Tris(η^5-cyclopentadienyl)alkyl and -alkenyl Compounds of Thorium(IV)

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Abstract: The syntheses of a number of (η^5-C$_5$H$_5$)$_3$ThR organometallics from (η^5-C$_5$H$_5$)$_3$ThCl and the corresponding RLi or RMgX reagents are reported. The new compounds have been characterized by chemical means, and by infrared, laser Raman, and proton NMR spectroscopy. The properties of these thorium organometallics are compared to those of the analogous (C$_5$H$_5$)$_3$UR compounds. With both elements the (C$_5$H$_5$)$_3$M(allyl) species is a fluxional η^1-allyl; the barriers to sigmatropic rearrangement are comparable. The Th–C bond reacts more readily with protonic solvents. The (C$_5$H$_5$)$_3$ThR compounds are more thermally stable in solution. The thermolysis pathway is similar to uranium, with intramolecular extrusion of R–H taking place (H derived from a cyclopentadienyl ring) rather than olefin elimination. For thorium, the other product of thermolysis is (η^5-C$_5$H$_5$)$_2$Th(η^1:η^5-C$_5$H$_4$)$_2$Th(η^5-C$_5$H$_5$)$_2$, which appears to arise via an intermediate η^1-C$_5$H$_4$ carbene complex-ylide. Coordinative saturation and 5f electron configuration play an important role in directing the course of certain types of reactions of organoactinides.

It is now well established that uranium(IV) alkyl and aryl complexes are chemically accessible[3] and that, given the appropriate choice of supporting ligands, these compounds can exhibit very high thermal stability.[3,4] A fundamental question in the understanding of organoactinide[5] chemical periodicity is whether alkyl and aryl compounds of other actinides exist, and if so, how their chemistry and spectroscopy is related to that of the uranium(IV) (5f^2) system.[3,4] Relatively few thorium(IV) (5f^0) organometallics are known[5] and detailed chemical comparisons between analogous pairs of uranium(IV) and thorium(IV) compounds[5,6] are almost nonexistent. In this paper, we report the first synthesis of triscyclopentadienylthorium alkyl compounds[7] and discuss some of the more interesting chemical and spectroscopic properties of these new molecules, especially as they compare to our previous results[3c] for the (C$_5$H$_5$)$_3$UR system.

Experimental Section

The synthesis and manipulation of all organothorium compounds was, of necessity, carried out under prepurified nitrogen with rigorous exclusion of oxygen and moisture. Sample handling was carried out in flame-dried Schlenk apparatus or in a glove box. All solvents were thoroughly dried in an appropriate manner and were distilled under nitrogen immediately prior to use. Melting points were determined in sealed, nitrogen-filled capillaries and are uncorrected. The reagent (C$_5$H$_5$)$_3$ThCl was prepared by our published procedure.[8] Elemental analyses were performed by Schwartzkopf Microanalytical Laboratory, Woodside, N.Y.

Tris(η^5-cyclopentadienyl)(n-butyl)thorium(IV). To 4.39 g (9.48 mmol) of (C$_5$H$_5$)$_3$ThCl was added 300 ml of toluene. After cooling this solution to −78°, 8.2 ml (13.2 mmol) of commercial 1.6 M butyllithium in hexane was added via syringe. Upon warming to −10° over 3 h, the solution turned black. It was then suction filtered and, upon evaporation of the cloudy yellow filtrate under high vacuum, a gray residue was obtained. The residue, after standing at room temperature for 2 days, was dissolved in 300 ml of toluene and filtered, yielding a water-white filtrate. The filtrate was evaporated under high vacuum, and the residue obtained was washed with two 10-ml portions of pentane and dried under high vacuum to yield 3.17 g (69%) of white microcrystalline (C$_5$H$_5$)$_3$ThC$_4$H$_9$, mp 210° dec. The solid turns ochre upon exposure to air. A somewhat purer product can be obtained by dissolution in toluene and filtration, evaporation of the filtrate, and washing the resulting powder with pentane. Ir data (cm^{-1}): 1440 w, 1400 w, 1376 m, 1350 w, 1125 w, 1093 w, 1065 w, 1015 s, 775 vs, 645 sh; Raman data (cm^{-1}): 3108 m, 3078 w, 1432 w, 1398 w, 1360 w, 1127 vs, 1117 w, sh, 1068 w, 1024 w, 790 w, 507 w, 256 s.

Anal. Calcd for C$_{19}$H$_{24}$Th: C, 47.11; H, 4.93; mol wt 484. Found: C, 47.37; H, 4.96; mol wt 489 (cryoscopic in benzene).

Tris(η^5-cyclopentadienyl)(neopentyl)thorium(IV). To a −78° solution of 0.64 g (1.38 mmol) of (C$_5$H$_5$)$_3$ThCl in 250 ml of toluene was added 5.0 ml (3.25 mmol) of 0.65 M neopentyllithium[9] in pentane. The reaction mixture was stirred and, upon warming to room temperature over 4 h, turned dark gray. It was then suction filtered and the filtrate evaporated under high vacuum yielding a white residue. The residue was washed with three 5-ml portions of hexane and vacuum-dried to yield 0.39 g (57%) of (C$_5$H$_5$)$_3$ThCH$_2$C(CH$_3$)$_3$ as a white microcrystalline solid, mp 200° dec. This material smokes upon exposure to air. Ir data (cm^{-1}): 1440 w, 1367 w, 1353 m, 1260 m, 1225 m, 1201 m, 1097 w, 1064 w, 1010 s, 930 w, 775 vs, 650 sh.

Anal. Calcd for C$_{20}$H$_{26}$Th: C, 48.19; H, 5.26. Found: C, 48.54; H, 5.01.

Tris(η^5-cyclopentadienyl)(allyl)thorium(IV). Allylmagnesium chloride was prepared by the literature procedure.[10] The product was stripped of ether and other organic impurities under high vacuum to yield a white free-flowing powder. To 1.81 g (18.0 mmol) of this reagent, suspended in 25 ml of diethyl ether and 100 ml of toluene at −78°, was added 1.40 g (3.03 mmol) of (C$_5$H$_5$)$_3$ThCl. The mixture was allowed to warm to 0° and was stirred for 24 h at this temperature and then for 1 h at room temperature. Next, the ether was removed from the dark gray mixture under high vacuum and 40 ml more of toluene was added. After 0.5 h additional stirring, suction filtration was carried out, and the water-white filtrate was evaporated under high vacuum. The white powder obtained was washed with three 10-ml portions of hexane and vacuum dried, to yield 0.59 g (42%) of (C$_5$H$_5$)$_3$ThC$_3$H$_5$ as a white microcrystalline powder, mp 210° dec. Ir data (cm^{-1}): 1675 m, br, 1584 m, 1451 w, 1447 w, 1260 w, 1190 m, 1070 m, 1012 s, 950 m, 932 m, 780 vs, 647 m, sh; Raman data (cm^{-1}): 3100 w, 1650 w, 1619 w, 1590 m, 1187 m, 1180 m, 1161 w, 1133 vs, 1124 s, 787 w, 260 s.

