LANTHANIDES AND ACTINIDES

ANNUAL SURVEY COVERING THE YEAR 1976

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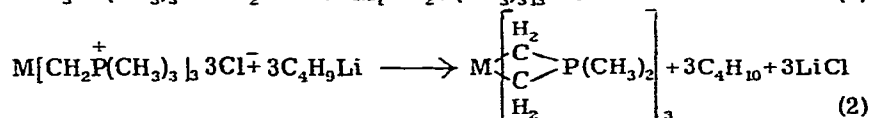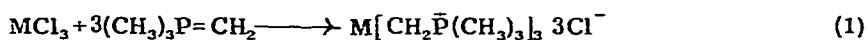
Evanston, Illinois 60201

General

Baker, Halstead, and Raymond (1) have published an extensive review article on the structural chemistry of lanthanide and actinide organometallics. They conclude that the properties of many of these complexes suggest bonding intermediate between the high covalency of transition metal organometallics and the ionicity of alkali metal organometallics. No effect analogous to a noble gas formalism appears operative. The observed molecular structures frequently represent a compromise between ligand-ligand nonbonded repulsions and the tendency of the metal ion to achieve a maximum coordination number. Variations in metal-ligand bond lengths as well as observed coordination numbers are largely attributable to changes in metal ionic radius. Tsutsui, Ely, and Dubois (2) have written a review of sigma-bonded f-element organometallics which presents their current views on structure and bonding. Two review articles by Marks (3,4) have appeared on organoactinide chemistry. The former article (3) deals with the relationship of organoactinide electronic configuration and coordination geometry to molecular

reactivity. Metal ion electronic configuration appears to exert the greatest influence on those transformations of actinide organometallics which involve formal changes in oxidation state (e.g. oxidative addition, reductive elimination). Coordination pattern in the form of ligational saturation or immobilization plays a major role in thwarting such processes as β-hydride elimination, which requires expansion of the metal ion coordination sphere. The second review article (4) presents a discussion of the chemistry and spectroscopy of organoactinide sigma-bonded, tetrahydroborato, and modified cyclopentadienyl systems.

Lanthanides

Schumann and Hohmann have reported the first synthesis of a series of uncharged homoleptic lanthanide alkyls (5). These highly air-sensitive complexes apparently owe their high thermal stability to the incorporation of chelating phosphorus ylide ligands. The synthetic procedure for these compounds is shown in equations (1) and (2).
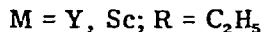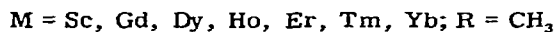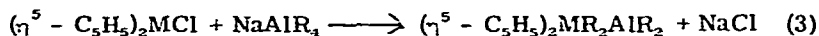
$$MCl_3 + 3(CH_3)_3P = CH_2 \longrightarrow M[CH_2\overset{+}{P}(CH_3)_3]_3\ 3Cl^- \tag{1}$$

$$M[CH_2\overset{+}{P}(CH_3)_3]_3\ 3Cl^- + 3C_4H_9Li \longrightarrow M\left\{\begin{matrix}H_2\\C\\C\\H_2\end{matrix}\hspace{-0.3em}>P(CH_3)_2\right\}_3 + 3C_4H_{10} + 3LiCl \tag{2}$$

M = La, Pr, Nd, Sm, Gd, Ho, Er, Lu.

These complexes are found to be monomeric in benzene solution.

Holton, Lappert, Scollary, Ballard, Pearce, Atwood, and Hunter(6) have communicated synthetic and structural results on an interesting series of inner transition metal (Sc, Y, lanthanide) tetraalkylaluminates, $(\eta^5 - C_5H_5)_2M(\mu - R)_2AlR_2$. The syntheses of these complexes, which con-

tain bridging alkyl groups, are given in eq. (3). The new compounds were

$$(\eta^5 - C_5H_5)_2MCl + NaAlR_4 \longrightarrow (\eta^5 - C_5H_5)_2MR_2AlR_2 + NaCl \quad (3)$$

$$M = Sc, Gd, Dy, Ho, Er, Tm, Yb; R = CH_3$$

$$M = Y, Sc; R = C_2H_5$$

characterized by standard chemical and spectroscopic techniques. ^{1}H and ^{13}C nmr studies reveal the diamagnetic Y complex to be fluxional at room temperature, undergoing rapid bridge-terminal R group exchange. The Sc complex, on the other hand, is rigid in this temperature range. The molecular geometries of the isostructural M = Y, R = CH$_3$ and M = Yb, R = CH$_3$ complexes were determined by X-ray diffraction and are illustrated in Figure 1. The geo-

metrical parameters for the two complexes are nearly identical, with M – Al distances (Yb in brackets, standard deviations in parentheses) of 3.056(2) [3.03 (4)] Å, Al – C(1) of 2.08(4)[2.02(4)] Å, Al · C(2) of 2.11(4)[2.24(4)] Å, M – C(1) of 2.56(2)[2.53(4)] Å, and M – C(2) of 2.60 (2)[2.58(4)] Å. The aluminum to terminal carbon distances are shorter than to the bridging carbons, with Al – C(3) = 1.90 (4)] Å and Al – C(4) = 1.97 (4)[1.94(4)] Å. The valence angles around aluminum are essentially tetrahedral. The average M-C-Al bridging angle is ca. 80(1)°. The above parameters can be compared with an Al-C (average) of 2.125Å and an ⟨ Al-C-Al (average) of 75.7° in [Al(CH$_3$)$_3$]$_2$ (7). Additional structural details for the Y and Yb compounds are ⟨ C(1)-M-C(2) = 85(1) [87(1)]° and average M – C (ring) = 2.62(2)[2.63 (4)] Å.

In a subsequent, related communication, Holton, Lappert, Ballard, Pearce, Atwood, and Hunter (8) have reported that the above tetraalkyl-
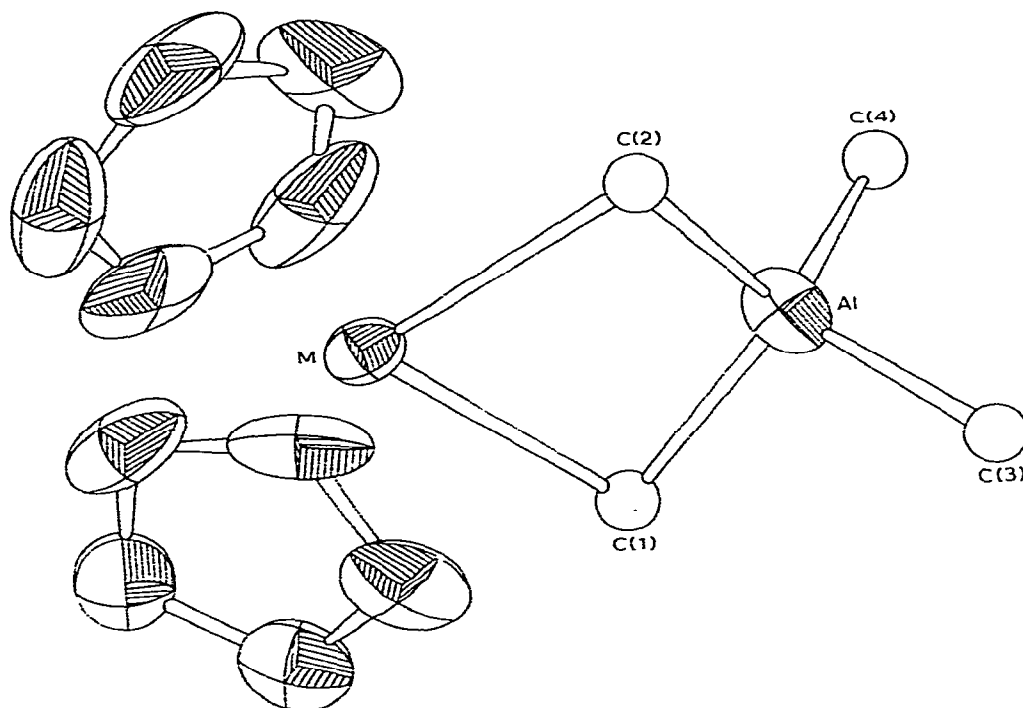
Figure 1. The molecular structures of $(C_5H_5)_2M(CH_3)_2Al(CH_3)_2$, M = Y, and Yb, from ref. 6.

