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LANTHANIDES AND ACTINIDES

ANNUAL SURVEY COVERING THE YEAR 1978

TOBIN J. MARKS, Department of Chemistry, Northwestern University,
Evanston, Illinois 60201

General

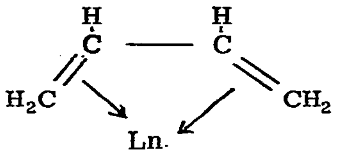
A NATO Advanced Study Institute entitled "Organometallics of the f-Elements" was held in Urbino, Italy in September 1978. Copies of the proceedings are available (1) and a monograph (2) based upon the contributions of the principal lecturers will be issued by summer of 1979.

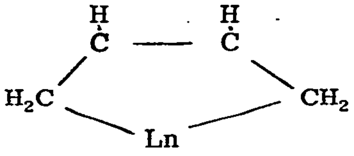
Lanthanides

A review article on the chemical and spectrochemical properties of lanthanide organometallic compounds has appeared (3). It contains large compilations of data and attempts to tie together what is known about the electronic structure, bonding, and chemical behavior of 4-f element organometallics.

Evans, Engerer, and Neville (4) have studied by metal atom vapor techniques the reactions of lanthanide atoms (La, Nd, Sm, Er) with 1,3-butadiene and 2,3-dimethyl-1,3-butadiene. The major products of the cocondensation of Nd, Sm, and Er atoms with 1,3-butadiene at -196° C are extremely air and moisture sensitive organometallics of the stoichiometry $Ln(C_4H_6)_3$. With 2,3-dimethyl-1,3-butadiene the compounds $Er[(CH_3)_2C_4H_4]_2$ and $La[(CH_3)_2C_4H_4]_2$ could be isolated. All of these unusual new compounds were characterized by complete elemental analysis, spectral (ir, electronic), and magnetochemical methods. The physical properties observed argue clearly against any bonding formulation involving simple trivalent lanthanide ions. Hydrolysis of the butadiene derivatives produces predominantly 2-butenes, in contrast to most transition metal butadiene complexes where either butadiene or 1-butene is produced. The bonding in the new lanthanide complexes was discussed in terms of mixtures of the two resonance hybrids shown below.

Lanthanides and actinides; Annual Survey covering the year 1977 see J. Organometal. Chem., Vol. 158 (1978) 325-343.





In other low-valent lanthanide chemistry, Evans, Wayda, Chang, and Cwirla (5) have found that a slurry produced by reducing anhydrous $PrCl_3$ with potassium metal in tetrahydrofuran reacts with 1,5-cyclooctadiene to yield, after oxidative work-up, 1, 3, 5, 7-cyclooctatetraene. The role of the lanthanide in this reaction is not clear and it may act either as a simple dispersant of the potassium atoms or as a complexing agent for $C_8H_8^{=}$. The authors found that, under more drastic thermal conditions, the $PrCl_3$ could be omitted from the synthesis.

DeKock, Ely, Hopkins, and Brault (6) have now published a complete account of their metal atom vapor syntheses of the compounds $[Ln(C_8H_8)(THF)_2]$-$[Ln(C_8H_8)_2]$ where Ln = La, Ce, Nd, and Er. Preparative procedure involved condensing the lanthanide atoms with cyclooctatetraene at -196° C and purifying the resulting product by Soxhlet extraction with tetrahydrofuran (THF). In the case of Ln = Yb, the divalent compound $Yb(C_8H_8)$ was obtained. The molecular structure of $[Nd(C_8H_8)(THF)_2][Nd(C_8H_8)_2]$ was investigated by single crystal X-ray diffraction and the result is shown in Figure 1. The structure can be most easily understood in terms of a $Nd(C_8H_8)_2^-$ anion (7) coordinated to a $Nd(C_8H_8)(THF)_2^+$ cation. The average Nd-C distance involving C(1) - C(8) is 2.68(1)Å while that for C(9) - C(16) is 2.79Å. Carbon atoms C(13), C(14), and C(15) are involved in an unusual bridging interaction between the two lanthanide ions, with Nd(2)-C distances of 2.76(2), 2.76(2), and 2.83(2)Å, respectively. The average Nd-C distance involving C(17)-C(24) is 2.68(1) Å, and the average Nd(2) - O(THF) distance is 2.57(2)Å.

The chemistry of organometallic compounds with lanthanide-to-carbon sigma bonds received much attention in 1978. Atwood, Hunter, Rogers, Holton, McMeeking, and Lappert (8) have reported a number of new neutral and anionic lanthanide alkyls. The reaction of three equivalents trimethylsilylmethyl lithium with anhydrous lanthanide chlorides proceeds as shown in equation (1).

$$LnCl_3 + 3\ LiCH_2Si(CH_3]_3 \xrightarrow{THF} Ln[CH_2Si(CH_3)_3]_3(THF)_2 + 3\ LiCl \qquad (1)$$

Ln = Tb, Er, Yb

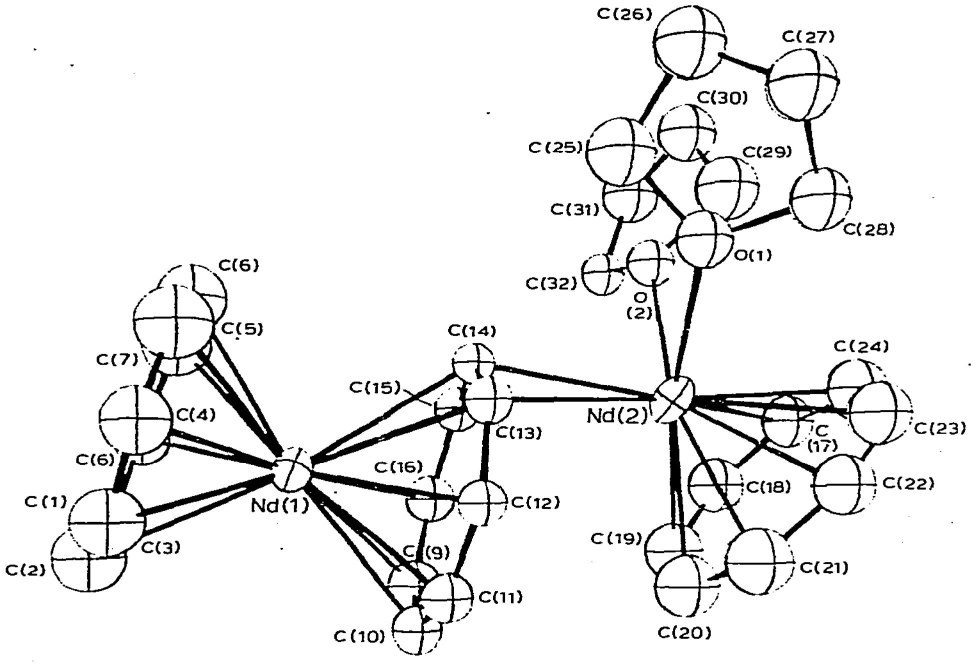


Fig. 1. The molecular structure of $[Nd(C_8H_8)(THF)_2][Nd(C_8H_8)_2]$ from ref. 6.

