LANTHANIDES AND ACTINIDES

ANNUAL SURVEY COVERING THE YEAR 1977

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General

S. A. Cotton (1) has written a thorough and thoughtful review article on contemporary developments in lanthanide and actinide organometallic chemistry. A recent review on covalent metal tetrahydroborate (BH_4^-) complexes by Marks and Kolb (2) discusses chemistry and spectroscopy of organolanthanide and organoactinide tetrahydroborates in detail.

Warren (3) has published an extensive treatise on the ligand field theory of lanthanide and actinide cyclooctatetraene sandwich compounds. The article reviews and extends earlier ligand field investigations (4) and complements one-electron molecular orbital studies by the same group (5). The ligand field work employed Wolfsberg-Helmholz molecular orbital calculations to determine the f orbital energy displacements in $Ce(C_8H_8)_2^-$ and $U(C_8H_8)_2$. A weak field basis set which assumes that the crystal field splitting is less than the separation between J levels (most valid for the cerium ion) was utilized. In both complexes, the dominant bonding interaction was determined to take place between metal f_{xyz}

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and $f_{z(x^2-y^2)}$ orbitals and the ligand e_{2u} orbitals. This is in accord with the bonding scheme originally introduced by Streitwieser for $U(C_8H_8)_2$(6). For uranocene, Warren finds a mixing of ca. 22% ligand character into the initially pure metal $5f_{xyz}$ and $5f_{z(x^2-y^2)}$ orbitals, as opposed to a ca. 3% mixing into the analogous 4f orbitals of $Ce(C_8H_8)_2^-$. As noted in many other studies, the greater spatial extension of 5f orbitals gives rise to higher metal-ligand bond covalency, although in the present case it must be recognized that the formal charges on the metal ions differ. The ground state of $U(C_8H_8)_2$ was found in the present work to be a $J_z = \pm 3$ level. Warren employed the calculated f orbital energy level orderings in the lanthanide and actinide sandwich compounds to predict the temperature dependence of the magnetic susceptibilities and magnetic anisotropies. The agreement appears to be somewhat better in the case of the actinide complexes; more experimental data are needed for the lanthanides.

Lanthanides

In an effort to probe for metal-ligand bond covalency, Dubois, Carver and Tsutsui (7) have studied the X-ray photoelectron spectra of a series of gadolinium organometallics. The relative intensity of 3d "shake-up" satellites (due to simultaneous photoionization and outer shell excitation) is believed to be related to 4f covalency. In the series $GdCl_3$, $Gd(C_5H_5)Cl_2$, $Gd(C_5H_5)_2Cl$, $Gd(C_5H_5)_3$, and $Gd(C_5H_5)_2R$, R = CH_3 or $C{\equiv}CC_6H_5$, the intensity of the satellite peak remains essentially constant. Thus, there is no evidence that metal-ligand bond covalency is a strong function of the nature of the ligand.

It has been known for some time that triscyclopentadienyl lanthanides are strong Lewis acids and form complexes with a variety of Lewis bases (8). Baker and Raymond (9) have now prepared and characterized a binuclear pyrazine complex of triscyclopentadienyl ytterbium. The synthetic procedure is illustrated in equation (1). The

$$2\ Yb(C_5H_5)_3 + NC_4H_4N \xrightarrow{\text{benzene}} (C_5H_5)_3YbNC_4H_4NYb(C_5H_5)_3 \qquad (1)$$

structure of this molecule was determined by single crystal X-ray diffraction, and the result is shown in Figure 1.

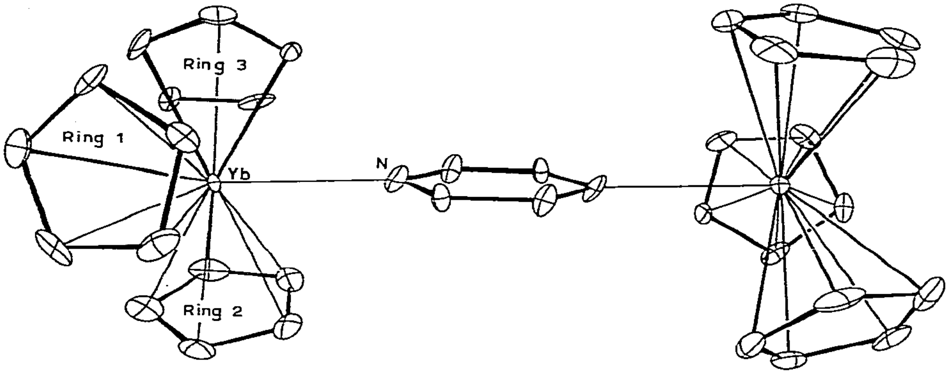


Figure 1. The molecular structure of $(C_5H_5)_3YbNC_4H_4NYb(C_5H_5)_3$ from ref. 9.