aluminates can be used to synthesize biscyclopentadienyl lanthanide alkyls in high yield [eq. (4)]. Several of these compounds had

$$(C_5H_5)_2M(CH_3)_2Al(CH_3)_2 + \text{pyridine} \longrightarrow (C_5H_5)_2MCH_3 + (CH_3)_3Al\cdot\text{pyridine} \quad (4)$$

$$M = Y, \ Dy, \ Ho, \ Er, \ Yb$$

previously been synthesized from the corresponding biscyclopentadienyl lanthanide chlorides and alkyl lithium reagents (9). An equally important part of the present communication was the report of the molecular structure of $(\eta^5 - C_5H_5)_2YbCH_3$. In surprising contrast to the original formulation, this complex is actually a dimer with unique bridging alkyl groups as shown in Figure 2. Important structural
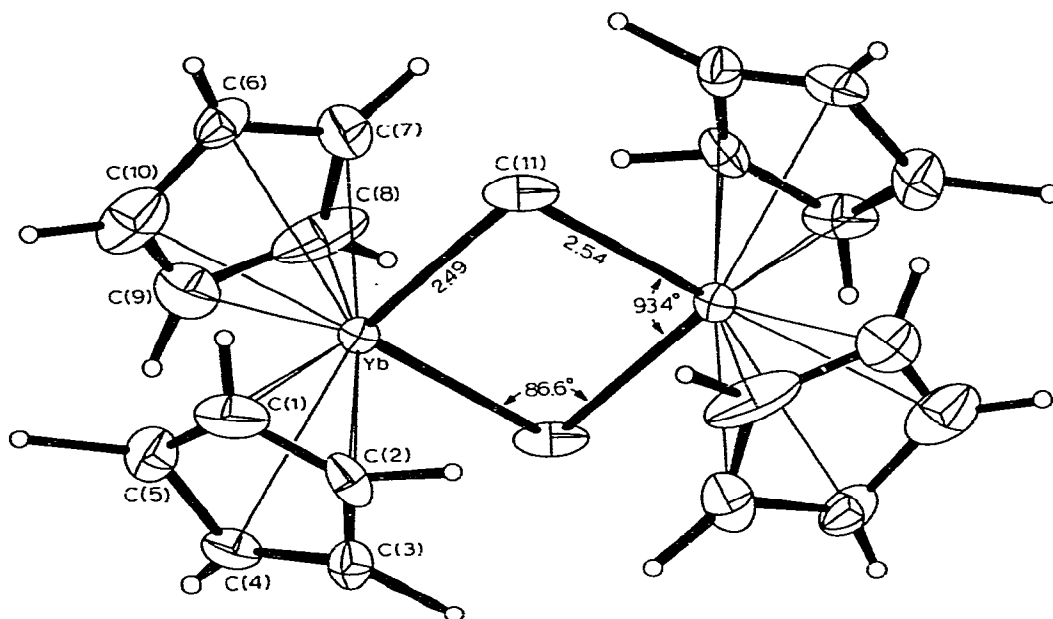
Figure 2. The molecular structure of $[(C_5H_5)_2Yb(CH_3)]_2$ from ref. 8.

parameters in the centrosymmetric dimer are, Yb – C = 2.49 and 2.54 Å, C(bridge) – Yb – C(bridge) = 93.4°, and Yb – C(bridge) – Yb = 86.6°. The average Yb – C(ring) distance was reported to be 2.613(13) Å. The over-all molecular geometry is reminiscent of that found in $[(\eta^5 - C_5H_5)_2YbCl]_2$ (10).

In another important contribution to the chemistry of sigma-bonded lanthanide organometallics, Deacon and Vince (11) reported the synthesis of the first pentafluorophenyl complex. The preparative procedure is shown in eq. (5).

$$Yb + (C_6F_5)_2Hg \xrightarrow{THF} (C_6F_5)_2Yb \cdot 4THF + Hg \tag{5}$$
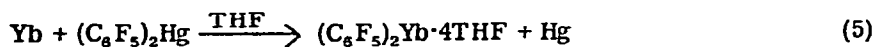
The highly air-sensitive divalent ytterbium complex is isolated as orange

crystals which are stable at room temperature for only short periods of time.

Ely, Hopkins, and DeKock (12) have used the promising new technique of metal atom vapor synthesis to prepare the novel neodymium complex [Nd(COT)(THF)$_2$][Nd(COT)$_2$], where COT = cyclooctatetraene. Nd atoms, generated by vaporizing the metal, were condensed with cyclooctatetraene at -196° C. The crude product was Soxhlet extracted with THF to yield green crystals. The molecular structure, determined by X-ray diffraction, is presented in Figure 3. It can best be
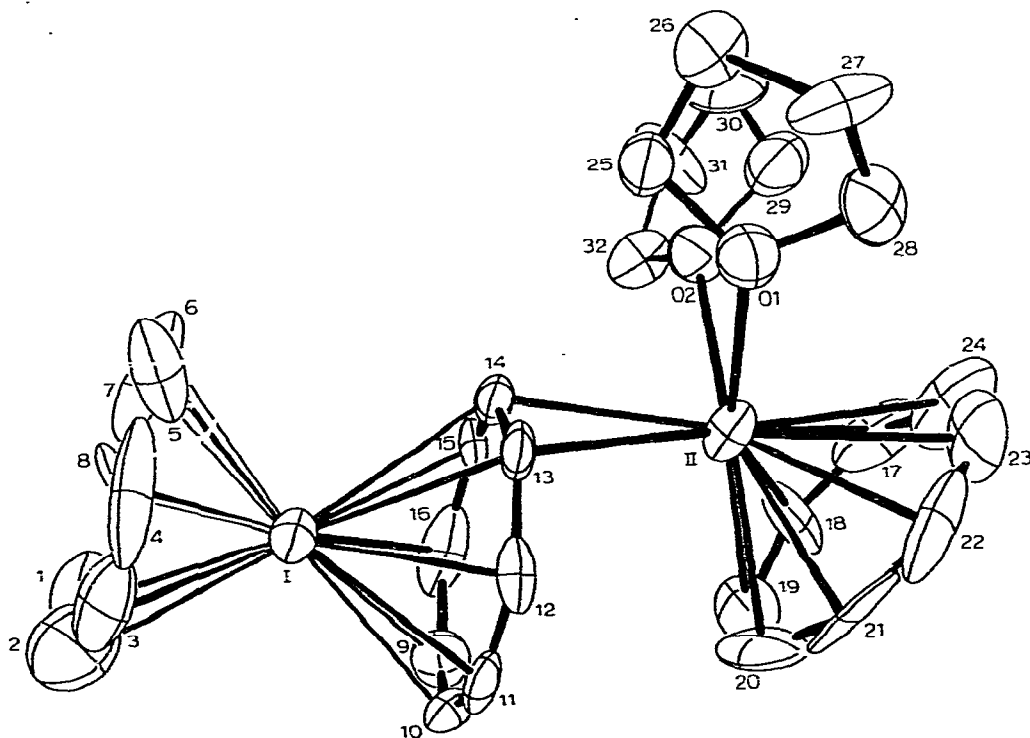

Figure 3. The structure of (Nd(C$_8$H$_8$)(THF)$_2$][Nd(C$_8$H$_8$)$_2$] from ref. 12.

described as a $Nd(COT)_2^-$ (13) anion coordinated by a $Nd(COT)(THF)_2^+$ cation. The average Nd – C distance involving the ring with carbon atoms 1-8 is 2.660(24) Å, while that for Nd(I) and carbon atoms 9–15 is 2.787 (19) Å. The average distance from Nd(II) to carbon atoms 17–24 is 2.673 (16) Å, and to the THF oxygen atoms is 2.577 (11) Å. An unusual trihapto bridging interaction between Nd(II) and carbon atoms 13, 14, and 15 is indicated by distances of 2.896(20), 2.700(18), and 3.059(19) Å, respectively. This type of interaction is similar to that observed in lanthanide triscyclopentadienyls and suggests considerable ionic character in the bonding (1, 13).