to yield neutral, five-coordinate lanthanide alkyls. With four equivalents of lithium reagent, anionic lanthanide tetraalkyls are produced (equation (2)). All of the new compounds were characterized by spectral (ir, nmr), analytical

$$LnCl_3 + 4\ LiCH_2Si(CH_3)_3 \xrightarrow{THF} LiL_4^+\ Ln[CH_2Si(CH_3)_3]_4^- + 3LiCl \qquad (2)$$

Ln = Er, Yb

L = THF, $\frac{1}{2}$ tetramethylethylenediamine

and magnetochemical methods. In the case of the bulkier bistrimethylsilylmethyl lithium reagent, complete substitution of halide does not occur, and as illustrated in equation (3), anionic chlorotrialkyls are obtained. The

$$4\ LiCH[Si(CH_3)_3]_2 \xrightarrow{ether/THF} LiL_4^+\ Ln\{CH[Si(CH_3)_3]_2\}_3Cl^- + 2LiCl \qquad (3)$$

Ln = Er, Yb
L = THF

molecular structure of the Yb derivative was studied by single crystal X-ray

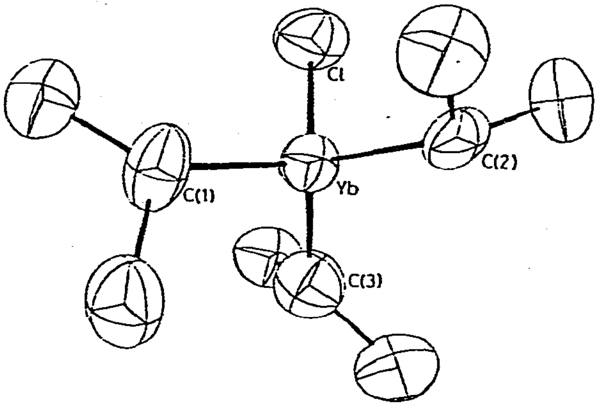
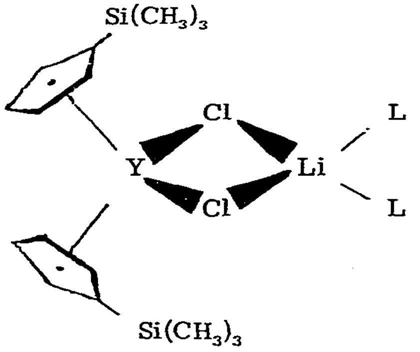


Fig. 2. The molecular structure of the anionic portion of $Li(THF)_4^+$-$Yb\{CH[Si(CH_3)_3]_2\}_3Cl^-$ from ref. 8.

diffraction. The coordination geometry about the ytterbium ion (Figure 2) is distorted tetrahedral with ∢ C(1)-Yb-C(2) = 115.9 (7)°, ∢ C(2)-Yb-C(3) = 107.6(8)°, ∢ C(1)-Yb-C(3) = 107.1(6)°, ∢ C(2)-Yb-Cl = 110.3(5)°, ∢ C(1)-Yb-Cl= 104.0(5)°, and ∢ C(1)-Yb-Cl = 112.0(6)°. The Yb-C distances range from 2.372(16) Å to 2.391(20) Å, and the Yb-Cl contact is 2.486(6) Å. It was noted that halotransition metal alkyls are rare and generally unstable. Heating the $Li(THF)_4^+$ $Er\{CH[Si(CH_3)_3]_2\}_3Cl^-$ complex in hexane induces what is apparently a ligand redistribution reaction, yielding $Er\{CH[Si(CH_3)_3]_2\}_4^-$ and what was presumed to be $Li^+[ErCl_4]^-$. Atwood <u>et. al</u> (8) also demonstrated that anionic biscyclopentadienyls of yttrium could be prepared (equation 4)). The structure

$$YCl_3 + 2\ LiC_5H_4Si(CH_3)_3 \xrightarrow{THF} LiL_2^+\ Y[\eta^5\text{-}C_5H_4Si(CH_3)_3]Cl_2^- + LiCl \qquad (4)$$

L = THF, ½ tetramethylethylenediamine
illustrated below was proposed.



In closely related lanthanide trimethylsilylmethyl investigations, Schumann and Müller (9) reported the synthesis of a trialkylerbium tris(tetrahydrofuranate) (equation (5)). This product was characterized by elemental analysis,

$$LnCl_3 + 3\,LiCH_2Si(CH_3)_3 \xrightarrow{THF} Ln[CH_2Si(CH_3)_3]_3(THF)_3 + 3LiCl \qquad (5)$$

$Ln = Er$

cryoscopic molecular weight, infrared and nmr spectroscopy. Reaction with $HgCl_2$ yields $Hg[CH_2Si(CH_3)_3]Cl$, while reaction with I_2 produces a mixture of $(CH_3)_3SiCH_2I$ and $(CH_3)_3SiCH_2CH_2Si(CH_3)_3$. Interestingly, when the reaction of equation (5) is carried out with Ln = Sm, Tb, and Dy, thermally unstable products are obtained which decompose by α-elimination to produce tetramethylsilane. With Ln = La and Nd, no reaction occurs in equation (5). Schumann and Müller (10) have also prepared new hexaalkyl lanthanide trianions via the approach of equation (6). These interesting new complexes

$$LnCl_3 + 6LiCH_3 \xrightarrow{L} LiL_3^+\ Ln(CH_3)_6^- + 3\ LiCl \qquad (6)$$

$Ln = Er, Lu$

L = tetramethylethylenediamine

are crystalline and very thermally stable.

Wayda and Evans (11) used the t-butyl functionality to synthesize anionic lanthanide tetraalkyls (equation (7)).

$$LnCl_3 + 4\,LiC(CH_3)_3 \xrightarrow{THF} Li(THF)_4^+\ Ln[C(CH_3)_3]_4^- + 4\,LiCl \qquad (7)$$

$Ln = Sm, Er, Yb$

These complexes are analogous to the trimethylsilylmethyl species prepared by Atwood, et al. (vide supra). They were characterized by elemental analysis, magnetic measurements, hydrolysis experiments, as well as by electronic and infrared spectroscopy. An important observation was that thermolysis of $Sm[C(CH_3)_3]_4^-$ in THF does not give organic products indicative of β-hydride elimination, i.e. no 2-methylpropene was formed. Rather, 3.25 mole of 2-methylpropane and 0.5 mole of ethylene are produced per mole of tetraalkyl.

Experiments with THF-d_8 indicated that only ca. 25% of the 2-methylpropane was present as deuterated (d_1) product. The ethylene formed was attributed to attack of free $LiC(CH_3)_3$ on THF (a known reaction).

