J. Am. Chem. Soc. 1982, 104, 1860-1869

Mechanistic Study of Photoinduced β-Hydride Elimination. The Facile Photochemical Synthesis of Low-Valent Thorium and Uranium Organometallics

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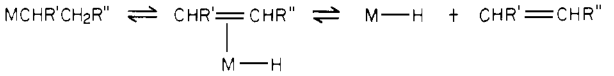
Abstract: This paper reports a mechanistic investigation of the photochemistry of the actinide hydrocarbyls $Th(C_5E_5)_3R$, E = H, D, R = CH_3, i-C_3H_7, n-C_4H_9; $Th(CH_3C_5H_4)_3(n\text{-}C_4H_9)$; $Th(indenyl)_3(n\text{-}C_4H_9)$; $U(C_5E_5)_3R$, E = H, R = CH_3, i-C_3H_7, n-C_4H_9, *sec*-C_4H_9, E = D, R = n-C_4H_9. For the thorium cyclopentadienyl compounds with R $\neq$ CH_3, UV photolysis in aromatic solvents produces 1:1 mixtures of alkane:alkene (RH:R − (H)) and the trivalent thorium complex $Th(C_5E_5)_3$ in nearly stoichiometric yield. On the basis of products, product yields, quantum yields, studies with ^2H labels, matrix photochemistry, added reagents, and the behavior of the R = CH_3 compound, a photoinduced β-hydrogen elimination mechanism is proposed. This reaction yields (irreversibly) olefin and $Th(C_5E_5)_3H$, the latter species then reacting with another molecule of $Th(C_5E_5)_3R$ to produce alkane and $Th(C_5E_5)_3$. A minor pathway for RH formation involves abstraction of C_5E_5 or solvent hydrogen (deuterium) atoms. On the basis of spectroscopic, magnetic, and chemical studies, the thorium photoproduct is formulated as a $Th(\eta^5\text{-}C_5E_5)_3$ compound, possibly with metal-bridging cyclopentadienyl ligands in the solid state. In contrast to these results, photolysis of the indenyl compound produces only alkane, the added hydrogen atom being derived from the indenyl ligand. For the uranium compounds in aromatic solvents, photoinduced β-hydrogen elimination (and $U(C_5H_5)_3$ formation) occurs but is not the major pathway. Rather, hydrogen atom abstraction from cyclopentadienyl rings (analogous to the thermolysis pathway) predominates, with lesser abstraction from the solvent molecules. Photolysis in THF greatly increases the yield of $U(C_5H_5)_3$.

Although there is now a considerable amount known about the structural, spectroscopic, chemical, and thermal properties of compounds with actinide-to-carbon σ bonds,[1] there is little known about the photochemical properties of these or, indeed, any actinide organometallic compounds.[2] Several years ago, we communicated[3] that while coordinatively saturated hydrocarbyls of the type $Th(\eta^5\text{-}C_5H_5)_3R$ (R = hydrocarbon functionality) strongly resist the well-known β-hydride elimination reaction (eq 1) under



$$MCHR'CH_2R'' \rightleftharpoons \underset{\displaystyle M{-}H}{\underset{|}{CHR'{=}CHR''}} \rightleftharpoons M{-}H + CHR'{=}CHR'' \quad (1)$$

thermal activation,[1,4] this process occurs facilely and cleanly for the R = isopropyl derivative under photochemical excitation.[3] Furthermore, the ultimate organometallic product of the reaction is the dark-green, paramagnetic complex $Th(C_5H_5)_3$. Complexes of thorium in oxidation states lower than 4+ are exceedingly rare[5] and present unique challenges in terms of understanding actinide ion electronic structure.[6] The estimate[7] that the Th(IV) → Th(III) reduction potential may be as large as −3.7 V presents an obvious synthetic challenge.

It has been of interest to explore the nature of the photoinduced β-hydride elimination in depth with a view toward developing new, selective ways of activating actinide hydrocarbyls. Such chemistry also offers a new approach to actinide complexes in unusual oxidation states[7] and to organoactinide hydrides. Furthermore, such investigations offer the possibility of drawing meaningful comparisons between actinide behavior and the growing field of transition-metal hydrocarbyl photochemistry.[8-17] In the present contribution, we discuss in detail our mechanistic studies of Th-

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(6) It is likely that the 6d levels will fall below the 5f levels in energy.[5a]

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$(C_5H_5)_3R$ photochemistry and photoinduced β-hydride elimination for a range of R substituents as well as for η^5-C_5H_5 ring modifications. Information on the chemical nature of the trivalent thorium complex $Th(C_5H_5)_3$ is also presented. In addition, we describe complementary studies of $U(C_5H_5)_3R$[4b,c] photochemistry[18] which provide a picture of how the various photoprocesses vary with metal ion 5f electron configuration (Th(IV) is $5f^0$; U(IV), $5f^2$).

Experimental Section

All operations involving organoactinide compounds were carried out under an atmosphere of prepurified nitrogen, with the rigorous exclusion of air and moisture, by using flame-dried Schlenk apparatus, a high vacuum line, or a Vacuum Atmospheres glovebox. Solvents were thoroughly dried and deoxygenated in a manner appropriate to each and were distilled under nitrogen immediately prior to use. Photochemical reactions were conducted with a Hanovia 679A36 450-W medium-pressure mercury lamp.[19a] Wavelength-dependence experiments were conducted with a set of Corning sharp-cut filters. Solutions of the organoactinides were sealed in flame-dried quartz tubes equipped with Teflon valves or, for NMR-scale experiments, in serum-capped quartz NMR tubes. The lamp and quartz tubes were clamped in a water bath and irradiations carried out at 10–15 °C. Low-temperature photolyses were carried out by placing the quartz tubes in a liquid nitrogen cooled Dewar equipped with quartz windows. Elemental analyses were performed by Galbraith Analytical Laboratories, Knoxville, TN. The compounds $Th(C_5H_5)_3Cl$,[19b] $U(C_5H_5)_3Cl$,[19b] $Th(C_5H_5)_3R$[4a] (R = n-C_4H_9, i-C_3H_7), $U(C_5H_5)_3R$[4c] (R = CH_3, n-C_4H_9, i-C_3H_7), violet $Th(C_5H_5)_3$,[5e] and $Th(C_9H_7)_3(n$-$C_4H_9)$[20] were prepared and purified according to the literature procedures.

Physical Measurements. Infrared spectra were recorded on Perkin-Elmer 267 or 283 spectrometers and were calibrated with polystyrene film. Sample mulls were prepared in a glovebox with dry, degassed Nujol or Fluorolube and were studied between KBr plates in an air-tight, O-ring sealed holder. Laser Raman spectra were observed with Ar^+ (5145 Å) excitation by using a Spex 1401 monochromator and photon-counting detection. Samples were studied in sealed Pyrex tubes spinning at 1200 rpm.

Nuclear magnetic resonance spectra were recorded on Hitachi Perkin-Elmer R20-B (CW, 60 MHz), Varian CFT-20 (FT, 80 MHz), JEOL FX 90 (FT, 90 MHz), or JEOL FX 270 (FT, 270 MHz) spectrometers. Samples were prepared in a glovebox in serum-capped NMR tubes or were filled and sealed on a vacuum line.

Gas chromatographic analyses were performed on a Hewlett-Packard 5750 gas chromatograph with a $^1/_4$ in. × 2 m 80/100 mesh silica gel column at 160 °C or a $^1/_8$ in. × 20 ft 10% EDO-1 on 100/120 Chromosorb PAW column at 30 °C, using flame ionization detection. Yields of gases were determined by removing measured volumes of the gases above the solutions with a gas syringe. Calibration of yield was achieved by comparison with samples prepared by the addition of known amounts of the appropriate gases to sample tubes containing an identical quantity of solvent. The estimated error in yields determined by this procedure is ±3%. Satisfactory agreement was obtained with yields measured on a vacuum line by Toepler pump.

Mass spectra were recorded on a Hewlett-Packard 6940A mass spectrometer interfaced with a Hewlett-Packard 5700 gas chromatograph or a Hewlett-Packard 5985 gas chromatograph–mass spectrometer system. Solid samples of organometallics were analyzed at 70 eV by use of the direct-inlet technique. Deuterium incorporation in the gaseous products of photochemical reactions was determined by separation and analysis on the GC–MS systems. Measurements were made at 15 eV, taking the appropriate precautions.[21] Integration of the mass spectrum over the entire GC peak was performed as a check against isotopic fractionation. We thank Dr. Doris Hung for assistance with these measurements.

Electronic spectra were recorded on Cary 17D or Perkin-Elmer 330 spectrophotometers. Samples were prepared as Nujol mulls between quartz plates or as solutions in matched cuvettes sealed with Teflon valves. Several scans were made of each sample to check for possible decomposition.

Magnetic susceptibility measurements were kindly performed by Professor Basil Kanellakopulos of the Institut für Heisse Chemie, Kernforschungszentrum, Karlsruhe, West Germany.

Tris(η^5-cyclopentadienyl)(methyl)thorium(IV). Following the procedure of Marks and Wachter for the preparation of $Th(C_5H_5)_3(n$-$C_4H_9)$,[4a] 5.00 g (10.8 mmol) of $Th(C_5H_5)_3Cl$ was dissolved in 175 mL of toluene and the mixture cooled to −78 °C. To this solution was added 15 mL of commercial methyllithium (1.05 M, 15.8 mmol). The solution was allowed to warm to room temperature and filtered, and the solvent was removed under vacuum. The crude gray product was allowed to stand at room temperature for 48 h and then was redissolved in 150 mL of toluene and filtered, and the solvent was then removed. The solid product was then washed with 2 × 25 mL of pentane and dried in vacuo, yielding 2.70 g of white microcrystalline $Th(C_5H_5)_3CH_3$ (57%): IR 3090 (w), 1440 (s), 1400 (w), 1105 (s), 1060 (w), 1015 (vs), 810 (vs), 780 (vs) cm^{-1}; ^1H NMR (C_6D_6 solution) δ 5.97 (s, 15 H), 0.82 (s, 3 H). Anal. Calcd for $C_{16}H_{18}Th$: C, 43.44; H, 4.10. Found: C, 43.05; H, 4.14.

Tris(η^5-cyclopentadienyl)(*sec*-butyl)uranium(IV). By using the same procedure as for the preparation of $Th(C_5H_5)_3CH_3$, 7.61 g of $U(C_5H_5)_3Cl$ (16.3 mmol) was dissolved in 150 mL of toluene and the mixture cooled to −78 °C. To this was added 23.3 mL of commercial *sec*-butyllithium (1.4 M, 32.6 mmol). Upon workup, 3.83 g (73%) of dark, black-green, microcrystalline $U(C_5H_5)_3[CH(CH_3)C_2H_5]$ was obtained: IR 3090 (m), 1440 (s), 1365 (m), 1355 (m), 1313 (w), 1216 (m), 1153 (w), 1105 (w), 1060 (w), 1013 (vs), 973 (w), 812 (vs), 783 (vs), 495 (m) cm^{-1}; ^1H NMR (C_6D_6 solution, ppm relative to internal benzene) 11.1 (s, 15 H), 14.4 (m, 3 H), 21.4 (m, 1 H), 23.4 (m, 3 H), 33.5 (m, 1 H), 186 (m, 1 H). Anal. Calcd for $C_{19}H_{24}U$: C, 46.53; H, 4.93. Found: C, 46.35; H, 5.01.

Synthesis of M(η^5-C_5D_5)$_3$R Compounds. Following the procedure of McLean et al.,[22] C_5D_6 was prepared by the base-catalyzed exchange of deuterium for hydrogen in C_5H_6 using a D_2O/Me_2SO mixture. The C_5D_6 was converted to TlC_5D_5,[23] which was then used to prepare $Th(C_5D_5)_3Cl$ and $U(C_5D_5)_3Cl$.[19] The alkyl derivatives were prepared by the reaction of the appropriate tris(cyclopentadienyl)metal chlorides with alkyllithium reagents. The extent of deuteration in the cyclopentadienyl rings, which was measured by NMR integration of the residual hydrogen atoms on the rings vs. the hydrogen atoms of the alkyl groups, was on the order of 95 ± 2%. This result was also confirmed by mass spectral analysis of the compounds.