It has been known for some time that triscyclopentadienyl lanthanide complexes form adducts with Lewis bases (14), however the molecular structures of the adducts have not been well defined. Burns and Baldwin (15) have now reported an X-ray diffraction study of the cyclohexyliso-cyanide derivative of $(\eta^5 - C_5H_5)_3Pr$. The result of this structure determination is presented in Figure 4. The immediate coordination geometry about the praseodymium ion is similar to that found for $(\eta^5 - C_5H_5)_3UX$ complexes (1), with the average ring centroid-Pr-ring centroid angle being 118.9 (1)°, which can be compared to 117 (1.3)° in $(\eta^5 - C_5H_5)_3UC_2C_6H_5(1)$. The same angle in the tetrameric $(CH_3C_5H_4)_3Nd$ is 117.4(1)°(13). The average Pr–C(ring) distance in the present structure is 2.78(1) Å, and the Pr–C(isocyanide) distance is 2.65(1) Å. The Pr–C-N angle is found to be 174.1(1.1)°. The cyclo-hexyl ring appears to be curiously flattened from the normal chair conformation; this may be the result of disorder about the C-N-C(cyclo-hexyl axis.
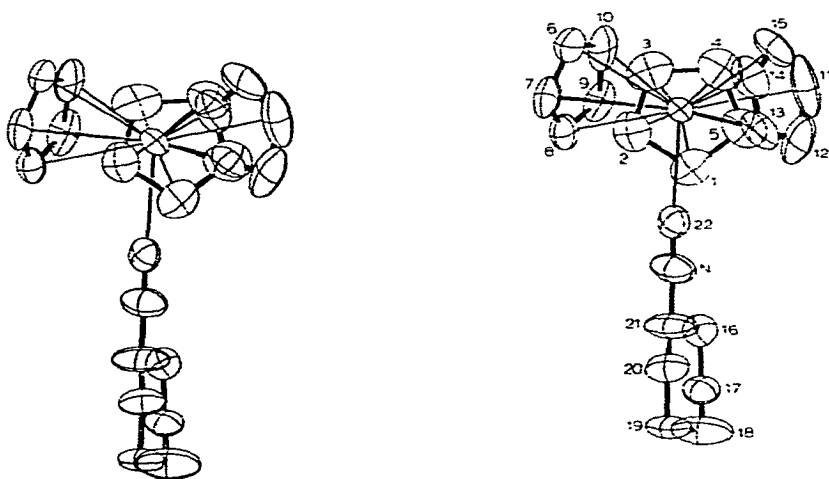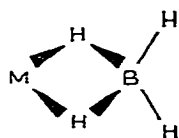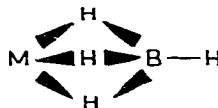
Figure 4. Stereoscopic view of the structure of $(C_5H_5)_3PrCNC_6H_{11}$ from ref. 15.

Marks and Grynkewich (16) have employed the lanthanide contraction to determine whether the mode of metal-tetrahydroborate (17) bonding (bidentate or tridentate) varies with metal ionic radius.
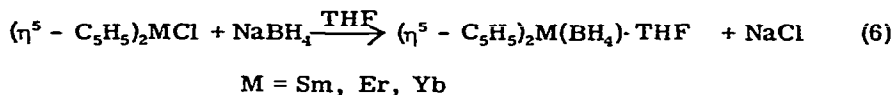

bidentate

tridentate

A series of organolanthanide tetrahydroborates, synthesized as shown in eq. (6), was studied by vibrational spectroscopy in the solid state and in solution.

$$(\eta^5 - C_5H_5)_2MCl + NaBH_4 \xrightarrow{\text{THF}} (\eta^5 - C_5H_5)_2M(BH_4) \cdot THF + NaCl \qquad (6)$$

$$M = Sm, \ Er, \ Yb$$

For M = Sm, tridentate $\overset{\bullet}{BH_4}{}^-$ coordination was assigned, whereas the complex of the smaller M = Yb ion was assigned bidentate ligation. For M = Er and Yb the THF can be removed by heating in vacuo (eq. (7)). Vibrational
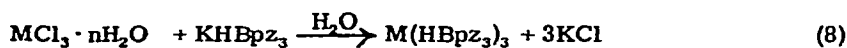
$$(\eta^5 - C_5H_5)_2M(BH_4) \cdot THF \xrightarrow{-THF} (\eta^5 - C_5H_5)_2M(BH_4) \qquad (7)$$

$$M = Er, \ Yb$$
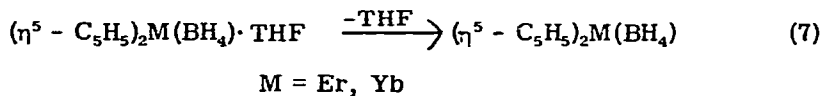
spectra of the resulting biscyclopentadienyl lanthanide tetrahydroborates are in accord with an oligomeric structure involving bridging $BH_4{}^-$ units, as schematized below.
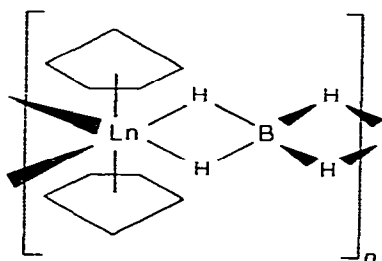
Despite the fact that metal pyrazolylborate complexes are not strictly organometallics, the great similarity in pyrazolylborate and cyclopentadienide chemistry prompts mention of the first lanthanide pyrazolylborates. Bagnall, Tempest, Takats, and Masino (18) have prepared these new compounds via the routes of eq. (8) and (9). The anhydrous

$$MCl_3 \cdot nH_2O + KHBpz_3 \xrightarrow{H_2O} M(HBpz_3)_3 + 3KCl \qquad (8)$$

$$M = La, \ Ce, \ Pr, \ Sm, \ Gd, \ Er, \ Y$$

$$HBpz_3 = \text{hydrotrispyrazolylborato}$$

$$ErCl_3 + nKHBpz_3 \xrightarrow{\text{THF}} Er(HBpz_3)_n Cl_{3-n} \cdot mTHF + nKCl \qquad (9)$$

$$n = 1, \ m = 1.5$$

$$n = 2, \ m = 1$$

products of eq. (3) precipitate from aqueous solutions in virtually quantitative yield. It is possible to synthesize $M(Bpz_4)_3$ complexes in an analogous manner. The $M(HBpz_3)_3$ species were found to be monomeric in benzene solution. In contrast to the above products, the chloro derivatives of eq. (9) are highly moisture sensitive. Attempts to prepare $M(H_2Bpz_2)_3$ derivatives in aqueous solution were unsuccessful.