In recent work, Deacon, Raverty, and Vince (12) reported that a thermally unstable bis(pentafluorophenyl)ytterbium tetrahydrofuranate could be prepared from ytterbium metal via the route of equation (8). Deacon and Koplick (13)

$$Hg(C_6F_5)_2 + Yb \xrightarrow{THF} Yb(C_6F_5)_2(THF)_4 + Hg \qquad (8)$$

have now applied this lanthanide metal/mercurial synthetic technique to the synthesis of an ytterbium phenylethynyl complex (equation (9)). Bis(phenyl-

$$Hg(C{\equiv}CC_6H_5)_2 + Yb \xrightarrow{THF} Yb(C{\equiv}CC_6H_5)_2 + Hg \qquad (9)$$

ethynyl)ytterbium could also be prepared by reacting $Yb(C_6F_5)_2(THF)_4$ with phenylacetylene. The phenylethynyl compound is thermally stable but exceedingly air and moisture sensitive. Hydrolysis of this compound gave ca. 80% phenylacetylene and ca. 20% styrene (from hydrogenation of the phenylacetylene as demonstrated by experiments with D_2SO_4). Molecular weight measurements in THF showed $Yb(C{\equiv}CC_6H_5)_2$ to be associated, probably as trimers and/or tetramers. Previously reported lanthanide acetylides, $Eu(C{\equiv}CCH_3)_2$ and $Yb(C{\equiv}CCH_3)_2$, were prepared by reacting the lanthanide metals with propyne in liquid ammonia (14).

Compounds involving metal-metal bonds between biscyclopentadienyl lanthanide functionalities and Group IV elements have been communicated by Schumann and Cygon (15). As indicated in equations (10) and (11), these

$$Er(C_5H_5)_2Cl + LiE(C_6H_5)_3 \xrightarrow{THF} Er(C_5H_5)_2E(C_6H_5)_3 + LiCl \qquad (10)$$

$$E = Ge,\ Sn$$

$$Yb(C_5H_5)_2Cl + LiSn(C_6H_5)_3 \xrightarrow{THF} Yb(C_5H_5)_2Sn(C_6H_5)_3 + LiCl \qquad (11)$$

compounds were prepared in THF from the corresponding lanthanide chlorides. They were purified by extraction with benzene and were characterized by elemental analysis, infrared spectroscopy, and magnetic measurements.

Dornberger, Klenze, and Kanellakopulos (16) have reported a highly efficient new method for synthesizing $M(C_5H_5)_{m-n}X_n$ complexes of lanthanides and actinides, starting from the corresponding $M(C_5H_5)_m$ compounds and employing ammonium salts as C_5H_5 substitution reagents. An example with lanthanide complexes is presented in equation (12). Further examples with 5f elements will be discussed in the section on actinides.

$$Ln(C_5H_5)_3 + NH_4{}^+Cl^- \longrightarrow Ln(C_5H_5)_2Cl + C_5H_6 + NH_3 \qquad (12)$$
$$Ln = Sm, Yb$$

Actinides

Fischer and coworkers have reported new results on compounds evidencing expansion of the uranium coordination sphere in the $U(C_5H_5)_3X$ systems. Thus, Fischer, Klähne, and Kopf (17) have isolated complexes of the composition $U(C_5H_5)_3Cl(CH_3CN)$ by recrystallizing $U(C_5H_5)_3Cl$ from acetonitrile. By metathesis in acetonitrile, the chloride ion can be replaced by thiocyanate (equation (13)). The molecular structure of the acetonitrile adduct of tris-

$$U(C_5H_5)_3Cl + KNCS \xrightarrow{CH_3CN} U(C_5H_5)_3NCS(CH_3CN) + KCl \qquad (13)$$

cyclopentadienyl uranium thiocyanate has been determined by single crystal X-ray diffraction. The result (Figure 3) is an unusual pseudo-five-coordinate configuration in which the three pentahaptocyclopentadienyl ligands occupy the equatorial vertices of a trigonal bipyramid. The average ring centroid-U-ring centroid angle is 119.9°, while the average N1-U-ring centroid angle is 92.2°, and the average N2-U-ring centroid angle is 87.8°. The U-N1

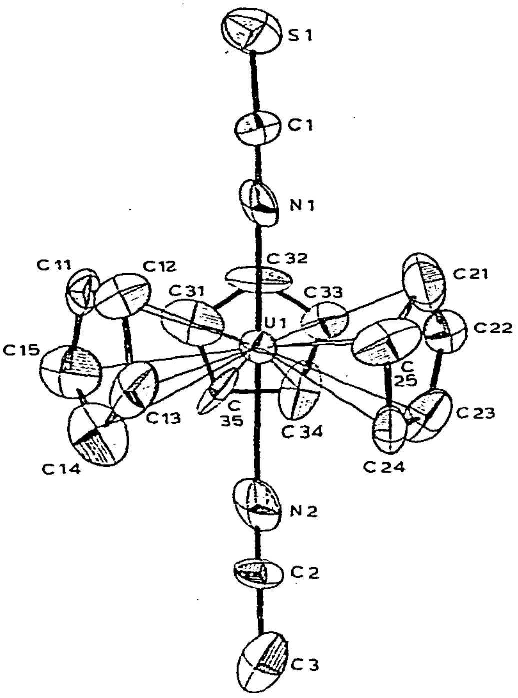


Figure 3. The molecular structure of $U(C_5H_5)_3NCS(CH_3CN)$ from ref. 17.

distance is 2.407(15) Å and the U-N2 distance is 2.678(16) Å; the average U-ring centroid contact is 2.484 Å. Treating $U(C_5H_5)_3NCS(CH_3CN)$ with water yields the aquo adduct, $U(C_5H_5)_3NCS(H_2O)$; under high vacuum this compound is converted to anhydrous $U(C_5H_5)_3NCS$. In related triscyclopentadienyl uranium investigations, Fischer and Sienel (18) found that metathesis reactions of $U(C_5H_5)_3Cl$ also produced tetracyanonickelates and tetracyanoplatinates (equation (14)). These complexes were characterized by elemental analysis,

$$2U(C_5H_5)_3Cl + K_2M(CN)_4 \xrightarrow{H_2O} [U(C_5H_5)_3]_2M(CN)_4 + 2KCl \qquad (14)$$

$$M = Ni, Pt$$

infrared spectroscopy, and magnetochemical methods. A structure composed of networks of pseudo-trigonal bipyramidal $U(C_5H_5)_3{}^+$ units and bridging $M(CN)_4{}^=$ groups was proposed (Figure 4).