Anal. Calcd for C$_{18}$H$_{20}$Th: C, 47.30; H, 4.85. Found: C, 47.31; H, 4.60.

Tris(η^5-cyclopentadienyl)(isopropyl)thorium(IV). The procedure employed for the n-butyl derivative (vide supra) was followed with 1.55 g (3.35 mmol) of (C$_5$H$_5$)$_3$ThCl and 5.0 ml (6.3 mmol) of 1.26 M isopropyllithium in pentane, to yield 0.75 g (48%) of (C$_5$H$_5$)$_3$Th(i-C$_3$H$_7$) as a white microcrystalline solid, mp 220° dec. Ir data (cm^{-1}): 3080 w, 2822 s, sh, 2770 m, sh, 1780 w, br, 1675 w, br, 1570 w, br, 1440 s, 1122 w, 1058 w, 1013 vs, 858 m, 805 vs, sh, 782 vs, 656 w.

Anal. Calcd for C$_{18}$H$_{22}$Th: C, 45.95; H, 4.71. Found: C, 45.80; H, 4.73.

Tris(η^5-cyclopentadienyl)(2-*trans*-2-butenyl)thorium(IV). The procedure for the n-butyl derivative was followed using 2.76 g (5.96 mmol) of (C$_5$H$_5$)$_3$ThCl and 22 ml (8.8 mmol) of 0.4 M 2-*trans*-2 butenyllithium[11] in ether to yield 0.54 g (19%) of white microcrystalline (C$_5$H$_5$)$_3$Th[2-*trans*-CH$_3$CCH(CH$_3$)], mp 215° dec. Ir data (cm^{-1}): 3085 w, 1783 w, br, 1670 w, br, 1567 w, 1444 s, 1065 w, 1055 w, 1006 s, 836 w, 797 vs, sh, 774 s, 770 s, 645 s, 603 m.

Anal. Calcd for $C_{19}H_{22}Th$: C, 47.30; H, 4.60. Found: C, 47.21; H, 4.58.

Tris(η^5-cyclopentadienyl)(2-cis-2-butenyl)thorium(IV). The above procedure was carried out with 1.50 g (3.12 mmol) of $(C_5H_5)_3ThCl$ and 13.0 ml (4.55 mmol) of 2-cis-2-butenyllithium[11] to yield 0.38 g (24%) of $(C_5H_5)_3Th$-2-cis-$(CH_3)CCH(CH_3)$ as a white solid, mp 215° dec. Ir data (cm^{-1}): 1660 m, 1570 w, 1265 w, 1123 w, 1070 w, 1013 s, 926 m, br, 840 w, 880 s, 772 vs, 723 w; Raman data (cm^{-1}): 3109 m, 3094 w, 3072 w, 1649 w, 1507 w, 1440 w, 1360 w, 1304 w, 1236 w, 1128 s, 1125 s, sh, 1107 w, 1070 m, 1008 w, 937 w, 872 w, 750 w, 259 m.

Anal. Calcd for $C_{19}H_{22}Th$: C, 47.30; H, 4.60. Found: C, 47.33; H, 4.82.

Tris(η^5-cyclopentadienyl-d_5)(n-butyl)thorium(IV). Cyclopentadiene-d_6 was synthesized via the procedure of McLean et al.[12] and was converted into C_5D_5Tl, $(C_5D_5)_3ThCl$,[8] and, finally, into $(C_5D_5)_3Th(n$-$C_4H_9)$. Integration of the ^1H NMR spectrum indicated the compound was 95 ± 2% deuterated in the cyclopentadienyl rings.

Isolation of the Thermal Decomposition Product, the μ-di(η^1:η^5-cyclopentadienyl)-dithorium(IV) Complex. A 4-ml tube fitted with a Teflon high vacuum stopcock was washed with 5 ml of concentrated HCl, 25 ml of distilled water, 5 ml of dilute ammonia, and 25 ml of distilled water. It was then flamed under high vacuum and flushed with nitrogen. To it was added 0.65 g (0.134 mmol) of $(C_5H_5)_3Th(n$-Bu) and 2.5 ml of toluene. The stopcock was then closed and the mixture heated at 167°C for 9 days, during which time white needles precipitated out. The tube was then cooled and the supernatant syringed off. After washing the residue with three 4-ml portions of benzene and one 4-ml portion of pentane, 0.49 g (75%) of $[(C_5H_5)_2C_5H_4]_2Th_2$ was obtained. The kinetic data (Table III) indicate the thermolysis was ca. 90% complete at this point. Mass spectrum, parent ion at m/e 851 ± 1 (852 calcd); ir (Nujol mull, cm^{-1}): 1137 w, 1074 w, 1040 m, 1027 ms, 872 w, 852 w, 787 vs, br.

Anal. Calcd for $[(C_5H_5)_2C_5H_4]_2Th_2$: C, 42.26; H, 3.31. Found: C, 41.13; H, 3.33.

Spectroscopic Measurements. Infrared spectra were recorded on Beckman IR-9 and Perkin-Elmer 267 spectrophotometers and were calibrated with polystyrene film. Nujol mulls were prepared in a nitrogen-filled glove box with dry, degassed Nujol. Routinely, mulled samples were deliberately exposed to air to ascertain the effect on spectra.

Raman spectra were obtained with a Spectra Physics Model 164 argon (5145 Å, 0.30–0.40 W) or krypton (6471 Å, 0.30–0.40 W) laser in train with a Spex 1400 II double monochromator with photon counting detection.[13] Samples were examined as powders in sealed Pyrex capillaries.

Nuclear magnetic resonance spectra were recorded on Varian T-60, Hitachi Perkin-Elmer R-20B (60 MHz), and Bruker HFX-90 (90 MHz) instruments. On the R-20B, a Takeda-Riken TR-3824x frequency counter and Hitachi R-201SD proton spin decoupler were used for decoupling experiments. On the HFX-90, chemical shifts were calibrated by measuring the frequency separation from the internal locking signal with a Hewlett-Packard 5216 A electronic counter. Variable temperature studies were accomplished with the calibrated Bruker B-ST 100/700 temperature control unit. Sample solutions were examined under nitrogen in sample tubes capped with serum stoppers.