Photolysis of Th(η^5-C_5H_5)$_3$(n-C_4H_9). A solution of 1.21 g of $Th(C_5H_5)_3(n$-$C_4H_9)$ in 300 mL of benzene was irradiated for 3 h. After allowing the finely divided green photolysis product to settle, the colorless supernatant was removed via cannula. The solid product was washed with 3 × 25 mL portions of benzene and then dried under vacuum. The yield of $Th(C_5H_5)_3$ was 0.97 g (91%). In a separate reaction, 0.0388 g of $Th(C_5H_5)_3(n$-$C_4H_9)$ (0.0802 mmol) was dissolved in 10 mL of toluene and irradiated for 4 h. Gas chromatographic analysis of the gaseous mixture above the solution showed the production of a total of 0.072 mmol of a mixture comprised of 58% butane and 42% 1-butene (90% yield based on the starting alkyl). IR (Nujol mull) $Th(C_5H_5)_3$ 3085 (w), 1432 (w), 1120 (w), 1070 (w), 1012 (m), 835 (w), 800 (s, sh), 780 (vs), 680 (w), 640 (m), 610 (w), 568 (w) cm^{-1}; Raman spectrum (ν_o = 5145 Å) 1870 (vw), 1866 (vw), 1854 (w), 1436 (vw), 1136 (w), 1121 (s), 1068 (vw), 1007 (vw), 900 (vw), 893 (vw), 885 (w), 840 (s), 806 (vw), 790 (vw), 780 (w), 515 (w), 254 (s), 234 (s), 157 (s) cm^{-1}; mass spectrum, *m/e* (relative intensity) 427 ($Th(C_5H_5)_3^+$, 100), 362 ($Th(C_5H_5)_2^+$, 21). Anal. Calcd for $C_{15}H_{15}Th$: C, 42.16; H, 3.54. Found: C, 42.05, H, 3.90.

Photolysis of Th(η^5-C_5H_5)$_3$(i-C_3H_7). By using the same conditions as for the irradiation of $Th(C_5H_5)_3(n$-$C_4H_9)$, 0.105 g of $Th(C_5H_5)_3(i$-$C_3H_7)$ (0.223 mmol) was dissolved in 10 mL of toluene and the mixture photolyzed for 4 h. Analysis of the gaseous reaction products revealed that 0.208 mmol of gas (93% yield) consisting of 54% propane and 46% propene had been produced.

Photolysis of Th(η^5-C_5H_5)$_3$$CH_3$. In a quartz tube equipped with a ground-glass joint on the side arm, 0.348 g of $Th(C_5H_5)_3CH_3$ (0.787 mmol) was dissolved in 20 mL of toluene. After being irradiated for 20 h, the gaseous products were measured by use of a Toepler pump. The major product was methane (0.416 mmol, 53%) along with traces of hydrogen (0.027 mmol, 3.5%) and another gas which could be trapped at −196 °C (found to be ethane from its mass spectrum, 0.020 mmol, 2.5%). The brownish green thorium-containing product isolated from this

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reaction gave a similar infrared spectrum as compared to that of the photolysis products of the isopropyl and butyl analogues, although the peaks at 835 cm^{-1} and in the 600–700-cm^{-1} range were visibly less intense in this product.

$Th(\eta^5-C_5H_4CH_3)_3$. By using the procedure of Wachter for the preparation of $Th(C_5H_4CH_3)_3(i-C_3H_7)$,[24] $Th(C_5H_4CH_3)_3(n-C_4H_9)$ was prepared. Photolysis of a solution of this compound in toluene (ca. 0.02 M) resulted in the formation of green, microcrystalline $Th(C_5H_4CH_3)_3$,[3] identified by absorbances at 431, 477, and 572 nm in the optical spectrum (Nujol mull). Unlike $Th(C_5H_5)_3$, this thorium(III) product is somewhat unstable when left in contact with the mother liquor, slowly decomposing to yield a soluble brown product which was not characterized.

Photochemical Preparation of $Th(\eta^5-C_5H_5)_4$. A mixture of 0.59 g of $Th(C_5H_5)_3CH_3$ (1.33 mmol) and 1.18 g of diphenylacetylene (6.62 mmol) was dissolved in 15 mL of toluene and photolysis initiated. The solution began to darken to a reddish brown color after a few minutes. After 24 h of irradiation, small colorless crystals were visible in the reaction mixture. The photolysis was continued for 168 h, at which time the supernatant solution was removed and the solid product washed with 3 × 20 mL of pentane, yielding 0.15 g of crude, yellow tetrakis(cyclopentadienyl)thorium. This material was placed in a sublimation apparatus and sublimed under high vacuum at 250 °C overnight to yield 0.13 g of pure $Th(C_5H_5)_4$ (20% based on starting $Th(C_5H_5)_3CH_3$). The product was identified by the ^1H NMR spectrum ($CDCl_3$ solution, δ 6.35, s; lit. δ 6.4),[25a] mass spectrum (major peaks at m/e 492 [$Th(C_5H_5)_4^+$], 427 [$Th(C_5H_5)_3^+$], 362 [$Th(C_5H_5)_2^+$], as well as other characteristic fragmentation peaks), and elemental analysis (Anal. Calcd for $C_{20}H_{20}Th$: C, 48.78; H, 4.09. Found: C, 48.79; H, 4.03.)

In a separate experiment, 0.103 g of $Th(C_5H_5)_3CH_3$ (0.232 mmol) and 1.00 g of $C_6H_5C{\equiv}CC_6H_5$ (5.61 mmol) dissolved in 15 mL of toluene were irradiated for 99 h. Again, a colorless, crystalline precipitate was observed to form. Analysis of the gaseous products by Toepler pump revealed a mixture of methane (0.0434 mmol, 19%), hydrogen (0.0085 mmol, 4%), and ethane (0.0170 mmol, 8%).

When $Th(C_5H_5)_3(n-C_4H_9)$ was substituted for the methyl analogue, similar results were obtained. The gaseous products from this reaction were n-butane and 1-butene (85% and 15% relative yield, respectively). Tetrakis(cyclopentadienyl)thorium, but none of the characteristic green precipitate of $Th(C_5H_5)_3$, was visible in this reaction. Mixtures of $Th(C_5H_5)_3R$ and diphenylacetylene yielded no $Th(C_5H_5)_4$ after several days' heating at 100 °C in the absence of light.

Photolysis of a Mixture of $Th(\eta^5-C_5H_5)_3(n-C_4H_9)$ and $Th(\eta^5-C_5D_5)_3(n-C_4H_9)$. A mixture of 0.30 g of $Th(C_5H_5)_3(n-C_4H_9)$ and 0.10 g of $Th(C_5D_5)_3(n-C_4H_9)$ was dissolved in 20 mL of toluene. One half the solution was subjected to 4 h of irradiation while the other half was stored in the dark at ambient temperature for one week. The green photolysis product was analyzed by mass spectroscopy, revealing the presence not only of $Th(C_5H_5)_3$ and $Th(C_5D_5)_3$ but also peaks which could be attributed to species of the type $Th(C_5D_5)(C_5H_5)_2$ and $Th(C_5D_5)_2(C_5H_5)$ as evidenced by major peaks at m/e 427, 432, 437, and 442 ($Th(C_5H_5)_n(C_5D_5)_{3-n}^+$, n = 3,2,1,0) and 362, 367, and 372 ($Th(C_5H_5)_n(C_5D_5)_{2-n}^+$, n = 2,1,0) as well as fragmentation peaks attributable to such species. The mass spectrum of the unphotolyzed mixture showed no peaks which could not be attributed to the starting materials. A solution containing a similar mixture of $Th(C_5H_5)_3(n-C_4H_9)$ and $Th(C_5D_5)_3(n-C_4H_9)$ in toluene was subjected to 0.5 h of photolysis. This partially photolyzed solution was then filtered to remove the $Th(C_5H_5)_n(C_5D_5)_{3-n}$ that had been produced. The toluene was then vacuum distilled from the filtered solution, and the resultant solid product was analyzed by mass spectroscopy, revealing only the presence of $Th(C_5H_5)_3(n-C_4H_9)$ and $Th(C_5D_5)_3(n-C_4H_9)$. No $Th(C_5H_5)_n(C_5D_5)_{3-n}(n-C_4H_9)$ compounds were detectable.

Photolysis of $Th(\eta^5-C_5H_5)_3R$ and $Th(\eta^5-C_5D_5)_3R$ Compounds in Benzene and Benzene-d_6. Dilute solutions (0.010 M) of $Th(C_5D_5)_3R$ (R = $n-C_4H_9$, $i-C_3H_7$, CH_3) in benzene and benzene-d_6 and $Th(C_5H_5)_3R$ in benzene-d_6 were irradiated and the gaseous products analyzed by GC–MS to determine the extent and source of any deuterium incorporation in these gases. The alkenes produced (propene and 1-butene) contained no more than 1% of the monodeuterated compound. The alkanes produced upon photolysis of $Th(C_5D_5)_3R$ (R = $i-C_3H_7$, $n-C_4H_9$) in deuterated solvent contained 3.6% propane-d_1 and 8.5% n-butane-d_1 whereas when the irradiation was performed in nondeuterated solvent, the amounts were 2.8% and 2.6%, respectively. Photolysis of the $Th(C_5H_5)_3R$ compounds in benzene-d_6 resulted in the production of 3.8% propane-d_1 and 2.7% butane-d_1. Photolysis of the methyl derivatives resulted in the formation of methane-d_1 in the amounts of 15.6%, 25.6%, and 38.9% when the solutions contained $Th(C_5H_5)_3CH_3$ in C_6D_6, $Th(C_5D_5)_3CH_3$ in C_6H_6, and $Th(C_5D_5)_3CH_3$ in C_6D_6, respectively.

Quantum Yield Determinations. The quantum yield for the disappearance of $Th(C_5H_5)_3(i-C_3H_7)$ was determined for 0.020 M solutions in C_6D_6. Sample solutions (3.0 mL + 25 μL of C_6H_6) were sealed in 10-mL NMR tubes under high vacuum. Reaction progress was monitored by careful integration of the 270-MHz ^1H NMR spectrum vs. internal C_6H_6. Precipitated $Th(C_5H_5)_3$ was removed from the sample area by inverting the tubes and centrifuging. Samples were irradiated ($\leq$20% conversion) on a merry-go-round apparatus at 10 °C with the Hanovia 450-W lamp and a potassium chromate filter solution to isolate 313-nm light. Lamp intensities were determined with use of C_6D_6 solutions of *trans*-stilbene and monitoring the known conversion to *cis*-stilbene by GC.[25b] Based upon results for three $Th(C_5H_5)_3(i-C_3H_7)$ samples, $\Phi = 1.7 \pm 0.1$.

Low-Temperature Photolysis of $Th(\eta^5-C_5H_5)_3(n-C_4H_9)$. A toluene solution of $Th(C_5H_5)_3(n-C_4H_9)$ (0.010 M) was frozen in liquid nitrogen prior to irradiation. During the course of the photolysis of this frozen solution, the color of the toluene glass changed from colorless to a deep violet. Upon warming to room temperature after photolysis, this violet color was replaced by the familiar green color of $Th(C_5H_5)_3$. Analysis of the gaseous products by gas chromatography showed a mixture of n-butane (relative yield 29%) and 1-butene (71%) had been produced. Attempts to isolate the transient violet species by performing the irradiation in the presence of a Lewis base such as THF were unsuccessful. The characteristic green compound was the ultimate product when the sample was warmed.