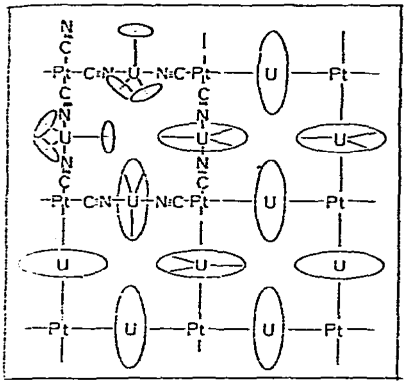
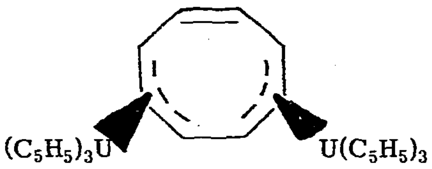


Fig. 4. Proposed structure of $[U(C_5H_5)_3]_2Pt(CN)_4$ from ref. 18.

Sienel, Spiegl, and Fischer (19) have also studied the reaction of $U(C_5H_5)Cl$ with cyclooctatetraene dianion. As illustrated in equation (15), the reaction

$$2U(C_5H_5)_3Cl + K_2C_8H_8 \xrightarrow[-30°]{THF} [U(C_5H_5)_3]_2C_8H_8 + 2KCl \qquad (15)$$

yields a thermally unstable organometallic containing two uranium moieties per cyclooctatetraene ligand. The complex loses cyclooctatetraene at 0° under high vacuum (the other product is not the known $U(C_5H_5)_3$). The proton nmr spectrum of $[U(C_5H_5)_3]_2C_8H_8$ exhibits two isotropically shifted singlets in a 30:8 ratio at all accessible temperatures. Based upon this evidence and infrared bands typical of metal-allyl interactions, a bisallyl structure such as that shown below was proposed. Evidently the $U(C_5H_5)_3$ units are executing



rapid motion about the eight-membered ring; such dynamic processes are not unexpected for uranium allyls (20) or cyclooctatetraene metal complexes (21).

Stutte and Schmid (22) have published metathesis chemistry of $U(C_5H_5)_3Cl$ which serves to incorporate uranium into a metal atom cluster (via an alkoxide linkage) as shown in equation (16). The new compound was charac-

$$U(C_5H_5)_3Cl + Li[OCCo_3(CO)_9] \xrightarrow{THF} U(C_5H_5)_3OCCo_3(CO)_9 + LiCl \qquad (16)$$

terized by the usual spectroscopic and analytical methods as well as by magnetic susceptibility measurements. The proposed structure for this molecule is shown in Figure 5 and features a common bonding arrangement for the tricobalt enneacarbonyl cluster (23).

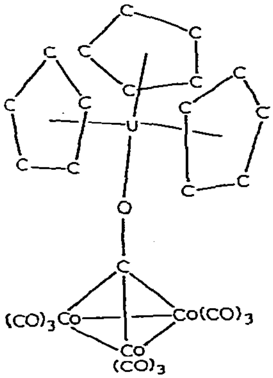


Fig. 5. Proposed structure for $U(C_5H_5)_3OCCo_3(CO)_9$ from ref. 22.

As noted in the lanthanide section, Dornberger, Klenze, and Kanellakopulos (16) used a new ammonium salt technique for displacing cyclopentadienyl ligands in f-element compounds. As illustrated by the examples of equation (17), this method appears to have very wide applicability. Work-up is particularly

$$An(C_5H_5)_4 + NH_4^+X^- \xrightarrow[\text{benzene}]{\text{THF or}} An(C_5H_5)_3X + C_5H_6 + NH_3 \tag{17}$$

An = Th, Pa, U, Np
$X^- = F^-, Cl^-, NO_3^-, ClO_4^-, B(C_6H_5)_4^-, ReO_4^-$

straightforward since C_5H_6 and NH_3 are both soluble and volatile; yields are generally high, sometimes quantitative. In the case of dinegative anions, binuclear complexes are produced (equation (18)). It was also possible to apply

$$An(C_5H_5)_4 + (NH_4^+)_2Y^= \xrightarrow{\text{THF}} [An(C_5H_5)_3]_2Y + 2C_5H_6 + 2NH_3 \tag{18}$$

An = U
$Y = SO_4^=, C_2O_4^=$

this procedure to trivalent actinides as shown in equation (19). In the case of

$$Th(C_5H_5)_3 + NH_4^+Cl^- \xrightarrow{\text{THF}} Th(C_5H_5)_2Cl + C_5H_6 + NH_3 \tag{19}$$

U(IV), excess $NH_4^+B(C_6H_5)_4^-$ produced the interesting new complex $U[B(C_6H_5)_4]_4$ (equation (20)). All new compounds were characterized by elemental analysis,

$$U(C_5H_5)_4 + 4NH_4^+B(C_6H_5)_4^- \xrightarrow{\text{THF}} U[B(C_6H_5)_4]_4 + 4C_5H_6 + 4NH_3 \tag{20}$$

ir and electronic absorption spectroscopy, and by magnetic susceptibility.

The bonding in $U(C_5H_5)_3X$ compounds continues to be of interest, and Aderhold, Baumgärtner, Dornberger, and Kanellakopulos (24) have conducted an extremely detailed study (1-300°K over a range of magnetic field strengths) of the magnetic susceptibility of UX_4 and $U(C_5H_5)_3X$ complexes where X = F, Cl, Br, I. In agreement with crystal field calculations, all eight compounds were found to have a maximum of three cyrstal field levels populated at room temperature. Electronic absorption spectra recorded at 77°K were used to assign crystal field levels at higher energies. It was concluded that the nature of X has a very strong influence on the crystal field in $U(C_5H_5)_3X$ compounds.

Bagnall, Edwards, and Tempest (25) have published a detailed study of the coordination chemistry of $U(C_5H_5)Cl_3$ and $U(C_5H_5)Br_3$ with oxygen-donor ligands. Complexes prepared were of the type $U(C_5H_5)X_3L_2$, X = Cl or Br, L = $(C_6H_5)_3PO$ or $(CH_3)_3CCON(CH_3)_2$; $U(C_5H_5)Cl_3L_2$, L = N,N-dimethylacetamide; and $[U(C_5H_5)X_3L]_2$, X = Cl or Br, L = $(C_6H_5)_2P(O)CH_2CH_2P(O)(C_6H_5)_2$. Synthetic routes to these compounds are shown in equations (21) and (22). Products were

$$U(C_5H_5)X_3(THF)_2 \xrightarrow[THF]{L} U(C_5H_5)X_3L_2 \qquad (21)$$

$$UX_4L_2 + Tl(C_5H_5) \xrightarrow{THF} U(C_5H_5)X_3L_2 + TlX \qquad (22)$$

characterized by the usual chemical and spectral procedures. Reaction of the $U(C_5H_5)X_3L_2$ complexes with one equivalent of $Tl(C_5H_5)$ or $Tl(CH_3C_5H_4)$ yielded mixtures which appear to be principally comprised of $U(C_5H_5)_3X$ (or $U(C_5H_5)(CH_3C_5H_4)_2X$) and $U(C_5H_5)X_3L_2$ (or $U(CH_3C_5H_4)X_3L_2$) compounds. The instability of $U(C_5H_5)_2X_2$ compounds with respect to ligand redistribution has been noted previously (26). The only stable uranium biscyclopentadienyl species which could be prepared by $Tl(C_5H_5)/X$ substitution was of the type $[U(C_5H_5)_2X_2L]_2$ where L was the bidentate ligand, $(C_6H_5)_2P(O)CH_2CH_2P(O)(C_6H_5)_2$. The lability of the cyclopentadienyl ligands in $U(C_5H_5)_3X$ compounds was demonstrated by the surprising redistribution reaction shown in equation (23).

