the very powerful base n-butyllithium (TMEDA) [9], eq. 4.



(4)

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

From a consideration of the known organolanthanide and organoactinide chemistry, an ionic bonding, polarization model is most likely responsible for the observed increase in acidity. Although weak covalency resulting from $\pi$-bond formation has been attributed to many organoactinide compounds [12,16], $\pi$-bonding in organolanthanide compounds is not chemically significant [17].

Metal ions may be thought of as functioning to increase the methylene carbon—hydrogen acidities in the cycloheptadienyl ligand by acting as a strong electron-withdrawing group polarizing ligand $\pi$-electron density toward the metal ion. As the methylene proton is lost, the resulting negative charge on the methylene carbon is stabilized by distributing that charge throughout the delocalized $\pi$-orbital system. The electron-withdrawing effect of the metal ion decreases the electron density on the carbon atoms with the greatest negative charge, the odd dienyl carbon atoms which are located adjacent to the methylene carbon atoms. As a result of the decreased electron density on the carbon atom adjacent to the methylene carbon, the conjugate base of the cycloheptadienyl ligand is stabilized relative to the conjugate base of the free cycloheptadienide ion. The primary increase in acidity of the cycloheptadienyl anion is attributed to the stabilization of the conjugate base by the metal ion. There are many examples in organic chemistry of an electron-withdrawing group increasing the acidity of an adjacent carbon—hydrogen bond.

In this study lanthanide and actinide ions have been observed to increase cycloheptadienyl reactivity following coordination to the metal ion. Specifically, the cycloheptadienyl ligand displays increased methylene carbon—hydrogen acidity leading to the facile formation of the cycloheptatrienyl trianion. In the presence of either lanthanide or actinide ions, reaction times for the formation of the cycloheptatrienyl trianion have been reduced from approximately ten days to 30 min. In addition, the base strength required to remove the methylene hydrogen atoms has been reduced from the very powerful base n-butyllithium (TMEDA) to the weakly basic cycloheptadienyl anion. The ability of a metal ion to activate organic molecules and increase reaction rates (lower activation energies) is one of the most important molecular properties of an organometallic catalyst. In the future it is likely that lanthanide and actinide ions will function in stoichiometric and catalytic reactions as polarization centers activating organic molecules by inductive effects [16,18].

## Experimental

### *General considerations*

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

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

### *Preparation of cycloheptadienide anions*

The preparation of lithium cycloheptadienide [4] and lithium 6-n-butylcycloheptadienide [19] have been previously described. Lithium 6-methylcycloheptadienide may be prepared in the following manner. In 40 ml of $Et_2O$, 0.91 ml (0.93 mmol) of freshly distilled cycloheptatriene was added to 6.62 ml (0.93 mmol) of 1.4 *M* MeLi and 1.40 ml of TMEDA. After stirring for 24 hours at room temperature all of the cycloheptatriene had reacted, producing a dark red solution of lithium 6-methylcycloheptadienide. Aliquots (1.0 ml) of the resulting red solution were taken for hydrolysis, deuterolysis and alkylation reactions. The substituted cycloheptadiene isomers may be isolated by VPC (1/8" × 8', 15% Carbowax 20 M). Results obtained for lithium 6-methylcycloheptadienide were identical with those obtained from other cycloheptadienide anions. Average yields were 80% based on added cycloheptatriene.

### *1,3- and 1,4-cycloheptadiene*

Authentic samples of 1,3- and 1,4-cycloheptadiene were prepared by the reduction of cycloheptatriene by sodium metal in liquid ammonia [19,20]. At —60°C, 10 ml of liquid ammonia were added to 0.22 g (0.96 mmol) Na. The metal dissolved, resulting in a blue solution. Cycloheptatriene (0.50 ml) was added at —60° C, and the solution carefully hydrolyzed with ethanol. Approximately 15 ml of $Et_2O$ were added and the temperature was raised to 0° C. The $NH_3$ was removed under vacuum and 1,3- and 1,4-cycloheptadiene were obtained by preparative VPC (1/4″ × 8′, 10% Carbowax 4000). $^1H$ NMR spectra were identical to those reported in the literature [20].