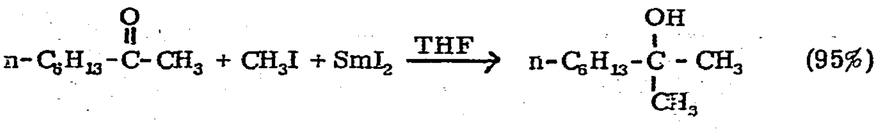
The coordination geometry about the ytterbium ion is approximately C_{3v} with ring centroid-Yb-ring centroid angles ranging from 115.6° to 102.5°. A similar ligation geometry was observed in the cyclohexylisocyanide adduct of triscyclopentadienyl praseodymium (10). In the present example, the Yb-N distance was found to be 2.61(1)Å and the average Yb-C distance, 2.684(11)Å. The intramolecular Yb-Yb distance is 8.047(2)Å. The magnetic susceptibility of this compound was studied from 3-100°K. The susceptibility obeys the Curie-Weiss law with $\mu_{eff} = 3.48\mu_\beta$, C = 1.51(4) and θ = 1.3(6)°K. Significantly, there is no evidence of appreciable magnetic coupling between the two ytterbium ions, suggestive of a high degree of ionic character in the metal-ligand bonding.

An interesting new cyclooctatetraene complex of Ce(IV) has recently been reported. Greco, Cesca, and Bertolini (11) have prepared the black, extremely oxygen-sensitive complex bis(cyclooctatetraene)-cerium by the route shown in equation (2). Infrared

$$Ce(O\text{-}i\text{-}C_3H_7)_4 \cdot i\text{-}C_3H_7OH + C_8H_8 + Al(C_2H_5)_3 \xrightarrow{140^\circ C} Ce(C_8H_8)_2 \qquad (2)$$

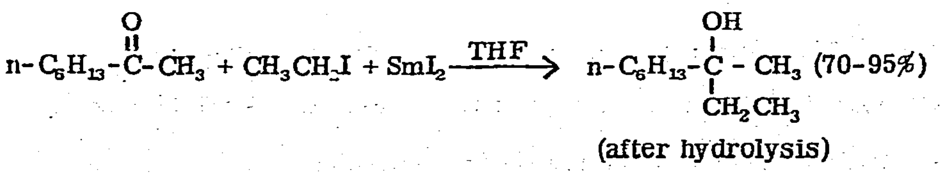
and proton NMR spectra of the new compound are consistent with η^8-C_8H_8 bonding. Preliminary X-ray diffraction studies reveal $Ce(C_8H_8)_2$ to be isomorphous with the D_{8h} sandwich complex, $Th(C_8H_8)_2$. Surprisingly, $Ce(C_8H_8)_2$ is not particularly reactive toward water. Reduction with one equivalent of potassium yields the known (12) compound $K^+Ce(C_8H_8)_2^-$, while reduction with an excess of potassium produces the unusual divalent species $[K(monoglyme)]_2^{+2}\,[Ce(C_8H_8)_2]^{-2}$. When the reaction of equation (2) is conducted at lower temperatures using cycloheptatriene as the solvent and a C_8H_8:Ce ratio of less than 5, a green compound of stoichiometry $Ce_2(C_8H_8)_3$ can be isolated. Infrared spectra suggest that this compound possesses two different types of C_8H_8 ligand.

In the area of organic synthesis, Namy, Girard, and Kagan (13) have reported that SmI_2 and YbI_2 can be used in combination with alkyl iodides or bromides for the Grignard-like alkylation of ketones (equations (3) and (4)).



$$n\text{-}C_6H_{13}\text{-}\overset{\overset{\large O}{\|}}{C}\text{-}CH_3 + CH_3I + SmI_2 \xrightarrow{THF} n\text{-}C_6H_{13}\text{-}\underset{\underset{\large CH_3}{|}}{\overset{\overset{\large OH}{|}}{C}}\text{-}CH_3 \quad (95\%) \qquad (3)$$

(after hydrolysis)



$$n\text{-}C_6H_{13}\text{-}\overset{\overset{\large O}{\|}}{C}\text{-}CH_3 + CH_3CH_2I + SmI_2 \xrightarrow{THF} n\text{-}C_6H_{13}\text{-}\underset{\underset{\large CH_2CH_3}{|}}{\overset{\overset{\large OH}{|}}{C}}\text{-}CH_3 \quad (70\text{-}95\%) \qquad (4)$$

(after hydrolysis)

The same methodology, when applied to alkyl aldehydes, produced the desired product but also competing reduction of the aldehyde to the corresponding alcohol.

