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Synthesis and Properties of Bis(pentamethylcyclopentadienyl) Actinide Hydrocarbyls and Hydrides. A New Class of Highly Reactive f-Element Organometallic Compounds

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Abstract: This paper reports the synthesis and chemical and physicochemical properties of thorium and uranium bis(pentamethylcyclopentadienyl) chlorides, hydrocarbyls, chlorohydrocarbyls, and hydrides. The reaction of the precursor compounds $M[\eta^5\text{-}(CH_3)_5C_5]_2Cl_2$ with 2 equiv of lithium reagent RLi produces $M[\eta^5\text{-}(CH_3)_5C_5]_2R_2$ compounds where R = CH_3, $CH_2Si(CH_3)_3$, $CH_2C(CH_3)_3$, $CH_2C_6H_5$, and C_6H_5 (M = Th) and R = CH_3, $CH_2Si(CH_3)_3$, $CH_2C_6H_5$, and C_6H_5 (M = U) in good yield. With 1 equiv of lithium reagent, $M[\eta^5\text{-}(CH_3)_5C_5]_2(R)Cl$ compounds where R = $CH_2C(CH_3)_3$, $CH_2Si(CH_3)_3$, $CH_2C_6H_5$, and C_6H_5 (M = Th) and R = $CH_2C(CH_3)_3$, $CH_2Si(CH_3)_3$, $CH_2C_6H_5$, and C_6H_5 (M = U) are formed in high yield. The $M[\eta^5\text{-}(CH_3)_5C_5]_2(CH_3)Cl$ compounds can be synthesized by redistribution between the corresponding dimethyl and dichloro complexes. The new organoactinides were thoroughly characterized by elemental analysis, ^1H NMR and vibrational spectroscopy, and in many cases cryoscopic molecular weight measurements. The hydrocarbyls and chlorohydrocarbyls generally exhibit high thermal stability. However, the diphenyl compounds react readily with C_6D_6 to yield, via a benzyne complex, the corresponding $M(C_6D_5)_2$ compounds. The thorium bis(neopentyl) complex reacts with benzene to produce the corresponding diphenyl complex. In probes of bond polarity, the dimethyl complexes react rapidly with acetone, alcohols, and iodine to produce respectively the corresponding *tert*-butoxides, alkoxides plus methane, and iodides plus methyl iodide. Competition experiments at −78 °C indicate that the thorium complexes are more reactive than those of uranium. The $M[\eta^5\text{-}(CH_3)_5C_5]_2R_2$ compounds undergo hydrogenolysis to yield organoactinide hydrides, $\{M[\eta^5\text{-}(CH_3)_5C_5]_2(\mu\text{-}H)H\}_2$, and RH. While the thorium hydride exhibits high thermal stability, that of uranium readily (and reversibly) eliminates H_2, forming a uranium(III) hydride. The new hydrides react vigorously with methyl chloride to produce methane and the corresponding chloro complexes, with acetone to produce isopropoxy complexes, and with alcohols to produce alkoxides and H_2. The thorium chlorohydride, $\{Th[\eta^5\text{-}(CH_3)_5C_5]_2(\mu\text{-}H)Cl\}_2$, can be prepared by redistribution of the dichloride and dihydride; an alkoxyhydride, $Th[\eta^5\text{-}(CH_3)_5C_5]_2[OC(CH_3)_3]H$, can be prepared by hydrogenolysis of $Th[\eta^5\text{-}(CH_3)_5C_5][OC(CH_3)_3]CH_3$. In solution, the metal-bound hydrides of $\{Th[\eta^5\text{-}(CH_3)_5C_5]_2(\mu\text{-}H)H\}_2$ rapidly exchange with dissolved H_2; this hydride also reacts with ethylene to yield the corresponding diethyl complex. The olefin addition and hydrogenolysis reactions can be coupled to effect homogeneous, catalytic olefin hydrogenation. The differences between thorium and uranium chemistry appear largely to reflect differences in accessible oxidation states and in metal–ligand bond polarity.

