

LANTHANIDES AND ACTINIDES
ANNUAL SURVEY COVERING THE YEAR 1979

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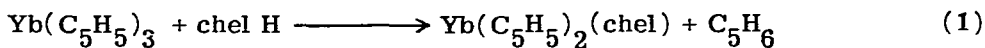
General

A NATO Advanced Study Institute entitled "Organometallics of the f-Elements" was held in Urbino, Italy in September 1978. A 517 page monograph of the same title appeared in 1979 which is comprised of chapters written by the 15 principal lecturers at the Institute (1). This book endeavors to present a detailed and coherent picture of the present state of knowledge in organo-f-element chemistry. It is currently the only monograph of its kind.

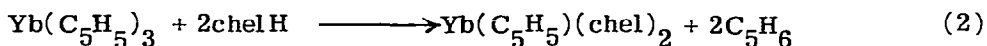
Lanthanides

A concise review of rare earth organometallic chemistry by Schumann has been published (2). The article begins with an interesting historical note and surveys the general classes of known compounds according to ligand type.

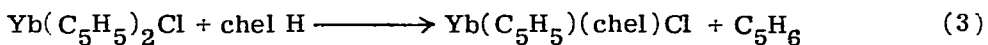
Bielang and Fischer (3) have reported on the synthesis and properties of mixed ligand organolanthanides containing cyclopentadienyl and classical chelate ligands. Thus, $\text{Yb}(\text{C}_5\text{H}_5)_3$ and $\text{Yb}(\text{C}_5\text{H}_5)_2\text{Cl}$ were reacted in hydrocarbon solvents with the conjugate acids of several β -diketonates and β -aminoketones as shown in eqs. (1) - (3).



chel = acetylacetonate
 2,2,6,6-tetramethyl-3,5-heptanedionate
 4-anilino-3-pentene-2-onate



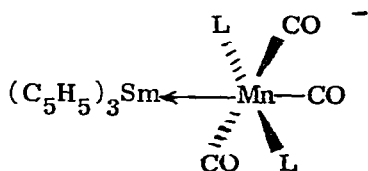
chel = 4-anilino-3-pentene-2-onate



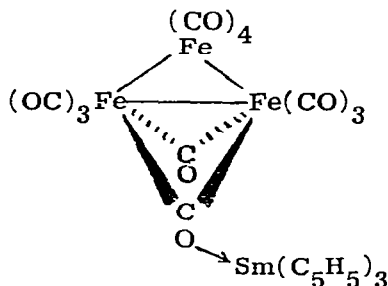
chel = 4-anilino-3-pentene-2-onate

The new compounds were characterized by elemental analysis, mass spectrometry, optical spectroscopy, and, where possible, ^1H NMR spectroscopy. Complexes of the β -aminoketonate were found to be considerably more tractable and readily purified than those of the β -diketonates.

Onaka and Furuichi (4) have studied the interaction of $\text{Sm}(\text{C}_5\text{H}_5)_3$ with a variety of metal carbonyl compounds by infrared and ^1H NMR spectroscopy. In the case of $\text{Mn}(\text{CO})_x\text{L}_{5-x}\text{Br}$ ($\text{L} = \text{P}(\text{OC}_6\text{H}_5)_3$) derivatives, a lowering of the carbonyl C-O stretching frequencies was attributed to interaction of the acidic lanthanide with the carbonyl oxygen atoms. It was recognized, however, that interaction (reaction ?) with the MnBr functionality might also be occurring. Indeed, it is surprising that the interaction took many hours to reach equilibrium. The reaction of $\text{Sm}(\text{C}_5\text{H}_5)_3$ with the corresponding anionic $\text{Mn}(\text{CO})_x\text{L}_{5-x}^-$ complexes resulted in a shift of the C-O stretching frequencies to higher energy. This was interpreted in terms of metal-metal interactions (5) as shown below. With large excesses of $\text{Sm}(\text{C}_5\text{H}_5)_3$, lower energy ν_{CO}



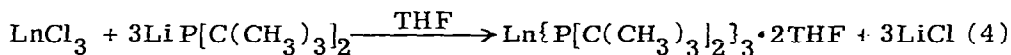
signals were also noted, indicative of $\text{MnCO} \cdots \text{Sm}$ coordination. For $\text{Sm}(\text{CH}_3)_{4-x}[\text{Mn}(\text{CO})_5]_x$ compounds ($x = 1, 2, 3$) lowering of the C-O stretching frequencies was also noted. Rather long time periods were required for equilibration. Studies with iron carbonyls revealed that $\text{Fe}(\text{CO})_5$ was slowly decomposed by $\text{Sm}(\text{C}_5\text{H}_5)_3$, while $\text{Fe}_3(\text{CO})_{12}$ interacted to produce a ν_{CO} signal (1786 cm^{-1}) characteristic of a bridging carbonyl complexed by a Lewis acid. A possible structure is shown below. Curiously, $\text{Fe}_2(\text{CO})_9$ reacts with $\text{Sm}(\text{C}_5\text{H}_5)_3$



to yield $\text{Fe}_3(\text{CO})_{12}$. The reaction of $\text{H}_3\text{Mn}_3(\text{CO})_{12}$ with $\text{Sm}(\text{C}_5\text{H}_5)_3$ resulted in disappearance of the hydride ^1H NMR signal and a down-shifting of the terminal C-O stretching modes. In THF, $\text{Mn}_2(\text{CO})_{10}$ reacted with $\text{Sm}(\text{C}_5\text{H}_5)_3$ to produce (after 135 hr.) the aforementioned infrared spectrum observed for $\text{Mn}(\text{CO})_5^- + \text{Sm}(\text{C}_5\text{H}_5)_3$. With $[\text{Mn}(\text{CO})_4\text{L}]_2$, only an infrared absorption attributable to terminal $\text{MnCO} \cdots \text{Sm}$ coordination was noted. It would be of interest to examine some of the above reactions in terms of possible Sm-to-transition metal C_5H_5^- transfer.

The cocondensation of erbium metal vapor with 3-hexyne at -196°C has been studied by Evans, Engerer, Piliero, and Wayda (6). Three products are obtained by successive extraction of the dark brown product with pentane, toluene, and tetrahydrofuran (THF). The middle fraction appears to be $\text{Er}_2(\text{C}_6\text{H}_{10})_3$ by elemental analysis and molecular weight measurements. The THF-soluble fraction exhibited molecular weights as high as decamers. Infrared spectra indicate strong perturbation of the $\text{C}\equiv\text{C}$ bond in all three fractions. At room temperature and one atmosphere of hydrogen pressure, the first two fractions catalyze the hydrogenation of 3-hexyne to cis-3-hexene (97% cis) with turnover frequencies of 0.02-0.04 3-hexyne molecules/minute/Er atom. In contrast, 3-hexene is hydrogenated at approximately one-tenth the rate of the alkyne. Cocondensation of samarium and ytterbium vapors with 3-hexyne produces THF-soluble materials of empirical formulae $\text{SmC}_6\text{H}_{10}$ and $\text{YbC}_6\text{H}_{10}$. These compounds can also function as 3-hexyne hydrogenation catalysts, as can products resulting from the condensation of lanthanum vapor with 3-hexyne and erbium vapor with alkynes such as diphenylacetylene.

Dialkylphosphido derivatives of lanthanides have been reported by Schumann and Frisch (7). The crystalline products were



$\text{Ln} = \text{Ho, Er, Tm, Yb, Lu}$

characterized by standard analytical methodology. The tetrahydrofuran can be removed to yield the pure $\text{Ln}\{\text{P}[\text{C}(\text{CH}_3)_3]_2\}_3$ complexes.

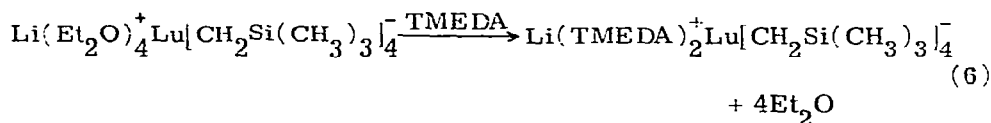
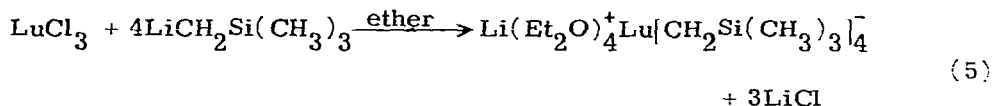
Molecular weight measurements show these latter species to be polymeric.

Schumann and Müller (8) have prepared neutral and anionic

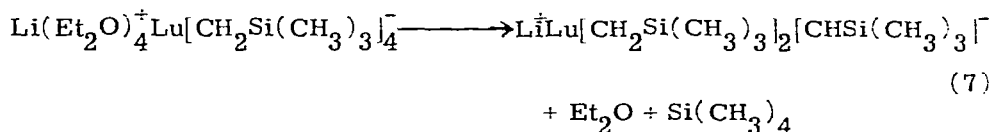
trimethylsilylmethylidene complexes of erbium and lutetium. Earlier results indicated that anionic complexes of the formula

$\text{Ln}[\text{CH}_2\text{Si}(\text{CH}_3)_3]_4^-$ ($\text{Ln} = \text{Er}, \text{Tm}, \text{Yb}, \text{Lu}$) were thermally unstable (9).