Razuvaev, Bochkarev, Kalinina, and Bochkarev (14) have prepared the first metal-metal bonded compound involving a lanthanide and a main group metal. Thus, the reaction of equation (5) produces a pale green,

$$5[(C_6F_5)_3Ge]_2Hg + 2Pr \xrightarrow[20^\circ C]{1,2\text{-dimethoxyethane}} 2[(C_6F_5)_3Ge]_3Pr\cdot Hg[Ge(C_6F_5)_3]_2 + 3Hg \quad (5)$$

moisture-sensitive product which was characterized by vibrational spectra and elemental analyses. The ionic structure $[(C_6F_5)_3Ge]_2Pr^+Hg[Ge(C_6F_5)_3]_3^-$ was suggested. Not surprisingly, the Pr-Ge bonds can be cleaved with HCl to yield hydrido-germanium and chloro-praseodymium fragments.

Actinides

Activity in the area of actinide-to-carbon sigma bonds continues at a high level. Sigurdson and Wilkinson (15) have reported detailed studies on homoleptic U(IV) and U(V) polyalkyls. The thermally unstable hexaalkyl uranates, prepared by the approach of equation (6), were characterized by

$$UCl_4 + \text{excess } RLi \xrightarrow{S} Li_2UR_6\cdot 8S \quad (6)$$

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

$$S = \text{diethyl ether, tetrahydrofuran}$$

spectroscopic techniques and by quantitative analysis of the hydrolysis products. The ionic structure $(LiS_4)_2^{+2}UR_6^{-2}$ was suggested. Even considering that the ligand field about uranium is approximately cubic and that dipolar shifts should be negligible, the reported proton NMR isotropic shifts are surprisingly small. A considerably larger shift was observed in the reaction product of UCl_4 with four equivalents of methyllithium (16). Sigurdson and Wilkinson reported magnetic moments in the range 2.7 - 2.9 BM, which are unusually large for an octahedral system where the second-order Zeeman effect is expected to dominate the susceptibility. The reaction of uranium (V) pentaethoxide with lithium reagents, followed by dioxane precipitation, yields what were formulated as octaalkyl uranium(V) trianions (equation (7)). These products

$$U_2(OC_2H_5)_{10} + \text{excess } RLi \longrightarrow Li_3UR_8 \cdot 3 \text{ dioxane} \qquad (7)$$

$$R = CH_3,\ CH_2Si(CH_3)_3,\ CH_2C(CH_3)_3$$

are stable at room temperature; NMR but not magnetic data were reported. Discrete, eight-coordinate UR_8^{-3} ions with dodecahedral or bicapped trigonal prismatic or antiprismatic structures, possibly with the lithium ions bridging the polyhedral faces, were considered to be consistent with the experimental data. Coordination numbers higher than seven have never previously been observed for mononuclear U(V) complexes with monodentate, uninegative ligands (17).

Goffart, Gilbert, and Duyckaerts (18) have reported on trisindenyl alkyls of thorium and uranium. These new organometallics were synthesized by the route shown in equation (8) and were

$$M(C_9H_7)_3Cl + RLi \xrightarrow[-70°]{THF} M(C_9H_7)_3R + LiCl \qquad (8)$$

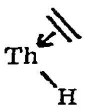
$$M = Th,\ R = CH_3,\ n\text{-}C_4H_9 \qquad M = U,\ R = CH_3$$

characterized by electronic, mass, infrared, and Raman spectroscopy, and by elemental analysis. Trisindenylmethyluranium was found to react quantiatively with methanol to give the methoxy derivative (equation (9)). This result is in contrast

$$U(C_9H_7)_3CH_3 + CH_3OH \xrightarrow{THF} U(C_9H_7)_3OCH_3 + CH_4 \qquad (9)$$

to the behavior of $U(C_5H_5)_3R$ compounds (19,20) where both alkyl and ring alcoholysis occur. Thus, the pentahaptoindenyl ligand is more strongly bound or at least more resistant to protolytic attack.