Two-electron σ bonds between metal ions and the carbon atoms of organic molecules play a central role in stoichiometric and catalytic organometallic chemistry. While for many main-group and d elements, the chemistry of this type of linkage has reached an advanced stage of development,[1] the nature of actinide (5f) hydrocarbyls is largely unexplored. Indeed, until recently, there was even doubt that organoactinide[2] molecules with actinide-to-carbon σ bonds would be isolable. Research in this laboratory and elsewhere has now altered this picture, and it is apparent that thermally stable, coordinatively saturated tris(cyclopentadienyl) ($M(\eta^5\text{-}C_5H_5)_3R$)[2,3] and related species,[2] as well as far less stable and less coordinatively saturated homoleptic[2,4] hydrocarbyls, can be prepared. Our goal in organoactinide research has been to capitalize upon the unique features of actinide ions (large coordination numbers, high kinetic lability, 5f valence orbitals, marked oxophilicity) to promote unusual types of chemical reactivity and also to develop meaningful chemical comparisons between organo–5f-element reaction patterns and those of transition-metal organometallics.

We recently communicated that bis(pentamethylcyclopentadienyl)thorium and -uranium hydrocarbyls could be prepared and that such complexes underwent a variety of unusual reactions with surprising vigor.[5,6] In the present contribution we relate in detail the synthesis and a number of the chemical/physicochemical properties of this new class of actinide hydrocarbyls. Much new information on actinide-to-carbon σ bonds is presented. We also include here hydrogenolysis chemistry which has afforded the first organoactinide hydride complexes[5] and describe some of the interesting properties of actinide hydrides. We defer discussion of certain mechanistic details for several reactions[7] as

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well as results on carbon monoxide activation[8] until later contributions.

Experimental Section

Physical and Analytical Measurements. ^{1}H NMR spectra were recorded on a Perkin-Elmer R-20B (60-MHz, CW) or JEOL FX-90Q (90-MHz, FT) spectrometer. Chemical shifts are reported relative to internal $Si(CH_3)_4$. Samples were prepared either in a glovebox or on a high vacuum line. Deuterated aromatic solvents were dried over Na/K alloy and were degassed by freeze–thaw cycles on a vacuum line. Mass spectra were recorded on a Hewlett-Packard 5985 instrument.

Gas chromatography was performed with a Varian 920 instrument using thermal conductivity detection. Infrared spectra were recorded on a Perkin-Elmer 267 or Perkin-Elmer 283 spectrometer and were calibrated with polystyrene film. Samples were prepared in a glovebox as mulls by using previously dried and degassed Nujol or Fluorolube. Mulls were sandwiched between polished KBr plates contained in an O-ring sealed, airtight holder.

Elemental analyses were performed by Dornis and Kolbe Mikroanalytiches Laboratorium, West Germany.

Cryoscopic molecular weights were measured by using an apparatus similar to that described previously,[9] but modified for use on a vacuum line.[10] In a glovebox, a weighed amount of the sample was charged into a side arm tube through the Teflon vacuum valve. The apparatus was connected to the high vacuum line, and a weighed amount of benzene was condensed in vacuo into the bottom portion of the apparatus at −78 °C. The desired atmosphere (N_2 or Ar, 1 atm) was then introduced, and three freezing curves were recorded. The apparatus was next tipped to allow benzene to flow into the side arm dissolving the sample. Three freezing curves were then recorded for the solution. In general, ca. 5–8 g of benzene and 150–250 mg of compound were used for the molecular weight determinations. The experimental error in the cryoscopic molecular weights is estimated to be ±10%.

Materials and Methods. All procedures were performed in Schlenk-type glassware using normal bench-top Schlenk techniques, in Schlenk-type glassware interfaced to a high vacuum (10^{-4}–10^{-5} torr) line, or in a dinitrogen (or argon) filled glovebox. Argon (Matheson, prepurified), dinitrogen (Matheson, prepurified), and dihydrogen (Linde) were purified further by passage through a supported MnO oxygen removal column[11] and a Davison 4-Å molecular sieve column. Reactions with gases were performed in an enclosed volume on the vacuum line. Gas uptake was monitored with a mercury manometer. Toluene, diethyl ether, benzene, tetrahydrofuran, and pentane (previously distilled from Na/K/benzophenone) were condensed and stored in vacuo in bulbs on the vacuum line. Diphenylacetylene (Aldrich) was sublimed before use. Deuterium gas (Matheson, 99.5%), TlCl (Aldrich), and lithium wire (Alfa, 0.02% Na, 3.2-mm diameter) were used as obtained. Ethylene (Matheson, 99.5%) and methyl chloride (Matheson, 99.5%) were purified by freezing the gases in a flask at liquid-nitrogen temperature, removing any volatile residual gases in vacuo, and warming to −78 and −40 °C, respectively, to obtain the desired pressure. Acetone was dried over freshly activated and degassed 4-Å molecular sieves and was degassed by freeze–thaw cycles on a vacuum line before use. The hydrogenation substrate, 1-hexene (Aldrich, distilled), was dried over Na metal and degassed in vacuo.