Mass spectra were recorded on a C.E.C. 21-104 or on a Hewlett-Packard 5930 mass spectrometer. The latter was interfaced with a Hewlett-Packard 5700 gas chromatograph and a data system based upon a Data General Nova 840 minicomputer with software written by Professor D. DeFord of this department. Organometallics were examined by the direct inlet technique. Deuterium incorporation studies on organic thermolysis products were conducted either by injection of pure components into the C.E.C. machine or by separating and analyzing mixtures on the H.P. GC-mass spectrometer. For the column and conditions employed (10% EDO-1 on 100/120 Chromosorb P AW $\frac{1}{8}$ in. × 20 ft at room temperature. EDO-1 = ethyl N,N-dimethyloxamate) multiple cuts of the GC peaks showed isotopic fractionation to be negligible. All quantitative deuterium incorporation measurements were made with the appropriate precautions.[14] We thank Dr. L. A. Raphelian for assistance.
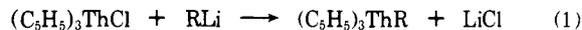
Thermolysis Studies. The relative rates of thermal decomposi-

tion of the various purified $(C_5H_5)_3ThR$ compounds were studied by NMR in solutions of toluene-d_8 or benzene-d_6. The solvent along with a calibrated internal standard (benzene) was dried over sodium–potassium alloy. This was used to prepare sample solutions of the organothorium compounds. Prior to filling and sealing under high vacuum, the NMR tubes had been carefully cleaned[3c] and flamed under high vacuum. Sample solutions were maintained in a constant temperature bath at 167 ± 1°, and were periodically removed. The decrease in intensity of the C_5H_5 resonance (and the CH_3 resonance in the case of the isopropyl and 2-cis-2-butenyl compounds) relative to the benzene peak was determined by averaging at least three integral scans. Kinetic data were analyzed by standard procedures,[15] using a program written by Mr. J. Bartmess of this department. Standard deviations reported are derived from least-squares fitting of the data.

Product analysis studies were performed by thermolyzing toluene solutions of the organometallics in ampules which could be sealed with Teflon needle valves.[3c,4a] The gases above the solutions were examined by removing measured volumes with a gas syringe and analyzing them by gas chromatography on a Barber-Coleman Series 5000 instrument (flame ionization detection). Columns employed were a $\frac{1}{4}$ in. × 10 ft Porapak QS (95–120°) and a $\frac{1}{8}$ in. × 16 ft 15% tris(cyanoethoxy)propane on Chromosorb W (27°). Calibration of yield was achieved by chromatographing control samples prepared from toluene and known amounts of hydrocarbons. For most of the compounds, thermolysis product identity and yield were also verified from the ^1H NMR spectra of the kinetics samples. Assignments were confirmed with spectra of known hydrocarbons. In several cases, the thermolysis solutions were trap-to-trap distilled, and the distillate was analyzed by GC. The deuterium content of the hydrocarbons above the thermolysis solutions was determined by removing samples from the thermolysis tubes with a gas syringe and injecting them into the mass spectrometer (see previous section). Known mixtures of deuterated or undeuterated hydrocarbons served as a control.

Results

Synthesis and Characterization. The new organothorium compounds could be synthesized via the following reactions:

$$(C_5H_5)_3ThCl + RLi \longrightarrow (C_5H_5)_3ThR + LiCl \qquad (1)$$

$$(C_5H_5)_3ThCl + RMgX \longrightarrow (C_5H_5)_3ThR + MgXCl \qquad (2)$$

where R can be the following: Ia, R = allyl; Ib, R = i-C_3H_7; Ic, R = 2-cis-2-butenyl; Id, R = 2-trans-2-butenyl; Ie, R = n-C_4H_9; If, R = neopentyl. The products, when pure, are colorless, air-sensitive microcrystalline solids. In general, reaction conditions for a successful preparation are somewhat more critical than in the uranium series.[3] Considerable reduction to thorium metal competes with alkylation, and best results in terms of product yield and purity are obtained at low temperatures in noncoordinating solvents. Even so, it has not been possible to synthesize either the phenyl or tert-butyl derivatives in a pure state. The thorium alkyls are less soluble in common organic solvents than the uranium analogues (a similar situation obtains for the $(\eta^8$-$C_8H_8)_2M$ series[16]) rendering crystallization considerably more difficult.

The new thorium compounds have been characterized by elemental analysis, infrared and laser Raman spectroscopy (see Experimental Section for data), and by proton magnetic resonance with homonuclear decoupling. The infrared spectra exhibit the characteristically simple pattern of η^5-cyclopentadienyl groups (C_{5v}):[3c] A_1 and E_1 C–H out-of-plane wagging ≈ 780 cm^{-1} (strong), and E_1 in-plane wagging ≈ 1010 cm^{-1} (medium). The laser Raman spectra exhibited corroboratory[17] emissions at ca. 3100 cm^{-1}, A_1 C–H stretch (strong); ca. 1130 cm^{-1}, A_1 ring breathing (strong); and ca. 260 cm^{-1}, A_1 metal-ring stretch (strong). Other features were more difficult to discern due to interference by fluorescence. In general, the vibrational spectra are quite similar to the uranium system, strongly supporting

Table I. Nuclear Magnetic Resonance Data for
$(\eta^5\text{-}C_5H_5)_3$ThR Compounds[a-c]

Com-pound	
1a	6.50 (1 H, quint, J = 12 Hz), 5.84 (15 H, s), 3.94 (4 H, d, J = 12 Hz)[d]
1b	5.95 (15 H, s), 1.89 (6 H, d, J = 6.5 Hz),[d] 0.98 (1 H, m, J = 6.5 Hz)
1c	6.45 (1 H, m, J = 6 Hz),[d] 6.10 (15 H, s,), 2.18 (3 H, m), 2.05 (3 H, d of m, J = 6 Hz)
1d	6.95 (1 H, m, J = 6 Hz),[d] 6.16 (15 H, s), 2.56 (3 H, m), 2.11 (3 H, d of m, J = 6 Hz)
1e	6.00 (15 H, s), 1.39 (9 H, m)
1f	6.09 (15 H, s), 1.41 (9 H, s), 1.28 (2 H, s)

[a] ¹H NMR data in δ (ppm). [b] All data at 25°C. [c] Key: s = singlet; d = doublet; quint = quintuplet; m = multiplet. [d] Assignment verified by spin decoupling.

our proposed structure (A), well established for $(\eta^5\text{-}C_5H_5)_3$U compounds by diffraction studies.[18]

A
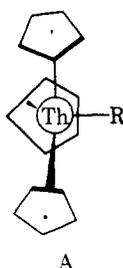
The proton NMR spectra (Table I) are in accord with the proposed structure. The data also indicate, as expected for Th(IV) (5f⁰), that the compounds are diamagnetic. The resonance positions for the C_5H_5 protons are at rather low field (δ 6.14–5.97) as commonly found for complexes of the early transition metals.[19]