Actinides

Templeton, Templeton, and Walker (19) have now published synthetic and X-ray structural details on the air stable organoactinide, octaphenyluranocene. The complex was synthesized by the reaction of the dianion of 1, 3, 5, 7 - tetraphenylcyclooctatetraene with uranium tetrachloride (eq. (10)), and was purified by sublimation.

$$2(C_8H_5)_4C_8H_4^{-2} + UCl_4 \longrightarrow [(C_6H_5)_4C_8H_4]U + 4Cl^- \qquad (10)$$
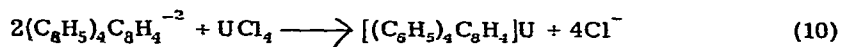
The molecular structure of this sandwich complex, viewed perpendicular to the ligand plane, is shown in Figure 5. The planar cyclooctatetraene rings are essentially eclipsed with the phenyl substituents in staggered positions, tilted by an average angle of 42° from the cyclooctatetraene plane. The U-C (hydrogen substituted) distances average 2.63(2) Å while the U-C (phenyl substituted) distances average 2.68 (1) Å.

Photoelectron spectroscopy, which is a powerful tool for studying bonding in organometallic molecules, has recently been applied to
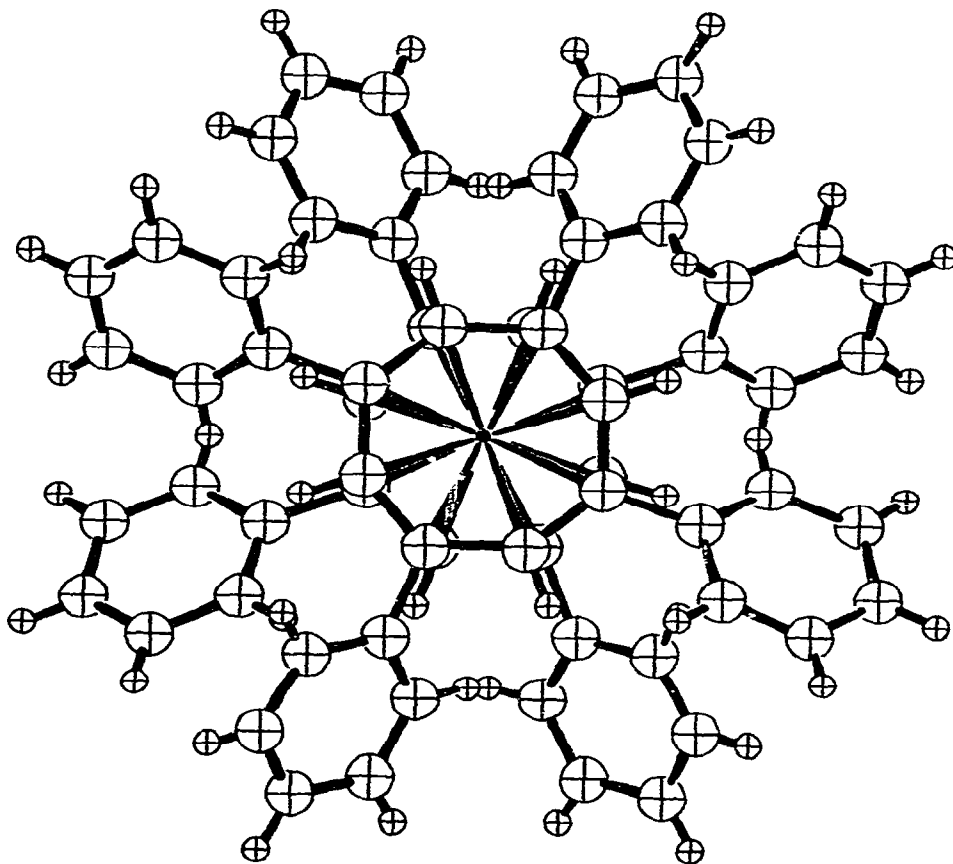
Figure 5. The structure of $[(C_6H_5)_4C_8H_4]_2U$ from ref. 19.

organoactinides. Clark and Green (20), have analyzed the He(I) photo-electron spectra of throcene and uranocene. They find the spectra to be remarkably similar to those of transition metal sandwich compounds. The ionization energy of the uranocene $5f^2$ electrons is estimated to be 6.2 eV. Fragala, Ciliberto, Fischer, Sienel, and Zanella (21) have reported photoelectron spectra of $(C_5H_5)_3MCl$, M = Th and U; $(CH_3C_5H_4)_3$ MCl, M = Th and U; $(CH_3C_5H_4)_3UBr$, and $(CH_3C_5H_4)_3U(BH_4)$. The spectra

can be qualitatively assigned in terms of a simple molecular orbital scheme. A band at 6.35 ~ 7.10 eV is only observed for the uranium derivatives and is energetically rather sensitive to the nature of the ligands in the metal coordination sphere. It is presumably associated with 5f electron ionization.

Fronczek, Halstead and Raymond (22) have communicated the synthesis and molecular structure of the first actinide carborane complex. The preparation, employing the 1,2-dicarbollide dianion, is shown in eq. (11). Figure

$$2Li_2B_9C_2H_{11} + UCl_4 \xrightarrow{\text{THF}} (B_9C_2H_{11})_2UCl_2 2Li^{+} \cdot 8THF \qquad (11)$$
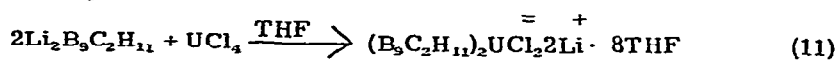
6 illustrates the structure of the uranium containing portion of the complex as determined by X-ray diffraction.
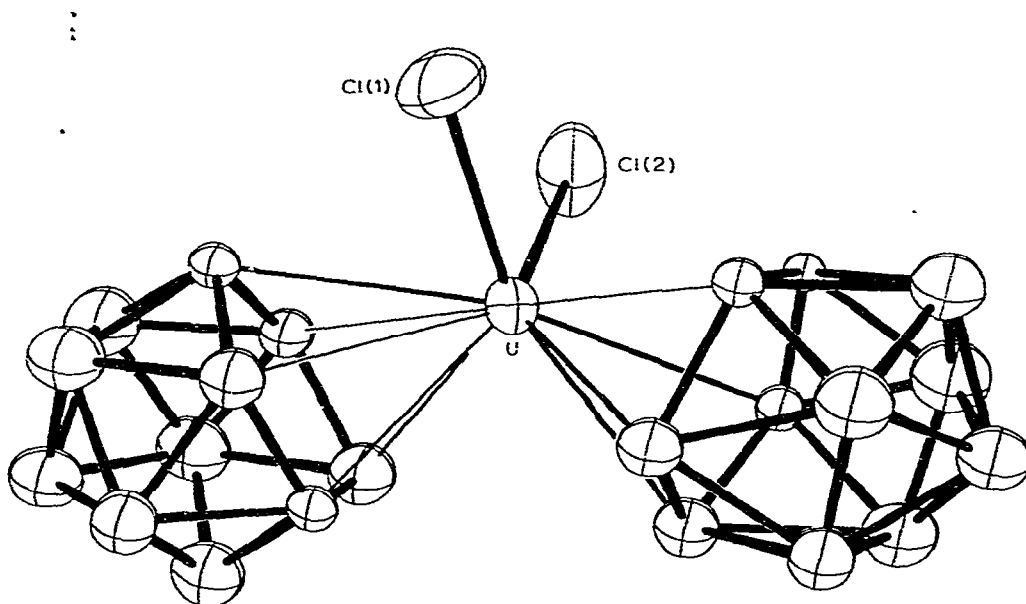

Figure 6. The molecular structure of $(B_9C_2H_{11})_2UCl_2^{=}$ from ref. 22.