Commercially obtained diethyl ether solutions of $LiCH_3{\cdot}LiBr$ (Aldrich) and *i*-C_3H_7MgCl (Alfa) were used without further purification. The solid lithium reagents $LiCH_2C(CH_3)_3$[12] (recrystallized from cold (−78 °C) pentane), $LiCH_2Si(CH_3)_3$[13] (recrystallized from cold (−78 °C) pentane), and LiC_6H_5[14] (recrystallized from diethyl ether) were prepared according to literature procedures. The lithium reagent $LiCH_2C_6H_5{\cdot}2C_4H_8O$ was obtained by metalation of toluene with *sec*-butyllithium (Aldrich) in the presence of tetrahydrofuran.[15] Yellow needles of the complex were isolated from cold (−78 °C) toluene/THF solutions. Pentamethylcyclopentadiene was prepared according to our procedure.[16] The preparation of UCl_4 was accomplished by the literature procedure.[17a,b] The synthesis of $ThCl_4$ was accomplished by slow passage of a nitrogen stream saturated with CCl_4 vapor over hot (450–500 °C) ThO_2.[17c] The resulting product was crushed to a fine powder, was washed with dry, deoxygenated CCl_4, and was then dried in vacuo.

$Mg[(CH_3)_5C_5]Cl{\cdot}C_4H_8O$. A one-necked, 1-L round-bottom flask with a Teflon vacuum valve side-arm was equipped with a glass stopper and a magnetic stirring bar. After the flask was evacuated and filled with argon three times, 281 mL of isopropylmagnesium chloride (1.95 M in diethyl ether) was syringed into the flask under a flush of argon. As much of the diethyl ether as possible was then removed in vacuo with the aid of a warm water bath, leaving a gelatinous cloudy-white mass in the flask. Toluene (250 mL) was then added to the flask under a flush of argon. The vacuum valve was closed, one inlet of an ice-cooled trap was connected to the vacuum valve, and the other inlet was connected to the vacuum line. The trap was evacuated and filled with argon three times and was then opened to the flask. Pentamethylcyclopentadiene (88 mL) was syringed into the flask under a flush of argon. The flask was then lowered into an oil bath maintained at 110 °C. The reaction mixture began to froth vigorously as it warmed, and the flask was removed from the oil bath periodically to prevent violent frothing. As the reaction progressed, diethyl ether distilled into the ice-cooled trap. After ca. 10 min, gas evolution subsided, and the reaction mixture was allowed to stir at 110 °C for 2.5 h. A yellow precipitate was observed. The reaction mixture was next cooled to room temperature, and tetrahydrofuran (110 mL) was syringed into the flask. The reaction mixture became warm, and after the mixture was stirred for 15 min, a crystalline solid was observed to form. Solvents were then removed in vacuo. Tetrahydrofuran (500 mL) was added to the flask dissolving the majority of the solids. The solution was filtered, and the tetrahydrofuran was removed in vacuo. Toluene (100 mL) was added via syringe to the filtrate residue, and the crystalline solid was isolated by filtration. After being washed three times with 20-mL portions of toluene, the white crystalline product was dried in vacuo. Yield: 80–90% (based on isopropylmagnesium chloride).

^{1}H NMR (C_6D_6): δ 2.13 (15 H, s), 3.64 (4 H, br m), 1.33 (4 H, br m).

$Th[\eta^5\text{-}(CH_3)_5C_5]_2Cl_2$. A 1-L round bottom flask with a Teflon vacuum valve side arm was charged with 14.0 g (37.4 mmol) of finely powdered $ThCl_4$ and 23.0 g (86.1 mmol) of $Mg[(CH_3)_5C_5]Cl{\cdot}C_4H_8O$. Under a flush of argon, toluene (500 mL) was then added to the flask. The flask was lowered into an oil bath maintained at 95–100 °C, and the reaction mixture was stirred under argon for 48 h. Stirring was then halted, and the white solids were allowed to settle. The solution was next filtered while hot through a coarse porosity glass frit on which rested a small amount of Celite 545 filter aid. The residual solids were washed with 50 mL of toluene, and this washing was combined with the filtrate. Toluene was then removed in vacuo, leaving a crystalline solid. Diethyl ether (40 mL) was added via syringe, and the product was dislodged from the sides of the flask with the aid of an external magnet. After the solid was slurried in the diethyl ether, it was isolated by filtration and was washed with 20 mL of diethyl ether. The white crystalline product was then dried in vacuo. Yield: 80–85%. The product as obtained is suitable for further use. If desired, the complex may be recrystallized from hot toluene in a manner similar to the isolation procedure.