### *Lithium n-butylcycloheptatrienyl trianion, $Li_3C_7H_6$-n-Bu*

Authentic samples of the $d_3$-deuterolysis products from the n-butylcycloheptatrienyl trianion were obtained by $D_2O$ addition to $Li_3C_7H_6$-n-Bu. In 35 ml of hexane, $Li_3C_7H_6$-n-Bu was prepared, according to the literature [9], by the addition of 0.30 ml (3.06 mmol) of cycloheptatriene and 1.5 ml (9.96 mmol) TMEDA to 5.75 ml of 1.6 *M* (9.2 mmol) n-BuLi. After approximately 4 hours, the solution turned green. Lithium 6-n-butylcycloheptadienide is rapidly formed. After stirring the green solution for 11 days, a black solid had precipitated. Deuterolysis of the entire reaction mixture resulted in the 35% formation of six n-butylcycloheptadiene-$d_3$ isomers. The degree of deuterium labeling was determined by VPC mass spectrometry.

### *Formation and characterization of the cycloheptatrienyl trianion-uranium(IV) complex*

A solution of lithium 6-n-butylcycloheptadienide was prepared from 7.4 ml (11.8 mmol) of 1.6 *M* n-BuLi and 1.16 ml (11.8 mmol) of cycloheptatriene in 35 ml $Et_2O$. A suspension of 1.5 g (3.95 mmol) of $UCl_4$ in 35 ml $Et_2O$ was cooled to —20° C. The solution of lithium 6-n-butylcycloheptadienide was added to the $UCl_4$ over approximately 10 min. After 15 min, the temperature was rapidly brought to room temperature. After an additional 30 min of stirring, the solution was pale yellow, and a dark red, insoluble uranium-containing cycloheptatrienyl trianion compound had been formed. The solid was filtered and washed with 3 × 15 ml of $Et_2O$. The reaction solution and washings were combined and analyzed by VPC. 6-n-butyl-1,3-cycloheptadiene, 5-n-butyl-1,4-cycloheptadiene and 5-n-butyl-1,3-cycloheptadiene were identified by a comparison of VPC retention times with authentic samples. Calibration was made using an external standard, yield 1.39 g (4.3 mmol, 78%). Mass spectral analysis of the reaction solution treated with $D_2O$ gave no evidence of deuterium incorporation into the cycloheptadiene products.

The cycloheptatrienyl trianion-uranium(IV) complex was dissolved in THF and filtered. Addition of pentane to the filtered THF solution precipitated the red uranium complex. The precipitate was filtered and washed with 3 × 15 ml of pentane and dried under vacuum ($10^{-3}$ mmHg) for no more than 30 minutes. Prolonged vacuum drying causes extensive decomposition. The solids obtained by this procedure fumed when exposed to air or oxygen and were decomposed by protic solvent. Qualitative analysis of this solid showed both lithium and chloride present as well as uranium. Cycloheptatrienyl trianion compounds were soluble in strongly coordinating solvents, THF, DME or pyridine, but were insoluble in $Et_2O$, hexane or benzene. Solutions of the cycloheptatrienyl trianion compound were stable for approximately three hours at 20°C where upon the initial red solution irreversibly turned black and solids began to precipitate. Isolated solids could be stored under $N_2$ for slightly longer periods although all reactions and spectra were obtained on freshly synthesized material.

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

### *Hydrolysis*

THF solutions of the freshly isolated cycloheptatrienyl trianion-uranium(IV) compound were hydrolyzed (deuterolyzed) with $H_2O$ ($D_2O$). The resulting mixture was acidified with 1 *M* HCl. Organic products were isolated as described above. Hydrolysis products were identified by identical comparisons with authentic samples by VPC retention times, $^1H$ NMR and mass spectra. The degree of deuterium labeling was determined by VPC mass spectrometry, Table 2. No cycloheptatriene was observed under these conditions.