One important feature of $Th(C_5H_5)_3R$ chemistry is the resistance of these species to β-hydride elimination upon thermolysis (21). This distinctive characteristic has been attributed to saturation and congestion of the actinide coordination sphere, which renders intermediates such as that shown below, prohibitively

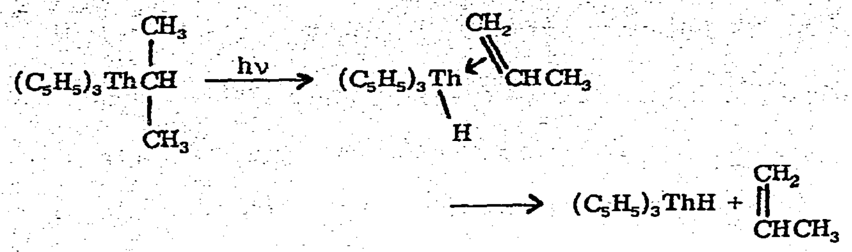


high in energy. Thus, instead of β-hydride elimination, transfer of a ring hydrogen atom takes place yielding RH. Kalina, Wachter, and Marks (22) have now reported completely different behavior on photolysis. Irradiation of $Th(C_5H_5)_3$(i-propyl) or $Th(CH_3C_5H_4)_3$(i-propyl) in benzene solution proceeds according to equation(10) to produce a dark green

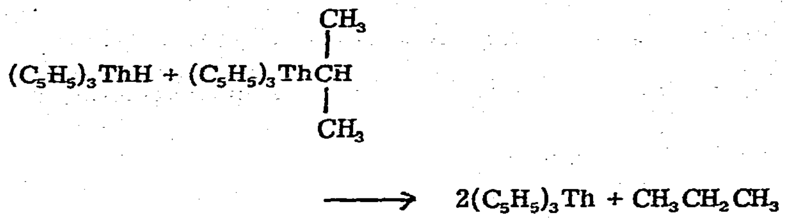
$$2Th(RC_5H_4)_3(i\text{-}C_3H_7) \xrightarrow{h\nu} 2Th(RC_5H_4)_3 + C_3H_8 + C_3H_6 \qquad (10)$$

$$R = H,\ CH_3$$

triscyclopentadienyl thorium species and propane to propene in a 53:47 ratio. The spectral and magnetic properties of the thorium organometallic are consistent with a tris(pentahaptocyclopentadienyl) $5f^1$ formulation, and differ distinctly from the deep violet compound produced by reducing $Th(C_5H_5)_3Cl$ with sodium naphthalide (23). The mechanism of reaction (8) was proposed to involve photoinduced β-hydride elimination as shown in equations (11)and (12). In



$$(C_5H_5)_3Th\overset{CH_3}{\underset{CH_3}{CH}} \xrightarrow{h\nu} (C_5H_5)_3Th(H)\leftarrow\overset{CH_2}{\underset{CHCH_3}{\|}} \longrightarrow (C_5H_5)_3ThH + \overset{CH_2}{\underset{CHCH_3}{\|}} \qquad (11)$$



$$(C_5H_5)_3ThH + (C_5H_5)_3Th\overset{CH_3}{\underset{CH_3}{CH}} \longrightarrow 2(C_5H_5)_3Th + CH_3CH_2CH_3 \qquad (12)$$

the initial step, photochemical labilization of an η^5-C_5H_5 ligand is proposed to take place (there is precedent for such processes (24)); this process is followed by olefin extrusion, and the resulting thorium hydride reacts with another thorium isopropyl molecule to produce propane. There is considerable precedent for an analogous two-step thermal sequence in transition metal alkyl β-hydride elimination chemistry (25). Further support for this mechanism is derived from deuterium labelling and frozen solution studies, and from the observation that $Th(C_5H_5)_3(CH_3)$ is far less reactive. Photolysis of $U(C_5H_5)_3$(i-propyl) produces the known compound $U(C_5H_5)_3$ (26) as well as some products *via* the thermal pathway (22b).

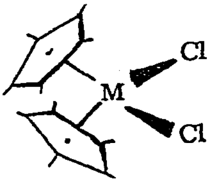
Seyam and Eddein (27) have synthesized bisindenyl dialkyls of uranium by the route shown in equation (13). These new compounds

$$UCl_4 + 2C_9H_7Li \xrightarrow[-70°C]{THF} \xrightarrow[-70°C]{2RLi} U(C_9H_7)_2R_2 \qquad (13)$$

were characterized by elemental analysis and infrared spectroscopy. They appear to have appreciable thermal stability.