IR (Nujol mull): 1019 (m) and 799 (w) cm^{-1}. Anal. Calcd for $C_{20}H_{30}Cl_2Th$: C, 42.60; H, 5.44. Found: C, 41.89; H, 5.27.

$U[\eta^5\text{-}(CH_3)_5C_5]_2Cl_2$. Maroon crystalline $U[\eta^5\text{-}(CH_3)_5C_5]_2Cl_2$ was synthesized in a manner identical with that for $Th[\eta^5\text{-}(CH_3)_5C_5]_2Cl_2$ (described above) by using 15.0 g (39.5 mmol) of UCl_4 and 24.3 g (91.0 mmol) of $Mg[\eta^5\text{-}(CH_3)_5C_5]Cl{\cdot}C_4H_8O$. Yield: 82–88%.

IR (Nujol mull): 1020 (m) and 800 (w) cm^{-1}. Anal. Calcd for $C_{20}H_{30}Cl_2U$: C, 41.46; H, 5.22; Cl, 12.24. Found: C, 41.36; H, 5.41; Cl, 12.52.

$Th[\eta^5\text{-}(CH_3)_5C_5]_2(CH_3)_2$. A 100-mL round-bottom flask with a stopcock-side arm was charged with 3.00 g (5.23 mmol) of $Th[\eta^5\text{-}(CH_3)_5C_5]_2Cl_2$. Diethyl ether (25 mL) was condensed into the flask in vacuo at −78 °C. Under a flush of argon, 6.70 mL of $CH_3Li{\cdot}LiBr$ (1.75 M in diethyl ether; 11.7 mmol) was syringed into the flask. The reaction mixture was stirred for 10 min at −78 °C and was then allowed to warm to room temperature. After 1.5 h, the diethyl ether was removed in vacuo. Toluene (25 mL) was then condensed into the flask, and after being stirred, the solution was filtered. The solids were washed twice by

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Soxhlet extraction in vacuo by condensing 5-mL portions of toluene from the filtrate into the upper portion of the filtration apparatus. Each of the washings was combined with the filtrate which was then cooled to −78 °C. The white crystalline precipitate was then isolated by cold filtration and was dried in vacuo. Yield: 60–70%. Recrystallization of this complex may be accomplished from cold (−78 °C) toluene.

IR (Nujol mull): 1019 (m) and 799 (w) cm^{-1}. Anal. Calcd for $C_{22}H_{36}Th$: C, 49.62; H, 6.81; mol wt, 532 g/mol. Found: C, 48.50; H, 6.93; mol wt (cryoscopic in benzene) 530 ± 10% g/mol.

$U[\eta^5\text{-}(CH_3)_5C_5]_2(CH_3)_2$. Orange needles of $U[\eta^5\text{-}(CH_3)_5C_5]_2(CH_3)_2$ were synthesized in a manner identical with that for $Th[\eta^5\text{-}(CH_3)_5C_5]_2(CH_3)_2$ (described above) by using 3.00 g (5.18 mmol) of $U[\eta^5\text{-}(CH_3)_5C_5]_2Cl_2$ and 6.65 mL of $CH_3Li{\cdot}LiBr$ (1.75 M in diethyl ether). Yield: 60–70%.

IR (Nujol mull): 1020 (m) and 799 (w) cm^{-1}. Anal. Calcd for $C_{22}H_{36}U$: C, 49.06; H, 6.75; mol wt 539 g/mol. Found: C, 49.24; H, 6.40; mol wt (cryoscopic in benzene) 546 ± 10% g/mol.