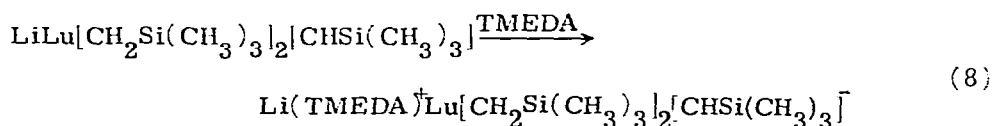
In the present work, the corresponding lutetium complex was isolated as a stable salt by replacing the lithium counterion ligand (diethylether) with tetramethylethylenediamine (TMEDA) (eqs. (5) and (6)).



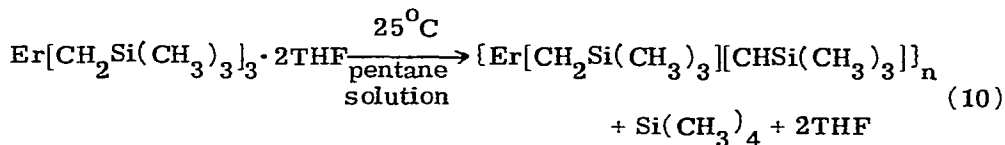
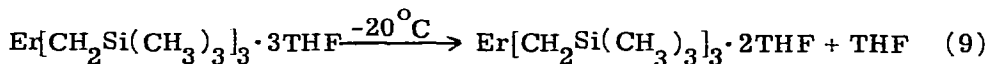
The ether-coordinated product decomposes thermally to produce, via α -hydrogen atom abstraction (10), an alkylidene complex (eq. (7))



which was characterized by standard analytical techniques. Furthermore, a counterion-coordinated complex could be isolated (eq.(8)) and was further characterized by ^1H and ^{13}C NMR spectroscopy.



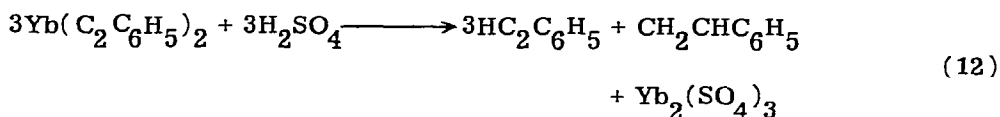
Signals due to the alkylidene functionality could not be located. Work on the previously reported (9) $\text{Ln}[\text{CH}_2\text{Si}(\text{CH}_3)_3]_3 \cdot n\text{THF}$ compounds ($\text{Ln} = \text{Er}, \text{Tm}, \text{Yb}, \text{Lu}$) was expanded in the present communication to report that the Er derivative undergoes thermolysis via α -hydrogen atom abstraction as indicated in eqs. (9) and (10).



Deacon, Koplick, Raverty, and Vince (11) have studied the transmetal-
lation reactions of fluoroaryl and alkynyl mercurials with ytterbium,
europium, and samarium metals in THF (eq. (11)).

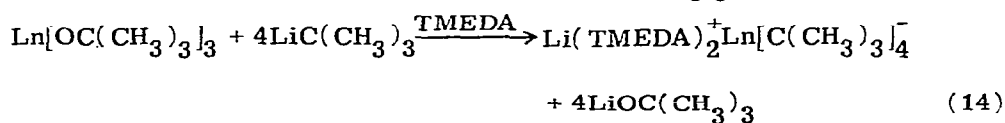
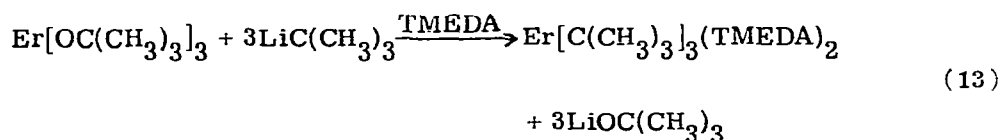


Product analysis was by acidolysis of the filtered reaction mixtures.
For $\text{R} = \text{C}_6\text{F}_5$, $\text{p-C}_6\text{F}_4\text{H}$, $\text{C}_6\text{H}_5\text{C}_2$, and $\text{Ln} = \text{Yb}$, the results indicate
nearly quantitative formation of previously reported $\text{Yb}(\text{C}_2\text{C}_6\text{H}_5)_2$ (12)
and $\text{Yb}(\text{C}_6\text{F}_5)_2 \cdot 4\text{THF}$ (13). Evidence for $\text{Eu}(\text{C}_6\text{F}_5)_2$, $\text{Yb}(\text{p-C}_6\text{F}_4\text{H})_2$,
and $\text{Yb}(\text{o-C}_6\text{F}_4\text{H})_2$ (stable only at 0°C) was also obtained. While
transmetalation to produce $\text{Yb}(\text{C}_6\text{F}_5)_2$ also occurred readily in
diethyl ether, no reaction took place between Yb and $\text{Hg}(\text{C}_2\text{C}_6\text{H}_5)_2$
under these conditions. Acidolysis of $\text{Yb}(\text{C}_2\text{C}_6\text{H}_5)_2$ produces, in
addition to phenylacetylene, styrene and traces of ethylbenzene.
These hydrogenation products are explicable in terms of reactions
such as that shown in eq. (15). The reactions of Yb with $\text{Hg}(\text{o-C}_6\text{F}_4\text{H})_2$

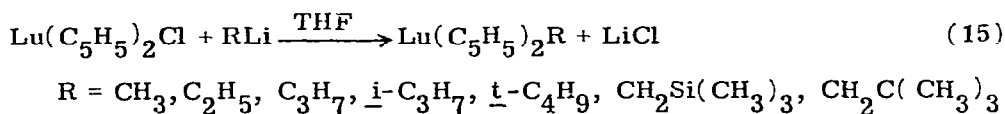


and Sm with $\text{Hg}(\text{C}_6\text{F}_5)_2$ in THF at room temperature are rather
complex and evidence thermal decomposition of the organolanthanides by
ortho-fluorine atom abstraction to produce fluorobenzynes. Reduction
of the fluoroaromatics by the divalent lanthanides and hydrogen atom
abstraction from THF are also detected.

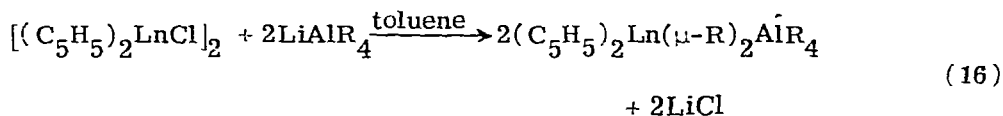
Schumann, Müller, and Genthe (14) have described some additional reactions between lanthanide compounds and lithium reagents. Thus, TbCl_3 and ErCl_3 react with three equivalents of $\text{LiC}(\text{CH}_3)_3$ in THF at $-78^\circ - -10^\circ \text{C}$ to form what appear to be $\text{LnR}_3 \cdot \text{THF}$ complexes. With four equivalents of lithium reagent, Wayda and Evans had previously prepared $\text{Li}(\text{THF})_4^+ \text{Ln}[\text{C}(\text{CH}_3)_3]_4^-$ salts for $\text{Ln} = \text{Sm}, \text{Er}, \text{Yb}$ (15). Using lanthanide alkoxides rather than chlorides, Schumann, Müller, and Genthe were able to prepare both neutral and anionic t-butyl lanthanides (eqs. (13) and (14)). Lutetium members of the



known (16, 17) $\text{Ln}(\text{C}_5\text{H}_5)_2\text{R}$ series were prepared for a wide variety of alkyl residues (eq. (15)).



Full discussions of the synthesis and properties of $(\text{C}_5\text{H}_5)_2\text{Ln}(\mu\text{-R})_2\text{AlR}_2$ (16) and $[(\text{C}_5\text{H}_5)_2\text{Ln}(\mu\text{-CH}_3)]_2$ (17) compounds by Holton, Lappert, Ballard, Pearce, Atwood, and Hunter have now appeared. The former compounds were prepared as shown in eq. (16). All of the $\text{R}=\text{CH}_3$ derivatives possess high thermal



Ln = Sc, Y, Gd, Dy, Ho, Er, Tm, Yb

R = CH₃

Ln = Sc, Y, Ho

R = C₂H₅

stability while the R=C₂H₅ complexes slowly decompose at room temperature. Solubility properties for these compounds suggest increasing covalency for the derivatives of the heavier lanthanides. Attempts to prepare (C₅H₅)₂Y(μ-CH₃)₂In(CH₃)₂ from [(C₅H₅)₂YCl]₂ and LiIn(CH₃)₄ yielded only [(C₅H₅)₂Y(μ-CH₃)₂]₂. The molecular structure of (C₅H₅)₂Yb(μ-CH₃)₂Al(CH₃)₂ has been determined by single crystal diffraction techniques and the result is shown in Figure 1.