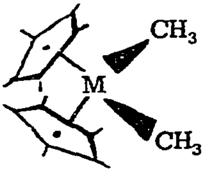
Manriquez, Fagan, and Marks (28) have prepared the first pentamethylcyclopentadienyl actinide complexes. The reaction of thorium or uranium tetrachloride with an excess of pentamethylcyclopentadienyl lithium or Grignard reagent produces crystalline bis(pentamethylcyclopentadienyl) dichlorides (equation (14)). The new compounds were characterized by elemental analysis as well as by proton NMR and infrared spectroscopy. The uranium compound is sufficiently soluble for cryoscopic molecular weight determinations in benzene, and the structure shown below has been proposed (28). The thorium and uranium dichlorides can be alkylated with methyllithium to produce thermally stable dialkyls (equation (15)). These highly reactive new compounds were characterized by the same techniques as the dichlorides. These results suggest the structure below. The bis(pentamethylcyclopentadienyl)-

$$MCl_4 + \text{excess } (CH_3)_5C_5^- \longrightarrow M[(CH_3)_5C_5]_2Cl_2 + 2Cl^- \quad (M = Th,\ U) \quad (14)$$



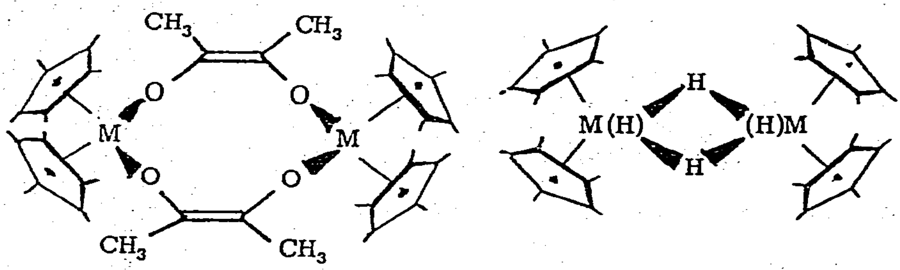
$$M[(CH_3)_5C_5]_2MCl_2 + 2CH_3Li \longrightarrow M[(CH_3)_5C_5]_2(CH_3)_2 + 2LiCl \quad (15)$$

$$(M = Th,\ U)$$

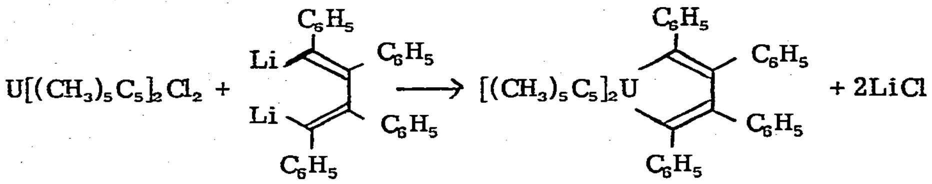


(M = Th, U)

actinide dimethyls react rapidly with hydrogen to yield the first isolable organoactinide hydrides, and with carbon monoxide to yield O-bonded insertion products (28). On the basis of elemental analysis, spectroscopic data, and cryoscopic molecular weights in benzene, the structures shown below have been put forward. The uranium dichloride can also be used to synthesize a metallocycle (equation (16)). Clearly the pentamethylcyclopentadienyls offer a wealth of fascinating new organoactinide chemistry.



M = Th, U



(16)

Fronczek, Halstead and Raymond (29) have now published a full account of their investigations of actinide 1,2-dicarbollide chemistry. Bis(dicarbollide) complexes of uranium (IV) were prepared via the metathesis approach of equation (17).

$$UCl_4 + 2A_2C_2B_9H_{11} \xrightarrow{THF} A_2U(C_2B_9H_{11})_2Cl_2 + 2ACl \qquad (17)$$

$A = Li, Na, K, \frac{1}{2} Ba$

Single crystals of the lithium salt, $[Li(THF)_4]_2[U(C_2B_9H_{11})_2Cl_2]$, were grown from tetrahydrofuran solution, and the result of a single crystal X-ray diffraction study is shown in Figure 2.