### *Oxidation*

Solutions of the uranium(IV)-cycloheptatrienyl trianion compound were observed to change irreversibly from red to black in approximately 8 hours at room temperature. This reaction occurred at nearly the same rate at —78°C. Hydrolysis (deuterolysis) of the resulting black mixture, followed by previously described work-up procedures, indicated the presence of cycloheptatriene

TABLE 2

MASS SPECTRAL PARENT ION FRAGMENTATION PATTERN OF HYDROLYSIS (DEUTEROLYSIS) PRODUCTS OF $C_7H_8R^-$, $C_7H_6R^{3-}$, $C_7H_6R^-$ (R = H, n-Bu, Me)

| Hydrolysis product | *M*(*m*/*e*) | Ion intensity (%) | | | |
|---|---|---|---|---|---|
| | | (*M* — 2) | (*M* — 1) | *M* | (*M* + 1) |
| $C_7H_{10}$ | 94 | 3.9 | 14.0 | 36.7 | 3.4 |
| $C_7H_9D$ | 95 | 4.7 | 18.9 | 66.0 | 5.4 |
| $C_7H_7D_3$ | 97 | 6.1 | 18.0 | 68.0 | 5.2 |
| $C_7H_8$ | 92 | 0.8 | 100.0 | 47.5 | 3.2 |
| $C_7H_7D$ | 93 | 100.0 | 91.9 | 30.4 | 1.4 |
| $C_7H_9$n-Bu | 150 | 0.3 | 0.2 | 34.5 | 4.1 |
| $C_7H_8$Dn-Bu | 151 | 1.8 | 1.7 | 43.8 | 5.8 |
| $C_7H_6D_3$n-Bu | 153 | 0.5 | 1.4 | 64.1 | 9.0 |
| $C_7H_7$n-Bu | 148 | | 1.4 | 19.1 | 2.1 |
| $C_7H_6$Dn-Bu | 149 | | 8.9 | 19.3 | 2.6 |
| $C_7H_9$Me | 108 | 1.4 | 8.6 | 80.9 | 7.5 |
| $C_7H_6D_3$Me | 111 | 4.3 | 17.8 | 96.9 | 11.6 |
| $C_7H_7$Me | 106 | 2.2 | 21.9 | 47.6 | 3.4 |
| $C_7H_6$DMe | 107 | 10.7 | 35.5 | 63.6 | 6.1 |

(cycloheptatriene-$d_1$). The degree of deuterium labeling was determined by VPC-mass spectrometry, Table 2.

Attempts to oxidize the cycloheptatrienyl trianion by air, $O_2$ or nitrobenzene were unsuccessful, causing complete decomposition of the uranium-trianion compound. No cycloheptatriene was observed.

### *Alkylation*

All attempts to alkylate the cycloheptatrienyl trianion were unsuccessful. THF solutions of the uranium-bound trianion were decomposed by MeI, EtBr, $CCl_4$, $(EtO)_2SO_2$ and $FSO_3Me$. The only identifiable products isolated from these reactions were non-alkylated isomers of cycloheptadiene.

### *Spectra*

$^1$H NMR spectra were obtained on freshly prepared cycloheptatrienyl trianion-uranium(IV) compounds. Solid trianion samples were dissolved in dry,