The room temperature proton NMR spectrum of $(C_5H_5)_3$Th(allyl) is shown in Figure 1. The allyl portion of the molecule exhibits a simple A_4X pattern; the position of the X quintet has been confirmed via spin decoupling, as illustrated in the figure. This spectral pattern is characteristic of both fluxional monohapto and trihapto metal allyls.[6b,20] In $(C_5H_5)_3$U(allyl), the ground state geometry, i.e., the instantaneous structure of the allyl group, was shown to be monohapto by variable temperature ¹H NMR studies and by the infrared spectrum.[3c] X-Ray diffraction studies on $(C_6H_5CH_2C_5H_4)_3$U(2-methylallyl) further support this deduction.[21] In the case of $(C_5H_5)_3$Th(allyl), sufficiently low temperatures required to observe the slow exchange limit spectrum could not be reached. However, collapse of the allylic resonances (Figure 1) by ca. −80° was observed in both toluene-d_8 and toluene-d_8-pentane solutions (which differ considerably in viscosity), and this strongly suggests slowing of the dynamic process. Unfortunately, assignment of a ground state geometry based upon chemical shift and/or coupling constant arguments is not unambiguous. For example, the low field resonance position of the X proton (δ 6.55) is near to that found for most σ-allyls, i.e., the olefinic region,[22] and also to that of the π-allyl, $(\eta^3\text{-}C_3H_5)_4$Th, δ 6.03.[6b] Similar difficulties arise in examination of the methylene proton chemical shifts[22,23] and J_{A-X}, which is invariably in the range 10–12 Hz,[22,6b] regardless of the instantaneous structure. Fortunately, some structural information can be obtained from the vibrational spectra of metal allyls.[6b,17,24] The most characteristic infrared-active vibration for η^1-allyls is $\nu_{C=C}$ at about 1600 cm⁻¹. This is absent in trihapto structures; however, strong to medium diagnostic bands are observed in the 1460–
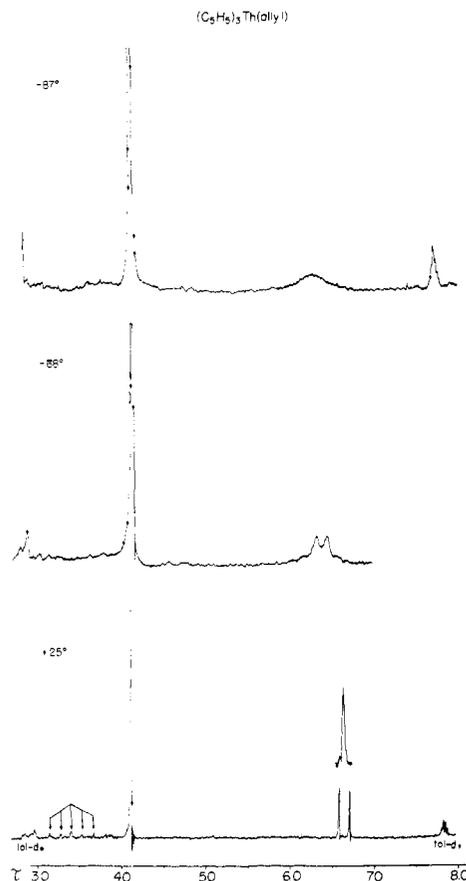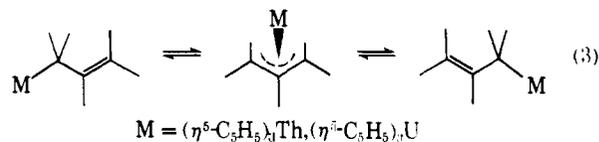

Figure 1. Variable temperature 90-MHz ¹H NMR spectra of $(C_5H_5)_3$Th(allyl) as a solution in toluene-d_8. The room temperature spectrum also indicates by an inset resonance the result of applying decoupling irradiation to the center of the low field quintet.

1500-cm⁻¹ region (CH_2 deformations) and around 1380–1400 cm⁻¹ (probably the antisymmetric C–C–C stretch). The vibrational spectrum of $(C_5H_5)_3$Th(allyl) (see Experimental Section for data) is similar to η^1-allyls,[6b,24] including $(C_5H_5)_3$U(allyl)[25] and unlike most π-allyls.[6b,24] The laser Raman spectrum of the thorium compound (Experimental Section for data) also exhibits $\nu_{C=C} \approx 1650$ cm⁻¹, and is unlike the spectra of the η^3-allyls which have been examined to date.[24] Thus, the ground state structure of the allyl ligand is monohapto for both the uranium and thorium tris(cyclopentadienyls).
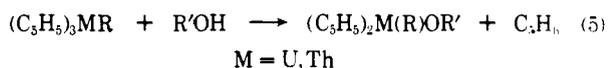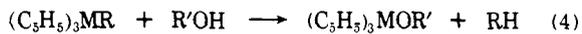
Returning to the dynamic process, it is possible to roughly estimate $\Delta G^\ddagger$,[26] assuming the coalescence temperature to be ca. −100 ± 10° and $\Delta\nu \approx 110 \pm 20$ Hz.[22] This treatment yields $\Delta G^\ddagger \approx 7.6$–8.7 kcal/mol, a value which is surprisingly close to that found for the analogous uranium system, 8 ± 1 kcal/mol.[3c] These results suggest that the potential energy surface for the tautomeric process given by eq 3,

$$M\text{—}\mathrel{\rlap{\raisebox{-2pt}{$\rightleftharpoons$}}} \quad \overset{M}{\text{—}} \quad \mathrel{\rlap{\raisebox{-2pt}{$\rightleftharpoons$}}} \quad \text{—}M \qquad (3)$$

$$M = (\eta^5\text{-}C_5H_5)_3Th, (\eta^5\text{-}C_5H_5)_3U$$

changes little when thorium is substituted for uranium. Whether these observations will be general for stereochemically nonrigid organoactinides remains to be seen. In the tetraallyl series,[6b] $(\eta^3\text{-}C_3H_5)_4$Th begins to exhibit (on the NMR time scale) fluxional behavior above ca. +10°. The uranium analogue appears to be too thermally unstable to allow measurements at these temperatures.[6b] In general, the large isotropic shifts of U(IV) complexes will facilitate