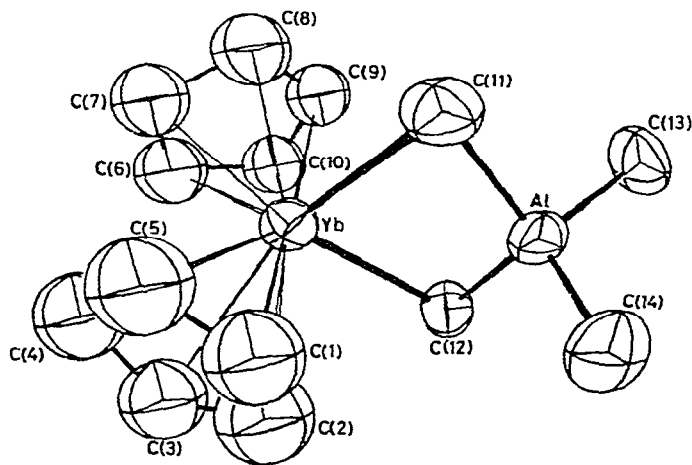
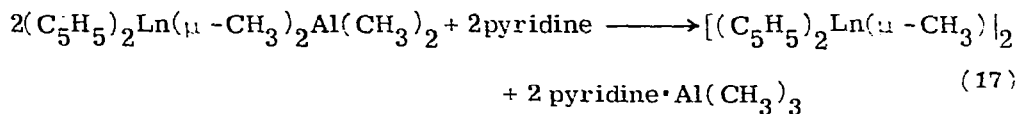


Fig. 1 The molecular structure of (C₅H₅)₂Yb(μ-CH₃)₂Al(CH₃)₂ from ref. 16.

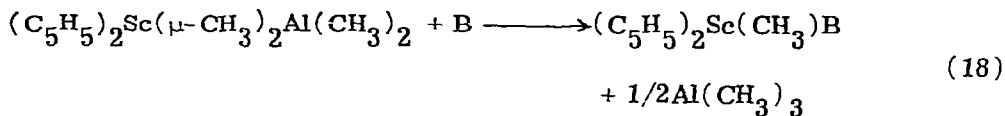
Relevant metrical parameters are Yb-Al = 3.014(6) Å, Yb-C(11) = 2.609(23) Å, Yb-C(12) = 2.562(18) Å, Al-C(11) = 2.165(22) Å, Al-C(12) = 2.096(18) Å, Al-C(13) = 2.014(25) Å, Al-C(14) = 1.991(24) Å, Yb-C(cyclopentadienyl) = 2.61(3) Å (average), ∠C(11)-Yb-C(12) = 87.1(6)°, ∠Yb-C(11)-Al = 77.7(7)°, ∠Yb-C(12)-Al = 80.0(6)°, ∠C(11)-Al-C(12) = 113.3(8)°, and ring centroid-Yb-ring centroid = 133.1°. As is typical of three-center two-electron bonding, the metal-C(bridge)-metal angle is rather acute, and the metal-C(bridge) bond distances (although limited in accuracy by high thermal motion) appear to be rather large. Both ¹H and ¹³C NMR studies of (C₅H₅)₂Y(μ-R)₂AlR₂ reveal rapid bridge-terminal methyl and ethyl group exchange which is fast on the NMR timescale at +40°C. Limiting, slow exchange limit spectra are reached at -40°C. The free energy for bridge-terminal alkyl interchange in the methyl compound is estimated to be 15.9 kcal/mol at 392°K. In contrast, the (C₅H₅)₂Sc(μ-R)₂AlR₂ complexes are static at +40°C, but at higher temperatures (>100°C) the methyl signals of the R=CH₃ compound collapse to a singlet.

The reaction of the aforementioned lanthanide tetramethylaluminates with pyridine yields dimeric methyl compounds (eq. (17) in high yield.



Ln = Y, Dy, Ho, Er, Tm, Yb

The same reaction with Ln = scandium revealed that Sc⁺³ was the more acidic site, since the pyridine remained coordinated to scandium; a similar observation was made for THF (eq. (18)).



Single crystal X-ray diffraction studies indicated that $[(\text{C}_5\text{H}_5)_2\text{Y}(\mu\text{-CH}_3)]_2$ and $[(\text{C}_5\text{H}_5)_2\text{Yb}(\mu\text{-CH}_3)]_2$ are isostructural. The molecular configuration of the Y compound is presented in Figure 2.

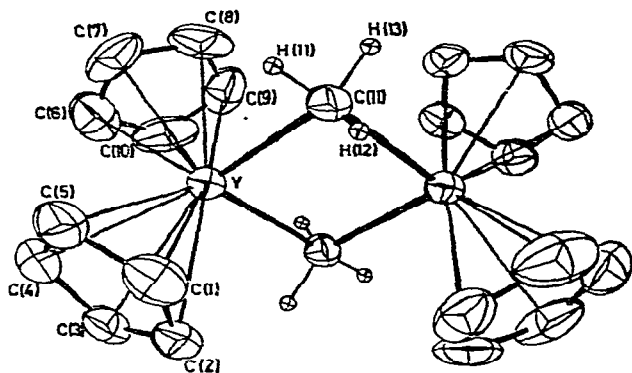
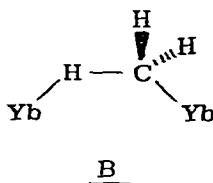
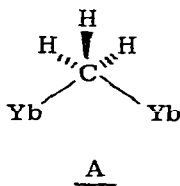


Fig. 2. The structure of $[(\text{C}_5\text{H}_5)_2\text{Ln}(\mu\text{-CH}_3)_2]_2$, Ln = Y and Yb, from ref. 17.

The hydrogen atoms of the bridging methyl groups were located in the yttrium complex. As in $[\text{Al}(\text{CH}_3)_3]_2$, the bonding is best described in terms of an electron-deficient bridging methyl (A) rather than a hydrogen-bridged structure (B).



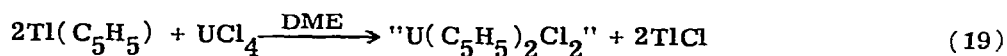
Important bond distances for the yttrium complex are Yb-C(11) = 2.536(17) Å, Yb-C(11') = 2.486(17) Å, and Yb-C(cyclopentadienyl) = 2.613(13) (average), while important angles are C(11)-Yb-C(11') =

93.4(5)^o, Yb-C(11)-Yb' = 86.6(5)^o, and ring centroid-Yb-ring centroid = 128.2^o. As in the tetramethylaluminates, an acute M-C(bridge)-M angle is observed. The Y-CH₃(bridge) and Yb-CH₃(bridge) distances may be slightly shorter than the corresponding contacts in the analogous tetramethylaluminates, but any differences are not statistically significant.

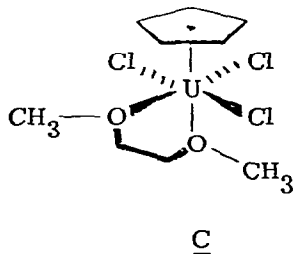
Actinides

Two review articles have recently appeared on organoactinide chemistry. Sokolov and Vasil'ev have summarized a number of aspects of organouranium chemistry with one-electron hydrocarbyl and π-allyl ligands(18). Legin(19) has reviewed the chemistry of uranocene (U(C₈H₈)₂) and other actinide cyclooctatetraene complexes. Electronic, magnetic, and chemical characteristics are discussed.

The year 1979 saw significant progress made in a number of areas of experimental organoactinide chemistry. In the area of cyclopentadienyl chemistry, Ernst, Kennelly, Day, Day, and Marks (20) have published a detailed study of the nature of U(C₅H₅)₂Cl₂ both in solution and in the solid state. The compound prepared in 1,2-dimethoxyethane (DME) according to eq. (19) is actually a



mixture of U(C₅H₅)₃Cl and U(C₅H₅)Cl₃(DME). In solution this conclusion was verified by FT ¹H NMR and optical spectroscopy, and in the solid state by X-ray powder diffraction and infrared spectroscopy. A pseudooctahedral (C) structure was assigned for U(C₅H₅)Cl₃(DME)



on the basis of NMR spectroscopy. Furthermore, the crystal structure of the related complex $U(CH_3C_5H_4)Cl_3(THF)_2$ was determined by diffraction methods and the result is shown in Figure 3. The coordination

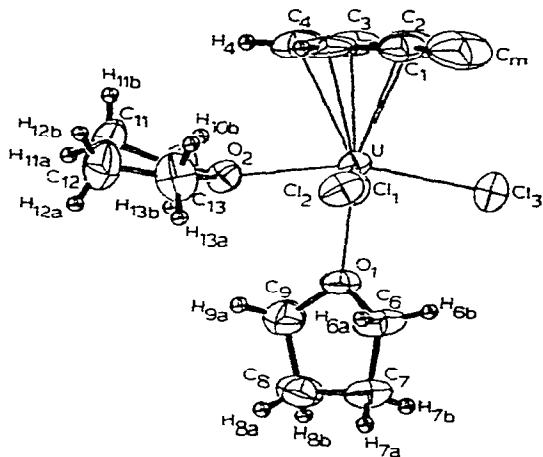


Fig. 3. The molecular structure of $U(CH_3C_5H_4)Cl_3 \cdot 2THF$ from ref. 20.

geometry about the uranium ion is essentially mer octahedral with $U-C(\text{cyclopentadienyl}) = 2.720(14) \text{ \AA}$ (average), $U-Cl = 2.623(3) \text{ \AA}$ (average), and $U-O = 2.450(8) \text{ \AA}$ (average). The major distortion of the coordination geometry from octahedral reflects ligand-ligand nonbonded repulsions and is a 0.47 \AA displacement of the uranium ion out of the equatorial plane toward the $CH_3C_5H_4$ ligand. This structure

is similar to those reported for $U(C_5H_5)Cl_3[OP(C_6H_5)_3]_2$ (21) and $U(C_5H_5)Cl_3\{OP[N(CH_3)_2]_3\}_2$ (22). The latter result was reported at a conference by Benetollo, Bombieri, DePaoli, Zanella, and Bagnall; the pseudooctahedral molecular configuration is presented in Figure 4.