Photolysis of $Th(\eta^5-C_5H_5)_3(n-C_4H_9)$ under H_2. On a vacuum line, 10 mL of toluene was distilled into a quartz tube containing 0.049 g of $Th(C_5H_5)_3(n-C_4H_9)$ (0.101 mmol). The tube was then charged with 0.388 mmol of hydrogen and sealed with a Teflon needle valve. After 45 min of photolysis, the residual hydrogen was collected and measured via a Toepler pump. A total of 0.390 mmol of hydrogen was recovered. An additional photoreaction was carried out with conditions similar to those in which the hydrocarbon products were analyzed by gas chromatography. The product gas mixture contained the same ratio of n-butane to 1-butene (58:42) as found for the photolysis of $Th(C_5H_5)_3(n-C_4H_9)$ in the absence of H_2.

Photolysis of a Mixture of $Th(\eta^5-C_5H_5)_3CH_3$ and $Th(\eta^5-C_5H_5)_3(i-C_3H_7)$. An irradiation tube containing 0.170 g of $Th(C_5H_5)_3CH_3$ (0.385 mmol) and 0.030 g of $Th(C_5H_5)_3(i-C_3H_7)$ (0.064 mmol) dissolved in 10 mL of toluene produced, after 1 h of photolysis, a mixture of 0.054 mmol of CH_4, 0.031 mmol of propene, and 0.009 mmol of propane. A parallel experiment with only $Th(C_5H_5)_3CH_3$ (0.170 g, 0.385 mmol) produced considerably less methane: 0.036 mmol.

Photolysis of $Th(\eta^5-C_5H_5)_3(n-C_4H_9)$ in the Presence of Ethylene. To a quartz tube containing 0.10 g of $Th(C_5H_5)_3(n-C_4H_9)$ (0.21 mmol) dissolved in 10 mL of toluene was added 0.223 mmol of ethylene. The solution was subjected to 1 h of photolysis followed by gas chromatographic analysis of the gaseous products. It was found that the mixture of gases in the reaction tube contained the usual ratio of butane to butene found for the photolysis of $Th(C_5H_5)_3(n-C_4H_9)$, as well as the ethylene. No ethane (<2% of the gaseous product), produced by the hydrogenation of ethylene, could be detected.

Photolysis of $U(\eta^5-C_5H_5)_3(n-C_4H_9)$. A solution of $U(C_5H_5)_3(n-C_4H_9)$, prepared by dissolving 0.96 g of the compound in 100 mL of toluene, was irradiated for 12 h, producing a green-brown precipitate. After removal of the colorless supernatant, the residue was extracted with 3 × 25 mL of THF. The resulting dark brown solution was taken to dryness under vacuum, yielding 0.12 g (12%) of solid identified as $U(C_5H_5)_3{\cdot}THF$ by the characteristic optical and mass spectra.[26,27] In a similar experiment, 1.26 g of $U(C_5H_5)_3(n-C_4H_9)$ was dissolved in 100 mL of THF and photolyzed for 12 h. The resulting brown solution was filered to remove a gray precipitate, and then the solvent was removed from the filtrate in vacuo to yield 0.39 g of $U(C_5H_5)_3{\cdot}THF$ (30%). In a separate experiment, 0.103 g of $U(C_5H_5)_3(n-C_4H_9)$ (0.209 mmol) was dissolved in 10 mL of toluene and irradiated for 8 h. Gas chromatographic analysis of the product gases revealed a mixture of 91% n-butane and 9% 1-butene. A total gas yield of 0.190 mmol (91% based on the starting alkyl compound) was produced.

Photolysis of $U(\eta^5-C_5H_5)_3(i-C_3H_7)$. A solution containing 1.05 g of $U(C_5H_5)_3(i-C_3H_7)$ in 100 mL of toluene was subjected to 12 h of ultraviolet irradiation. Following the procedure for the photolysis of $U(C_5H_5)_3(n-C_4H_9)$, the solid precipitate was extracted with 100 mL of THF and dried, yielding 0.30 g (27%) of $U(C_5H_5)_3{\cdot}THF$. When the

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irradiation of 1.11 g of $U(C_5H_5)_3(i\text{-}C_3H_7)$ was carried out using THF as the solvent, the yield of the uranium(III) product was 0.75 g (64%). Irradiation of 0.099 g of $U(C_5H_5)_3(i\text{-}C_3H_7)$ (0.207 mmol) dissolved in 10 mL of toluene produced a mixture of 0.195 mmol of propane and propene in an 83:17 ratio (93% total yield based upon the starting organometallic).

Photolysis of $U(\eta^5\text{-}C_5H_5)_3(sec\text{-}C_4H_9)$. Under the same conditions as for the above photolyses, 1.07 g of $U(C_5H_5)_3(sec\text{-}C_4H_9)$ in 100 mL of toluene yielded, after workup, 0.45 g of $U(C_5H_5)_3\cdot THF$ (41%). When the reaction was carried out in THF solution, the yield was increased to 59%. In an additional experiment, 0.152 g of $U(C_5H_5)_3(sec\text{-}C_4H_9)$ (0.311 mmol) dissolved in 10 mL of toluene yielded, after photolysis, a mixture of *n*-butane, 1-butene, and 2-butenes with relative yields of 74%, 19%, and 7%, respectively, and a total gas yield of 0.298 mmol (96% based on the starting uranium alkyl).

Photolysis of $U(\eta^5\text{-}C_5H_5)_3CH_3$. A solution containing 0.314 g of $U(C_5H_5)_3CH_3$ (0.701 mmol) was dissolved in 15 mL of toluene and irradiated for 19.5 h. Analysis of the gaseous products at this point revealed that 0.412 mmol of methane (59% based on starting alkyl) and 0.006 mmol of ethane (0.9%) had been produced. The solution still retained a deep green-brown color due to the incomplete reaction of $U(C_5H_5)_3CH_3$.

Photolysis of $U(\eta^5\text{-}C_5H_5)_3CH_3$ in the Presence of Diphenylacetylene. A mixture of 0.293 g of $U(C_5H_5)_3CH_3$ (0.653 mmol) and 1.00 g $C_6H_5C{\equiv}CC_6H_5$ (5.61 mmol) was dissolved in 15 mL of toluene. After a total irradiation period of 121 h, the gaseous reaction products were analyzed, revealing a mixture of methane (0.095 mmol, 15% based on $U(C_5H_5)_3CH_3$), hydrogen (0.026 mmol, 4.0%), and ethane (0.029 mmol, 4.5%). When the photoreaction was conducted and monitored in an NMR tube, no peak attributable to $U(C_5H_5)_4$ (20.42 ppm from internal benzene)[28] was observed.

Low-Temperature Photolysis of $U(\eta^5\text{-}C_5H_5)_3(sec\text{-}C_4H_9)$ and $U(\eta^5\text{-}C_5H_5)_3(n\text{-}C_4H_9)$. Toluene solutions of $U(C_5H_5)_3(n\text{-}C_4H_9)$ and $U(C_5H_5)_3(sec\text{-}C_4H_9)$ (0.010 M) were frozen in liquid nitrogen, and photoreactions were carried out on these frozen solutions. After 4 h of irradiation, the resultant gases were identified by gas chromatography. In the case of $U(C_5H_5)_3(n\text{-}C_4H_9)$, *n*-butane, and 1-butene were produced in a 58:42 ratio. Photolysis of $U(C_5H_5)_3(sec\text{-}C_4H_9)$ produced a mixture containing 53% butane and 47% butenes.

Deuterium Incorporation in the Photoproducts of $U(\eta^5\text{-}C_5H_5)_3R$ and $U(\eta^5\text{-}C_5D_5)_3R$. Solutions of $U(C_5D_5)_3(n\text{-}C_4H_9)$ in C_6H_6 and C_6D_6 as well as $U(C_5H_5)_3(n\text{-}C_4H_9)$ in C_6D_6 (0.010–0.020 M) were photolyzed for 3 h. Following irradiation, the gaseous products were analyzed by GC–MS to determine the extent of deuterium incorporation in the gases produced. The resultant butane contained C_4H_9D in the amounts of 20.0%, 41.1%, and 73.4% for the photolysis of $U(C_5H_5)_3(n\text{-}C_4H_9)$ in C_6D_6, $U(C_5D_5)_3(n\text{-}C_4H_9)$ in C_6H_6, and $U(C_5D_5)_3(n\text{-}C_4H_9)$ in C_6D_6, respectively, while the butene contained 4.3%, 23.9%, and 22.2% butene-d_1.

Reaction of $Th(\eta^5\text{-}C_5H_5)_3CH_3$ with $\{Th[\eta^5\text{-}(CH_3)_5C_5]_2H_2\}_2$. In an NMR-scale experiment, $Th(C_5H_5)_3CH_3$ and $\{Th[(CH_3)_5C_5]_2H_2\}_2$ (20:1 mole ratio) were loaded into a sample tube. Benzene-d_6 was next distilled into the tube on a vacuum line and the tube was sealed. Upon warming to room temperature, the initially colorless solution darkened over a period of ca. 15 min, producing a green precipitate. The NMR spectrum of the resulting solution showed the presence of residual $Th(C_5H_5)_3CH_3$, but no $\{Th[(CH_3)_5C_5]_2H_2\}_2$. However, new peaks attributable to the known[1d] $Th[(CH_3)_5C_5]_2(CH_3)_2$ were plainly visible. When the experiment was repeated and the sample tube allowed to warm to room temperature in the probe of the NMR spectrometer, the signals due to $Th[(CH_3)_5C_5]_2(CH_3)_2$ could be seen to increase in intensity as those due to $\{Th[(CH_3)_5C_5]_2H_2\}_2$ decreased. No other species was evident in the NMR spectrum.

When an NMR-scale experiment was conducted in which the hydride compound was present in nearly stoichiometric amounts (0.106 g of $Th(C_5H_5)_3CH_3$, 0.239 mmol, and 0.0706 g of $\{Th(CH_3)_5C_5]_2H_2\}_2$, 0.0700 mmol), the complete loss of peaks due to $Th(C_5H_5)_3CH_3$ in the NMR spectrum was evidenced. The loss of intensity of the peaks due to $\{Th[(CH_3)_5C_5]_2H_2\}_2$ and the growth of the $Th[(CH_3)_5C_5]_2(CH_3)_2$ peaks were noticed as well as the appearance of other, unidentified peaks in the region of the $(CH_3)_5C_5$ resonances (δ 2.25, 2.14, 2.07, s), a peak at δ 0.47, s, and a new peak in the C_5H_5 region (δ 6.07, s).

Attempted Reaction of $Th(\eta^5\text{-}C_5H_5)_3CH_3$ with H_2. An NMR tube containing 0.10 g of $Th(C_5H_5)_3CH_3$ was attached to vacuum line. After distillation of benzene-d_6 into the tube, it was filled with an atmosphere of hydrogen and sealed. The tube was placed in an oil bath at 100 °C and monitored by NMR spectroscopy periodically for several days. No new peaks were detected which could be attributed to a species such as $Th(C_5H_5)_3H$ or any other new organothorium compounds. After extended heating, the presence of small amounts of a white precipitate (presumably the thermolysis product $[Th(C_5H_5)_2(C_5H_4)]_2$, which would be expected under these conditions[29]) was the only observable change in the solution.