NMR studies of processes with low activation energies,[3c,27] since, for a given rate of exchange, increased chemical shift separations expand the time resolution of the NMR experiment.[27,28] For the same reason, processes with high activation energies will be more difficult to study. The $(C_5H_5)_3M(allyl)$ and $(allyl)_4M$ systems serves as illustrations of these points, and it is apparent that activation parameters will not be obtainable for all pairs of compounds (at least not at the same magnetic field strength[28b]).
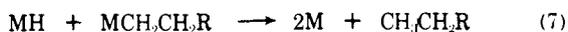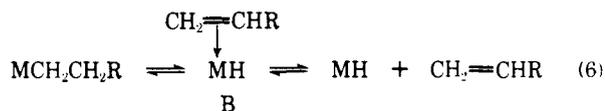
Chemistry. Reactions. It has already been noted[3c,d] that $(C_5H_5)_3UR$ compounds suffer alcoholysis at both mono-hapto and pentahapto linkages, eq 4 and 5. We find that the

$$(C_5H_5)_3MR \ + \ R'OH \ \longrightarrow \ (C_5H_5)_3MOR' \ + \ RH \quad (4)$$

$$(C_5H_5)_3MR \ + \ R'OH \ \longrightarrow \ (C_5H_5)_2M(R)OR' \ + \ C_5H_6 \quad (5)$$

$$M = U, Th$$

new $(C_5H_5)_3ThR$ compounds undergo similar reactions, with two differences. First, the alcoholysis of the thorium organometallics, as monitored by ^1H NMR, is faster than that of the analogous uranium compounds by several orders of magnitude for R and R' constant. This result mirrors the findings for the $(\eta^8-C_8H_8)_2M$ compounds;[16] i.e., uranocene is considerably more stable to hydrolysis than thorocene.[29] However, we also find that alcoholysis is considerably more selective for the thorium compounds, and that, upon incremental addition of alcohol, cleavage of the C_5H_5 ligands (best identified by appearance of C_5H_6 in the pmr spectrum) does not take place until all of the η^1-alkyl ligands have been cleaved. No such ligand selectivity is observed for the uranium organometallics,[30] and we have, at present, no explanation for these differences. A priori, the reaction with higher activation energy would be expected to exhibit greater selectivity.[31] Further studies are in progress.

As in the case of the uranium organometallics,[3c] no nucleophilic addition of $(C_5H_5)_3ThR$ compounds to acetone was observed over the course of several hours.

Chemistry. Thermal Behavior. The initial qualitative observations[3a] of strikingly high thermal stability for the $(C_5H_5)_3UR$ compounds led us to undertake a thorough examination of thermolysis kinetics and product yields in solution.[3c] The objective was to better understand those factors which stabilize actinide-to-carbon σ bonds. One surprising conclusion of this mechanistic investigation was that the commonly observed β-hydrogen elimination reaction,[32,33] eq 6 (sometimes attended by eq 7), was not operative to an appreciable extent in the thermal decomposition reaction.

$$MCH_2CH_2R \ \overset{CH_2=CHR}{\underset{\displaystyle \;}{\rightleftharpoons}} \ MH \ \rightleftharpoons \ MH \ + \ CH_2=CHR \quad (6)$$
$$B$$

$$MH \ + \ MCH_2CH_2R \ \longrightarrow \ 2M \ + \ CH_3CH_2R \quad (7)$$

Instead, stereospecific, intramolecular abstraction of a cyclopentadienyl ring hydrogen was found to take place, producing RH. It was suggested[3c] that inability to suffer β-elimination was a significant stabilizing factor for a number of the $(C_5H_5)_3UR$ compounds, and that this inability might be due to partial or complete coordinative saturation of the uranium ion (destabilization of structure B). The observation[4a] that a number of thermally unstable, presumed uranium tetraalkyls, R_4U, readily undergo olefin elimination is further substantiation of this hypothesis, since facile expansion of the coordination sphere would, in this case, seem energetically more feasible.

Similar studies of organothorium compounds were important for clarifying certain aspects of the uranium systems and, on a more general level, for exploring the effect of

Table II. Volatile Organic Thermolysis Products for $(C_5H_5)_3ThR$ Compounds

Compound	Product	Overall yield[a]	% R–D[b]
Ib	Propane	97	
	Propene	<2	
Ic	cis-2-Butene	90	
	trans-2-Butene	<5	
Id	trans-2-Butene	90[c]	
	cis-2-Butene	6[c]	
Ie	n-Butane	98	5[c]
	1-Butene	<1	
	Octane	<1	
If	Neopentane	100[c]	

[a] Based on starting thorium alkyl; estimated error ±2%. [b] Thermolysis in benzene-d_6. [c] Overall yield not measured; this represents composition of volatile organic product.

chemical periodicty on reactions of actinide-to-carbon σ bonded organometallics. Hence, the thermolysis of the $(C_5H_5)_3ThR$ compounds was investigated in toluene solution. Both product and kinetic analyses were carried out. The major *organic* product of $(C_5H_5)_3ThR$ thermolysis was invariably the corresponding R–H compound in high yield (Table II). In no case were products which would arise from β-hydrogen elimination detected in greater than trace amounts. The dimer, R–R, which might arise from free R· radicals[34,35] or from a nonradical bimolecular elimination[36] was sought in several cases and was either undetectable or present, at most, in only trace amounts. As found for the uranium system,[3c] thermolysis in benzene-d_6 resulted in only a minor yield of R–D (Table II).

Several experiments designed to identify free R· radicals which might be produced by Th–R homolysis were also carried out. In solution, free vinylic radicals are known to undergo inversion (eq 8) at rates (ca. 10^{10} sec^{-1} [37,38]) which

$$ (8) $$
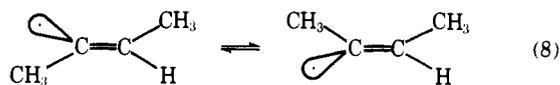
are competitive with radical atom transfer from solvents or potent scavengers.[3c,11a,37,38] For $(C_5H_5)_3Th(2-cis-2-bute-nyl)$ and $(C_5H_5)_3Th(2-trans-2-butenyl)$, the thermolysis products were, respectively, cis-2-butene and trans-2-butene (Table II). These results indicate the hydrogen abstraction occurs with essentially complete retention of configuration at the carbon atom bound initially to thorium, and free butenyl radicals are apparently not present for any length of time along the reaction coordinate. Another useful, supplemental test for free radicals was based upon the rapid cyclization of 5-hexenyl radicals,[39] eq 9. This process