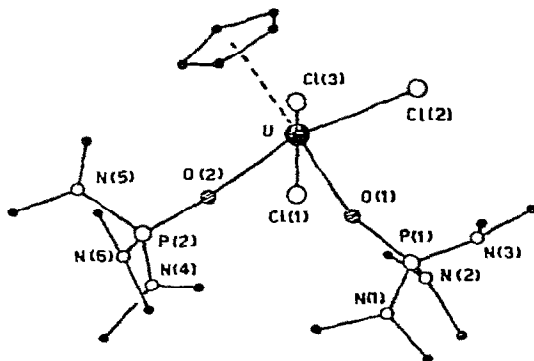
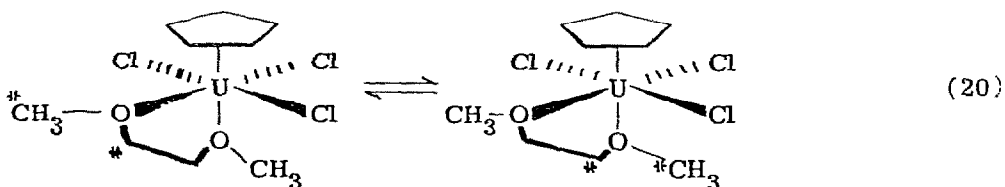


Fig. 4. Solid state structure of $U(C_5H_5)Cl_3\{OP[N(CH_3)_2]_3\}_2$ from ref. 22.

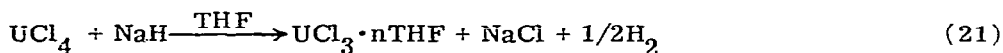
In all three structures, one bulky ligand is trans to the cyclopentadienyl ring and one cis. This arrangement apparently best minimizes the repulsions between the cumbersome organic ligands. Solution NMR studies (20) indicate that $U(C_5H_5)Cl_3(DME)$ is stereochemically dynamic, with the dimethoxyethane ligands undergoing the averaging process shown in eq. (20). Complexes of the formula $U(C_5H_5)Cl_3(L)$



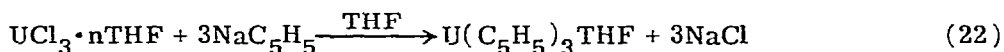
where L is a nitrogenous base such as 2,2'-bipyridyl or

1, 10-phenanthroline were prepared from the THF complex; a large number of oxygen donor complexes are already known (23).

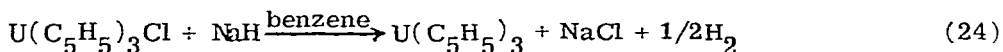
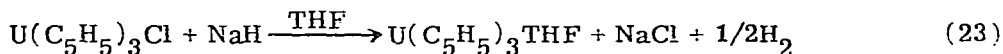
Three new routes to trivalent $U(C_5H_5)_3$ compounds have been reported. Moody and Odom (24) found that the reaction of uranium tetrachloride with sodium hydride in THF produces a soluble, reactive form of UCl_3 (eq.(21)). Reaction with sodium cyclopentadienide yields the known



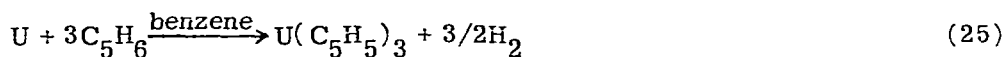
triscyclopentadienyluranium THF adduct (eq. (22)).



Zanella, Rossetto, DePaoli, and Traverso (25) reported a convenient synthesis of this compound as well as the THF-free material by reduction of $U(C_5H_5)_3Cl$ as shown in eqs. (23) and (24). Chang, Sung-Yu,



Hseu, and Chang have prepared finely divided uranium by evaporating the mercury from electrolytically prepared uranium amalgam (26). The reaction of this highly active uranium powder with cyclopentadiene yields (30%) $U(C_5H_5)_3$ (eq. (25)); in addition, the reaction of this

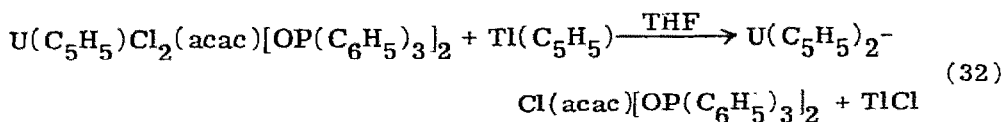
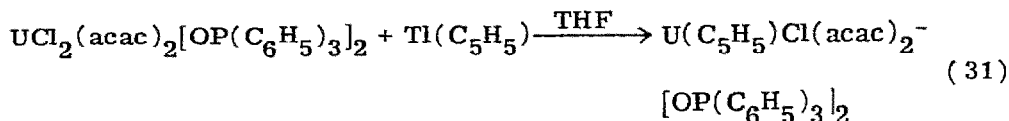
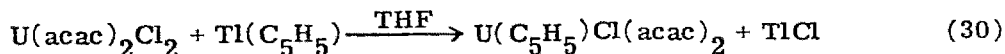
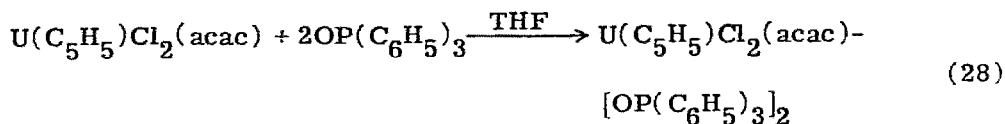
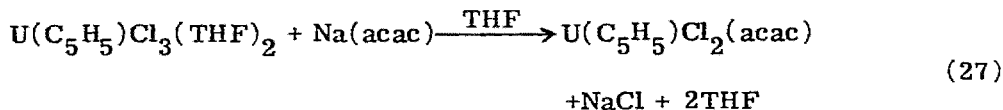


powder with cyclooctatetraene yields uranocene (eq. (26)).

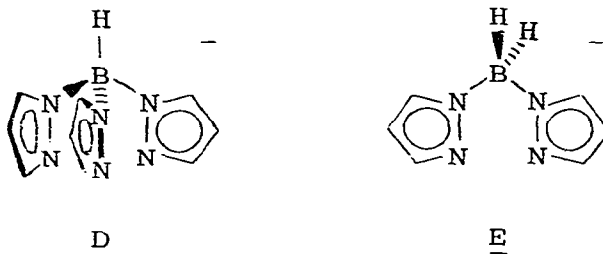


In other cyclopentadienyl actinide chemistry, Bagnall, Edwards, Rickard, and Tempest (27) have synthesized cyclopentadienyl uranium(IV)

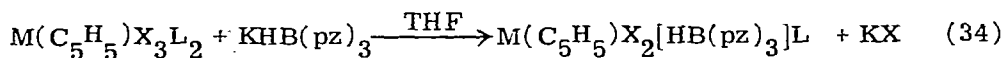
acetylacetonate complexes by the routes of eqs. (27) - (34). The new



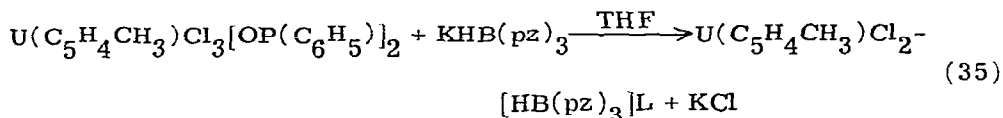
compounds were characterized by standard analytical and spectroscopic techniques. Unlike $\text{U}(\text{C}_5\text{H}_5)_2\text{Cl}_2$, neither $\text{U}(\text{C}_5\text{H}_5)_2(\text{acac})_2$ nor $\text{U}(\text{C}_5\text{H}_5)_2\text{Cl}(\text{acac})\text{[OP}(\text{C}_6\text{H}_5)_3\text{]}_2$ is unstable with respect to ligand redistribution. On the other hand, $\text{U}(\text{C}_5\text{H}_5)_2\text{Cl}(\text{acac})$ does undergo facile redistribution. Bagnall, Beheshti, Edwards, Heatly, and Tempest (28) have also prepared cyclopentadienyl thorium and uranium complexes of the hydrotris(pyrazolyl)borate (D) and dihydrobis(pyrazolyl)borate (E) ligands. As can be seen in



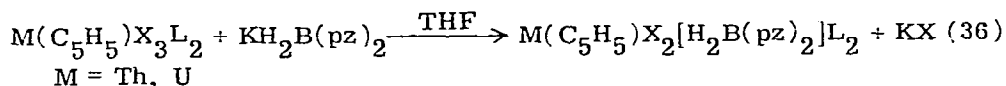
eqs. (34) and (35), a variety of cyclopentadienyl hydrotris(pyrazolyl)-borate compounds can be prepared from the appropriate $M(C_5H_5)_3X_2L_2$ (23, 29) precursors. Analogous complexes could also be prepared