$$U(C_5H_5)_3Cl + 2UCl_4[(C_6H_5)_3PO]_2 + 2(C_6H_5)_3PO \rightleftharpoons 3U(C_5H_5)Cl_3[(C_6H_5)_3PO]_2 \qquad (23)$$

A complementary structural study of an $U(C_5H_5)Cl_3L_2$ compound has been carried out by Bombieri, de Paoli, Del Prà, and Bagnall (27). As can be seen in Figure 6, the geometry about the uranium ion in $U(C_5H_5)Cl_3[(C_6H_5)_3PO]_2$

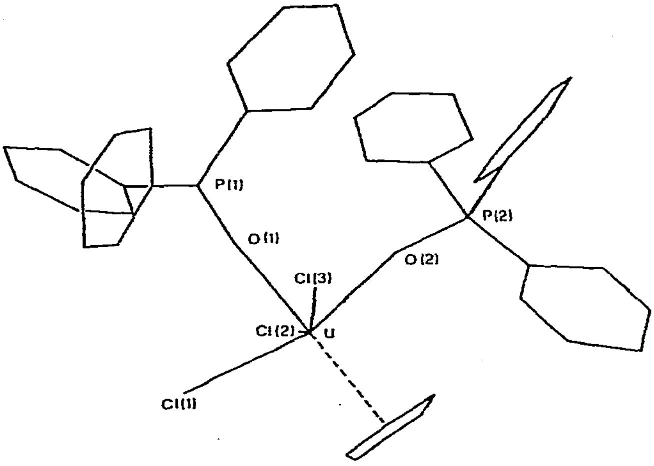


Fig. 6. The molecular structure of $U(C_5H_5)Cl_3[(C_6H_5)_3PO]_2$ from ref. 27.

is approximately pseudo-octahedral, with the angles Cl(1)-U-Cl(2) = 91.2(3)°, Cl(1)-U-Cl(3) = 94.6(3)°, Cl(1)-U-Cl(2) = 162.3(5)°, Cl(2)-U-O(2) = 81.3(5)°, Cl(2)-U-Cl(3) = 158.8(3)°, Cl(1)-U-O(1) = 81.8(5)°, Cl(2)-U-O(1) = 81.1(5)°, and Cl(3)-U-O(1) = 79.5(5)°. From these data it is evident that the four "equatorial" ligands, Cl(1), Cl(2), Cl(3), and O(2), bend away from the pentahaptocyclopentadienyl ligand. A similar structure was observed for $U(CH_3C_5H_4)Cl_3(THF)_2$ (28). In the present case, the U-O distances were 2.28(2) (O(1))and 2.33(2) Å (O(2)), and the U-Cl distances were 2.653(6) (Cl(1)), 2.654(7) (Cl(2)), and 2.668(7) Å (Cl(3)).

In the area of modified cyclopentadienyl ligands, Goffart and Duyckaerts (29) have extended the indenyl chemistry of thorium and uranium by synthesizing the trisindenyl iodides (equation (24)). The extremely oxygen and moisture

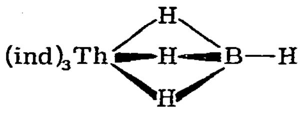
$$3M(ind) + AnI_4 \xrightarrow{THF} An(ind)_3I + 3MI \qquad (24)$$

M = Na, K
An = Th, U

sensitive new organometallics were characterized by elemental analysis as well as by ir, nmr, and mass spectroscopy. Further studies by Goffart, Michel, Gilbert, and Duyckaerts (30) have centered on trisindenyl tetrahydroborate complexes. Thus, reaction of $Th(ind)_3Cl$ with $NaBH_4$ (or $NaBD_4$) as given in equation (25) yields the corresponding tetrahydroborate (or

$$Th(ind)_3Cl + NaBH_4 \xrightarrow[\text{reflux 10 days}]{THF} Th(ind)_3BH_4 + NaCl \qquad (25)$$

tetradeuteroborate) complex. This substitution reaction failed in the case of $U(ind)_3Cl$ and only $U(ind)_3(THF)$ was obtained. The infrared and Raman spectra of $Th(ind)_3BH_4$ and $Th(ind)_3BD_4$ were assigned, and it was concluded that the tetrahydroborate ligand was bound in a tridentate (31) fashion as depicted below.



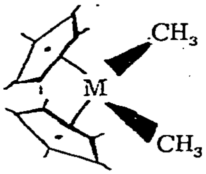
The chemistry of peralkylcyclopentadienyl (R_5C_5) actinide organometallics continued to expand in 1978. Manriguez, Fagan, and Marks (32) have communicated the synthesis and properties of bis(pentamethylcyclopentadienyl) actinide dichlorides and dimethyls. These new compounds were prepared in high yield via the procedure of equations (26) and (27); they were characterized by elemental analysis, cryoscopic molecular weight measurements, and by infrared and ^1H nmr spectroscopy. Interestingly, it was not possible to introduce greater than two pentamethylcyclopentadienyl rings through the procedure of equation(26). This observation stands in contrast to results for C_5H_5 and appears to reflect the strong steric influence of the five ring methyl substituents. The structure given below was proposed for the methyl compounds.

$$MCl_4 + 2\,(CH_3)_5C_5^- \xrightarrow{\text{toluene}} M[(CH_3)_5C_5]_2Cl_2 + 2Cl^- \qquad (26)$$

$$M[(CH_3)_5C_5]_2Cl_2 + 2CH_3Li \longrightarrow M[(CH_3)_5C_5]_2(CH_3)_2 + 2LiCl \qquad (27)$$

M = Th, U

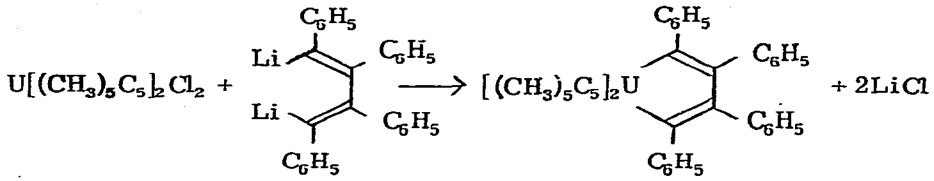
These metal-to-carbon sigma bonded organometallics are the most thermally stable actinide polyalkyls prepared to date. Half-lives in toluene solution at 100° C are ca. 1 week (M=Th) and ca. 16 hr. (M=U). The mixed chloroalkyls can be prepared by ligand redistribution (equation (28)), and a metallocycle can be synthesized as indicated in equation (29). The bis(pentamethylcyclopentadienyl) thorium and uranium dimethyls are extraordinarily reactive. They