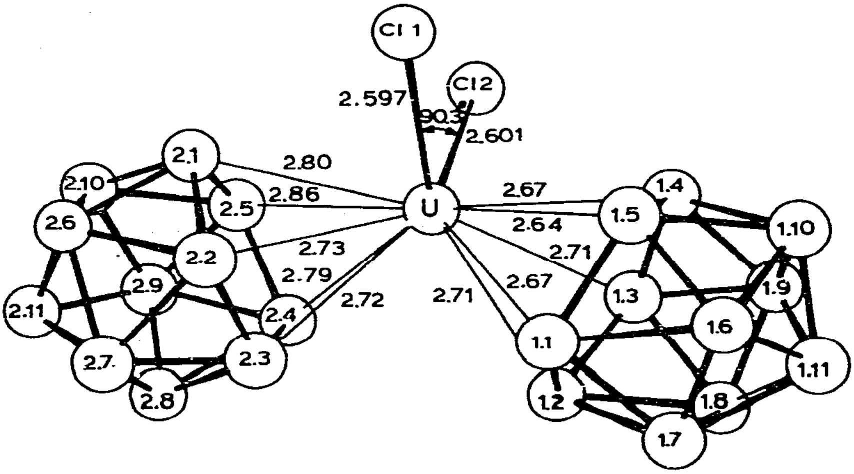


Figure 2. Molecular structure of the anionic portion of $[Li(THF)_4]_2$-$[U(C_2B_9H_{11})_2Cl_2]$ from ref. 29.

The coordination configuration about the uranium ion is distorted tetrahedral with pentahapto dicarbollide ligands. The Cl-U-Cl angle is 90.3(5)°, and the dicarbollide face centroid-U-dicarbollide face centroid angle is 137°. The average U-Cl distance is 2.599(6)Å. Due to apparent disorder and/or thermal motion of the dicarbollide ligands about the axes perpendicular to the bonding faces, it was not possible to unambiguously distinguish U-C from U-B bond distances. An average U-to-face atom distance of 2.73(2)Å was reported; this value is comparable to previously determined U-C(ring) distances in several η^5-C_5H_5 complexes of U(IV)(30). The reaction of $U(C_2B_9H_{11})_2Cl_2^{-2}$ with $K_2C_8H_8$ yields predominantly $U(C_8H_8)_2$, while the reaction with NaC_5H_5 appears to produce a mixed ligand complex which was not isolated. Attempts to prepare an analogous bis(dicarbollide) of thorium (IV) were unsuccessful.

Vasil'ev, Sokolov, and Kondratenkov (31) have found that triscyclopentadienyl uranium alkyls readily exchange monohapto ligands with aluminum alkyls, as shown in equation (18). These

$$U(C_5H_5)_3R + AlR'_3 \rightleftharpoons U(C_5H_5)_3R' + AlR_2'R \qquad (18)$$

$R = C_2H_5,\ n-C_4H_9,\ \text{allyl},\ C_6H_5,\ OC_2H_5$
$R' = CH_3,\ C_2H_5,\ i-C_4H_9$

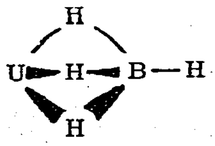
processes are conveniently monitored in the isotropically shifted proton NMR spectra.

A synthetic route to biscyclopentadienyl uranium bistetrahydroborate, $U(C_5H_5)_2(BH_4)_2$, has been reported by Zanella, DePaoli, Bombieri, Zanotti, and Rossi (32), and is shown in equations (19) and (20). The red-brown

$$UCl_4 + 2NaBH_4 \xrightarrow[\text{or THF}]{\text{1,2-dimethoxyethane}} UCl_2(BH_4)_2 + 2NaCl \qquad (19)$$

$$UCl_2(BH_4)_2 + 2TlC_5H_5 \xrightarrow[\text{or THF}]{\text{1,2-dimethoxyethane}} U(C_5H_5)_2(BH_4)_2 + 2TlCl \qquad (20)$$

highly air-sensitive complex can be sublimed at 60° C/10^{-2} mm. to yield a crystalline product. The authors concluded from infrared spectra that the tetrahydroborate ligands are coordinated in a tridentate manner, as shown below. Preliminary single crystal



X-ray diffraction results were also reported for $U(C_5H_5)_2(BH_4)_2$. There are two crystallographically unique molecules in a unit cell, and U-B distances were found to be 2.61(8) and 2.58(8)Å for one molecule, and 2.63(8) and 2.63(8)Å for the other. The B-U-B angles were reported to be 99.6(12)° and 102.5(12)°. Disorder of the cyclopentadienyl carbons about the ring fivefold axes was observed.