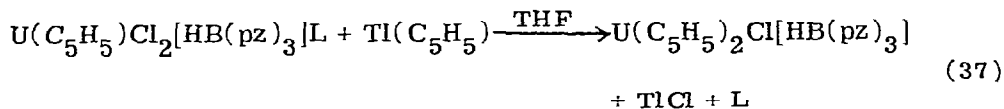
M = Th, U
 X = Br, Cl
 L = Lewis base



with the dihydrobis(pyrazolyl)borate ligand (eq. (36)). The new

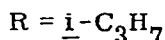
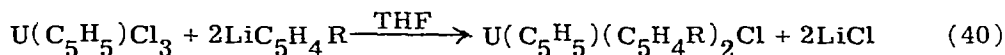
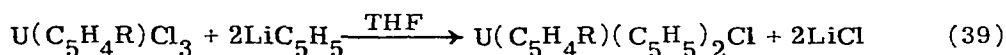
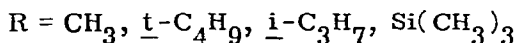
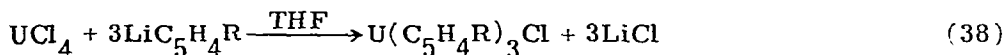


compounds were characterized by standard analytical and spectroscopic techniques. Two cyclopentadienyl rings could be introduced to form products which were stable with respect to ligand redistribution in the case of the hydrotris(pyrazolyl)borate ligand (eq. (37)) but not in the



case of dihydrobis(pyrazolyl)borate. Attempts to synthesize $U(C_5H_5)_3[HB(pz)_3]$ were unsuccessful.

Dormond and Duval (30) have synthesized a variety of ring-substituted triscyclopentadienyl uranium(IV) chlorides for ^1H NMR investigations. The NMR spectra of such $5f^2$ complexes typically exhibit large isotropic shifts (of both contact and dipolar origin) and narrow linewidths (31). The compounds of interest were prepared as indicated in eqs. (38) - (40).



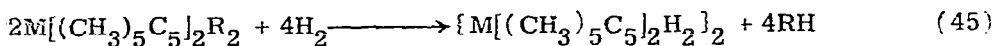
The organouranium compound prepared in the last equation is particularly interesting since the paramagnetism greatly enhances the anisochrony of the $\text{C}_5\text{H}_4\text{R}$ ring and methyl protons. At room temperature, the ring proton pairs exhibit magnetic nonequivalences of 3.9 and 1.6 ppm., while the methyl protons exhibit a nonequivalence of 1.1 ppm.

Mössbauer spectroscopy of ^{237}Np is a powerful technique for investigating bonding in organoactinides (32). Karraker and Stone (33) have now measured isomer shifts, quadrupole splittings, and magnetic hyperfine constants in the compounds $\text{Np}(\text{C}_5\text{H}_5)_3\text{R}$ ($\text{R} = \text{n-C}_4\text{H}_9, \text{C}_6\text{H}_5, \text{p-C}_6\text{H}_4\text{C}_2\text{H}_5$), $\text{Np}(\text{C}_5\text{H}_5)_3\text{Cl}$, $\text{Np}(\text{C}_5\text{H}_5)_3\text{OR}$ ($\text{R} = \text{i-C}_3\text{H}_7, \text{t-C}_4\text{H}_9, \text{CH}(\text{CF}_3)_3$), $\text{Np}(\text{C}_5\text{H}_4\text{CH}_3)_3\text{BH}_4$, $\text{Np}(\text{C}_5\text{H}_4\text{CH}_3)_3\text{O}(\text{i-C}_3\text{H}_7)$, $\text{Np}(\text{C}_5\text{H}_4\text{CH}_3)_4$, $\text{Np}(\text{C}_5\text{H}_4\text{CH}_3)\text{Cl}_3(\text{THF})_2$, and $\text{Np}(\text{indenyl})_3(\text{THF})_x$. Using the isomer shift as a measure of the electron density donated to the $\text{Np}(\text{IV})$ ion, it was concluded that in the $\text{Np}(\text{C}_5\text{H}_5)_3\text{X}$ series the electron-donating power of X^- varies approximately as $\text{Cl}^- \approx \text{BH}_4^- > \text{OR}^- > \text{R}^- > \text{C}_5\text{H}_5^-$. The cyclo-

pentadienide result was explained in terms of the increased metal-ring distances in the neptunium tetracyclopentadienyl. The anomalously low isomer shift in $\text{Np}(\text{C}_5\text{H}_4\text{CH}_3)\text{Cl}_3(\text{THF})_2$ suggests metal-ring bonding which is different from that in the triscyclopentadienyls.

In other organoneptunium work, Stollenwerk, Klenze, and Kanellakopoulos (34) have communicated the magnetic susceptibility of a series of $\text{Np}(\text{IV})(5f^3, {}^4I_{9/2})$ organometallics, $\text{Np}(\text{C}_5\text{H}_5)_3\text{X}$, where $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}, (\text{SO}_4)_{1/2}$. The temperature dependence of the susceptibility was measured from 300-1⁰K, and the crystal field strengths of the X ligands could be assessed.

Considerable activity has recently occurred in the area of actinide pentaalkylcyclopentadienyls. It has previously been reported (35) that bis(pentamethylcyclopentadienyl)thorium and uranium dialkyls suffer rapid hydrogenolysis to yield the corresponding dihydrides (eq. (45)).



$\text{M} = \text{Th}, \text{U}$

The molecular structure of the dimeric organothorium hydride has now been determined by single crystal neutron diffraction. Broach, Schultz, Williams, Brown, Manriquez, Fagan, and Marks (36) have reported the structure shown in Figure 5, which reveals both terminal and bridging Th-H interactions. The mean Th-H(terminal) and Th-H(bridge) distances are 2.03(1)Å and 2.29(3)Å, respectively. The first value is close to the sum of the covalent radii for hydrogen and thorium, and the bridging value is ca. 0.2Å longer. The H-Th-H angle, 58(1)⁰, is decidedly acute while the Th-H-Th angle, 122(4)⁰ is obtuse. The long Th-Th distance (4.007(8)Å) suggests minimal metal-metal bonding. The metal-metal distance in thorium metal is 3.59Å. The mean

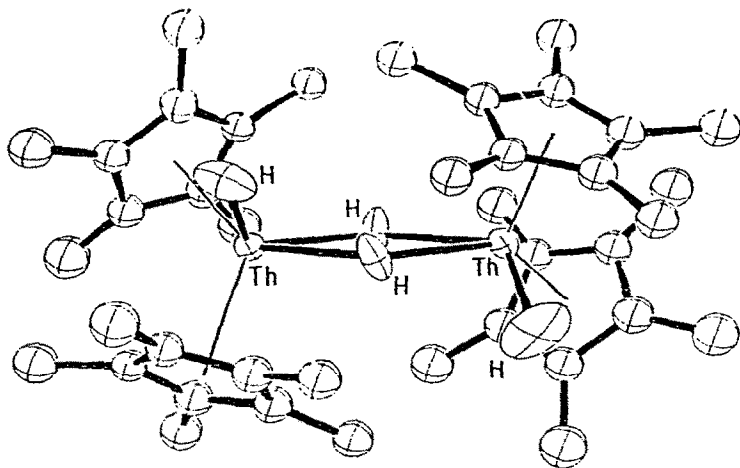
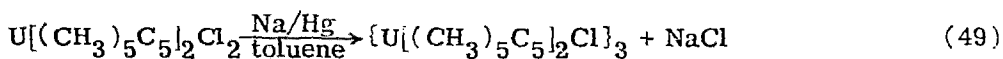
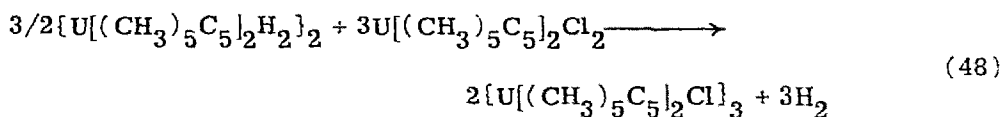
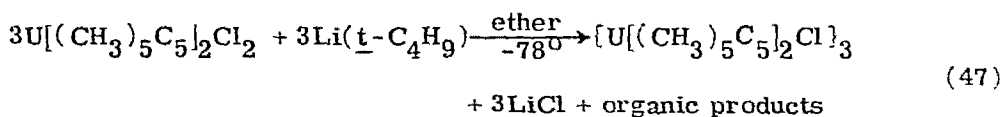
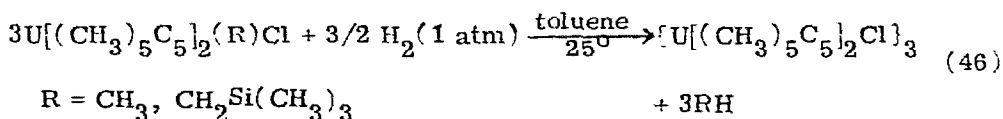


Fig. 5. Molecular structure of $\{\text{Th}[(\text{CH}_3)_5\text{C}_5\text{H}_2]\}_2$ from reference 36.