$$ (9) $$

is competitive with hydrogen abstraction from most solvents,[39] though the rate (ca. 10^5 sec^{-1} [39a]) is not as great as the inversion of vinyl radicals. The reaction of $(C_5H_5)_3ThCl$ with 5-hexenylmagnesium bromide[39a] under the usual alkylation conditions (see Experimental Section) produced a thorium organometallic which was identified by its ^1H NMR spectrum (no olefinic or allylic protons, C_5H_5:aliphatic protons in a ratio of ca. 15:11) not as the 5-hexenyl derivative but as the cyclopentylmethyl derivative,
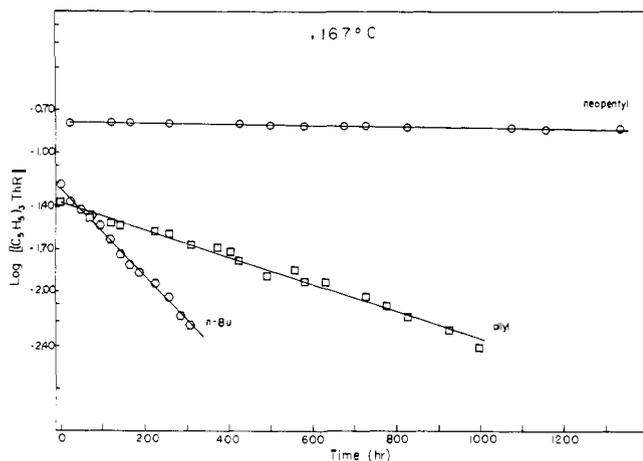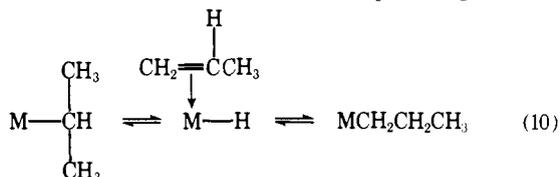
$$C$$
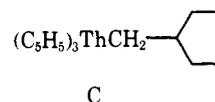
Figure 2. Kinetic plots for the thermal decomposition of various (η^5-C$_5$H$_5$)$_3$ThR compounds in solution.

Figure 3. Kinetic plots for the thermal decomposition of several (η^5-C$_5$H$_5$)$_3$ThR compounds. Functional groups in parentheses indicate which ^{1}H NMR resonances were monitored for the data.

(C). Such a cyclization accompanying metal–carbon bond formation has been observed before in silver–phosphine systems.[36]

Kinetic studies were also undertaken to determine the effect of the various organic substituents on the rate of thermal decomposition and also to secure additional mechanistic information. Rates were measured at various concentrations by following the disappearance of various (C$_5$H$_5$)$_3$ThR resonances in the NMR. The thermolysis reactions, as expected for a unimolecular rate-determining step, are first order in thorium alkyl (Figures 2 and 3), and rate constants, half-lives, and free energies of activation are presented in Table III. In all cases, considerably greater thermal stability was found than in the uranium series;[3c] comparative data can be seen in Table IV. A feature common to both uranium and thorium systems is the instability of the secondary alkyl (isopropyl) in comparison to the primary. Other trends, e.g., allyl vs. alkyl, neopentyl vs. *n*-butyl, are not clear-cut. The kinetic analysis also provided information on the possibility that, though decomposition did not proceed via β-hydrogen elimination, substantial elimination–readdition such as shown in eq 10, might occur

$$\underset{\underset{\text{CH}_3}{|}}{\overset{\overset{\text{CH}_3}{|}}{\text{M}-\text{CH}}} \rightleftharpoons \underset{\underset{}{}}{\overset{\overset{\text{CH}_2=\text{CCH}_3}{}}{\text{M}-\text{H}}} \rightleftharpoons \text{MCH}_2\text{CH}_2\text{CH}_3 \qquad (10)$$

prior to or competitively with the destruction of the M–C bond.[33d,40,41] This possibility was shown to occur less than 5% in pure (C$_5$H$_5$)$_3$U(*i*-Pr) since ^{1}H NMR isotropic shifts of paramagnetic products were large enough to allow easy identification of any new organouranium species (e.g., (C$_5$H$_5$)$_3$U(*n*-Pr)).[3c,42] However, resonances of the various diamagnetic thorium alkyls (such as the C$_5$H$_5$ singlet) frequently overlap at 60 MHz, so instead, the rate of decrease of the conspicuous isopropyl methyl doublet was compared to that of the C$_5$H$_5$ singlet (Figure 3). Isomerization (eq 10) would diminish the CH$_3$ resonance at a rate greater than the C$_5$H$_5$, since the *n*-propyl and isopropyl C$_5$H$_5$ resonances are nearly degenerate. As can be seen in Figure 3, data for C$_5$H$_5$ and CH$_3$ decay fall along the same plot for solutions of pure (C$_5$H$_5$)$_3$Th(*i*-Pr). Thus, we are unable to detect isomerization processes which would arise from reversible β-hydrogen elimination prior to actual disappearance of the isopropyl compound. A similar analysis of the 2-*cis*-2-butenyl complex (Figure 3) also revealed no evidence of isomerization prior to thermolysis.
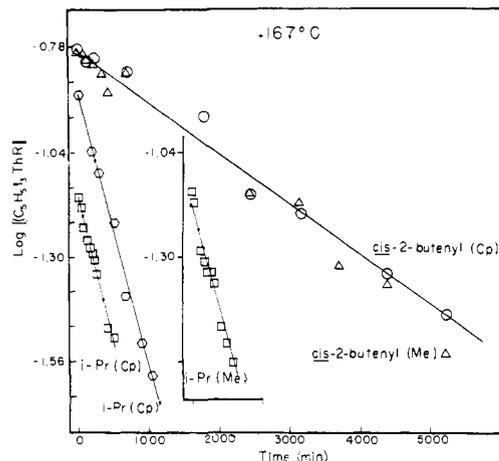
Table III. Kinetic Data for Thermolysis of (C$_5$H$_5$)$_3$ThR Compounds[a]

Compound	Concn (M)	Peak monitored	10^4k, h^{-1}	$t_{1/2}$, h	$\Delta G^{\ddagger}$, kcal/mol
Ia[b]	0.043	C$_5$H$_5$	22.6 ± 0.6	566	38.6
Ib[c]	0.068	C$_5$H$_5$	962 ± 4	7.21	35.3
Ib[c]	0.068	CH$_3$	1000 ± 7	6.93	35.3
Ib[c]	0.125	C$_5$H$_5$	942 ± 5	7.36	35.3
Ib[c,d]	0.02	C$_5$H$_5$	1010 ± 2	6.86	35.3
Ic[c]	0.162	C$_5$H$_5$	182 ± 7	38.1	36.8
Ic[c]	0.162	CH$_3$	175 ± 10	39.6	36.8
Id[c]	0.030	C$_5$H$_5$	326 ± 20	21.2	36.3
Ie[b]	0.054	C$_5$H$_5$	72.3 ± 2.3	95.9	37.6
Ie[c,d]	0.02	C$_5$H$_5$	70 ± 20	99	37.6
If[b]	0.0163	C$_5$H$_5$	0.92 ± 0.15	7500	41.4

[a] All compounds studied at 167 ± 1°. [b] Compounds examined in toluene-d_8. [c] Compounds examined in benzene-d_6. [d] Mixed thermolysis; Ib and Ie run together.
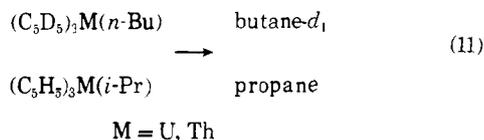
Table IV. Comparative Data for Thermolysis of (C$_5$H$_5$)$_3$MR Compounds in Solution