Reaction of $Th(C_5H_5)_3$ with I_2. After the complete photolysis of a solution containing 0.50 g of $Th(C_5H_5)_3(n\text{-}C_4H_9)$ (1.03 mmol) in 15 mL of toluene, followed by two 10-mL washes of the green precipitate with toluene, 5 mL of toluene was added, and the resulting suspension was frozen in liquid nitrogen. After 2.6 mL of a solution of iodine in toluene (0.05 g/mL, 0.51 mmol) was added, the mixture was allowed to warm slowly to room temperature with agitation. As the temperature increased, the color due to the iodine diminished as the green $Th(C_5H_5)_3$ reacted. After reaching room temperature, the nearly colorless solution was filtered and the solvent removed in vacuo to yield 0.45 g of gray solid. This solid material was then sublimed at 200 °C under the high vacuum over a period of 3 days, yielding 0.40 g (70%) of a pale-yellow product identified as $Th(C_5H_5)_3I$ by NMR (singlet at δ 6.12 in C_6D_6), mass spectrum[27] (major peaks at *m/e* 554 $[Th(C_5H_5)_3I^+]$, 489 $[Th(C_5H_5)_2I^+]$, 427 $[Th(C_5H_5)_3{}^+]$, 424 $[Th(C_5H_5)I^+]$, and 362 $[Th(C_5H_5)_2{}^+]$), and elemental analysis. Anal. Calcd for $C_{15}H_{15}ThI$: C, 32.51; H, 2.73. Found: C, 32.36; H, 2.80.

Reaction of $Th(C_5H_5)_3$ with $CDCl_3$. To approximately 0.020 g of $Th(C_5H_5)_3$ in an NMR tube was added 1 mL of $CDCl_3$. A vigorous reaction ensued, resulting in dissolution of the green thorium compound to yield a slightly yellow solution. The NMR spectrum revealed a singlet at δ 6.19 indicative of $Th(C_5H_5)_3Cl$.[19] In a larger scale reaction, 10 mL of $CHCl_3$ was added to a liquid nitrogen cooled Schlenk tube containing 0.52 g of $Th(C_5H_5)_3$. After slowly warming the tube to room temperature, we took the resulting yellow solution to dryness and extracted the residue with 50 mL of toluene. After filtration, the solvent was removed to yield 0.35 g of a pale yellow compound identified as $Th(C_5H_5)_3Cl$ on the basis of NMR,[19] IR,[19] and mass spectra[27] (63% yield).

Reaction of $Th(C_5H_5)_3$ with Hydrogen. A sample of the green $Th(C_5H_5)_3$ (0.096 g, 0.224 mmol) was weighed into a 25-mL flask equipped with a gas-addition bulb. On a vacuum line the system was evacuated and 10 mL of toluene was distilled in. The bulb was then charged with 1.197 mmol of hydrogen. The hydrogen (~300 torr) was admitted to the flask and the suspension was stirred in the dark for 12 h, resulting in the loss of the characteristic green color of the thorium(III) compound. The residual hydrogen was measured via a Toepler pump, revealing that 1.128 mmol remained or 0.069 mmol had reacted (mole ratio of H_2 to $Th(C_5H_5)_3$ = 0.310). The resulting off-white solid from this reaction was exceedingly photosensitive, rapidly reverting to a green color when exposed even to room light. Readdition of hydrogen resulted in the loss of this color. The infrared spectrum of this hydrogenated product showed the growth of a broad band in the 1550–1200-cm^{-1} region as well as new peaks at 1125, 938, and 682 cm^{-1}.

Reaction of $Th(C_5H_5)_3$ with Methanol. A sample of the green $Th(C_5H_5)_3$ (0.413 g, 0.966 mmol) was placed in a 10-mL flask and attached to a vacuum line. After evacuation of the flask, ca. 5 mL of dried, degassed methanol was distilled in. The resulting mixture was stirred for 1.5 h, during which time the green compound reacted, yielding colorless, insoluble $Th(OCH_3)_4$[30] (identified by the similarity of its infrared spectrum to that of $Ti(OCH_3)_4$[31,32]) and 0.531 mmol of hydrogen (collected by Toepler pump). The mole ratio of H_2 produced to $Th(C_5H_5)_3$ was 0.550.

Reaction of $Th(C_5H_5)_3$ with Ammonium Chloride. Following the procedure of Dornberger et al. for the preparation of $Th(C_5H_5)_2Cl$ from violet $Th(C_5H_5)_3$,[5f] we combined 0.26 g of $Th(C_5H_5)_3$ (0.61 mmol) and 0.04 g of NH_4Cl (0.75 mmol) with 25 mL of THF and heated the mixture under reflux for 16 h. At this time the supernatant solution was filtered from the unreacted starting material and the solvent was removed under vacuum, yielding only a trace of off-white product. An NMR spectrum of this solid identified it as $Th(C_5H_5)_3(OC_4H_9)$.[33]

Photolysis of $Th(\eta^5\text{-}C_9H_7)_3(n\text{-}C_4H_9)$. A sample of $Th(C_9H_7)_3(n\text{-}C_4H_9)$ (0.208 g, 0.328 mmol) was dissolved in 10 mL of toluene and photolyzed for 3 h. Analysis of the product gases above the red solution revealed 0.302 mmol of *n*-butane and 0.013 mmol of 1-butene (96% total yield based on the starting alkyl). In a larger scale reaction, 1.13 g of $Th(C_9H_7)_3(n\text{-}C_4H_9)$ was dissolved in 50 mL of toluene and photolyzed

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for 3 h. The resulting red solution was filtered to remove traces of a yellow precipitate, and then the solvent was removed in vacuo. The red solid obtained was dried under vacuum for 8 h, yielding 0.93 g of product that analyzed satisfactorily for the formulation $Th(C_9H_7)_3$ (90%): IR 3050 (br, w), 1334 (s), 1252 (m), 1216 (s), 1150 (w), 1119 (vw), 1055 (sh, m), 1040 (s), 999 (m), 968 (w), 940 (w), 865 (m), 780 (s), 745 (s), 674 (m) cm^{-1}; NMR (C_6D_6, relative to Me_4Si) δ 7.20 (singlet overlapping with broad peak, 18 H), 6.03 (d, 1 H), 5.82 (s, 1 H). Anal. Calcd for $C_{27}H_{21}Th$: C, 56.16; H, 3.67. Found: C, 55.93, H, 4.22.

Methanolysis of Th$(C_9H_7)_3$. A sample of $Th(C_9H_7)_3(n\text{-}C_4H_9)$ (0.115 g, 0.181 mmol) was dissolved in 10 mL of toluene and photolyzed for 3 h to yield $Th(C_9H_7)_3$. To this was added ca. 2 mL of methanol, which reacted with the thorium compound quite vigorously. Measurement of the hydrogen produced (collected by Toepler pump) revealed 0.083 mmol had been evolved (mole ratio of H_2:Th = 0.46).

Attempted Reaction of Th$(C_9H_7)_3$ **with** H_2. A flask containing 0.129 g of $Th(C_9H_7)_3$ (0.224 mmol) dissolved in 5 mL of toluene was charged with 0.357 mmol of hydrogen (~100 torr) on a vacuum line. After the solution was stirred in the dark for 1 week, no color change was apparent. Collection of the hydrogen remaining in the flask resulted in the recovery of 0.350 mmol of H_2, 98% of the initial charge, indicating that no reaction had occurred.

Reaction of Th$(C_9H_7)_3$ **with** $CHCl_3$. To a sample of 0.48 g of $Th(C_9H_7)_3$ in 10 mL of toluene at −196 °C was added 3 mL of chloroform. After warming of the solution to room temperature, it was filtered and the solvent was removed in vacuo. The NMR spectrum of the crude product agreed favorably with that reported in the literature for $Th(C_9H_7)_3Cl$[34] (although several additional, broad peaks in the range δ 6.08–6.21, 2.22 s, 1.46 s, 1.04 s were also detected). Sublimation of the crude product resulted in a yield of 0.19 g of pure $Th(C_9H_7)_3Cl$ (38%). The identity of the product was also confirmed by mass spectroscopy.

Reaction of Th$(C_9H_7)_3$ **with Iodine**. To a sample of 0.59 g of $Th(C_9H_7)_3$ (1.02 mmol) in 10 mL of toluene which had been cooled to −196 °C was added a solution containing 1 equiv of iodine (2.6 mL, 0.05 g/mL, 0.51 mmol). After the solution was warmed and filtered and the solvent removed in vacuo, the crude material was analyzed by mass and NMR spectroscopy. The mass spectrum of the product agreed favorably with the published spectrum of $Th(C_9H_7)_3I$, although it contained several extra peaks, while the NMR spectrum bore a close resemblance to that of $Th(C_9H_7)_3Cl$[34] (with the addition of spurious signals similar to those found in the crude product from the reaction of $Th(C_9H_7)_3$ with $CHCl_3$). Sublimation resulted in a yield of 0.329 (44%) of pure $Th(C_9H_7)_3I$, identified by ^1H NMR and mass spectroscopy.

Results

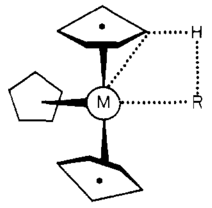
Cyclopentadienylthorium(IV) Compounds. Synthesis and Properties. Tris(cyclopentadienyl)thorium hydrocarbyls were prepared via the methodology of eq 2 and 3,[4a] starting with $Th(C_5H_5)_3Cl$, $Th(C_5D_5)_3Cl$, or $Th(CH_3C_5H_4)_3Cl$.

$$Th(C_5E_5)_3Cl + RLi \rightarrow \underset{\mathbf{1-6}}{Th(C_5E_5)_3R} + LiCl \qquad (2)$$

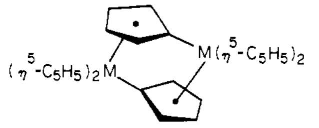
1, E = H, R = $i\text{-}C_3H_7$; **2**, E = D, R = $i\text{-}C_3H_7$; **3**, E = H, R = $n\text{-}C_4H_9$; **4**, E = D, R = $n\text{-}C_4H_9$; **5**, E = H, R = CH_3; **6**, E = D, R = CH_3

$$Th(CH_3C_5H_4)_3Cl + RLi \rightarrow \underset{\mathbf{7},\ R\,=\,n\text{-}C_4H_9}{Th(CH_3C_5H_4)_3R} + LiCl \qquad (3)$$

The thermolysis of the hydrocarbyls in solution has been studied in detail.[4] At 170 °C, β-hydride elimination is negligible, but rather intramolecular, stereospecific (R = 2-*cis*- or 2-*trans*-2-butenyl) abstraction of a ring hydrogen atom occurs ($k_H/k_D \approx 2.4 \pm 0.2$) (A) to yield the corresponding hydrocarbon, RH, and the colorless, crystalline $\eta^1:\eta^5$ thorium(IV) organometallic B[29] in essentially quantitative yield.



A



B

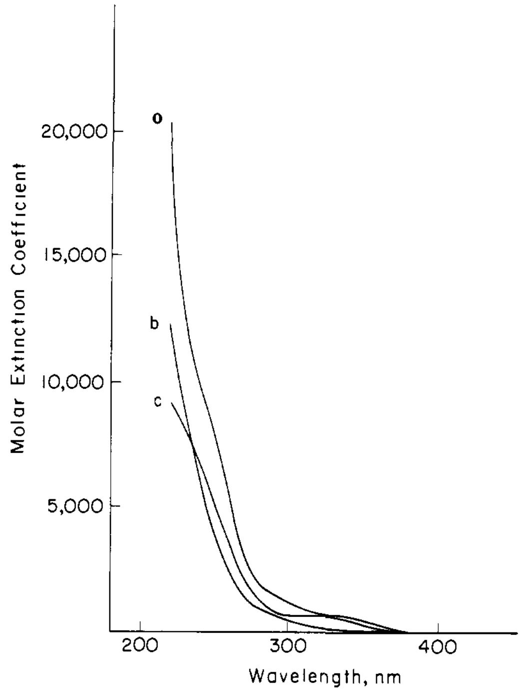


Figure 1. Electronic spectra of (a) $Th(C_5H_5)_3(n\text{-}C_4H_9)$, (b) $Th(C_5H_5)_3CH_3$, (c) $Th(C_5H_5)_3(i\text{-}C_3H_7)$, as solutions in cyclohexane.