Marquet-Ellis and Folcher (33) have studied the reduction of $U(C_5H_5)_3Cl$ in THF by $LiBH(C_2H_5)_3$ and $LiAlH_4$ using proton NMR and electronic spectroscopy. Two intermediate species were detected in the $LiBH(C_2H_5)_3$ reduction (one may be $U(C_5H_5)_3H$) with the final product being the known compound $U(C_5H_5)_3OC_2H_5$. Using $LiAlH_4$ as the reductant, two intermediate species are evident in the NMR at low temperature. The final product on warming to room temperature was identified as the known species $U(C_5H_5)_3THF$ (26).

Considerable progress is being made in the area of actinide cyclooctatetraene compounds. Harmon, Bauer, Berryhill, Hagiwara, and Streitwieser (34) have reported the synthesis of a number of new substituted uranocenes. These were prepared from substituted cyclooctatetraenes as represented in equation (21). Quaternization

$$UCl_4 + 2K_2RC_8H_7 \xrightarrow{THF} U(RC_8H_7)_2 + 4KCl \qquad (21)$$

$$\begin{array}{lll} R = & OCH_3 & OC(CH_3)_3 \\ & (CH_2)_3N(CH_3)_2 & OCH_2CH{=}CH_2 \\ & OC_2H_5 & N(CH_3)_2 \\ & & CH_2N(CH_3)_2 \end{array}$$

of the amino compounds with methyl iodide produced the corresponding $-\overset{+}{N}(CH_3)_3I^-$ and $-CH_2\overset{+}{N}(CH_3)_3I^-$ derivatives. The allyloxy uranocene was found not to undergo a Claisen rearrangement to a 1,2-allyl hydroxy compound upon refluxing in diglyme or several other solvents. The optical spectra of these compounds generally exhibit four transitions in the 600-700 nm region. Electron-donating substituents on the cyclooctatetraene rings shift the absorption bands to lower energy. Thus, these bands have been assigned to ligand-to-metal charge-transfer transitions, probably involving redistribution of π electron density from the ligand e_{2g} orbital to metal $J_z = \pm 1$ or ± 3 orbitals. There is no evidence in the electronic spectra that the nitrogen atoms in the compound with $(CH_2)_3N(CH_3)_2$ substituents interact with the uranium atom. The proton NMR spectra of the substituted uranocenes exhibit substantial isotropic shifts with resonances of all substituent protons being shifted to low field. Ring proton signals are shifted to high field. The carbon-13 NMR spectra reveal large downfield shifts of the ring carbon atoms.

Clark and Green (35) have recorded and analyzed the uv photoelectron spectra of $Th(C_8H_8)_2$ and $U(C_8H_8)_2$ using both He(I) and He(II) radiation. Ionizations were assigned on the basis of Hückel molecular orbital calculations as well as close analogies in level positions and bandshapes to

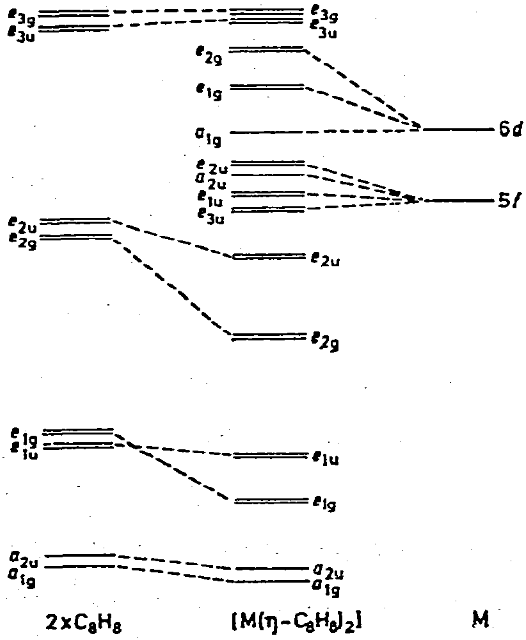


Figure 3. Proposed molecular orbital scheme for actinide $M(C_8H_8)_2$ sandwich compounds. From ref. 35.

those of transition metal metallocenes and bisarenes. Comparing the He(I) and He(II) results aided in spectral assignments and in deducing the compositions of molecular orbitals, since ionization cross-sections for U5f, U6d, and C2p orbitals are anticipated to have much different dependencies on ionization energy. The molecular orbital ordering shown in Figure 3 was proposed for actinide $M(C_8H_8)_2$ sandwich compounds. A highly significant conclusion of this study was that the major component of metal-ligand bonding in these compounds is between ligand e_{2g} π molecular orbitals and metal 6d orbitals ($d_{x^2-y^2}$ and d_{xy}). An appreciable covalent interaction was also detected between ligand e_{2u} orbitals and metal $5f_{x(x^2-y^2)}$ and $5f_{xyz}$ orbitals. This latter interaction is greater for uranium than for thorium because the uranium 5f orbitals are lower in energy than those of thorium.