$Th[\eta^5\text{-}(CH_3)_5C_5]_2(CH_3)Cl$. A 100-mL round-bottom flask was charged with 2.40 g (4.19 mmol) of $Th[\eta^5\text{-}(CH_3)_5C_5]_2Cl_2$ and 2.23 g (4.19 mmol) of $Th[\eta^5\text{-}(CH_3)_5C_5]_2(CH_3)_2$. Toluene (60 mL) was condensed into the flask in vacuo, and ca. 600 torr of argon was then admitted. The solution was heated with an oil bath maintained at 50 °C for 2 h and was then stirred at room temperature for an additional hour. The solution was filtered, and the upper portion of the filtration apparatus was washed several times by Soxhlet extraction in vacuo by condensation of 5-mL portions of toluene from the filtrate into the upper portion of the filtration apparatus. These washings were combined with the filtrate which, after being concentrated to 30 mL, was cooled to −78 °C. The white crystalline product was isolated by cold filtration and was dried in vacuo. Yield: 80%. Recrystallization of this complex may be accomplished from cold (−78 °C) toluene.

IR (Nujol mull): 1020 (m) and 799 (w) cm^{-1}. Anal. Calcd for $C_{21}H_{33}ClTh$: C, 45.61; H, 6.02; Cl, 6.41; mol wt 553 g/mol. Found: C, 45.56; H, 6.13; Cl, 6.52; mol wt (cryoscopic in benzene) 620 ± 10% g/mol.

$U[\eta^5\text{-}(CH_3)_5C_5]_2(CH_3)Cl$. Maroon crystalline $U[\eta^5\text{-}(CH_3)_5C_5]_2(CH_3)Cl$ was synthesized in a manner identical with that for $Th[\eta^5\text{-}(CH_3)_5C_5]_2(CH_3)Cl$ (described above) by using 2.30 g (3.97 mmol) of $U[\eta^5\text{-}(CH_3)_5C_5]_2Cl_2$ and 2.17 g (4.03 mmol) of $U[\eta^5\text{-}(CH_3)_5C_5]_2(CH_3)_2$. Yield: 80%.

IR (Nujol mull): 1019 and 799 cm^{-1}. Anal. Calcd for $C_{21}H_{33}ClU$: C, 45.12; H, 5.95; Cl, 6.34; mol wt, 559 g/mol. Found: C, 44.98; H, 5.89; Cl, 6.39; mol wt (cryoscopic in benzene), 570 ± 10% g/mol.

$Th[\eta^5\text{-}(CH_3)_5C_5]_2[CH_2Si(CH_3)_3]_2$. A 50-mL round-bottom flask was charged with 3.50 g (6.10 mmol) of $Th[\eta^5\text{-}(CH_3)_5C_5]_2Cl_2$ and 1.40 g (15.1 mmol) of $LiCH_2Si(CH_3)_3$. Diethyl ether (25 mL) was condensed into the flask in vacuo at −78 °C, and the reaction mixture was allowed to stir for 10 min at this temperature. The mixture was then allowed to warm to room temperature. After 2 h, diethyl ether was removed in vacuo, and pentane (12 mL) was condensed into the flask. The solution was filtered, and the residual solids were washed by condensing some of the pentane from the filtrate into the upper portion of the filtration apparatus. The washings were combined with the filtrate which was then cooled to −78 °C. Crystallization of the product was initiated by vigorously scratching the solution interface with the magnetic stirring bar with the aid of an external magnet. The resulting crystalline white precipitate was isolated by cold filtration and was dried in vacuo. Yield: 72%. Recrystallization of this complex may be accomplished from cold (−78 °C) pentane.

IR (Nujol mull): 1253 (m), 1241 (s), 1020 (m), 898 (s), 877 (s), 849 (s), 820 (s), 738 (s), 710 (s), and 671 (s) cm^{-1}. Anal. Calcd for $C_{28}H_{52}Si_2Th$: C, 49.68; H, 7.74; mol wt, 677 g/mol. Found: C, 49.57; H, 7.71; mol wt (cryoscopic in benzene) 645 ± 10% g/mol.

$U[\eta^5\text{-}(CH_3)_5C_5]_2[CH_2Si(CH_3)_3]_2$. Orange needles of $U[\eta^5\text{-}(CH_3)_5C_5]_2[CH_2Si(CH_3)_3]_2$ were synthesized by a procedure identical with that for $Th[\eta^5\text{-}(CH_3)_5C_5]_2[CH_2Si(CH_3)_3]_2$ by using 3.50 g (6.04 mmol) of $U[\eta^5\text{-}(CH_3)_5C_5]_2Cl_2$ and 2.42 g (15.1 mmol) of $LiCH_2Si(CH_3)_3$. Yield: 76%.