Th-C(cyclopentadienyl) distance in $\{\text{Th}[(\text{CH}_3)_5\text{C}_5\text{H}_2]\}_2$ is $2.83(1)\text{\AA}$ and the ring centroid-Th-ring centroid angle is $130(1)^\circ$.

Compared to U(IV), there is a paucity of chemical information on the organometallic chemistry of U(III). Manriquez, Fagan, Marks, Vollmer, Day, and Day (37) have now reported on the chemistry and structural properties of pentamethylcyclopentadienyl trivalent uranium compounds. Bis(pentamethylcyclopentadienyl) uranium monochloride can be prepared by any of the reductive schemes shown in eqs. (46)-(49).



Reactions (46)-(48) appear to involve the intermediacy of $U[(CH_3)_5C_5H_2(H)Cl]$, which is unstable with respect to elimination of H_2 . Eq. (47) is thought to proceed via β -hydride elimination in a transitory t-butyl derivative.

The molecular structure of the uranium monochloride has been determined by X-ray diffraction and the trimeric structure is shown in Figure 6. The

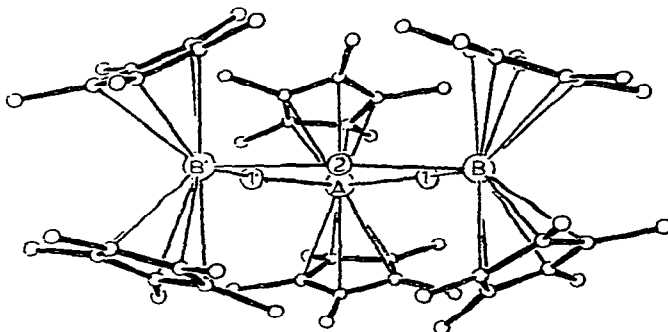
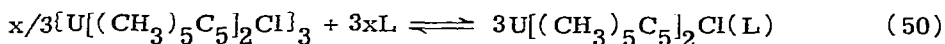


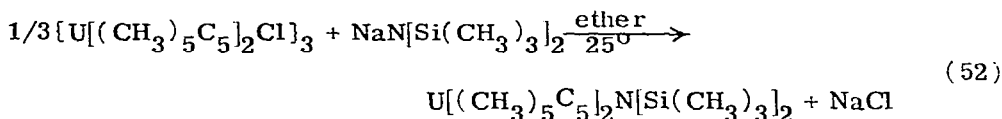
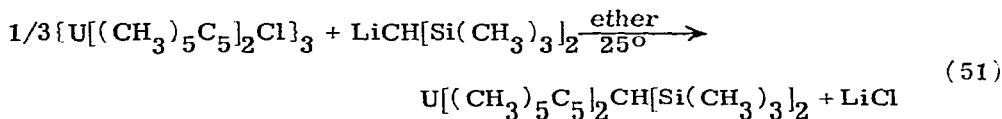
Fig. 6. Solid state structure of $\{U[(CH_3)_5C_5H_2Cl]\}_3$ from ref. 37.

structure features an approximately D_{3h} arrangement of pseudotetrahedral $U[(CH_3)_5C_5H_2Cl]$ units bridged by chloride ligands in a nearly planar six-membered ring. The average U-Cl distance is $2.901(5)\text{\AA}$, the average U-C(cyclopentadienyl) distance is $2.76(3)\text{\AA}$, and the average U-U distance is $5.669(2)\text{\AA}$. The average ring centroid-U-ring centroid angle is 127.9° . The monochloride has a number of informative chemical properties. It forms adducts with a variety of Lewis bases (including phosphines) according to eq. (50). The monochloride can

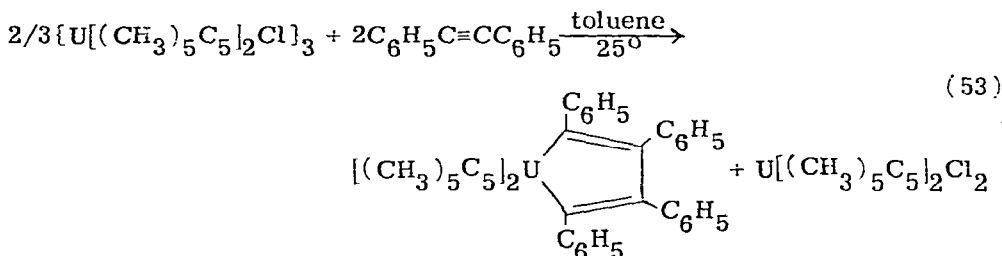


L = pyridine, $P(CH_3)_3$, THF, diethyl ether

also be converted to U(III) alkyls (eq.(51)) and dialkylamides (eq.(52)).

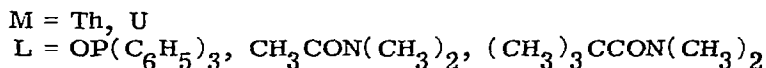
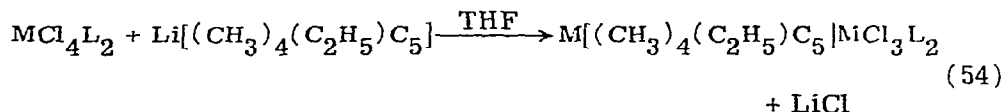


The above alkyl reacts rapidly with hydrogen to form the known dihydride, $\{U[(CH_3)_5C_5]_2H_2\}_2$, and $CH_2[Si(CH_3)_3]_2$. Finally, the monochloride reacts with diphenylacetylene in an unusual "disproportionation" reaction to produce the known U(IV) metallocycle (reductive coupling of the acetylene) and the U(IV) dichloride (eq. (53)).

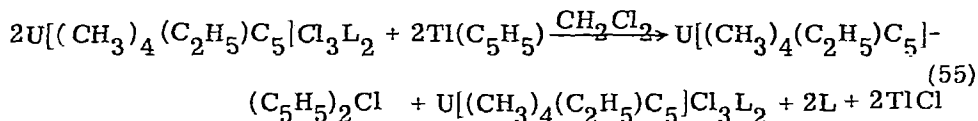


Fragalà, Ciliberto, Condorelli, Marks, Manriquez, and Fagan (38) have described the uv photoelectron spectra (He-I and He-II) of $M[(CH_3)_5C_5]_2X_2$ compounds where $M = Zr, Th, U$, and $X = Cl, CH_3$. Surprising similarities in bonding are observed when comparing the transition metal and actinide complexes. The major differences between the two classes appear to arise from metal-ligand bonding involving the actinide 5f orbitals. A distinctive $5f^2$ signal is observed in the spectra of both uranium compounds.

In related work on pentaalkylcyclopentadienyls, Bagnall, Beheshti, Heatley, and Tempest (39) have described the synthesis of tetramethylethylcyclopentadienyl ($(CH_3)_4(C_2H_5)C_5$) actinide trihalides. These compounds were prepared via the route of eq. (54) and were

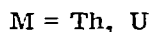
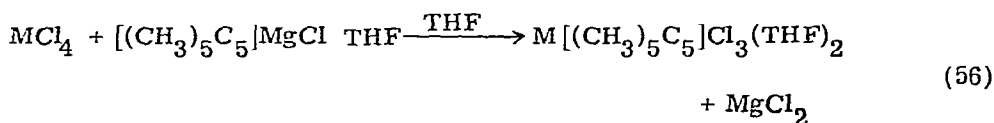


isolated as adducts of various Lewis bases. The complex with L = THF could not be obtained in a pure state. Attempts to synthesize $\text{U}[(\text{CH}_3)_4(\text{C}_2\text{H}_5)\text{C}_5](\text{C}_5\text{H}_5)_2\text{X}_2$ compounds resulted in ligand redistribution (eq. (55)), however, it was possible to prepare the three-ring complex

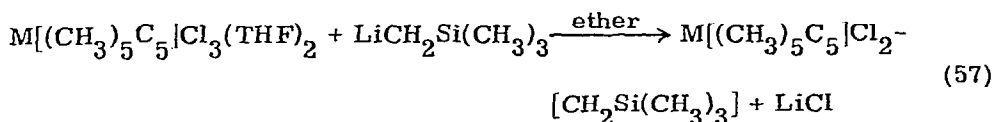


in good yield by doubling the quantity of $\text{Tl}(\text{C}_5\text{H}_5)$ employed.

Marks, Fagan, and Manriquez (40) have related the synthesis of pentamethylcyclopentadienyl thorium and uranium trichlorides using the approach of eq. (56). The structures of these complexes are presumably



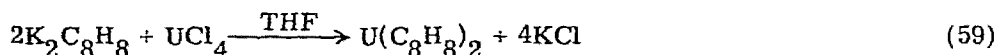
analogous to that of $\text{U}(\text{CH}_3\text{C}_5\text{H}_4)\text{Cl}_3(\text{THF})_2$ (*vide supra*). The thorium trichloride reacts with trimethylsilylmethyl lithium to produce a compound with a metal-carbon σ bond (eq. (57)).