M = Th, U

$$M[(CH_3)_5C_5]_2Cl_2 + M[(CH_3)_5C_5]_2(CH_3)_2 \xrightarrow[\text{temp.}]{\text{toluene}}_{\text{room}} 2M[(CH_3)_5C_5]_2(Cl)CH_3 \qquad (28)$$

M = Th, U

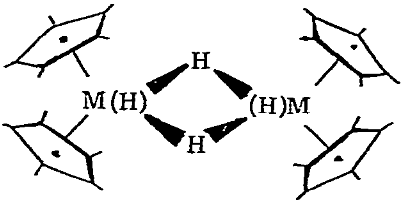


(29)

react rapidly with hydrogen gas at 1 atm. to yield the first organoactinide hydrides (equation (30)). The thorium derivative is thermally stable for prolonged periods at 80° C, however the uranium dihydride reversibly loses a mole of H_2 (per two uranium atoms). On the basis of molecular weight measurements and vibrational spectra (including studies with analogous compounds prepared using D_2) a dimeric structure with both bridge and terminal hydrogen atoms was proposed (see below). The hydridic nature of these new compounds is evidenced by the rapid and quantitative reduction of methyl chloride (equation (31)).

$$2M[(CH_3)_5C_5]_2(CH_3)_2 + 4H_2 \xrightarrow[\text{room temperature}]{\text{toluene}} \{M[(CH_3)_5C_5]_2H_2\}_2 + 4CH_4 \qquad (30)$$

M = Th, U



M = Th, U

$$\{M[(CH_3)_5C_5]_2H_2\}_2 + 4CH_3Cl \longrightarrow 2M[(CH_3)_5C_5]_2Cl_2 + 4CH_4 \qquad (31)$$

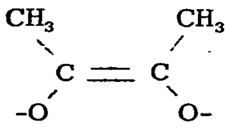
M = Th, U

In further work, Manriquez, Fagan, Marks, Day, and Day (33) have described the carbonylation chemistry of bis(pentamethylcyclopentadienyl) actinide alkyls. Migratory insertion of carbon monoxide has never been observed for an actinide-to-carbon sigma bond. Thus, it was noted with great surprise that the bis(pentamethylcyclopentadienyl) thorium and uranium dimethyls rapidly reacted with carbon monoxide according to equation (32). On the basis of infrared and ^1H nmr

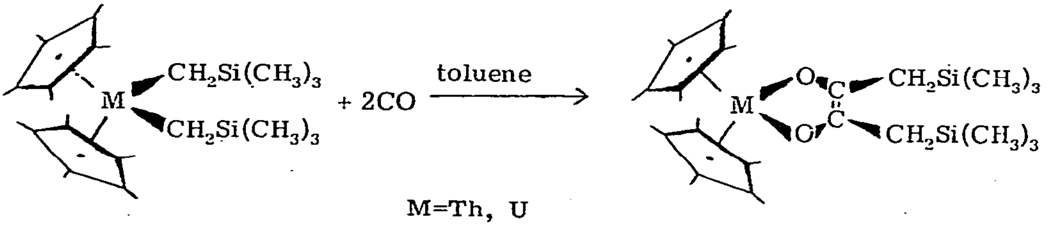
$$2M[(CH_3)_5C_5]_2(CH_3)_2 + 4CO \xrightarrow{\text{toluene}} \{M[(CH_3)_5C_5]_2(OC(CH_3){=}C(CH_3)O)\}_2 \qquad (32)$$

M=Th, U

spectroscopy, the presence of the cis-2-butene-2,3-diolate ligand (34) shown below could be clearly identified; molecular weight measurements indicated



that the carbonylation products were dimers. The actual molecular structure of the thorium compound was elucidated by a single crystal X-ray diffraction study, which revealed the molecular geometry shown in Figure 7. The overall molecular symmetry approximates C_{2h} with the two thorium atoms displaced by 0.59 Å above and below the otherwise planar (to within 0.01 Å) ten-atom metallocycle. The average Th-C distance was found to be 2.845(13)Å and the average Th-O distance, 2.154(8)Å. The course of the carbonylation reaction can be modified by the presence of bulky alkyl groups (equation (33)). Furthermore,



(33)

M=Th, U

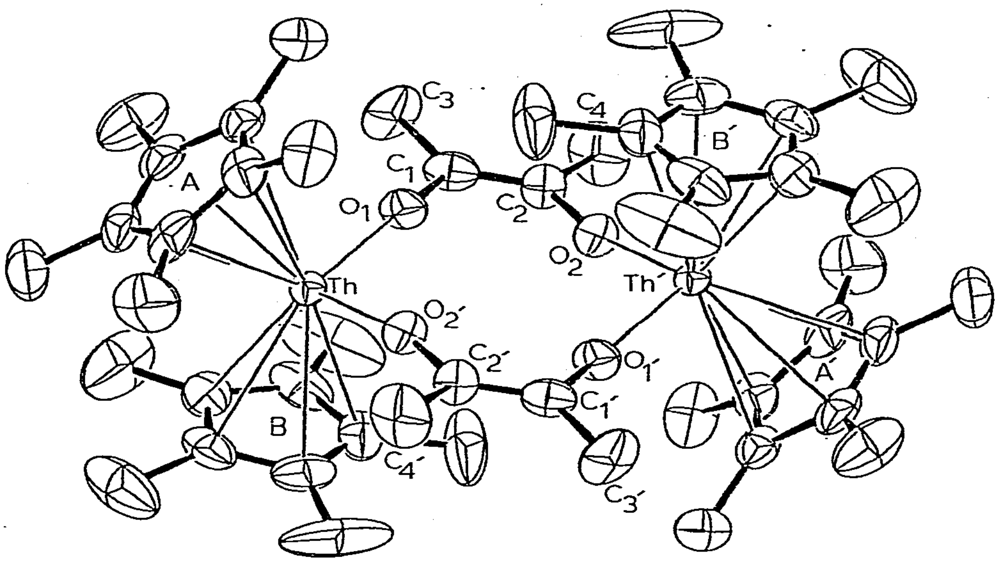
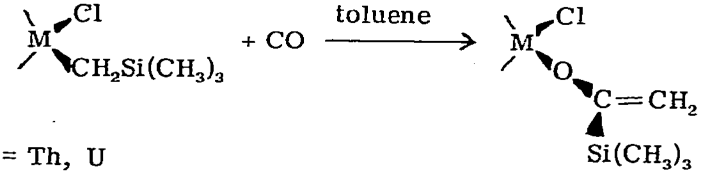


Figure 7. The molecular structure of $\{Th[(CH_3)_5C_5]_2[\mu\text{-}O_2C_2(CH_3)_2]\}_2$ from ref. 33.