IR (Nujol mull): 1253 (m), 1242 (s), 1020 (m), 898 (s), 877 (s), 848 (s), 820 (s), 738 (s), 710 (s), and 671 (s) cm^{-1}. Anal. Calcd for $C_{28}H_{52}Si_2U$: C, 49.25; H, 7.67; mol wt, 683 g/mol. Found: C, 48.96; H, 7.46; mol wt, 688 ± 10% g/mol.

$Th[\eta^5\text{-}(CH_3)_5C_5]_2[CH_2Si(CH_3)_3]Cl$. A 50-mL round-bottom flask was charged with 4.00 g (6.98 mmol) of $Th[\eta^5\text{-}(CH_3)_5C_5]_2Cl_2$ and 0.70 g (7.4 mmol) of $LiCH_2Si(CH_3)_3$. Diethyl ether (25 mL) was condensed into the flask in vacuo at −78 °C. The reaction mixture was then allowed to warm to room temperature. After 1.5 h, the diethyl ether was removed in vacuo. Toluene (20 mL) was then condensed into the flask, and after being stirred, the solution was filtered. The residual solids were washed several times by condensation of toluene from the filtrate into the upper portion of the filtration apparatus. The washings were combined with the filtrate, and toluene was then removed in vacuo. Pentane (12 mL) was condensed into the flask, and the mixture was cooled to −78 °C. The white crystalline precipitate was isolated by cold filtration and was dried in vacuo. Yield: 65%. Recrystallization of this complex may be accomplished from cold (−78 °C) pentane.

IR (Nujol mull): 1251 (m), 1238 (s), 1021 (m), 894 (s), 865 (s), 822 (s), 722 (s), 704 (s), and 678 (s) cm^{-1}. Anal. Calcd for $C_{24}H_{41}ClSiTh$: C, 46.11; H, 6.61; Cl, 5.67; mol wt, 625 g/mol. Found: C, 46.16; H, 6.56; Cl, 6.40; mol wt (cryoscopic in benzene) 660 ± 10% g/mol.

$U[\eta^5\text{-}(CH_3)_5C_5]_2[CH_2Si(CH_3)_3]Cl$. Maroon, crystalline $U[\eta^5\text{-}(CH_3)_5C_5]_2[CH_2Si(CH_3)_3]Cl$ was synthesized in a manner identical with that for $Th[\eta^5\text{-}(CH_3)_5C_5]_2[CH_2Si(CH_3)_3]Cl$ by using 4.10 g (7.08 mmol) of $U[\eta^5\text{-}(CH_3)_5C_5]_2Cl_2$ and 0.72 g (7.6 mmol) of $LiCH_2Si(CH_3)_3$. Yield: 68%.

IR (Nujol mull): 1251 (m), 1240 (s), 1020 (m), 890 (s), 870 (s), 850 (s), 823 (s), 720 (s), 702 (s), and 678 (s) cm^{-1}. Anal. Calcd for $C_{24}H_{41}ClSiU$: C, 45.67; H, 6.55; Cl, 5.62; mol wt, 631 g/mol. Found: C, 45.59; H, 6.54; Cl, 5.70; mol wt (crysoscopic in benzene), 634 ± 10% g/mol.

$Th[\eta^5\text{-}(CH_3)_5C_5]_2[CH_2C(CH_3)_3]_2$. A 100-mL round-bottom flask was charged with 4.00 g (6.98 mmol) of $Th[\eta^5\text{-}(CH_3)_5C_5]_2Cl_2$ and 1.15 g (14.7 mmol) of $LiCH_2C(CH_3)_3$. Diethyl ether (40 mL) was condensed into the flask in vacuo at −78 °C. After 10 min, the reaction mixture was allowed to warm to room temperature. After 1.5 h, the diethyl ether was removed in vacuo, and pentane (20 mL) was then condensed into the flask. The solution was filtered, and the residual solids were then washed by condensing some of the pentane from the filtrate into the upper portion of the filtration apparatus. The washings were combined with the filtrate which was then cooled to −78 °C. The white crystalline precipitate was isolated by cold filtration and was dried in vacuo. Yield: 56%. Recrystallization was accomplished from cold (−78 °C) pentane.