Rather high thermal motion of the atoms was observed and it was impossible to distinguish boron from carbon atoms in the dicarbollide ligand. The average uranium to complexing cage atom distance was found to be 2.73 (2) Å, the average U-Cl distance, 2.599(6) Å. The angle Cl-U-Cl was reported to 90.3(5)°, and the angle face centroid-U-face centroid, 137°.

Marks and Wachter have now reported full details on the synthesis, chemistry, and spectroscopy of triscyclopentadienyl thorium alkyl and alkenyl compounds (23). These complexes are best prepared at low temperatures in non-coordinating solvents (eq. 12). All are highly

$$(\eta^5 - C_5H_5)_3ThCl + RLi \text{ or } RMgX \xrightarrow[-78°]{\text{toluene}} (\eta^5-C_5H_5)_3ThR \qquad (12)$$
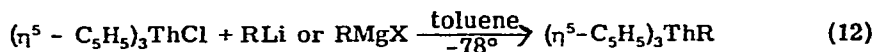
R = allyl, n-butyl, i-propyl, 2-cis-2-butenyl, 2-trans-2-butenyl, neopentyl

oxygen and moisture sensitive. The new compounds were assigned the $(\eta^5-C_5H_5)_3UR$ structure shown below. Vibrational
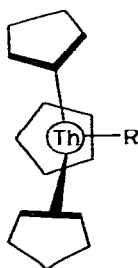

spectra are in accord with a monohapto geometry for the allyl complex, and variable temperature pmr studies indicate fluxional behavior (eq. 13) similar to that found for $(C_5H_5)_3U(allyl)(24)$ and with similar activation energetics

$$(13)$$
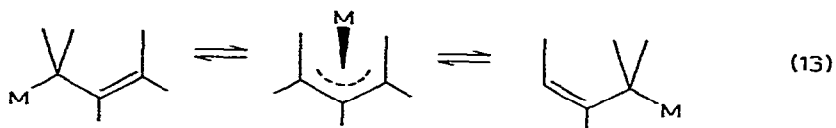
$(\Delta G^{\ddagger} \approx 7.6 - 8.7 \text{ kcal/mol.})$. These new thorium alkyls and alkenyls

possess extraordinarily high thermal stability in solution, and a study of

the thermal decomposition mechanism was reported. As in the case of

the analogous $(C_5H_5)_3UR$ compounds, β-hydride elimination was not found

to be an important pathway for thermolysis. Rather, stereospecific

intramolecular abstraction of a cyclopentadienyl hydrogen takes place as

shown in eq. (14). Unlike

$$2(C_5H_5)_3ThR \xrightarrow{\Delta} [(C_5H_5)_2Th(C_5H_4)]_2 + 2RH \qquad (14)$$
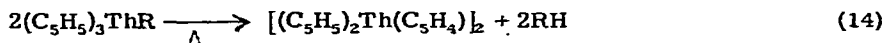
the $(C_5H_5)_3UR$ thermolysis, it is possible to isolate the thorium-containing

thermolysis product in crystalline form. The structure of this unique

$\eta^5 : \eta^1$ - cyclopentadienyl species (25) is shown below. The unimolecular
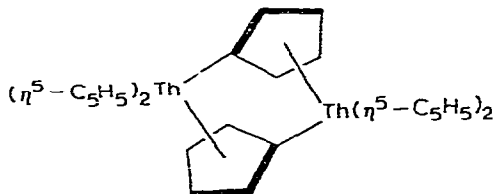
nature of $(C_5H_5)_3ThR$ thermolysis suggests that a carbene complex-acti-

nide cyclopentadienylide intermediate
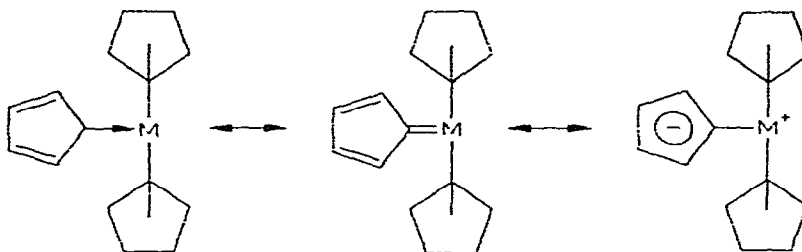
is the precursor of the $\eta^5 : \eta^1$ dimer. As in the uranium system, it was
not possible to rigorously differentiate between thermolysis mechanisms
involving tightly caged radical pairs, direct H^+ to R^- transfer, or ini-
tial C-H bond addition to the actinide.
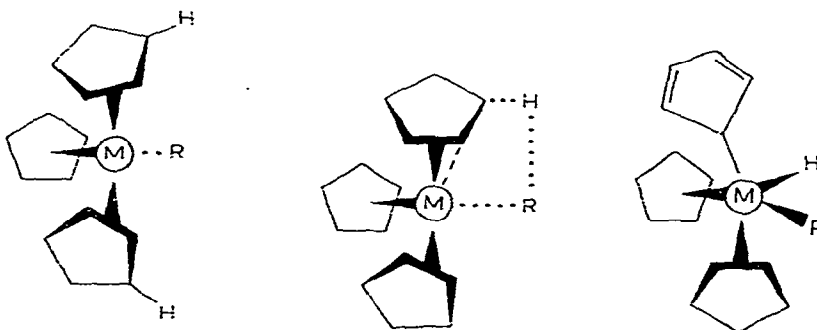
Kinetic studies yielded $\Delta G^{\pm}$ values for the $(C_5H_5)_3ThR$ thermolyses that
were 2 - 10 kcal/mole higher than for the analogous uranium compounds.

In work on related compounds of other actinide ions, Karraker and
Stone (26) have presented preliminary results on the synthesis and pro-
perties of neptunium (IV) alkyl compounds. The synthesis is shown in
eq. (15). It was

$$(\eta^5 - C_5H_5)_3NpCl + RLi \xrightarrow[-80°]{Et_2O} (\eta^5 - C_5H_5)_3NpR + LiCl \qquad (15)$$
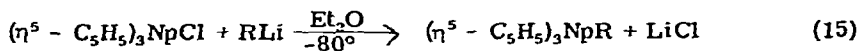
successful for R = n-butyl, however the R = phenyl reagent yielded only
$(C_5H_5)_4Np$ and $(C_5H_5)_3Np$. The R = n-butyl complex was characterized by
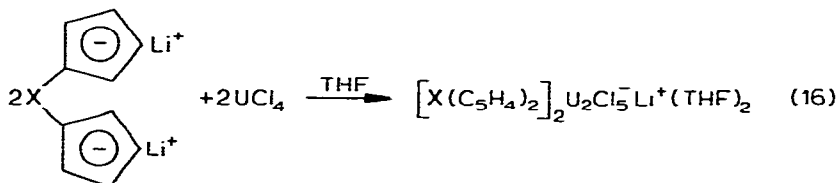
chemical analysis, magnetic susceptibility, electronic absorption

spectroscopy, and Np Mössbauer spectroscopy. The isomer shift of

$(C_5H_5)_3Np(n\text{-butyl})$ is 0.45 cm/sec less than that of $(C_5H_5)_4Np$, which was

interpreted as reflecting a smaller covalency.

Amberger, Fischer, and Kanellakopulos (27) have made a detailed

study of the magnetic susceptibility of $(C_5H_5)_4U$. The experimental data,

which reveal a non-magnetic ground state arising from slight distortion

of the crystal field from T_d to S_4 symmetry, can be explained rather well

on the basis of either of three approximate types of model calculations,

viz. electrostatic point charge, angular overlap, or Mulliken-Helmholz-

Wolfsberg molecular orbital. These results allow estimation of the

crystal field splitting parameters, the two-center e_σ and e_π angular over-

lap parameters, and the valence state ionization potential of the 5f elec-

trons in this complex. In related work, Amberger (28) has been able to

assign the room temperature electronic absorption spectrum of $(C_5H_5)_4U$.