R	M = U		M = Th	
	$\Delta G^{\ddagger}$ (kcal/mol)	$t_{1/2}$ (hr)	$\Delta G^{\ddagger}$ (kcal/mol)	$t_{1/2}$ (hr)
n-C$_4$H$_9$[b]	33.3 (97°)	1130	37.6 (167°)	96
Neopentyl[b]	32.2 (97°)	270	41.4 (167°)	7500
i-C$_3$H$_7$[a]	29.8 (72°)	201	35.3 (167°)	7.1
Allyl[b]	28.7 (72°)	40	38.6 (167°)	566
trans-2-Butenyl[a]	34.6 (97°)	6730	36.3 (167°)	21

[a] Samples studied in toluene and benzene-d_6 for M = U, Th, respectively. [b] Samples run in toluene and toluene-d_8 for M = U, Th, respectively.
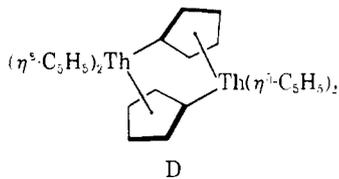
The kinetic measurements described above indicate that the rate-determining step in (C$_5$H$_5$)$_3$ThR thermal decomposition is unimolecular. However, these results do not rigorously exclude the possibility of a rate-determining intramolecular rearrangement (e.g., to produce a metal hydride) followed by a rapid bimolecular reaction for R–H formation, similar to eq 7. Though any bimolecular process seems unlikely in view of the great steric bulk surrounding the actinide,[43] two additional experiments were conducted. First, it was found that both (C$_5$H$_5$)$_3$Th(*n*-Bu) and (C$_5$H$_5$)$_3$Th(*i*-Pr) decompose at the same rate when mixed together as when separate (Table III). Since the isopropyl organometallic is considerably less stable than the *n*-butyl, it is rea-

sonable that any hypothetical rapid bimolecular reaction occurring subsequent to the rate-determining step would affect the rate of decomposition of the n-butyl compound. No such effect was observed. For the $(C_5H_5)_3UR$ series,[3c,42] an additional "cross-over" experiment was conducted (eq 11)

$$(C_5D_5)_3M(n\text{-Bu}) \qquad \text{butane-}d_1$$
$$\longrightarrow \qquad\qquad (11)$$
$$(C_5H_5)_3M(i\text{-Pr}) \qquad \text{propane}$$

$$M = U, Th$$

to further prove the unimolecularity of R–H formation. No cross-over was observed,[3c,42] as expected. The same experiment was then conducted for the thorium analogues. Considerable cross-over (butane which was 72% protonated, propane which was 35% deuterated) was observed. However, mass spectra of the starting triscyclopentadienylalkyls, isolated after partial thermolysis, indicated that random scrambling of the label had taken place prior to thermolysis. It is not certain whether the difference in behavior of the thorium vs. the uranium compounds reflects differences in thermolysis conditions ($97°$[3c] vs. $167°$), purity of the compounds (the uranium alkyls crystallize more readily), or reaction pathway. In any case, the cross-over experiment provides no mechanistic information on the molecularity of the thermal decomposition. However, the results of the other experiments conducted offer very strong support for the intramolecularity of R–H extrusion.

The discussion so far has centered principally on the *organic* products of $(C_5H_5)_3ThR$ thermolysis. Though, as shown above, considerable information can be obtained from the nature of these products, the resultant actinide-containing thermolysis species are of obvious interest. Solutions of $(C_5H_5)_3UR$ complex precipitate a pyrophoric brown solid upon thermal decomposition.[3c] This solid analyzes for $(C_5H_5)UH_n$, $n = 2$ or 3; the infrared spectrum clearly reveals the presence of an η^5-C_5H_5 functionality.[3c] We have so far been unable to crystallize this compound.[70] In the case of the $(C_5H_5)_3ThR$ series, thermolysis solutions deposit a colorless solid. If thermolysis is carried out slowly ($167°C$) the product can be isolated as colorless needles in essentially quantitative yield (see Experimental Section). These analyze (C, H, and mass spectrum) for $[(C_5H_5)_2Th(C_5H_4)]_2$. Again the infrared spectrum exhibits bands attributable to η^5-C_5H_5 rings. The molecular structure of this complex has been determined by x-ray diffraction to be D.[44] The configuration of this remarkable molecule can be viewed as that obtained by removing the elements R–H from a $(\eta^5$-$C_5H_5)_3ThR$ molecule and then dimerizing the resulting species. Each thorium is bonded to two η^5-cyclopentadienyl rings and shares a third via a double η^1:η^5-C_5H_4 bridge. The structure is in many ways similar to that of "niobocene".[45] Thus, it is possible to write out the complete stoichiometry for $(C_5H_5)_3ThR$ thermolysis, as depicted in eq 12.

D

$$2(C_5H_5)_3ThR \longrightarrow [(C_5H_5)_2ThC_5H_4]_2 + 2RH \qquad (12)$$
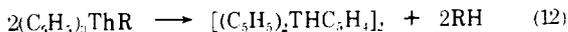
It should be noted that the product analysis and kinetic studies already described were carried out at $167°C$. In several cases, thermolysis was also conducted at even higher temperatures ($220°C$). In this case, gray-black material

precipitated from solution. For $(C_5H_5)_3Th(i\text{-Pr})$ the yield of organic product consisted of propane (80%) and propene (20%). Thus, though olefin elimination does not occur in the temperature range where the thermal decomposition appears to be relatively clean, it does take place under more drastic conditions.

Discussion

The absence of the β-hydrogen elimination reaction as a thermolysis pathway is a striking feature of $(C_5H_5)_3UR$ and, as shown in the present work, $(C_5H_5)_3ThR$ chemistry. Stabilization of these compounds with respect to this pathway is likely an important factor in the marked thermal stability which we observe. It is well established[32,33] that β-hydrogen elimination proceeds via intermediate hydride olefin complexes (B) (eq 6). These configurations are usually attained either by expansion of the metal coordination sphere or by dissociation of another ligand. In the coordinatively congested[43] $(C_5H_5)_3UR$ and $(C_5H_5)_3ThR$ complexes, apparently neither alternative can be achieved for a reasonable expenditure of free energy[46-49] and an alternate route is traversed. On the other hand, the thermally unstable actinide tetraalkyls presumably have coordination numbers as low as four, and here intermediates (or transition states) such as structure B are readily achieved, facilitating β-hydrogen elimination. Thus, for $M = U$, $R = n$-butyl, thermolysis in hexane yields 49% n-butane, 46% 1-butene, and 1% octane,[4a] while for $M = Th$, $R = n$-butyl, the yields are 60% n-butane, and 38% 1-butene.[50,51]
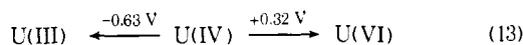
What pathways then are available for the thermal decomposition of the more coordinatively saturated $(C_5H_5)_3UR$ and $(C_5H_5)_3ThR$ compounds? Three descriptions of the primary event were put forward for the uranium system[3c,52] (E, F, G) and are the most reasonable choices.