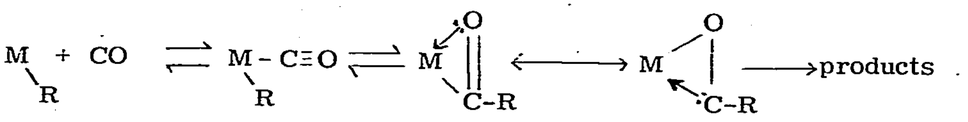
the carbonylation of the chlorotrimethylsilylmethyl derivative yields a trimethysilyl rearrangement product, as shown in equation (34). This result is strongly suggestive of alkoxycarbene rearrangement chemistry. The scheme



(34)

M = Th, U

below was proposed to explain the unusual CO insertion chemistry observed in the present case (and in several early transition metal systems as well (34,35)).



M = Th, U

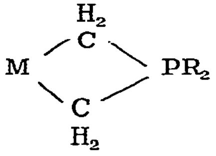
Central to this description is the hypothesis that sufficient metal ion coordinative unsaturation and oxygen affinity can produce bihaptoacyl species with carbene-like reactivity. An important observation that derives from the sum total of the new bis(pentamethylcyclopentadienyl) actinide work is that the organometallic chemistry of the actinides is far more like the early transition metals than heretofore supposed. A significant difference, however, is that given exactly the same ligands, the organoactinides appear to be far more reactive.

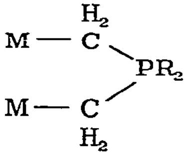
A bis(tetramethylethylcyclopentadienyl) uranium compound has been communicated by Green and Watts (36). Uranium tetrachloride was reacted with an excess of the cyclopentadienyl tin reagent to yield the corresponding uranium dichloride (equation (35)) as dark red crystals. Under the same conditions,

$$2Sn(C_4H_9)_3[(CH_3)_4(C_2H_5)C_5] + UCl_4 \xrightarrow{toluene} U[(CH_3)_4(C_2H_5)C_5]_2Cl_2 + 2Sn(C_4H_9)_3Cl \qquad (35)$$

$Sn(C_4H_9)_3C_5H_5$ yielded $U(C_5H_5)_3Cl$, illustrating the marked steric bulk of the cyclopentadienyl substituents. Both ^1H nmr and uv photoelectron data were reported for $U[(CH_3)_4(C_2H_5)C_5]_2Cl_2$.

Phosphorus ylides have an extensive organotransition metal chemistry (37), and have also been found to form complexes with lanthanides (38). Typical structures for the metal-ligand interaction are shown below. Cramer, Maynard, and Gilje (39) have now extended phosphorus ylide chemistry to organoactinides. Thus, the reaction of $U(C_5H_5)_3Cl$ with $Li(CH_2)_2P(C_6H_5)_2$ appears to proceed as shown in equation (36).





$$2U(C_5H_5)_3Cl + 4Li(CH_2)_2P(C_6H_5)_2 \xrightarrow{ether} \{U[\mu\text{-}(CH)(CH_2)P(C_6H_5)_2](C_5H_5)_2\}_2 + 2Li(C_5H_5) + 2CH_2P(CH_3)(C_6H_5)_2 \qquad (36)$$

The major organometallic product of this reaction was characterized by single crystal X-ray diffraction and the interesting result is illustrated in

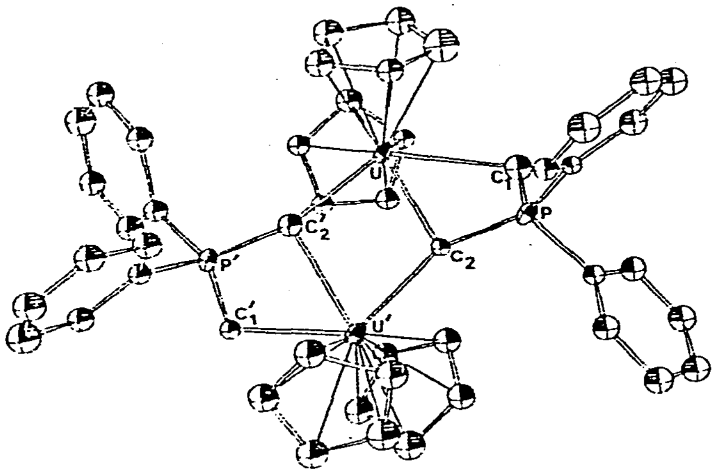


Figure 8. The molecular structure of $\{U[u\text{-}(CH)(CH_2)P(C_6H_5)_2](C_5H_5)_2\}_2$ from ref. 39.

Figure 8. An unusual dimeric structure of approximate C_2 symmetry is found, with two biscyclopentadienyl uranium units bridged by two apparently deprotonated (assuming U(IV)) ylide moieties. The coordination geometry about the uranium ions is highly distorted square-pyramidal with $\sphericalangle C_2\text{-}U\text{-}C_2' = 69(1)^\circ$ and $\sphericalangle C_1\text{-}U\text{-}C_2' = 130(1)^\circ$. Uranium-to-ylide carbon atom distances were found to be 2.66(4)Å ($U\text{-}C_1$) and 2.52(4)Å ($U\text{-}C_2$). The U-U distance of 3.810(2)Å suggests little metal-metal interaction when compared with a U-U distance of 3.12 Å in uranium metal.

The year 1978 also saw considerable progress in the area of actinide cyclooctatetraene complexes. Butcher, Chambers, and Pagni (40) have conducted an electrochemical study of uranocene ($U(C_8H_8)_2$). They find evidence upon oxidation for a uranocene cation (equation (37)). This species is unstable, however, and quasi-reversible cyclic voltammograms could only

$$U(C_8H_8)_2 \underset{}{\overset{-e^-}{\rightleftarrows}} U(C_8H_8)_2^+ \longrightarrow \text{products} \qquad (37)$$

be observed at subambient temperatures. Controlled potential electrolyses produce an air-stable solution of what may be a cluster complex such as $U_2(C_8H_8)_3^{+3}$. It could not be isolated in a pure state.

Grant and Streitwieser (41) have now published a detailed study of the reaction of uranocene (or substituted uranocenes) with organic nitro compounds to produce azo compounds (equation (38)). This deoxygenation reaction occurs

$$2U(C_8H_7R)_2 + 2R'NO_2 \xrightarrow{THF} R'\text{-}N{=}N\text{-}R' + 2UO_2 + 4C_8H_7R \tag{38}$$

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

rapidly with aromatic and aliphatic nitro compounds to produce the corresponding azo compounds in moderate to high yields. In several cases the amine, RNH_2, was also produced in appreciable quantities; the source of the hydrogen atoms appears to be the solvent. A number of well chosen mechanistic experiments strongly argue that the deoxygenation does not take place via free nitrene (R-N:) intermediates; also, direct electron transfer to form a nitro radical anion ($R\text{-}NO_2^{\cdot-}$) could be reasonably ruled out. Rather, it appears that the initial step of the transformation involves direct attack by a nitro oxygen atom at the uranium center. That nitrobenzene reacts more rapidly than 4-nitrotoluene (a Hammett ρ value of -1.7 was calculated) supports the idea that the nitro compound is being reduced in the transition state. The result of this initial reduction reaction was proposed to be a nitroso compound, R-NO, which was already known to be deoxygenated by uranocene to yield the corresponding azo compound. Azoxy compounds, RN(O)=NR, were shown to react only slowly with dibutyluranocene and could be ruled out as important intermediates.