IR (Nujol mull): 1379 (s), 1354 (s), 1227 (s), 1203 (s), 1019 (m), 801 (w), 761 (m), 741 (m), 510 (s), 474 (m) cm^{-1}. Anal. Calcd for $C_{30}H_{52}Th$: C, 55.88; H, 8.13. Found: C, 55.69; H, 8.91.

$Th[\eta^5\text{-}(CH_3)_5C_5]_2[CH_2C(CH_3)_3]Cl$. A 100-mL round-bottom flask with a female ball joint was charged with 2.00 g (3.49 mmol) of $Th[\eta^5\text{-}(CH_3)_5C_5]_2Cl_2$. A bent solid addition tube with a male ball joint was charged with 0.28 g (3.6 mmol) of $LiCH_2C(CH_3)_3$ and was then attached to the flask. Tetrahydrofuran (30 mL) was condensed into the flask in vacuo. Some of the tetrahydrofuran (2–3 mL) was then condensed into the adjoining solid addition tube dissolving the lithium reagent. The flask was cooled to 0 °C in an ice-water bath, and the $Th[\eta^5\text{-}(CH_3)_5C_5]_2Cl_2$ was slurried by stirring vigorously. The solution of $LiCH_2C(CH_3)_3$ was then added all at once by pivoting the addition tube. All the solids were dissolved upon addition, and stirring was continued for 5 min at 0 °C. Tetrahydrofuran was then removed, and the residual solids were dried in vacuo for 15 h. Pentane (20 mL) was then condensed into the flask, and the solids were broken by stirring. The solution was filtered, and the residual solids were washed once by condensing pentane from the filtrate into the upper portion of the filtration apparatus. The washing was combined with the filtrate which was then concentrated to 10 mL. The filtrate was cooled to −78 °C and the white crystalline precipitate was isolated by cold filtration and was dried in vacuo. Yield: 61%. Recrystallization was accomplished from cold (−78 °C) pentane.

IR (Nujol mull): 1353 (m), 1225 (m), 1205 (m), 1020 (m), and 801 (w) cm^{-1}. Anal. Calcd for $C_{25}H_{41}ClTh$: C, 49.30; H, 6.78; Cl, 5.82. Found: C, 49.54; H, 6.70; Cl, 6.30.

$U[\eta^5\text{-}(CH_3)_5C_5]_2[CH_2C(CH_3)_3]Cl$. The brown complex $U[\eta^5\text{-}(CH_3)_5C_5][CH_2C(CH_3)_3]Cl$ was synthesized in a manner similar to that for the preparation of $Th[\eta^5\text{-}(CH_3)_5C_5]_2[CH_2C(CH_3)_3]Cl$ (described above) by using 2.00 g (3.45 mmol) of $U[\eta^5\text{-}(CH_3)_5C_5]_2Cl_2$ and 0.27 g (3.55 mmol) of $LiCH_2C(CH_3)_3$. The reaction residue was kept at 0 °C while being dried, and the workup was carried out as quickly as possible. Yield: 20%. An ^1H NMR spectrum of the product was taken immediately after being dissolved in C_6D_6 at 25 °C. The product as obtained was ca. 80–85% pure and decomposed fairly rapidly in C_6D_6 solution at room temperature. In the solid state, it may be stored cold (−20 °C) without decomposition for extended periods of time.

$Th[\eta^5\text{-}(CH_3)_5C_5]_2(CH_2C_6H_5)_2$. A 100-mL round-bottom flask was charged with 2.00 g (3.49 mmol) of $Th[\eta^5\text{-}(CH_3)_5C_5]_2Cl_2$ and 1.72 g (7.10 mmol) of $LiCH_2C_6H_5{\cdot}2C_4H_8O$. Diethyl ether (25 mL) was condensed in vacuo into the flask at −78 °C. The reaction mixture was allowed to stir for 10 min at this temperature and was then allowed to warm to room temperature. After 1.5 h, the diethyl ether was removed in vacuo. Toluene (10 mL) was next condensed into the flask. After being stirred for 15 min, the solution was filtered and the residual solids were washed with 2-mL portions of toluene by condensing toluene from the filtrate into the upper portion of the filtrate apparatus. The washings were combined with the filtrate, and the filtrate was then concentrated in vacuo to ca. 2 mL. Pentane (20 mL) was condensed into the flask, and the flask was cooled to −78 °C. The yellow-white precipitate was isolated by cold filtration, and solvents were removed in vacuo. The product was then washed twice with 2-mL portions of diethyl ether to remove unreacted $LiCH_2C_6H_5{\cdot}2C_4H_8O$. The pale yellow crystalline product was then dried in vacuo. Yield: 67%. Recrystallization of this complex was carried out in a manner similar to the isolation procedure.