Assuming a tetrahedral f^2 system, an iterative procedure was employed

to derive the crystal field splitting, interelectronic repulsion, and spin-

orbit coupling parameters which produced the best agreement between

calculated and experimental spectral band maxima. The parameters

obtained are rather similar to those derived for $U(BH_4)_4$ in an $Hf(BH_4)_4$

matrix (29), suggesting that tridentate BH_4^- and $\eta^5 - C_5H_5^-$ have similar

ligand field strengths. This proposition gains further support from

related studies on the electronic absorption spectrum of $(C_5H_5)_3UBH_4$

by Amberger and Sienel (30). The spectrum is considerably simpler

than that found for most $(C_5H_5)_3UX$ complexes, which suggests (as do

earlier magnetic susceptibility studies) that the uranium ion environ-

ment in $(C_5H_5)_3UBH_4$ is only slightly distorted from tetrahedral. The absorption spectrum can be fit and the relevant crystal field parameters obtained by diagonalizing the energy matrix including crystal field, electron-electron, and spin-orbit interactions, as described above. In further work Amberger (31) has conducted a similar analysis of the $(C_5H_5)_3UCl$ electronic spectrum. Here the distortion of the crystal field from T_d to C_{3v} symmetry is substantial. The calculated positions and ordering of the crystal field levels can be used to predict the experimental temperature dependence of the magnetic susceptibility and pmr dipolar (magnetic anisotropy) shifts with good agreement. It appears that the contributions individual ligands make to actinide ion crystal field splittings are approximately additive.

In an effort to learn more about the nature of biscyclopentadienyl uranium (IV) chemistry ($(C_5H_5)_2 UCl_2$ is an unstable species) Secaur, Day, Ernst, Kennelly, and Marks (32) have studied the reactions of biscyclopentadienyl ligands in which the rings are joined by various bridging groups (eq. (16)). These air sensitive new compounds were character- ized by chemical, spectroscopic, and crystallographic means.

$$2X \begin{array}{c} \text{(−) Li}^+ \\ \text{(−) Li}^+ \end{array} + 2UCl_4 \xrightarrow{\text{THF}} \left[X(C_5H_4)_2\right]_2 U_2Cl_5^- Li^+(THF)_2 \quad (16)$$

$X = CH_2, (CH_3)_2Si, CH_2CH_2CH_2$

The molecular structure of the $X = CH_2$ derivative, determined by X-ray diffraction, is presented in Figure 7.
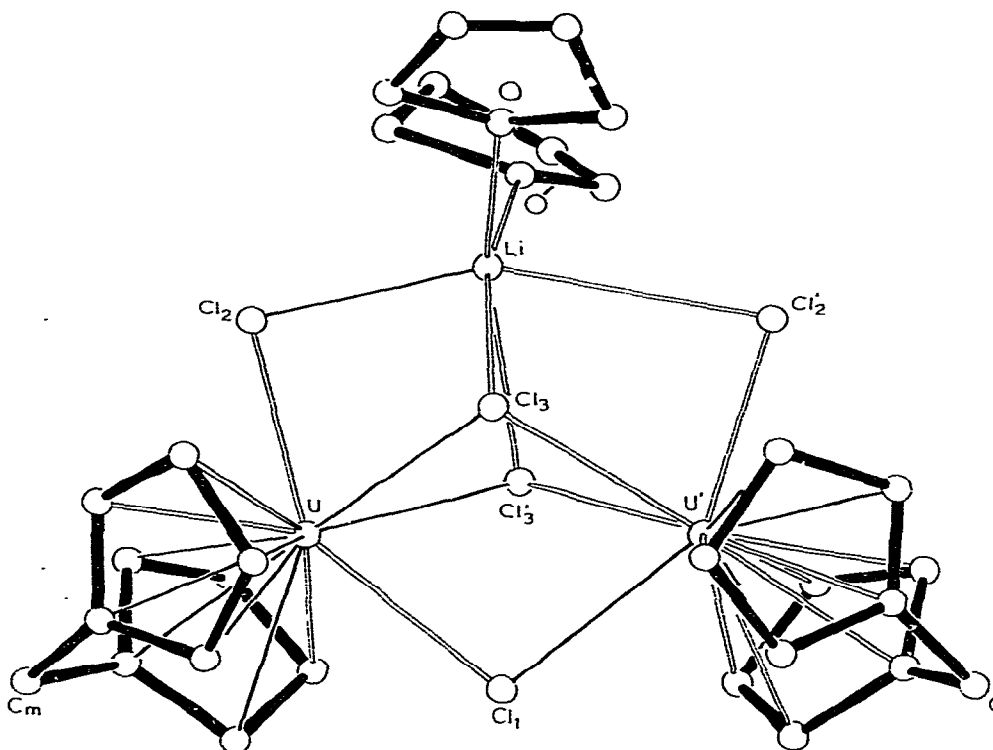
Figure 7. The structure of $LiU_2Cl_5[CH_2(C_5H_4)_2]_2 \cdot 2THF$ from ref. 32.

An unusual dimer (approximately C_{2v} symmetry) is found with a "cryptated" lithium ion and a triple chlorine bridge. The average U-Cl(bridge) distance was found to be 2.83(1) Å and the U-Cl(terminal) 2.68(1) Å. The average U-C (ring) distance was 2.72(5) Å, ∢ Cl_1-U-Cl_3, 73.3(3)°; ∢ Cl_2-U-Cl_3, 79.1(4)°; and ∢ Cl_1-U-Cl_2, 146.3(4)°. Pmr studies indicate that this unsymmetrical structure maintains its integrity in C_6D_6 solution, but that the THF molecules rapidly exchange with added THF. The chemistry of these dimers indicates that they provide ready sources of $X(C_5H_4)_2UCl_2$ as illustrated in the scheme below.

$$\left[X(C_5H_4)_2 \right]_2 U_2Cl_5^- Li^+$$
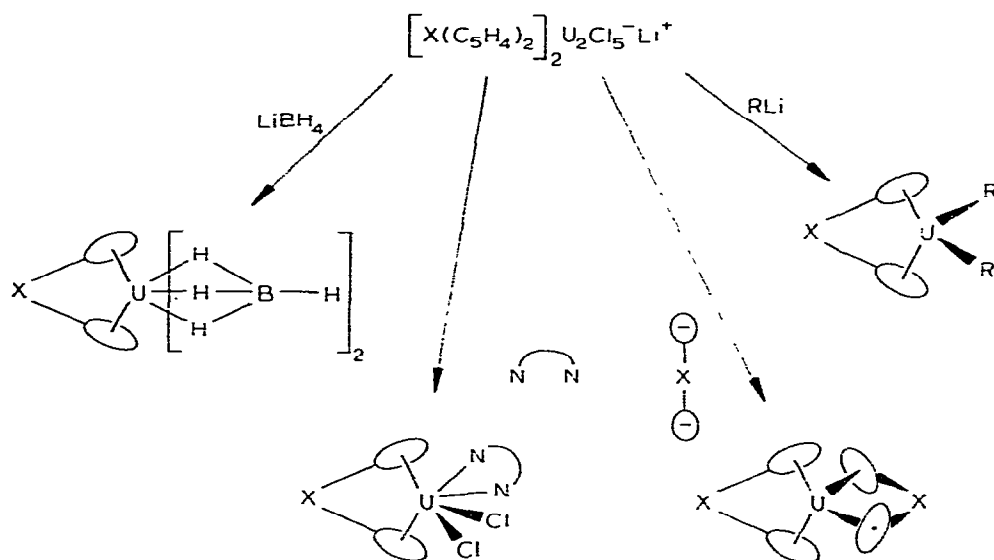
With lithium reagents such as R = n-butyl, the unstable dialkyls undergo

facile β-hydride elimination. With elimination-resistant alkyls such as

R = neopentyl, the derivatives have greater thermal stability. Reaction

with bidentate nitrogenous bases such as N͡   N = 2,2'-bipyridyl cleaves

the dimer to produce air stable, crystalline adducts. The molecular

structure of the X = CH₂ species, reported separately by Day, Secaur,

Fredrich, Ernst, Kennelly, and Marks (33) is shown in Figure 8.