Rösch and Streitwieser (42) have reported molecular orbital calculations on thorocene and uranocene. The treatment was at the SCF-Xα scattered wave level without incorporation of relativistic effects. The molecular orbital energy level schemes obtained are in good agreement with photoelectron spectroscopic data and are illustrated in Figure 9. It is evident in the results of the calculations that there is substantial interaction between the ring e_{2u} π molecular orbitals and the actinide $5f_{xyz}$ and $5f_{z(x^2-y^2)}$ ($l_z = \pm 2$) orbitals, as originally proposed for the bonding in these compounds. Less expected (but noted previously in photoelectron spectra (43)) was an equally strong interaction between the ring e_{2g} π molecular orbitals and the metal $6d_{xy}$ and $6d_{x^2-y^2}$ orbitals. The smaller energetic separation of the e_{2u} and e_{2g} molecular orbitals in uranocene as compared to thorocene was attributed to greater f orbital covalency in the former compound. Some shifting of the relative energies of the 6d and 5f orbitals is expected when relativistic corrections to the calculations are made (44).

Considerable debate has centered around the symmetry of the electronic ground state in uranocene. Different research groups have preferred, on the

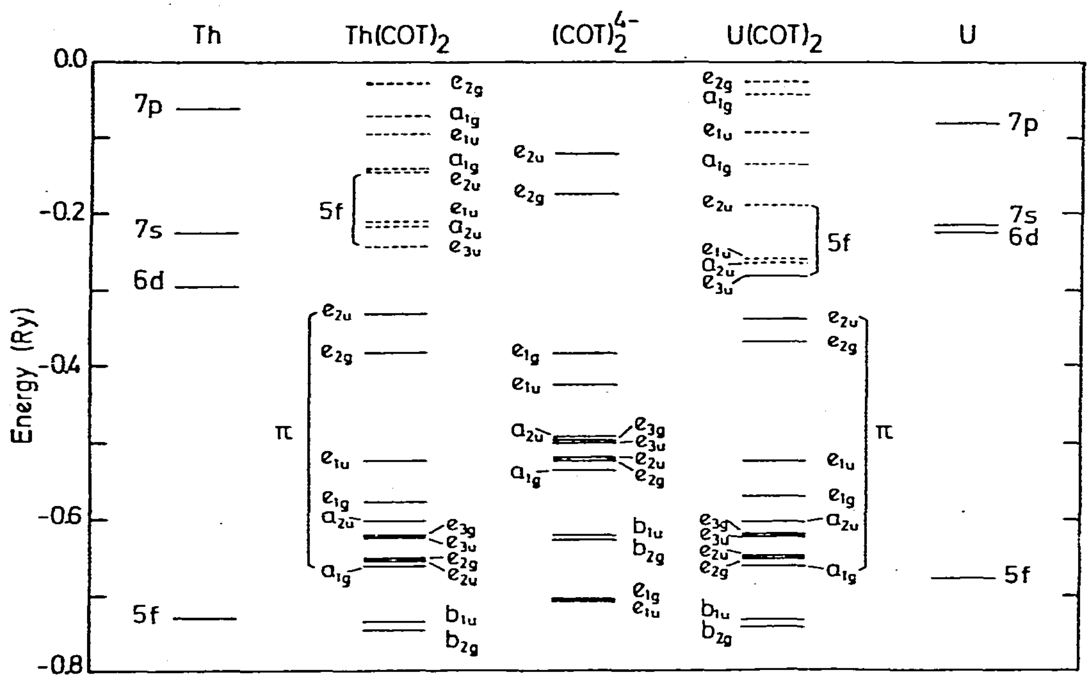
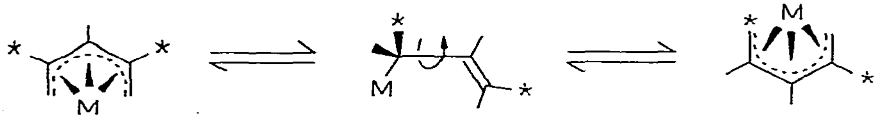


Figure 9. Molecular orbital energy level diagrams for thorocene, uranocene, and the two $C_8H_8^{=}$ ligands minus the metal ion. Unoccupied orbitals are indicated by dashed lines. From ref. 42.

basis of magnetic susceptibility studies as well as crystal field and molecular orbital calculations, either a $J_z = 0$ or a $J_z = \pm 3$ ground state of the $5f^2\ {}^3H_4$ manifold (45, 46) (in a crystal field description). Now Dallinger, Stein, and Spiro (47) have reported dye laser excited Raman experiments on uranocene (and perdeuterouranocene) which provide new information. The ring-metal stretching (211 cm^{-1}) and ring-breathing (754 cm^{-1}) modes were clearly identified in the resonance-enhanced spectra. More importantly, an anomalously polarized ($\rho_l > 0.75$) band was observed at 466 cm^{-1} which could be assigned to an electronic Raman transition (i.e. scattering involving a transition between electronic energy levels). Such transitions have been previously observed in solid lanthanide complexes (48). On the basis of circular polarization experiments and consideration of the electronic Raman selection rules, it was concluded that this band must involve a $\Delta J_z = \pm 1$ transition. Combining this conclusion with the existing magnetic susceptibility data, the authors were able to demonstrate that the most reasonable electronic structural description for uranocene is a $J_z = \pm 4$ ground state and a $J_z = \pm 3$ excited state lying 466 cm^{-1} above.

Allyl uranium compounds are known to be efficient catalysts or cocatalysts for diene polymerization (49). Khvostik, Sokolov, and Kondratenkov (50) have conducted an ^{1}H nmr investigation of the effect of adding 1,3-butadiene, isoprene, and tributylphosphate to tetraallyl uranium. It was found that the addition of both butadiene and isoprene caused substantial broadening of the multiplets in the A_2B_2X spectrum of the uranium compounds. These substrates also caused a change in the temperature dependence of the isotropic (due to the paramagnetism) chemical shifts. This led to the conclusion that the dienes are complexed by U(allyl)$_4$ and rapidly exchange with free diene. Addition of tributylphosphate causes complete collapse of the allyl spectral multiplets and coalescence to a single broad line. This is indicative of rapid syn-anti proton exchange and presumably involves a monohapto allyl intermediate (51) as shown below.



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