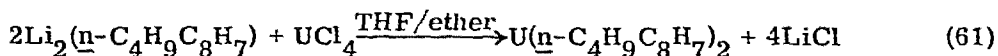
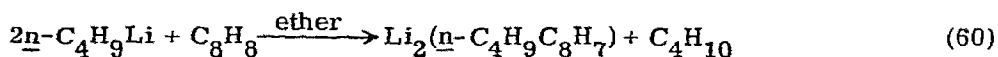
Goffart has employed the indenyl ligand to prepare complexes of

the type $M(\text{indenyl})X_3L$, where $M = \text{Th, U, Np}$; $X = \text{Cl or Br}$; and $L = \text{THF or OP}(\text{C}_6\text{H}_5)_3$ (41). It was also noted that $\text{U}(\text{indenyl})_3\text{Cl}$ reacts with UCl_4 to yield $\text{U}(\text{indenyl})\text{Cl}_3(\text{THF})$. All of the new compounds were characterized by vibrational, mass, and NMR spectroscopy, and by magnetic susceptibility.

More information on the synthesis of "uranocene" ($\text{U}(\text{C}_8\text{H}_8)_2$) as well as ring-substituted uranocenes has recently appeared. Streitwieser, Müller-Westerhoff, Mares, Grant, and Morrell (42) have published detailed directions for carrying out eqs. (58) and (59) in 82% overall yield.



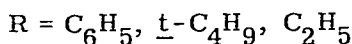
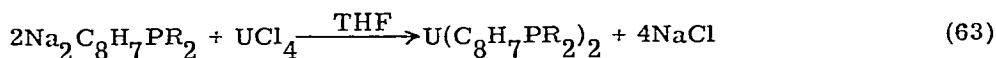
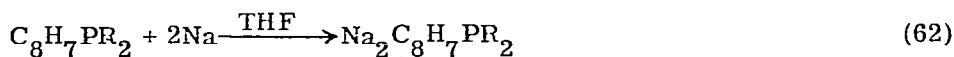
Rieke and Rhyne (43) have prepared an activated uranium slurry by reducing UCl_4 in DME with sodium-potassium alloy in the presence of naphthalene. This slurry reacts with cyclooctatetraene to produce uranocene in greater than 35% yield. In addition, the uranium slurry couples allyl iodide to give 1,5-hexadiene and benzophenone to give tetraphenylethylene. Miller and DeKock (44) have found that 1,1'-di-*n*-butyluranocene can be prepared via the sequence shown in eqs. (60) and (61).



Zalkin, Templeton, Berryhill, and Luke (45) have determined the crystal structure of bis(cyclobutenocyclooctatetraene)uranium(IV) by single crystal X-ray diffraction. The molecular geometry features

the uranocene sandwich configuration (Figure 7) with eclipsed, octahapto rings. The fused cyclobutane functionalities are positioned as far apart as possible. The plane of the cyclobutane ring is at an angle of 6.8° to the plane of the C_8 ring (tipped toward the uranium ion). The average U-C bonding distance in the present case is $2.64(2)\text{\AA}$, which compares favorably with that in uranocene, $2.647(4)\text{\AA}$ (46).

Uranium complexes of substituted cyclooctatetraenes have been described by Spiegl and Fischer (47). Phosphine-substituted cyclooctatetraenes were employed as in eqs. (62)-(63). A cyclooctatetraene-substituted



uranocene was prepared using cyclooctatetraenyl Grignard reagent

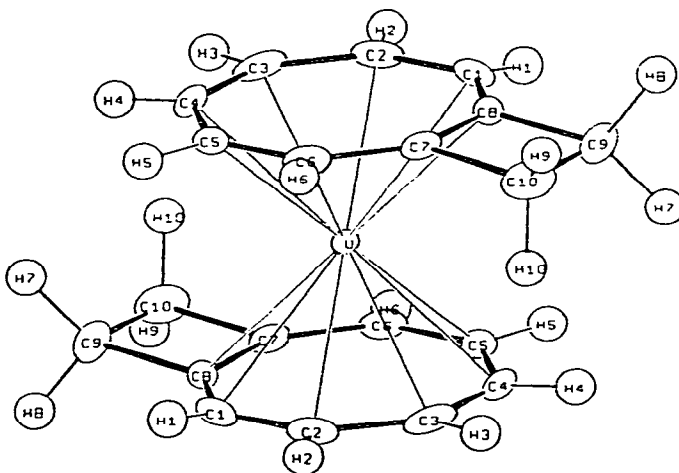
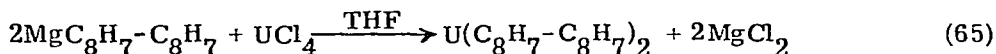
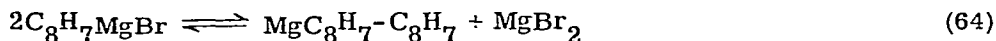


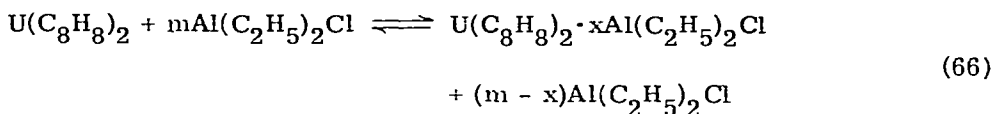
Fig. 7. The molecular structure of bis(cyclobutenocyclooctatetraene)-uranium from ref. 45.

(eqs.(64) and (65)). The structure presented in Figure 8 was proposed



for this complex. The temperature dependence of the $\text{U}(\text{C}_8\text{H}_7\text{-C}_8\text{H}_7)_2$ ^1H NMR spectrum was interpreted in terms of double bond shifting and ring inversion in the uncoordinated C_8 rings.

Shchelokov, Sokolov, Leonov, Bolotova, Khvostik, Korshunova, and Kondratenkov (48) have found that uranocene can be greatly solubilized by the addition of $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$. Variable temperature proton NMR studies indicate a dynamic equilibrium between complexed and uncomplexed uranocene (eq. (66)). The exact structure of the uranocene-



diethylaluminum chloride complex could not be determined (x is probably 2) but may involve slippage of the C_8H_8 rings to facilitate coordination of the uranium ion. Tel'noi, Rabinovich, Leonov, Solov'eva, and Gramoteeva (49) have determined heats of combustion, sublimation, and

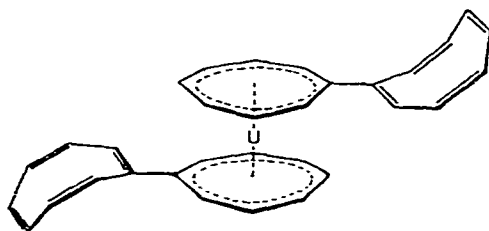
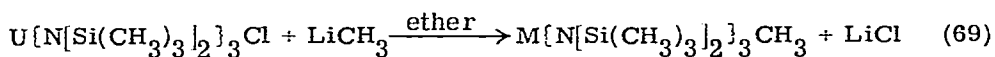
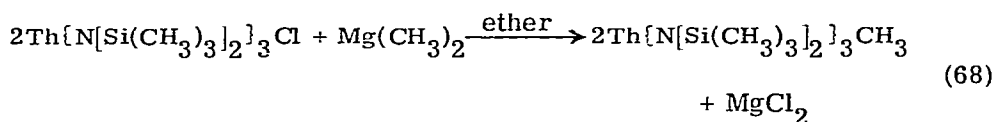
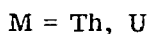
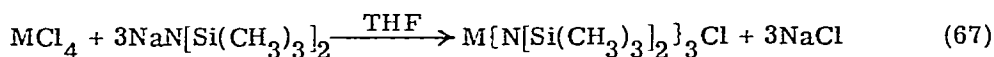


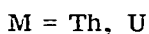
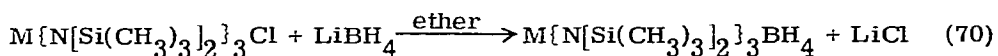
Fig. 8. Molecular structure proposed for $\text{U}(\text{C}_8\text{H}_7\text{-C}_8\text{H}_7)_2$ in ref. 47.

formation for $U(C_8H_8)_2$ and $U(C_5H_5)_4$. Mean metal-ligand bond dissociation energies of 59 kcal/mole ($U-C_5H_5$) and 83 kcal/mole ($U-C_8H_8$) were reported. The cyclopentadienyl value can be compared to 71 kcal/mole for ferrocene (50).

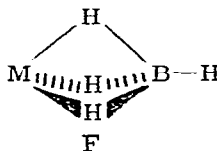
Turner, Andersen, Zalkin, and Templeton (51) have reported tris(hexamethyldisilylamido) thorium and uranium methyl compounds, prepared as shown in eqs. (67)-(69). It is also possible to prepare



tris(hexamethyldisilylamido) tetrahydroborate complexes (eq. (70)).