This monomeric species has no elements of sym-

metry (save C_1). The average U-Cl distance was

found to be 2.706(5) Å, the average U-C (ring), 2.72(3) Å, and the

average U-N, 2.68 (2) Å. The Cl-U-Cl angle is 86.2(2)°. Both this

structure and that of Figure 7 illustrate the pronounced tendency of

uranium (IV) organometallics to achieve a formal coordination number

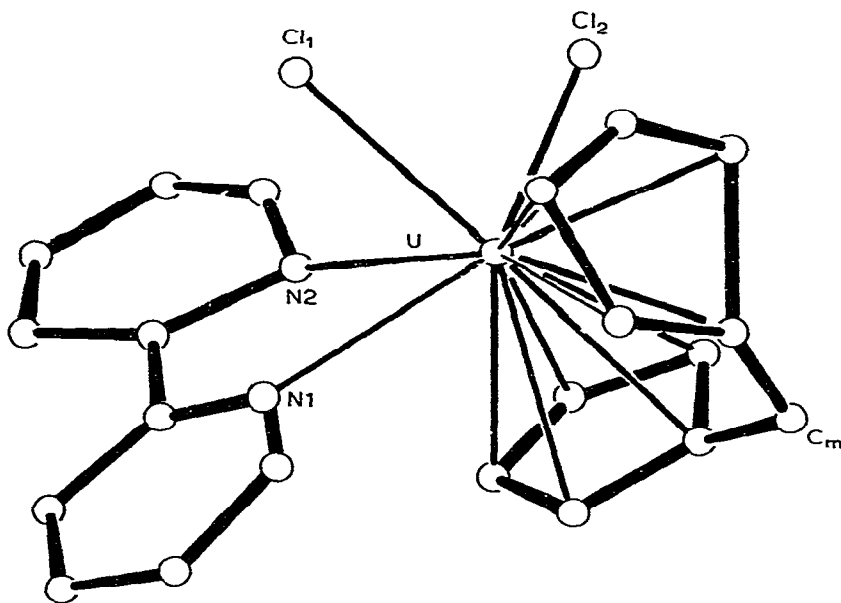of 10. Presumably as a consequence of increased coordinative satura-

Figure 8. The structure of $[(C_5H_4)_2CH_2]UCl_2 \cdot 2,2'$-bipyridyl from ref. 33

tion, the dialkyls of the bipyridyl complex have greater thermal stability.

Fischer and Sienel (34) have reported on triscyclopentadienyl uranium (IV) tricyanomethanide complexes, prepared via eq. (17). The new, air sen-

$$(\eta^5 - C_5H_4R)_3UCl + K^+ C(CN)_3^- \longrightarrow (\eta^5 - C_5H_5)_3UC(CN)_3 + KCl \qquad (17)$$

$$R = H, \ CH_3$$
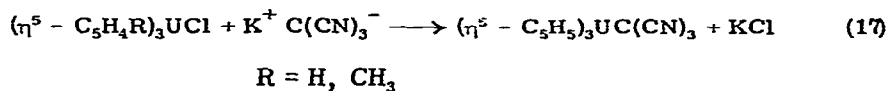
sitive complexes were characterized by vibrational and nmr spectroscopy. In the solid state these complexes are believed to have oligomeric structures with pentagonal bipyramidal $(C_5H_5)_3U^+$ units and bridging $C(CN)_3^-$ groups.
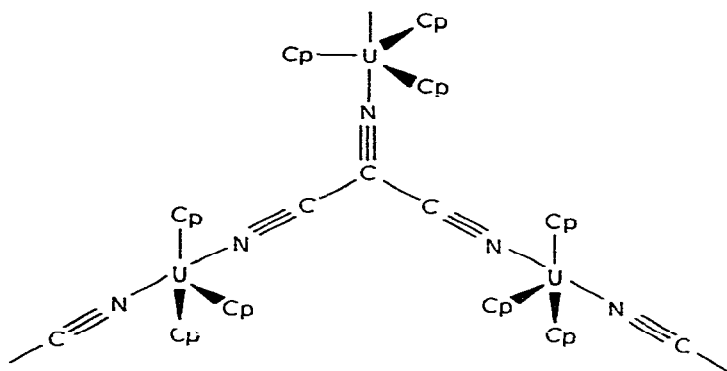
Marks, Seyam and Wachter (35) have now published tested "recipes"

for the highly useful precursors $(\eta^5 - C_5H_5)_3UCl$ and $(\eta^5 - C_5H_5)_3ThCl$.

These syntheses employ the air stable cyclopentadienylating reagent

C_5H_5Tl (eq. (18)) in 1,2-dimethoxyethane.

$$MCl_4 + 3C_5H_5Tl \xrightarrow{DME} (C_5H_5)_3MCl + 3TlCl \tag{18}$$

$$M = Th,\ U$$
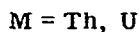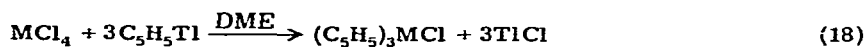
Perego, Cesari, Farina, and Lugli (36) now report the completely

refined X-ray diffraction structures of $(\eta^5 - C_5H_5)_3U(n\text{-butyl})$ and

$(\eta^5\ C_5H_5)_3UCH_2(p\text{-}CH_3C_6H_4)$. The molecular geometries are presented

in Figures 9 and 10. The uranium coordination polyhedra

are similar to other $(C_5H_5)_3UR$ complexes (1) with ring centroid–U–ring

centroid angles of 115.8–118.1° (R=n-butyl) and 115.6 – 120.6° (R =

p-methylbenzyl). The ring centroid–U–C(1) angles for the above two

compounds are 98.2 - 102.3° and 99.4 – 99.8°, respectively. The U–C (1)

distances are 2.426(23) Å (n-butyl) and 2.541 (15) Å (p-methylbenzyl).