E   F   G
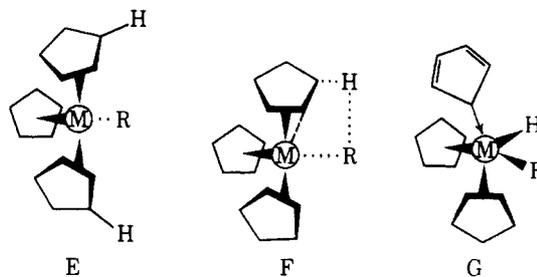
The free radical, homolytic cleavage (E) (involving a formal reduction of uranium(IV) to uranium(III) or thorium(IV) to thorium(III) as an initial step) has considerable precedent in transition metal alkyl systems which do not possess β-hydrogens or which (for stereochemical and/or electronic reasons) cannot undergo reductive elimination[53] (vide infra). The final product, RH, would be formed by subsequent hydrogen atom abstraction[34] within a very tightly constrained (perhaps unrealistically[3c]) solvent cage.[54,55] The existence of uranium(III) and thorium(III) organometallics such as $(C_5H_5)_3M$[6f] is further support for E. However, such a pathway is only compatible with the experimental data if it occurs in a solvent cage which is sufficiently "tight" to ensure complete retention of stereochemical configuration in RH. Considering the structure of the organoactinide in the ground state as well as the other spectroscopic evidence for coordinative congestion,[43] such a situation cannot be completely ruled out, since the α-carbon atom of R is within 3 Å of several of the surrounding ring hydrogens. The stability trend as a function of R, primary > secondary > tertiary, also suggests radical character. Still, the nearly complete retention of configuration observed for the hydrogen abstraction has never been previously observed for vinyl radical atom transfer reactions[38]

nor is such stereospecificity usually observed for caged radical pair recombination reactions in solution.[54,55] Furthermore, it should be pointed out that if a caged radical pair is sufficiently constrained, it is not legitimate to consider the radicals "free" and pathway E then verges upon a more reasonable concerted process. Path F is a concerted, four-center process, in which the hydrogen is transferred directly to R. It could also be viewed as an intramolecular interligand proton transfer reaction.[56] We have already noted that protonolysis of actinide-to-carbon σ bonds is facile with alcohols (eq 4). Finally, process G is a variant of an oxidative addition reaction in which a ligand C–H bond is added to a metal center. There is considerable precedent for this type of process in transition metal systems;[57-59] it is sometimes followed by reductive elimination.[58a,b,59]

The uncertainty in mechanistic course is essentially, then, reduced to the unanswered question of whether the cyclopentadienyl hydrogen is transferred directly to the R ligand, or whether it is transferred first to the actinide center and subsequently to R.[52] It is clear from our data that these transfers must be in a tightly controlled, intramolecular fashion. In considering possible differences in the $(C_5H_5)_3UR$ and $(C_5H_5)_3ThR$ thermolyses, it is instructive to examine the relative tendencies of uranium and thorium to shuttle between oxidation states.[60] The uranium potentials given in eq 13 and 14 are for aqueous solutions;[60] data for thorium were estimated from spectroscopic correlations.[61]

$$U(III) \xleftarrow{\;-0.63\ V\;} U(IV) \xrightarrow{\;+0.32\ V\;} U(VI) \qquad (13)$$

$$Th(III) \xleftarrow{\;-3.7\ V\;} Th(IV) \xrightarrow{\;\;/\!\!\!\!\longrightarrow\;} Th(VI) \qquad (14)$$

Uranium(IV) can be reduced or oxidized with relative ease. It is considerably more difficult to reduce thorium(IV) (few thorium(III) compounds are known)[6f,62] and impossible to oxidize it without removal of low-lying electrons from the closed 6p shell (no thorium(VI) compounds have been isolated). To the extent that organometallic reaction mechanisms can be described in terms of formal changes in oxidation state, then rate-determining processes involving either reduction or oxidation of the metal should be far more facile for uranium(IV) than for thorium(IV). The observed differences in the rates of $(C_5H_5)_3UR$ and $(C_5H_5)_3ThR$ thermolyses may well reflect such considerations. In this way the presence of two 5f electrons can strongly influence the chemistry of thorium and uranium organometallics.

The discussion above concerned the initial hydrogen transfer process. However, once R–H extrusion occurs, and by whatever mechanism, the resulting actinide-containing moiety must form the organometallic product which is isolated. This final product has been most securely characterized for thorium (vide supra).[44] For both uranium and thorium, the unimolecularity of R–H elimination implicates an intermediate such as H which is a carbene complex.[63]

H   I   J
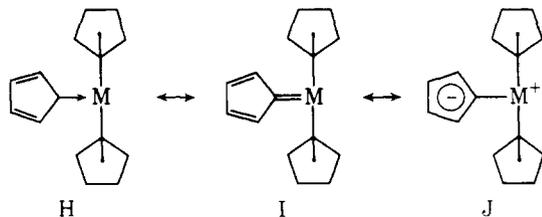
Though diaryl[64] and dialkyl[65] carbene complexes have been isolated, no d transition metal cyclopentadienylidene complexes have yet been prepared via rational approaches.[66] Considering the pronounced electrophilic character of this carbene,[67] this may not be surprising. Resonance hybrid

(H) possesses an antiaromatic four-electron π system. However, an electron-rich metal (one in actuality capable of undergoing a formal two-electron oxidation) such as divalent uranium or thorium might stabilize the aromatic ylide hybrid (J). Hence, an intermediate such as J might be reasonably stable, and in the case of thorium, apparently persists until dimerization takes place to yield the isolated product $[(C_5H_5)_2Th(C_5H_4)]_2$. We have previously suggested the importance of similar species in processes involving the intramolecular transfer of η^5-C_5H_5 hydrogens to coordinated borohydride.[56] Further rationale for the existence and postulated structure[68] of J is that triphenylphosphine forms a very stable complex with cyclopentadienylidene, i.e., triphenylphosphoniumcyclopentadienylide (K).[69] It is possible

K
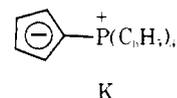
that carbene–ylide $(\eta^1$-$C_5H_4)M$ species are involved in a large number of thermolysis and group transfer reactions of both d and f transition metal $(\eta^5$-$C_5H_5)M$ compounds.[56]

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