Table I. Optical Spectroscopic Data for $M(\eta^5\text{-}C_5H_5)_3R$ Compounds[a,b]

compound	absorption, nm	log ε, M^{-1} cm^{-1}
$Th(C_5H_5)_3(i\text{-}C_3H_7)$, 1	220	3.94
	320 sh	
$Th(C_5H_5)_3(n\text{-}C_4H_9)$, 3	220	4.31
	300 sh	
$Th(C_5H_5)_3CH_3$, 5	219	4.10
$Th(C_5H_5)_3Cl$	234	
	220 sh	
	250 sh	
$Th(C_2H_5C_5H_4)_3(i\text{-}C_3H_7)$[c]	220	
$Th(C_2H_5C_5H_4)_3Cl$[c]	220 sh	4.13
	234	
	250 sh	
$U(C_5H_5)_3(n\text{-}C_4H_9)$, 11	215	3.85
$U(C_5H_5)_3CH_3$, 14	227	3.93
$U(C_5H_5)_3Cl$	217	
	250	
	310	

[a] Measured in cyclohexane solution. [b] sh = shoulder. [c] Reference 39.

In Figure 1 are shown solution optical spectra of several $Th(C_5H_5)_3R$ complexes. Full data are compiled in Table I. In general, the optical spectra of actinide complexes exhibit three types of transitions: 5f–5f, $5f\text{–}5f^{n-1}6d$, and ligand-to-metal charge transfer (LMCT).[1b,35] In principle, ligand-centered, $\pi\text{–}\pi^*$ transitions are also possible. For Th(IV), which has a $5f^0$ configuration, the 5f–5f and $5f\text{–}5f^{n-1}6d$ transitions need not be considered. As can be seen in Figure 1, the $Th(C_5H_5)_3R$ optical spectra are dominated by intense UV absorption. From Jørgensen's, empirical optical electronegativity considerations,[36] the energies of the $\eta^5\text{-}C_5H_5$ LMCT transitions[37] are anticipated

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(35) Carnall, W. T., in ref 1a, Chapter 9.

(36) (a) Jørgensen, C. K. "Modern Aspects of Ligand Field Theory"; North Holland: Amsterdam, 1971; chapter 23. (b) Jørgensen, C. K. *Prog. Inorg. Chem.* **1970**, *12*, 101–158. (c) Ryan, J. L. In MTP "International Review of Science, Inorganic Chemistry, Series One"; Bagnall, K. W., Ed.; University Park Press: Baltimore, 1972; Vol. 7, Chapter 9.

(37) (a) Clack, D. W.; Warren, K. D. *Struct. Bonding (Berlin)* **1980**, *39*, 1–41. (b) Gordon, K. R.; Warren, K. D. *Inorg. Chem.* **1978**, *17*, 978–994. (c) Warren, K. D. *Struct. Bonding (Berlin)* **1976**, *27*, 45–159.

Table II. Yields of Photolysis Products for $M(\eta^5\text{-}C_5H_5)_3R$ Compounds[a]

compound	yield of gaseous products,[b] %	organic products	relative yield, %	isolated yield of $M(C_5H_5)_3$, %
$Th(C_5H_5)_3(i\text{-}C_3H_7)$, 1	93	propane	54	94
		propene	46	
$Th(C_5H_5)_3(n\text{-}C_4H_9)$, 3	90	*n*-butane	58	91
		1-butene	42	
$Th(C_5H_5)_3CH_3$, 5	*c*	methane	90	
		hydrogen	6	
		ethane	4	
$U(C_5H_5)_3(i\text{-}C_3H_7)$, 10	95	propane	83	27
		propene	17	
$U(C_5H_5)_3(n\text{-}C_4H_9)$, 11	91	*n*-butane	91	12
		1-butene	9	
$U(C_5H_5)_3(s\text{-}C_4H_9)$, 13	96	*n*-butane	71	41
		butenes[d]	29	
$U(C_5H_5)_3CH_3$, 14	*c*	methane	98	
		ethane	2	

[a] Photolyses carried out in toluene solution at 10–15 °C. [b] Based on starting actinide alkyl; estimated error for gases is ±3%. [c] Complete reaction not achieved. [d] Mixture of isomeric butenes.

to be in the region of ca. 240 nm for a Th(IV) complex. The σ alkyl LMCT band should be at even shorter wavelengths[36]—ca. 150 nm. We assign the intense absorption in the $Th(C_5H_5)_3R$ complexes at wavelengths shorter than 300 nm to transitions which are predominantly $C_5H_5^-$ π HOMO[37] (a_1, a_2, and e under C_{3v} symmetry) to metal (5f and/or 6d) in character.[38] It will be seen that this assignment is in accord with the spectral data for the $U(C_5H_5)_3R$ analogues (vide infra). Although, a priori, these LMCT transitions might be expected to decrease in energy upon alkyl ring substitution,[37] the expected shifts in the present case (cf. $Th(C_2H_5C_5H_4)_3R$ compounds[39] in Table I) are likely too small to resolve, judging from metallocene[37] and substituted uranocene[40] data.

Tris(Cyclopentadienyl)thorium Hydrocarbyls. Photochemistry. In contrast to the high thermal stability of the $Th(C_5H_5)_3R$ compounds ($t_{1/2} \approx$ 10–1000 h at 170 °C in solution),[4a] the derivatives in which the R moiety contains a β-hydrogen atom (**1–4**, **7**) undergo facile photochemical decomposition upon irradiation at wavelengths shorter than 350 nm. The reaction proceeds according to eq 4 and 5, producing a nearly 1:1 ratio of alkane:alkene and a dark green precipitate, analyzing as $Th(C_5E_5)_3$ or $Th(CH_3C_5H_4)_3$[24] in nearly quantitative yield (Table II). Monitoring of these reactions by ^1H NMR spectroscopy gave no evidence for detectable concentrations of intermediate organometallics such as a thorium hydride[1] (arising from β-hydride elimination) or an *n*-propyl derivative[4a] (arising from isomerization of the isopropyl complex). Monitoring the alkane:alkene ratio through the course of the reaction showed it to remain essentially constant. Added ethylene or D_2 was not incorporated in the photoproducts or affected in any way by the photolysis. Labeling studies were conducted with deuterated cyclopentadienyl rings and solvents to determine the source of the hydrogen uptake in the RCH_2CH_2R' products. As can be seen in Table III, the solvent or rings are only a minor source. In addition, there is essentially no deuterium incorporation in the olefinic photoproduct. Photolysis of a mixture of **3** and **4** does not result in C_5H_5–C_5D_5 ring scrambling in the unconverted starting materials. The quantum yield for the disappearance of $Th(C_5H_5)_3(i\text{-}C_3H_7)$ was found to be 1.7 ± 0.1 for irradiation at 313 nm. When compound **3** is photolyzed in a glass at −196 °C, the relative yield of olefin increases and that of alkane decreases; H_2 is also detected as a product. Because of the apparatus employed in the matrix experiment, it was not possible to irradiate the entire sample, and overall yields are not meaningful.

$$2Th(C_5E_5)_3CHRCH_2R' \xrightarrow{h\nu} \underset{\mathbf{8},\ E\,=\,H,\ D}{2Th(C_5E_5)_3} + RCH_2CH_2R' + RCH{=}CHR' \quad (4)$$

$$2Th(CH_3C_5H_4)_3CHRCH_2R' \xrightarrow{h\nu} \underset{\mathbf{9}}{2Th(CH_3C_5H_4)_3} + RCH_2CH_2R' + RCH{=}CHR' \quad (5)$$

Table III. Deuterium Incorporation in the Organic Products of the Photolysis of $M(\eta^5\text{-}C_5H_5)_3R$ Compounds[a]

compound	solvent	product	% d_1 content
$Th(C_5H_5)_3(i\text{-}C_3H_7)$, 1	C_6D_6	propane	3.8
		propene	<1
$Th(C_5D_5)_3(i\text{-}C_3H_7)$, 2	C_6H_6	propane	2.8
		propene	<1
$Th(C_5D_5)_3(i\text{-}C_3H_7)$, 2	C_6D_6	propane	3.6
		propene	<1
$Th(C_5H_5)_3(n\text{-}C_4H_9)$, 3	C_6D_6	butane	2.7
		butene	<1
$Th(C_5D_5)_3(n\text{-}C_4H_9)$, 4	C_6H_6	butane	2.4
		butene	<1
$Th(C_5D_5)_3(n\text{-}C_4H_9)$, 4	C_6D_6	butane	8.5
		butene	<1
$Th(C_5H_5)_3CH_3$, 5	C_6D_6	methane	15.6
$Th(C_5D_5)_3CH_3$, 6	C_6H_6	methane	25.6
$Th(C_5D_5)_3CH_3$, 6	C_6D_6	methane	38.9
$U(C_5H_5)_3(n\text{-}C_4H_9)$, 11	C_6D_6	butane	20.0
		butene	4.3
$U(C_5D_5)_3(n\text{-}C_4H_9)$, 12	C_6H_6	butane	41.1
		butene	23.9
$U(C_5D_5)_3(n\text{-}C_4H_9)$, 12	C_6D_6	butane	73.4
		butene	22.2

[a] Determined by MS analysis of gases using 15-eV ionizing voltage. Estimated error, ±2%.

The photochemical response of $Th(C_5H_5)_3CH_3$, which contains no β-hydrogen atoms on the alkyl residue but displays an optical spectrum similar to that of the other tris(cyclopentadienyl)thorium hydrocarbyls, differs considerably from that of **1** and **3**. The reaction is appreciably slower as judged by the evolution of organic products (vide infra) and the formation of precipitate. Thus, while photolysis of **1** and **3** is complete in 2–4 h, photolysis of **5** under the same conditions is only ca. 50% complete after 20 h. As can be seen in Table II, the principal organic photolysis product of **5** is methane; however, significant amounts of ethane and hydrogen are also produced. Labeling studies (Table III) indicate that the cyclopentadienyl rings and the solvent are, in that order, major sources of hydrogen uptake in the production of methane. The yields from these two sources are approximately additive.

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(38) It should be noted that these energies approach those of what appear to be largely intraligand π–π* transitions in ionic cyclopentadienides: (a) Ford, W. G. *J. Organomet. Chem.* **1971**, *32*, 27–33. (b) Wagner, R. O.; Ebel, H. F. *Tetrahedron* **1970**, *26*, 5155–5167.

(39) Mintz, E. A.; Marks, T. J., unpublished results.

(40) Streitwieser, A., Jr.; Harmon, C. A. *Inorg. Chem.* **1973**, *12*, 1102–1104.

Photolysis of $Th(C_5H_5)_3CH_3$ in the presence of excess diphenylacetylene leads to the formation of a dark, red-brown solution. Over the period of several days of photolysis, ca. 20% yield of insoluble $Th(C_5H_5)_4$[25] crystallizes from this solution. An experiment was also conducted in which $Th(C_5H_5)_3(i\text{-}C_3H_7)$ was photolyzed in the presence of a ca. sixfold molar excess of $Th(C_5H_5)_3CH_3$. The result is an increase in methane yield relative to a $Th(C_5H_5)_3CH_3$ sample without added $Th(C_5H_5)_3(i\text{-}C_3H_7)$ and a marked drop in the propane:propene photoproduct ratio to 26:74. The sum of the moles of propane and additional methane produced is nearly identical, within experimental error, to the sum of the moles of propene produced, i.e., 0.027 mmol vs. 0.031 mmol.