The most surprising feature of both structures is the marked deviation

(ca. 20° openning) of the U–C(1)–C(2) angles from tetrahedral: 128.5

(16)° for R = n-butyl, and 128.6(9)° for R = p-methylbenzyl. For the
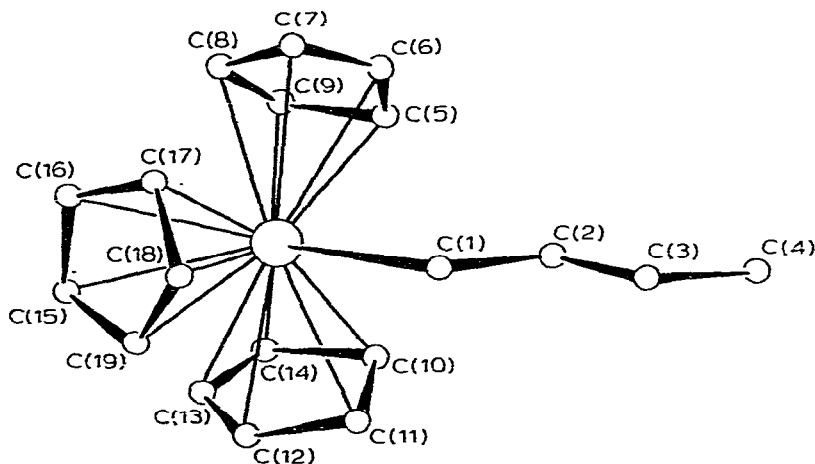
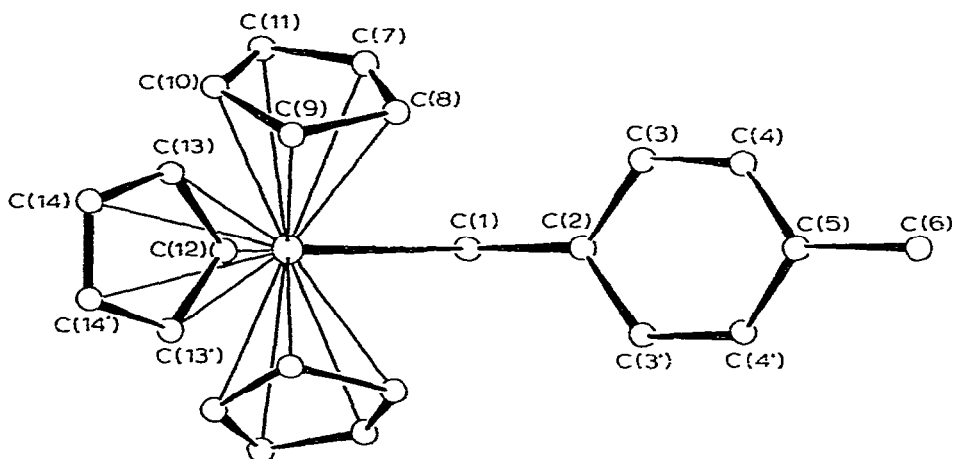Figure 9. The molecular structure of $(C_5H_5)_3U(n\text{-butyl})$ from ref. 36.

Figure 10. The molecular structure of $(C_5H_5)_3U(p\text{-methylbenzyl})$ from ref. 36.

former compound, the C(1)-C(2)-C(3) angle of 116.3(12)° is also unexpected. It seems unlikely that these distortions arise from intramolecular nonbonded repulsion, but rather they appear to reflect the nature

(ionic?) of the U-C sigma bond. In related work Atwood, Tsutsui, Ely, and Gebala (37) have presented full details on the molecular structure of $(C_5H_5)_3UC\equiv CH$. The uranium coordination geometry is similar to that of the above two structures with ring centroid-U-ring centroid angles of $116-121(4)^\circ$, ring centroid-U-C(ethynyl) angles of $94 - 99(4)^\circ$ and a U-C(ethynyl) distance of 2.36(3) Å. The two independent molecules in the unit cell have U-C(σ)-C(H) angles of 175(4) and 161(4)$^\circ$.

The importance of $(C_5H_5)UCl_3\cdot 1$, 2-dimethoxyethane (38) in the chemistry of "$(C_5H_5)_2UCl_2$" (32) and its potential utility as a precursor for new organoactinides (39) have led Day, Secaur, Fredrich, Ernst, Kennelly, and Marks (33) to investigate the solid state and solution structure of the related, more readily crystallized compound ($\eta^5 - CH_3$ $C_5H_4)UCl_3\cdot$ 2THF. This is conveniently prepared from the thallium reagent (33,39) as shown in eq. (19). The molecular structure,

$$(CH_3C_5H_4)Tl + UCl_4 \xrightarrow{\text{THF}} (CH_3C_5H_4)UCl_3 \cdot 2THF + TlCl \qquad (19)$$
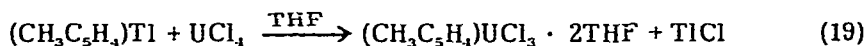
determined by X-ray diffraction, is shown in Figure 11. The molecule is monomeric, with a uranium coordination geometry surprisingly close to octahedral. Relevant metrical parameters are U-Cl (average) = 2.620 (9) Å, U-O (average) = 2.44(2) Å, and U-C (cyclopentadienyl, average) = 2.70 (4) Å. The angles Cl1-U-Cl3 = 90.0(3)$^\circ$, Cl1-U-O1 = 78.8(3)$^\circ$, Cl1-U-Cl2 = 155.6 (4)$^\circ$, and Cl1-U-O2 = 83.7(4)$^\circ$ illustrate the approximately octahedral geometry. Solution pmr studies indicate that several species are in dynamic equilibrium.

Bagnall and Edwards (40) have reported the synthesis and physical characterization of a number of new uranium (IV) pyrazolylborates.
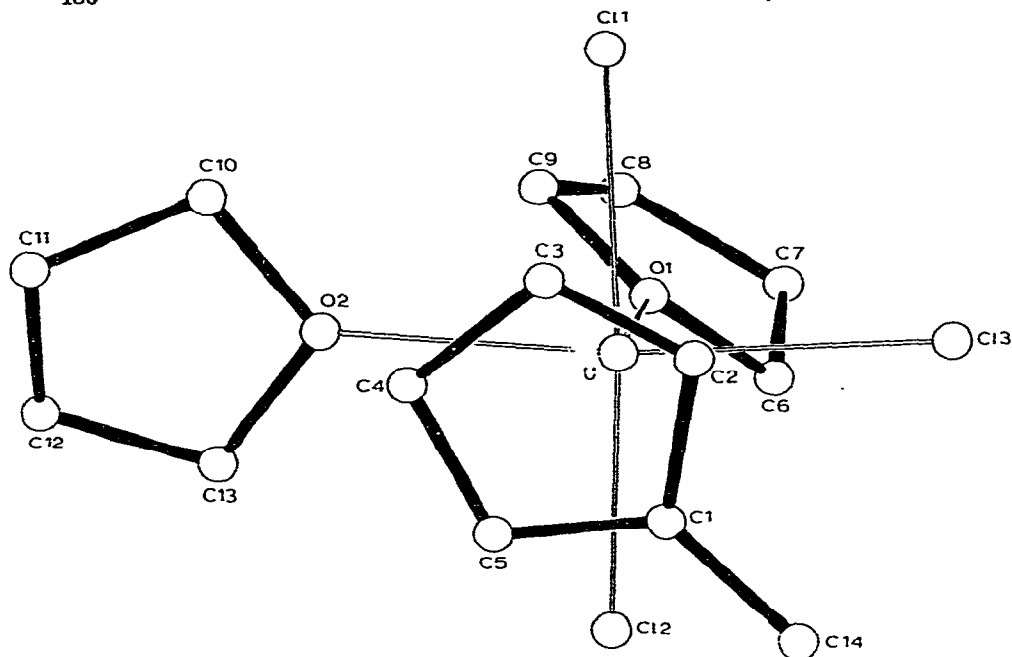
Figure 11. The structure of $(CH_3C_5H_4)UCl_3 \cdot 2THF$ from ref. 33.

These were prepared in several polar solvents by the route shown in eq. (20).

$$UCl_4 + 2H_nBX_{4-n} \longrightarrow Cl_2U(H_nBX_{4-n})_2 \tag{20}$$
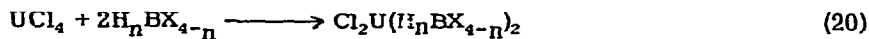
$$X = pyrazolyl, \ 3,5\text{-dimethylpyrazolyl}$$
$$n = 0,1,2$$

In cases where the ligation sphere is less bulky, e.g. X = pyrazolyl and n = 1 or 2, the complexes are isolated with coordinated solvent molecules, e.g. THF or dimethylformamide. Also synthesized were analogous bromide derivatives and non-halogenated complexes such as $U[H_2B$ $(3,5\text{-Me}_2pz)_2]_4$ and $U[H_2Bpz_2]_4 \cdot DMF$. The new compounds were characterized by infrared, proton nmr, and electronic spectroscopy.

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