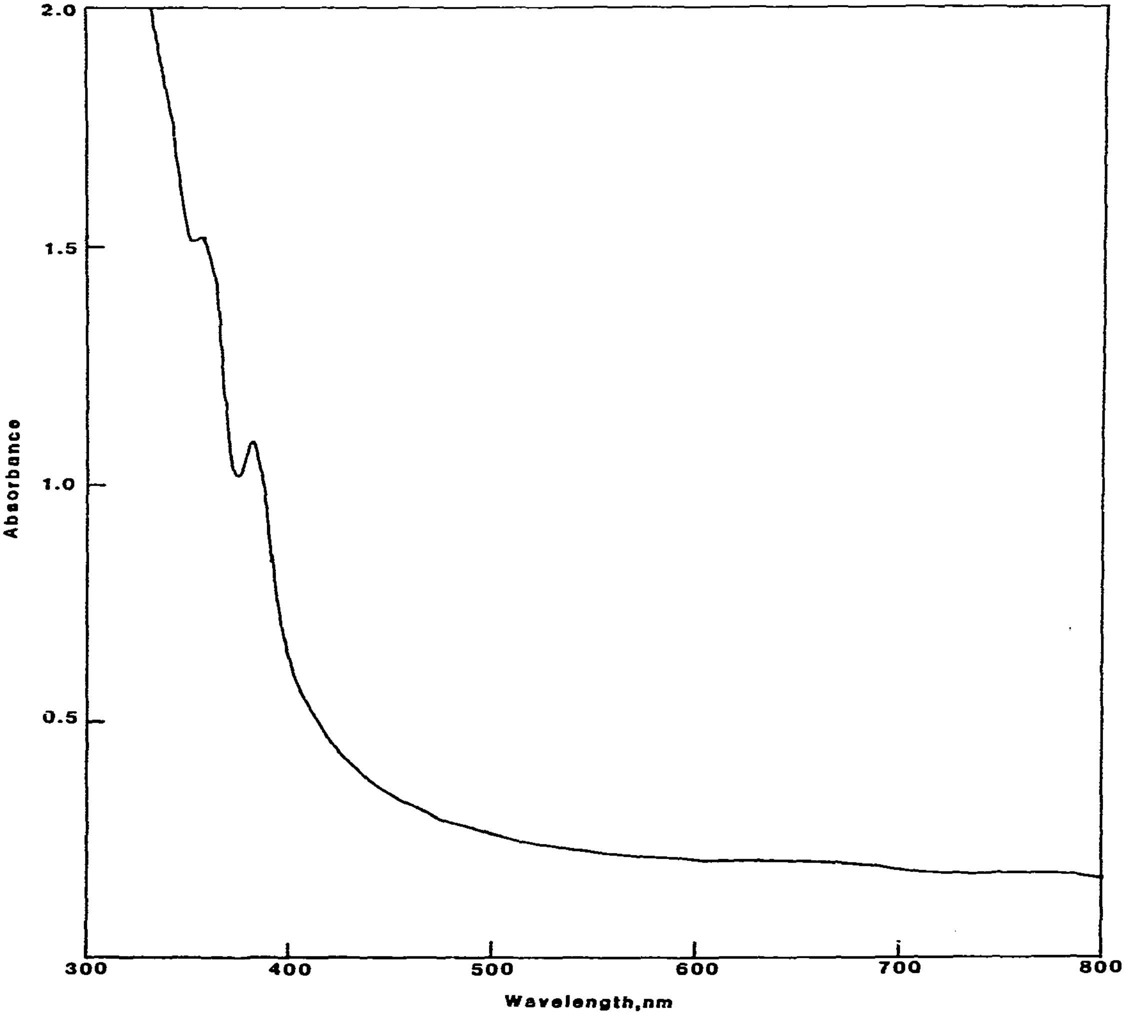


Fig. 2. The visible spectrum of the red solid dissolved in THF.

degassed pyridine-$d_5$ in a glove box. Samples were filtered through glass wool to remove undissolved solids and the NMR tube was sealed under $N_2$. Spectra were run immediately on a Varian HA 100 spectrometer at 20°C. Peak positions were determined using $^1$H pyridine peaks as an internal reference. After approximately one hour signal intensities became very weak and ultimately disappeared (including solvent peaks). Loss of signal intensity is probably due to the formation of paramagnetic solids.

The visible spectrum of the red solid dissolved in THF is shown in Fig. 2. The THF solution was approximately 0.001 *M* in uranium. Two transitions are observed at 380 and 357 nm and from their intensity and location are assigned to metal to ligand charge-transfer transitions. These transitions apparently obscure any *f—f* transitions of the $U^{IV}$. However, addition of dry air to dilute solutions resulted in a loss of both the 380 and 357 nm transitions followed by the appearance of a weaker band in the 400 to 450 nm region. Addition of a small amount of concentrated HCl to the oxidized solution gave rise to a weak series of bands located at 494, 476, 460, 442, and 429 nm. This spectrum is similar to that reported by Ryan for $UO_2Cl_4^{2-}$ in nitromethane to which water and HCl had been added.

Other lanthanide, erbium(III) and gadolinium(III), and actinide, thorium(IV), chlorides were found to convert solutions of lithium cycloheptadienide to the cycloheptatrienyl trianion under the same reaction conditions described for uranium(IV) tetrachloride. NOTE: For the lanthanide elements one equivalent of lithium cycloheptadienide per equivalent of lanthanide chloride was used.

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