Properties of Tris(cyclopentadienyl)thorium. The organometallic product of the $Th(C_5H_5)_3R$ photolysis is a dark-green, extremely air-sensitive complex analyzing as $Th(C_5H_5)_3$ (**8**). It is completely insoluble in nonpolar and ethereal organic solvents. To date, it has not proven possible to obtain diffraction quality crystals of **8** or of the ring-substituted analogues (vide infra). The vibrational spectra of **8** are typical of an $\eta^5\text{-}C_5H_5$ organometallic.[41] Thus, the infrared spectrum exhibits prominent cyclopentadienyl modes at 1012 m, 800 s, and 780 s cm^{-1} while the laser Raman spectrum (ν_0 = 5145 Å) displays strong scattering at 1121 s, 840 s, 254 s, 234 s, and 157 s cm^{-1}. There is no obvious indication of a metal hydride[1d] in these data. The mass spectrum exhibits intense signals for ions corresponding to $Th(C_5H_5)_3^+$ and $Th(C_5H_5)_2^+$; weaker features are noted for $Th(C_5H_5)_2C_3H^+$, $Th(C_5H_5)C_3H_3^+$, $Th(C_5H_5)C_3H_2^+$, and $Th(C_5H_5)C_3H^+$. This is a typical type of fragmentation pattern for an $\eta^5\text{-}C_5H_5$ metal compound.[42] Interestingly, while mass spectra of the mixed **3**/**4** reaction showed no C_5H_5–C_5D_5 scrambling in the unconverted starting materials, they do reveal extensive ring scrambling in the photoproduct; i.e., all possible parent ions for $Th(C_5H_5)_n(C_5D_5)_{3-n}$ species were detected. There was, however, no indication of appreciable H–D scrambling between the two types of rings. The optical spectrum of $Th(C_5H_5)_3$ as a Nujol mull shows three strong absorbances at 426, 480, and 622 nm. At room temperature, the magnetic moment of **8**, measured by Faraday techniques, is 0.404 μ_B. The moment is decidedly temperature dependent, falling to 0.10 μ_B at 4 K. Further details of the magnetic studies will be discussed elsewhere.[43]

The chemical reactions of **8** are also in accord with a $Th(C_5H_5)_3$ formulation. Thus, reaction with iodine produces $Th(C_5H_5)_3I$ in good yield, and reaction with chloroform produces $Th(C_5H_5)_3Cl$ in good yield (eq 6 and 7). The reaction with methanol indicates,

$$Th(C_5H_5)_3 + {}^1/_2I_2 \rightarrow Th(C_5H_5)_3I \qquad (6)$$

$$Th(C_5H_5)_3 + CHCl_3 \rightarrow Th(C_5H_5)_3Cl \qquad (7)$$

as expected, that Th(III) is a good reducing agent (eq 8). The

$$Th(C_5H_5)_3 + 4CH_3OH \rightarrow Th(OCH_3)_4 + {}^1/_2H_2 + 3C_5H_6 \qquad (8)$$

yield of hydrogen gas was within 10% of that expected, and that of cyclopentadiene (by NMR), within 5%. When **8** is exposed to hydrogen gas in the dark, the color fades and eventually 0.31 mol of H_2 is absorbed per $Th(C_5H_5)_3$ unit. The resulting, off-white product exhibits infrared transitions at 1375 (broad), 1125, 938, and 682 cm^{-1}. These are suggestive of metal hydride formation (cf. bands at 1404, 1370, 1215, 1114, 844, and 650 cm^{-1} in $(Th[(CH_3)_5C_5]_2H_2)_2$[1c,44]). Upon photolysis or prolonged exposure to room light, the hydrogenated material reverts to green **8**. It was found that **8** is relatively unreactive with respect to ammonium chloride (a cyclopentadienide cleavage reagent[5f]). The only product detected upon prolonged reflux with NH_4Cl in THF was a trace amount of $Th(C_5H_5)_3(O\text{-}n\text{-}C_4H_9)$. Similar THF ring-opening reactions have been observed for U(III) complexes or for Th(IV) complexes under reductive conditions.[45]

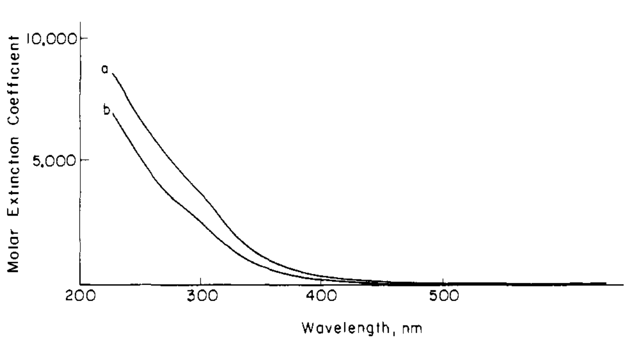

Figure 2. Electronic spectra of (a) $U(C_5H_5)_3CH_3$ and (b) $U(C_5H_5)_3(n\text{-}C_4H_9)$, as solutions in cyclohexane.

It was also possible to prepare ring-substituted thorium triscyclopentadienyls via the approach of eq 5. The complex $Th(CH_3C_5H_4)_3$ (**9**) exhibits an optical spectrum rather similar to that of **8** (431, 477, 572 nm, Nujol mull) and appears to be similar in other respects.[24] Although **9** is again insoluble, it is unstable to contact with aromatic solvents for a prolonged period. Slow decomposition yields a soluble, brown product which was not characterized. Photolysis of more soluble $Th(C_2H_5C_5H_4)_3R$ compounds in pentane yields a dark green precipitate with optical spectral properties similar to those of **8** and **9**. This complex, which will be discussed in more detail elsewhere,[39] dissolves in benzene or toluene with rapid discharge of the dark green color, hydrogen evolution, and the formation of pale-yellow, Th(IV) solutions.

Photochemistry of Th(indenyl)$_3$(*n*-C_4H_9). Extensive functionalization of the cyclopentadienyl ligands has profound effects on $Th(C_5H_5)_3R$ photochemistry. Thus, photolysis of $Th(C_9H_7)_3(n\text{-}C_4H_9)$ results in a 96% overall yield of organic product consisting of 96% butane and 4% 1-butene. Photolysis in C_6D_6 results in *n*-butane containing only 3.8% butane-d_1. The organometallic product of this reaction is a soluble, red-orange compound which analyzes as $Th(C_9H_7)_3$ (**15**). Reaction of **15** with methanol yields 0.46 mol of H_2 per mol of Th, in accord with the proposed formulation (cf. eq 8). Reaction of **15** with $CHCl_3$ and I_2 produces, respectively, $Th(C_9H_7)_3Cl$ and $Th(C_9H_7)_3I$. The latter yields are not, however, quantitative, and other organometallic products appear to be present. The ^1H NMR spectrum of **15** is too broadened to be meaningful. In contrast to the behavior of $Th(C_5H_5)_3$, $Th(C_9H_7)_3$ does not react with H_2. Further studies of the nature of **15** are in progress.

Tris(cyclopentadienyl)uranium(IV) Compounds. Synthesis and Properties. The $U(C_5H_5)_3R$ compounds for comparative photochemical studies were prepared from $U(C_5H_5)_3Cl$ or $U(C_5D_5)_3Cl$ as shown in eq 9. The tris(cyclopentadienyl)uranium hydrocarbyls

$$U(C_5E_5)_3Cl + RLi \rightarrow \underset{\textbf{10-14}}{U(C_5E_5)_3R} + LiCl \qquad (9)$$

10, E = H, R = $i\text{-}C_3H_7$; **11**, E = H, R = $n\text{-}C_4H_9$; **12**, E = D, R = $n\text{-}C_4H_9$; **13**, E = H, R = *sec*-C_4H_9; **14**, E = H, R = CH_3

are less thermally stable than those of thorium; however, solution thermolysis also yields organic products derived from intramolecular, stereospecific ring hydrogen atom transfer (RH).[4b,c] The uranium-containing product is an insoluble, U–($\eta^5\text{-}C_5H_5$) species of unknown structure.

Solution optical spectra of representative $U(C_5H_5)_3R$ compounds are shown in Figure 2; data are compiled in Table I. Excluding the sharp, weak ($\epsilon < 100$) f-electron transitions in the visible and near-infrared region,[1b,35] the major difference from the $Th(C_5H_5)_3R$ optical spectra of a shift of the intense UV absorption to lower energy. This displacement is in accord with the aforementioned ($\eta^5\text{-}C_5H_5$)-to-metal charge-transfer assignment since the U(IV) optical electronegativity is greater than that of

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[41] Maslowsky, E., Jr. "Vibrational Spectra of Organometallic Compounds"; Wiley-Interscience: New York, 1977; Chapter 3.

[42] (a) Cais, M.; Lupin, M. S. *Adv. Organomet. Chem.* **1970**, *8*, 211–333. (b) Müller, J. In "Mass Spectrometry of Metal Compounds", Charalambous, J., Ed.; Butterworths: London, 1975; pp 127–146.

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[44] Manriquez, J. M.; Fagan, P. J.; Marks, T. J. *J. Am. Chem. Soc.* **1978**, *100*, 3939–3941.

[45] McLaren, A. B.; Kanellakopulos, B.; Dornberger, E. *Inorg. Nucl. Chem. Lett.* **1980**, *16*, 223–225.

Table IV. Yields of Gases from $M(\eta^5\text{-}C_5H_5)_3R$ Photolyses at Liquid Nitrogen and Ambient Temperatures[a]

		yield, %	
compound	product	at ambient temperature	at −196 °C
$Th(C_5H_5)_3(n\text{-}C_4H_9)$, 3	*n*-butane	58	29
	1-butene	42	71
$U(C_5H_5)_3(n\text{-}C_4H_9)$, 11	*n*-butane	91	58
	1-butene	9	42
$U(C_5H_5)_3(s\text{-}C_4H_9)$, 13	*n*-butane	71	53
	butenes[b]	29	47

[a] Relative yields from toluene solutions. Estimated errors ±3%. [b] Mixture of isomeric butenes.

Th(IV).[36] Indeed, the Jørgensen equation[36] predicts a red shift of ca. 45 nm for the LMCT transitions on going from Th(IV) to U(IV). We thus assign the intense $U(C_5H_5)_3R$ spectral features in Figure 2 to $C_5H_5^-$ π HOMO LMCT excitations; the alkyl group σ LMCT energy is predicted[36] to lie at wavelengths shorter than ca. 200 nm.

Tris(cyclopentadienyl)uranium Hydrocarbyls. Photochemistry. The photolysis of compounds **10**–**14** follows a somewhat different course than that of the $Th(C_5H_5)_3R$ complexes. Relative to olefin, considerably larger quantities of alkane are produced (Table II). Olefin yields are greater for the secondary alkyls. Furthermore, substantial ^2H incorporation in the alkane (Table III) indicates that the cyclopentadienyl ligands and solvent molecules serve as hydrogen atom donors, with the former being the predominant source. The yields from these two sources are approximately additive. Also of interest is the observation that the olefin which is produced is partially deuterated and that the deuterium source is largely the $\eta^5\text{-}C_5D_5$ rings. In the case of the *sec*-butyl derivative, **13**, the butene photoproduct consists of a 2.7:1 ratio of 1-butene:2-butenes. There is no evidence for a soluble hydride or isomerization products such as $U(C_5H_5)_3(n\text{-}C_4H_9)$ when the photolysis is monitored by ^1H NMR. As in the case of the $Th(C_5H_5)_3R$ compounds, photolysis in a −196 °C glass increases the yield of olefin at the expense of alkane (Table IV). The organometallic product of $U(C_5H_5)_3R$ photolysis in toluene solution is a dark, green-brown precipitate. Evaporation of the toluene and extraction with THF yields, depending upon the R substituent, varying amounts of the known compound, $U(C_5H_5)_3\cdot THF$. There is a significant correlation between olefin and $U(C_5H_5)_3\cdot THF$ yield (Table II). The isolated yields indicate that the tris(cyclopentadienyl) is not the sole organometallic photoproduct. For $U(C_5H_5)_3(i\text{-}C_3H_7)$, photolysis in THF rather than toluene increases the $U(C_5H_5)_3$ yield from 27% to 64%.