Karraker (36) has prepared a bis(cyclooctatetraene) complex of trivalent americium. The synthetic procedure employed AmI_3 (equation (22)). There

$$AmI_3 + 2K_2C_8H_8 \xrightarrow{THF} KAm(C_8H_8)_2 + 3KI \qquad (22)$$

is no indication of THF incorporation in the product. The electronic absorption spectrum of $Am(C_8H_8)_2^-$ in THF exhibits red shifts of the bands on the order of ca. 250-450 cm^{-1} compared to Am(III) in aqueous solution. Thus, there is an indication of a small degree of metal-ligand bond covalency. Attempts to reduce this compound to an Am(II) species with potassium naphthalide or butyllithium were not successful. Karraker and Stone (37) have used ^{237}Mössbauer spectroscopy to study the products of the reaction between NpI_3 and one equivalent of K_2COT in THF (equation (23)). Earlier work (38) had characterized

$$NpI_3 + K_2C_8H_8 \xrightarrow{THF} Np(C_8H_8)I \cdot x\ THF \qquad (23)$$

the sandwich compound obtained with two equivalents of $K_2C_8H_8$ (equation (24)). In the present investigation

$$NpI_3 + 2K_2C_8H_8 \xrightarrow{THF} KNp(C_8H_8)_2 \cdot 2THF \qquad (24)$$

the product with an isomer shift of +3.83 cm/sec (versus $NpAl_2$) was suggested to be $Np(C_8H_8)I \cdot x\ THF$, which is analogous to known lanthanide complexes such as $(Ce(C_8H_8)Cl \cdot 2THF)_2$ (39). The neptunium compound is decomposed upon THF removal. The only product obtained by reacting $Np(C_8H_8)I \cdot xTHF$ with TlC_5H_5 was identified as $Np(C_5H_5)_3 \cdot THF$.

LeVanda and Streitwieser (40) have recently communicated the synthesis of a series of substituted thorocenes. These were prepared from substituted cyclooctatetraenes (equations (25) and (26)) and

$$2K_2RC_8H_7 + ThCl_4 \xrightarrow{1,2\text{-dimethoxyethane}} Th(RC_8H_7)_2 + 4KCl \qquad (25)$$

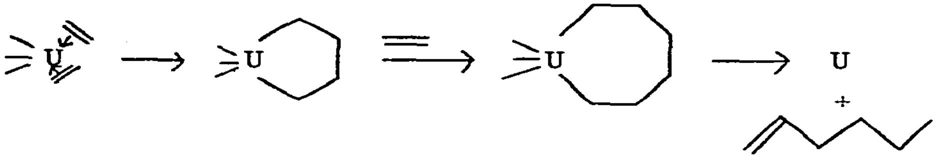
$$R = n\text{-}C_4H_9,\ C_6H_5$$

$$2K_2[1,3,5,7\text{-}(CH_3)_4C_8H_4] + ThCl_4 \xrightarrow{1,2\text{-dimethoxyethane}} Th[1,3,5,7\text{-}(CH_3)_4C_8H_4]_2 + 4KCl \qquad (26)$$

are considerably more soluble than thorocene. Proton and ^{13}C NMR spectra indicated considerably less electron density in the ligands than in the parent dianions. The chemical properties of the thorocenes appear to reflect greater ionic character in the metal-ligand bonding than in the corresponding uranocenes. Thorocene cleanly deoxygenates aryl nitro compounds to yield azo compounds, as shown in equation (27).

$$2\ ArNO_2 + 2Th(C_8H_8)_2 \longrightarrow ArN{=}NAr + 2ThO_2 + 4C_8H_8 \qquad (27)$$

In the area of catalysis, Manyik, Walker and Wilson (41) have reported that a soluble compound produced from partially hydrolyzed triisobutyl aluminum and various uranium salts (carboxylates, alkanoates, acetyacetonate) efficiently catalyzes the trimerization of ethylene to 1-hexene. A mechanism involving five- and seven-membered metallocycles was suggested (equation (28))



(28)

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