The mode of BH_4^- ligation was determined to be tridentate (F) from



vibrational spectroscopic criteria (52) and diffraction structure data (vide infra). The thorium tetrahydroborate and methyl compounds were found to be isomorphous. The molecular structure of the thorium tetrahydroborate was determined by single crystal X-ray diffraction and the result is illustrated in Figure 9. With the exception of the thorium,

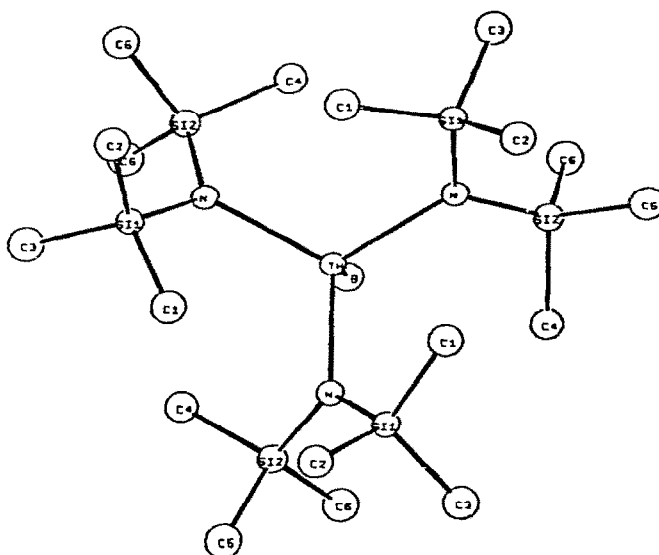
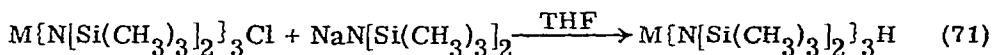


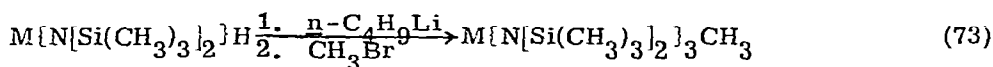
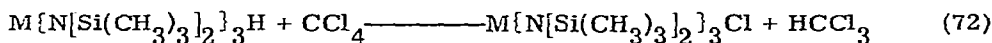
Fig. 9. The molecular structure of $\text{Th}\{\text{N}[\text{Si}(\text{CH}_3)_3]_2\}_3\text{BH}_4$ from ref. 51.

boron and terminal hydrogen atom of the BH_4^- ligand, all atoms in the structure are disordered. The thorium atom is on a threefold axis and lies 0.47 \AA above the plane of the three nitrogen atoms. Important bond distances are: $\text{Th-B} = 2.61(3) \text{ \AA}$, $\text{Th-N} = 2.32(2) \text{ \AA}$, and $\text{B-H} = 1.1(2) \text{ \AA}$. Important bond angles are: $\text{N-Th-N} = 115.9(2)^\circ$, $\text{Si}(1)\text{-N-Th} = 122(1)^\circ$, and $\text{Si}(2)\text{-N-Th} = 117(1)^\circ$. Turner, Simpson, and Andersen (53) have also reported the synthesis of tris(hexamethyldisilylamido) thorium and uranium hydrides by reacting the chloro derivatives with additional $\text{NaN}[\text{Si}(\text{CH}_3)_3]_2$ in refluxing THF (eq. (71)). Alternatively, $\text{LiB}(\text{C}_2\text{H}_5)_3\text{H}$ or $t\text{-C}_4\text{H}_9\text{Li}$ can be employed to convert the chloride to the hydride. Using deuterium labelling, the source of the hydride atom was determined to be the THF. The hydrides react with carbon tetrachloride



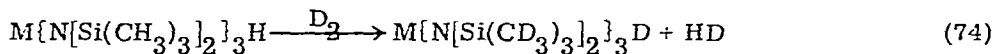
M = Th, U

to regenerate the chloro derivatives, and with butyllithium followed by methyl bromide to produce the aforementioned methyl compounds (eqs. (72) and (73)).



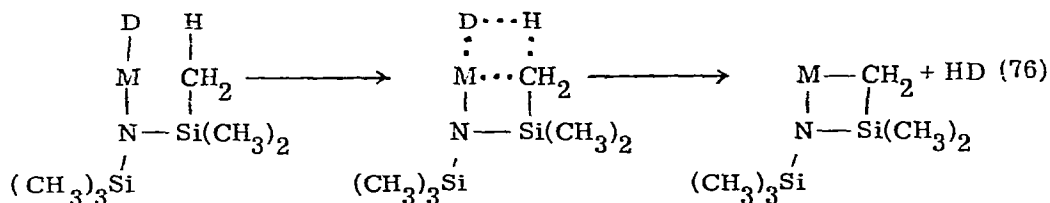
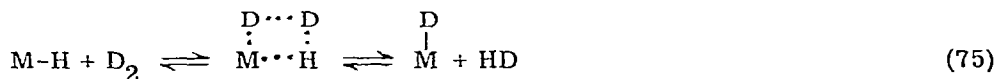
M = Th, U

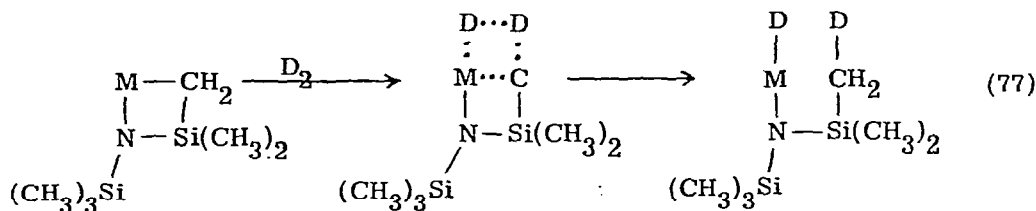
In closely related work, Simpson, Turner, and Anderson (54) have also discovered that both hydride and methyl hydrogen atoms in these compounds rapidly exchange with gaseous D₂ (eq. (74)). That this



M = Th, U

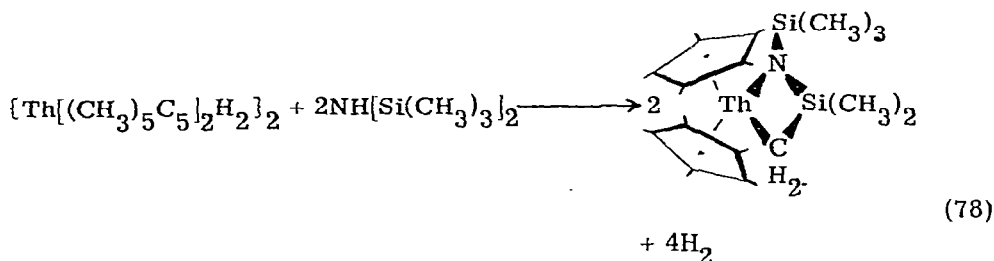
process is facile for both uranium, which has an accessible +6 oxidation state, and thorium, which should not suffer oxidative addition in the +4 oxidation state, argues for four-center mechanisms such as depicted in eqs. (75)-(77). There is precedent in previously reported



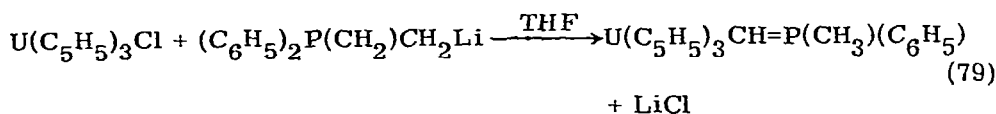


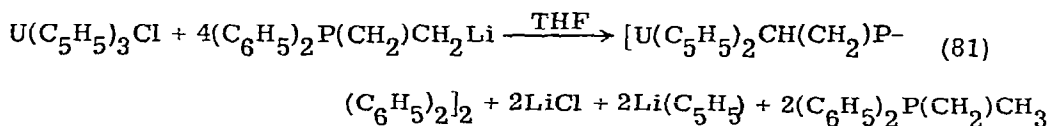
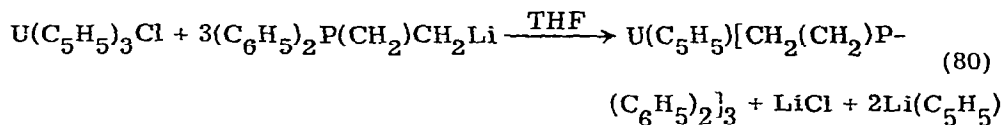
M = Th, U

organoactinide chemistry for metal hydride/D₂ exchange (35, 40), for metal-mediated C-H bond activation (31b, 40, 55), and for metal-carbon bond hydrogenolysis (35, 40). Simpson, Turner, and Andersen were also able to prepare the metallacycle shown in eq. (76) by thermolyzing the corresponding hydrides (eliminating H₂) or methyls (eliminating CH₄). It could be shown that the metallacycle reacts with H₂ (or D₂) to regenerate the corresponding metal hydride (or deuteride). A similar metallacycle-forming reaction was reported at a conference (56) (eq. (78)).

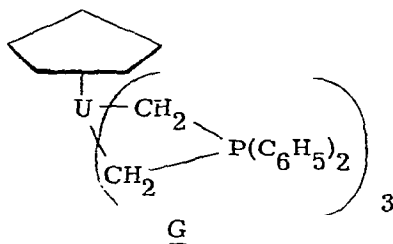


Cramer, Gilje, Maynard, and Mori (57) have described further results on the reaction of the phosphoylide (C₆H₅)₂P(CH₂)CH₂Li with triscyclopentadienyl uranium chloride (eqs. (79)-(81)). The dimeric





product of eq. (81) has already been structurally characterized (58). In the present contribution, the organouranium complex from eq. (80) was reported on the basis of X-ray diffraction studies to possess a formally nine-coordinate geometry (G).



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