Discussion

Thorium Photochemistry. The photochemistry of the $Th(C_5E_5)_3CHRCH_2R'$ compounds **1**–**4** (and **7**) is consistent with a photoinduced β-hydride elimination reaction to yield a thorium hydride (**15**) and olefin (eq 10), followed by bimolecular reductive elimination of alkane (eq 11). In the discussion which follows,

$$Th(C_5E_5)_3CHRCH_2R' \xrightarrow{h\nu} \underset{\mathbf{15}}{Th(C_5E_5)_3H} + RCH{=}CHR' \quad (10)$$

$$Th(C_5E_5)_3H + Th(C_5E_5)_3CHRCH_2R' \rightarrow 2Th(C_5E_5)_3 + CH_2RCH_2R' \quad (11)$$

we summarize the evidence for this mechanistic sequence (it now appears that the basic process depicted in eq 10 may have considerable generality[10a,b,11,46]) and discuss why a number of alternative mechanisms are highly unlikely. First, the sequence of reactions given by eq 10 and 11 should produce a 1:1 ratio of olefin:alkane with all hydrogen uptake in the alkane originating from another alkyl group; this is observed. If eq 11 is fast compared to eq 10, then the olefin:alkane ratio should remain constant throughout the reaction; this is also observed. The matrix results in which the bimolecular, alkane-forming second step (eq 11) is hindered (producing a higher percentage of olefin) and the lowered reactivity of $Th(C_5H_5)_3CH_3$ (which possesses no β-hydrogen atoms) are also in accord with the proposed mechanism. Especially significant is the observation that the less photoreactive $Th(C_5H_5)_3CH_3$, when added in excess to a $Th(C_5H_5)_3(i\text{-}C_3H_7)$ photolysis, results in a diminished propane yield and a corresponding enhanced methane yield. This is consistent with the hydride formation and scavenging processes shown in eq 12 and 13 in which the methyl and isopropyl compounds now compete for the intermediate hydride. That the quantum yield for $Th(C_5H_5)_3(i\text{-}C_3H_7)$ disappearance (1.7 ± 0.1) is greater than 1.0 but less than 2.0 also supports the proposed mechanism.

$$Th(C_5H_5)_3(i\text{-}C_3H_7) \xrightarrow{h\nu} Th(C_5H_5)_3H + C_3H_6 \quad (12)$$

$$Th(C_5H_5)_3H \begin{array}{l} \xrightarrow{Th(C_5H_5)_3CH_3} 2Th(C_5H_5)_3 + CH_4 \\ \xrightarrow{Th(C_5H_5)_3(i\text{-}C_3H_7)} 2Th(C_5H_5)_3 + C_3H_8 \end{array} \quad (13)$$

Barring some unusual reactivity of the alkyl moiety β C–H bonds (vide infra), classical free-radical processes can also be discounted as a major pathway. Thus, 1:1 alkane:olefin production via free-radical disporportionation would require the production of large amounts of the dimer $(-CHRCH_2R')_2$, since dimerization:disproportionation ratios for the *n*-butyl and isopropyl radicals are 7.1 and 0.8, respectively.[47] Such dimerization products are not present in significant quantities. Under normal conditions it would also be expected that $\cdot CHRCH_2R'$ radicals would abstract hydrogen atoms from the solvent molecules or cyclopentadienyl rings. This process occurs to only a minor extent in the deuterium labeling studies, and even assuming a relatively large kinetic isotope effect (k_H/k_D) of ca. 5–6 for C–H/C–D abstraction by the alkyl radical,[48] it is apparent that this pathway is not important when the alkyl moiety possesses β-hydrogen atoms.[49] Interestingly, it can be seen in Tables II and III that the slight excess of alkane over olefin that arises when **1**–**4** are photolyzed correlates approximately with the deuterium uptake in the alkane. This suggests that a minor C–H activating side reaction, possibly radical in character (vide infra), is operative. In the case of $Th(C_5H_5)_3CH_3$, no β-hydrogen atoms are present, and the far slower methane-forming reaction occurs with substantial (and additive) hydrogen (deuterium)[50] uptake from solvent and cyclopentadienyl rings. Ethane and hydrogen are also produced in this reaction.

Yet to be discussed is the possibility that $Th(C_5E_5)_3CHRCH_2R'$ photolysis involves only Th–C bond homolysis but also that the β-hydrogen atoms of the Th–alkyl group display a greatly enhanced reactivity with respect to abstraction by the photogenerated radicals (eq 14). A similar C–H selectivity has been suggested

$$Th(C_5H_5)_3CHRCH_2R' + \cdot CHRCH_2R' \rightarrow Th(C_5H_5)_3 + RCH{=}CHR' + CH_2RCH_2R' \quad (14)$$

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(46) For further cases where photoinduced β-hydride elimination may be occurring, see: (a) Duong, K. N. V.; Ahond, A.; Merienne, C.; Gaudemer, A. *J. Organomet. Chem.* **1973**, *55*, 375–382. (b) Müller, J.; Gösser, P. *Angew. Chem. Int. Ed. Engl.* **1967**, *6*, 364–365. (c) Müller, J.; Fischer, E. O. *J. Organomet. Chem.* **1966**, *5*, 275–282. (d) Fischer, E. O.; Müller, J. *Chem. Ber.* **1963**, *96*, 3217–322.

(47) (a) Ingold, K. U. In "Free Radicals"; Kochi, J. K., Ed.; Wiley: New York Vol. I, 1973; Chapter 2. (b) Koenig, T.; Fischer, H., in ref 47a, Chapter 4. (c) Gibian, M. J.; Corley, R. C. *Chem. Rev.* **1973**, *73*, 441–464.

(48) (a) Evans, J.; Okrasinski, S. J.; Pribula, A. J.; Norton, J. R. *J. Am. Chem. Soc.* **1977**, *99*, 5835–5837, and references therein. (b) Russell, G. A., in ref 47a Chapter 7.

(49) As an example, when photolysis of a $Th(C_5D_5)_3R$ compound (R = alkyl, 95% ring deuteration) in C_6H_6 yields 97% RH and 3% RD, then for $k_H/k_D = 5$, ring abstraction (H + D) accounts for only 3.8% of the alkane formation.

(50) This reaction, which was not carried to completion, is not as clean as the other $Th(C_5H_5)_3R$ photolyses. The total deuterium content of the organic products (entries in Table III) and reasonable estimations of possible kinetic isotope effects[48] suggest that nonradical-CH_3 hydrogen abstraction may be a significant source of methane. The additivity of the methane deuterium contents argues that either ring and solvent abstraction do not occur via a common intermediate (e.g., a methyl radical) or that the abstraction does not exhibit a kinetic isotope effect.

for an organomercurial free-radical chain reaction.[51] However, the mercurial studies were performed in a chlorinated solvent at concentrations on the other of at least 100 times greater than those of the present studies. For such an abstraction process to be operative in the photochemistry of **3**, for example, would require the *n*-butyl radical to exhibit a selectivity for $Th(n\text{-}C_4H_9)$ β-hydrogen atoms over C_6D_6 D atoms greater than 7600 for the concentrations at the *outset* of the reaction yielding the products in Tables II and III (assuming $k_H/k_D = 5$).[52] Judging from existing data on analogous abstraction processes, this selectivity appears unreasonable.[53] Furthermore, if all $Th(C_5H_5)_3R$ photolyses proceeded by such a homolysis/intermolecular β-hydrogen abstraction process, then the diminished reactivity of the R = CH_3 complex becomes less understandable, as do the results of the **1**/**5** mixed photolysis (eq 12 and 13).

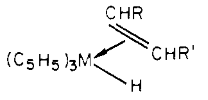
The question must also be entertained as to whether *100%* of the $Th(C_5E_5)_3CHRCH_2R'$ compound suffers photoinduced β-hydride elimination with $Th(C_5E_5)_3$ and the alkane arising via some process other than eq 11. One possible scenario would be be subsequent thermal or photochemical decomposition of the thorium hydride **15** to produce 0.5 equiv of H_2 and some species (possibly in trace quantities) which was an efficient thermal or photochemical olefin hydrogenation catalyst. Thus, one-half of the olefin would be catalytically hydrogenated to alkane. That the alkane:olefin ratio remains constant during the reaction requires that the hydrogenation process be relatively rapid. However, since added ethylene and D_2 are not incorporated in the photochemical products or affected by the reaction, the olefin hydrogenation mechanism is concluded to be unimportant.

In regard to precedent for eq 11, the existence of organothorium hydrides is well established (e.g., $\{Th[(CH_3)_5C_5]_2H_2\}_2$, $\{Th[(CH_3)_5C_5]_2(H)Cl\}_2$, etc.[1c,44]) although $Th(C_5H_5)_3H$ has not been isolated in a pure state.[54] Furthmore, support for eq 11 derives from the reaction of $\{Th[(CH_3)_5C_5]_2H_2\}_2$ with excess **5** to yield $Th(C_5H_5)_3$ (eq 15). The mixed photolysis experiment of eq 12

$$\{Th[(CH_3)_5C_5]_2H_2\}_2 + 8Th(C_5H_5)_3CH_3 \rightarrow 2Th[(CH_3)_5C_5]_2(CH_3)_2 + 8Th(C_5H_5)_3 + 4CH_4 \quad (15)$$

and 13 is also good evidence for eq 11. Of course, such bimolecular alkane reductive elimination processes are amply documented in transition-metal organometallic chemistry.[55]

Of the possible structures of the photoexcited species leading to β-hydride elimination, a ligand-to-metal charge-transfer state is most plausible. If excitation is $\pi(C_5H_5) \rightarrow$ metal in character, weakened ring–metal bonding would plausibly facilitate formation of an olefin–hydride intermediate such as C. There is precedent for η^5-C_5H_5 photolabilization (and subsequent intermolecular ring interchange) in transition-metal photochemistry.[14,15,56] The mechanism of this process is not entirely understood. There is no evidence in the present case for intermolecular C_5H_5–C_5D_5 exchange which is more efficient than β-hydride elimination. That mass spectra of the trivalent photoproduct reveal $Th(C_5H_5)_n(C_5D_5)_{3-n}$ species raises the possibility that ring labilization and exchange may compete with or trigger β-hydride elimination (the production of $Th(C_5H_5)_4$ on prolonged photolysis of **5** and diphenylacetylene is somewhat less direct evidence of ring photolabilization); however, such products may also simply be an artifact of the $Th(C_5H_5)_3$ crystal structure (vide infra). In regard to transition-state intermediate C, it is important to note that it is not sufficiently long-lived to allow olefin readdition and alkyl group isomerization. However, we show elsewhere[57] that migratory CO insertion in such compounds is photochemically accelerated. What of the minor (for **1**–**4**) non-β-hydrogen elimination pathway(s) observed? A homolytic Th–R bond scission process (possibly a consequence of σ(alkyl) $\rightarrow$ metal charge transfer) would be expected to produce R· radicals which in turn would abstract cyclopentadienyl or solvent hydrogen atoms. Alternatively, a photochemical entry to the known thermolysis pathway[4] would result in ring hydrogen atom abstraction.



C

All spectroscopic, magnetic, and chemical evidence strongly support a $Th(\eta^5\text{-}C_5H_5)_3$ formulation for **8**. If the crystal structure is similar to that of the tris(cyclopentadienyl) lanthanides,[1c,58] then extensive C_5H_5 bridging between metal ions reasonably explains the $Th(C_5H_5)_n(C_5D_5)_{3-n}$ mass spectral features without invoking photoinduced ring exchange. The present green $Th(C_5H_5)_3$ differs in a number of important chemical and physical respects from the violet $Th(C_5H_5)_3$ prepared by sodium naphthalide reduction of $Th(C_5H_5)_3Cl$ in THF.[5e] These will be discussed in detail elsewhere.[43] We note here that the violet compound is more soluble, possesses a far lower magnetic moment, and in reactions with iodine and methanol, gives ca. one-half the expected yields of $Th(C_5H_5)_3I$ and H_2, respectively.

The substitution of indenyl for cyclopentadienyl completely eliminates the β-hydrogen elimination pathway. Instead, intramolecular ligand hydrogen abstraction is the predominant photochemical pathway. Upon consideration of the increased bulk of the indenyl ligand (evident in metrical parameters[1c,59]), it may be that species such as C become prohibitively high in energy, and the commonly observed alternative to β-hydrogen elimination in organoactinide chemistry prevails. Similar hydrogen atom abstraction processes have been identified in the photochemistry of group 4B $M(indenyl)_2R_2$ complexes.[10g]

$U(C_5H_5)_3R$ Photochemistry. The products of $U(C_5H_5)_3CHRCH_2R'$ photolysis again indicate the operativity of β-hydrogen elimination; however, it is not the predominant photochemical pathway. The olefin production which is observed (without $(\text{–}CHRCH_2R')_2$ formation) is in accord with β-hydrogen elimination. Also, the 2.7:1 1-butene:2-butene ratio measured for **13** (Table II) is not the 1.25:1 ratio expected for disproportionation of the *sec*-butyl radical[60] and is more in accord with a β-hydrogen elimination pathway. The relative olefin yields *sec*-butyl > isopropyl > *n*-butyl are also interpretable in terms of decreasing tendency toward β-hydrogen elimination with decreasing steric congestion. That the $U(C_5H_5)_3$ yield for photolysis in toluene adheres to the same trend (Table II) argues that the β-hydride elimination is the major source of $U(C_5H_5)_3$.[61] The predominant organic product of the reaction is the alkane CH_2RCH_2R', with the added hydrogen atoms derived from the C_5H_5 ligands and solvent molecules, in that order. Since the trivalent oxidation state is far more accessible for uranium than for thorium,[7a] a homolytic bond scission to yield alkyl radicals could be postulated.[62]

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(51) Nugent, W. A.; Kochi, J. K. *J. Organomet. Chem.* **1977**, *124*, 327–347.

(52) This calculation assumes $Th(C_5H_5)_3(n\text{-}C_4H_9)$ concentrations on the order of 10 mM. These will, of course, decrease as the reaction proceeds, so the measured selectivity should be even higher.

(53) Pryor, W. A. "Free Radicals"; McGraw-Hill; New York, 1966; Chapter 12.

(54) The coordinative saturation of the $Th(C_5H_5)_3$-ligation sphere is likely a severe impediment to most synthetic approaches. Thus, while hydrogenolysis of the Th–CH_3 bonds in $Th[(CH_3)_5C_5]_2(CH_3)_2$ is rapid at 0 °C,[1d,44] no reaction could be observed for $Th(C_5H_5)_3CH_3$ over the course of days at elevated temperature (see Experimental Section for details).

(55) Collman, J. P.; Hegedus, L. S. "Principles and Applications of Organotransition Metal Chemistry"; University Science Books: Mill Valley, CA, 1980; 245–251, and references therein.

(56) Harrigan, R. W.; Hammond, G. S.; Gray, H. B. *J. Organomet. Chem.* **1974**, *81*, 79–85.

(57) Mintz, E. A.; Sonnenberger, D. C.; Marks, T. J., manuscript in preparation.

(58) Marks, T. J. *Prog. Inorg. Chem.* **1978**, *24*, 51–107.

(59) Burns, J. H.; Laubereau, P. G. *Inorg. Chem.* **1971**, *10*, 2789–2792.

(60) Shelton, R. A.; Kochi, J. A. *J. Am. Chem. Soc.* **1970**, *92*, 4395–4405.

(61) Indeed, there is a linear proportionality between olefin yield and $U(C_5H_5)_3$ yield.

(62) Studies carried out in ref 18b under a combination of thermal and photochemical excitation led to the suggestion of a homolytic pathway for $U(C_5H_5)_3(n\text{-}C_4H_9)$ photolysis in THF. The extent of this pathway, identified primarily on the basis of spin-trapping experiments (which should be interpreted with caution[63]), was not quantified.

(63) (a) Wong, P. K.; Lau, K. S. Y.; Stille, J. K. *J. Am. Chem. Soc.* **1974**, *96*, 5956–5957. (b) Whitesides, G. M.; Bergbreiter, D. E.; Kendall, P. E. *J. Am. Chem. Soc.* **1974**, *96*, 2806–2813.

However, it should be noted that $U(C_5H_5)_3$ yields are relatively low, and any radical must be sufficiently constrained that attack on the cyclopentadienyl rings predominates. Alternatively, the lower thermal stability of the $U(C_5H_5)_3R$ complexes may allow more facile population of the known, possibly concerted, ring hydrogen abstraction thermolysis pathway.[4b,c] It is not even certain that hydrogen abstraction from solvent molecules must be exclusively free radical in nature. For example, recent results in organoactinide $M[(CH_3)_5C_5]_2R_2$ chemistry reveal examples of facile, nonradical thermal hydrocarbon metathesis (e.g., eq 16).[1d]

$$M\text{-}R + C_6D_6 \rightarrow M\text{-}C_6D_5 + RD \qquad (16)$$

It is also interesting to note in Table II that the olefin produced in $U(C_5D_5)_3$(*n*-butyl) experiments contains appreciable amounts of deuterium. The mechanism of deuterium transfer from the rings to the olefin likely involves initial transfer to the metal to produce a metal deuteride, followed by reversible addition and elimination of the olefin. Facile deuteride–ring methyl scrambling is observed in $\{U[(CH_3)_5C_5]_2D_2\}_2$.[1d,64] When the $U(C_5H_5)_3R$ compounds are photolyzed in THF, the yield of $U(C_5H_5)_3$ (isolated as the THF adduct) increases significantly. This reaction was not investigated in detail; however, it is possible that the donor solvent alters the reaction pathway by intercepting intermediates such as C (with THF displacing the olefin) or by stabilizing caged radical pairs.[62]

Conclusions

This study demonstrates that nonthermal transformations can be brought about readily by the UV photolysis of organoactinides. In certain systems, photoinduced β-hydride elimination is facile and represents an efficient and clean route to new organoactinide hydrides and to actinide organometallics in unusual oxidation states. Such processes are, however, highly sensitive to the nature of the metal coordination sphere and to the 5f electron configuration; they may also be dependent, to a significant degree, on the properties of the solvent.

Acknowledgment. We are grateful to the National Science Foundation for support of this research (CHE8009060) and to Professor F. D. Lewis and Dr. W. A. Wachter for helpful discussions.

Registry No. 1, 58920-13-1; **2**, 80410-04-4; 3, 54067-92-4; **4**, 58920-16-4; **5**, 80410-05-5; **6**, 80410-06-6; **7**, 80410-07-7; **8**, 52550-20-6; **9**, 63372-74-7; **10**, 37298-79-6; **11**, 37298-84-3; **12**, 80410-08-8; **13**, 80410-09-9; **14**, 37205-28-0; **15**, E = H, 80410-10-2; $Th(C_5H_5)_3Cl$, 1284-82-8; $U(C_5H_5)_3Cl$, 1284-81-7; $Th(\eta^5\text{-}C_9H_7)_3(n\text{-}C_4H_9)$, 63643-43-6; $Th(C_9H_7)_3$, 80410-11-3; $Th(C_9H_7)_3Cl$, 11133-05-4; $Th(C_9H_7)_3I$, 66775-24-4; $Th(\eta^5\text{-}C_5H_5)_4$, 1298-75-5; $U(C_5H_5)_3\cdot THF$, 74237-38-0; $(Th[\eta^5\text{-}(CH_3)_5C_5]_2H_2)_2$, 67506-92-7; $Th[\eta^5\text{-}(CH_3)_5C_5]_2(CH_3)_2$, 67506-90-5; $Th(C_5H_5)_3I$, 80410-12-4; $C_6H_5C{\equiv}CC_6H_5$, 501-65-5; I_2, 7553-56-2; $CHCl_3$, 67-66-3; CH_3OH, 67-56-1; NH_4Cl, 12125-02-9; $U(C_5H_5)_3$, 54007-00-0; propene, 115-07-1; *n*-butane, 106-97-8; 1-butene, 106-98-9; methane, 74-82-8; hydrogen, 1333-74-0; ethane, 74-84-0; (*E*)-2-butene, 624-64-6; (*Z*)-2-butene, 590-18-1; propane, 74-98-6.

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[64] Fagan, P. J.; Marks, T. J., unpublished results.

Stable Precursors of Transition-Metal Carbene Complexes. Simplified Preparation and Crystal Structure of (η^5-Cyclopentadienyl)[(dimethylsulfonium)methyl]dicarbonyliron(II) Fluorosulfonate

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Abstract: The sulfonium salt $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_2S(CH_3)_2^+\ FSO_3^-$ (**4**), a possible precursor of an iron–carbene complex, is prepared in one simple sequence of reactions starting with commercially available $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$. The structure of **4** was determined by single-crystal X-ray diffraction techniques. This salt crystallizes in the space group *Pbca* (orthorhombic) with $a = 13.340\ (7)$ Å, $b = 15.096\ (3)$ Å, $c = 14.388\ (6)$ Å, and $Z = 8$. The structure was solved straightforwardly by a combination of Patterson and difference Fourier peak searches and was refined to values of $R = 0.045$ and $R_w = 0.057$. One structural parameter which is consistent with **4** behaving as a carbene-like complex is the Fe–C σ-bond length of 2.036 (3) Å, which is somewhat shorter than in the cases of other related iron alkyls. However, other structural parameters do not provide consistent support for the iron–carbene nature of **4**. Alternatively, the shortening of the Fe–C bond may be due to the operation of an inductive effect of the sulfonium group.

Transition-metal carbene complexes have been the subject of intensive investigation during the past two decades.[1] In recent years the involvement of these species in various important types of reactions has been realized. Among these reactions are alkene metathesis[2] and the conversion of alkenes into cyclopropanes.[1,3] One system that has been studied especially thoroughly is the cationic (η^5-cyclopentadienyl)dicarbonylalkylideneiron(II) group

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[1] For some selected reviews of transition-metal carbene complexes, see: (a) Fischer, E. O. *Pure Appl. Chem.* **1970**, *24*, 407–423; **1972**, *30*, 353-372. (b) Cardin, D. J.; Cetinkaya, B.; Lappert, M. F. *Chem. Rev.* **1972**, *72*, 545-574. (c) Cotton, F. A.; Lukehart, C. M. *Prog. Inorg. Chem. 16*, 487–613. (d) Cardin, D. J.; Cetinkaya, B.; Doyle, M. J.; Lappert, M. F. *Chem. Soc. Rev.* **1973**, *2*, 99–144. (e) Dötz, K. H. *Naturwissenschaften* **1975**, *62*, 365–371. (f) Fischer, E. O. *Adv. Organomet. Chem.* **1976**, *14*, 1–32. (g) Casey, C. P. *J. Organomet. Chem. Libr.* **1976**, *1*, 397–421. (h) Casey, C. P. *CHEMTECH* **1979**, 378–383. (i) Brown, F. J. *Prog. Inorg. Chem.* **1980**, *27*, 1–122. (j) Cardin, D. J.; Norton, R. J. *Organomet. Chem.* **1980**, *8*, 286–292; see also the earlier volumes of this series.

[2] For some recent reviews on the mechanism of alkene metathesis, see: (a) Rooney, J. J.; Stewart, A. *Catalysis (London)* **1977**, *1*, 277–334. (b) Katz, T. J. *Adv. Organomet. Chem.* **1977**, *16*, 283–317. (c) Grubbs, R. H. *Prog. Inorg. Chem.* **1978**, *24*, 1–50. (d) Calderon, N.; Lawrence, J. P.; Ofstead, E. A. *Adv. Organomet. Chem.* **1979**, *17*, 449–492.

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