IR (Nujol mull): 3050 (w), 1588 (s), 1559 (m), 1482 (s), 1296 (w), 1240 (w), 1209 (s), 1171 (m), 1148 (w), 1041 (w), 1026 (m), 1017 (m), 1004 (m), 978 (s), 900 (s), 876 (w), 852 (s), 802 (m), 790 (s), 737 (s), and 692 (s) cm^{-1}. Anal. Calcd for $C_{34}H_{44}Th$: C, 59.64; H, 6.48. Found: C, 59.19; H, 6.23.

$U[\eta^5\text{-}(CH_3)_5C_5]_2(CH_2C_6H_5)_2$. Black-green crystalline $U[\eta^5\text{-}(CH_3)_5C_5]_2(CH_2C_6H_5)_2$ was synthesized in a manner identical with that for $Th[\eta^5\text{-}(CH_3)_5C_5]_2(CH_2C_6H_5)_2$ (described above) by using 2.00 g (3.45 mmol) of $U[\eta^5\text{-}(CH_3)_5C_5]_2Cl_2$ and 1.70 g (7.02 mmol) of $LiCH_2C_6H_5{\cdot}2C_4H_8O$. Yield: 67%.

IR (Nujol mull): 3058 (w), 1587 (s), 1560 (m), 1481 (s), 1298 (w), 1238 (w), 1209 (s), 1172 (m), 1150 (w), 1029 (m), 1019 (m), 1008 (m), 982 (s), 901 (s), 880 (w), 863 (s), 803 (m), 790 (s), 736 (s), and 691 (s) cm^{-1}. Anal. Calcd for $C_{34}H_{44}U$: C, 59.12; H, 6.42. Found: C, 59.10; H, 6.66.

$Th[\eta^5\text{-}(CH_3)_5C_5]_2(CH_2C_6H_5)Cl$. A 100-mL round-bottom flask was charged with 2.00 g (3.49 mmol) of $Th[\eta^5\text{-}(CH_3)_5C_5]_2Cl_2$ and 0.86 g (3.55 mmol) of $LiCH_2C_6H_5{\cdot}2C_4H_8O$. Diethyl ether (25 mL) was condensed into the flask in vacuo at −78 °C. The reaction mixture was allowed to warm to room temperature. After 1.5 h, the solvent was removed in vacuo. Toluene (25 mL) was then condensed into the flask. The solution was filtered, and the residual solids were then washed by condensing some of the toluene from the filtrate into the upper portion of the filtration apparatus. The washings were combined with the filtrate which was next concentrated to ca. 2 mL. Pentane (20 mL) was condensed into the flask in vacuo. The precipitate was broken up by stirring, and the mixture was then cooled to −78 °C. The white crystalline precipitate was isolated by cold filtration and was dried in vacuo. Yield: 77%.

IR (Nujol mull): 3052 (w), 1591 (s), 1561 (w), 1478 (s), 1298 (w), 1212 (m), 1177 (m), 1021 (m), 980 (m), 895 (m), 841 (m), 792 (s), 737 (s), and 698 (s) cm^{-1}. Anal. Calcd for $C_{27}H_{37}ClTh$: C, 51.55; H, 5.93; Cl, 5.64. Found: C, 51.45; H, 6.36; Cl, 5.54.

$U[\eta^5\text{-}(CH_3)_5C_5]_2(CH_2C_6H_5)Cl$. Black-green crystalline $U[\eta^5\text{-}(CH_3)_5C_5]_2(CH_2C_6H_5)Cl$ was synthesized in a manner identical with that for $Th[\eta^5\text{-}(CH_3)_5C_5]_2(CH_2C_6H_5)Cl$ (described above) by using 2.00 g (3.45 mmol) of $U[\eta^5\text{-}(CH_3)_5C_5]_2Cl_2$ and 0.85 g (3.51 mmol) of $LiCH_2C_6H_5{\cdot}2C_4H_8O$. Yield: 75%.

IR (Nujol mull): 3060 (w), 1591 (s), 1564 (w), 1485 (s), 1300 (w), 1212 (m), 1178 (w), 1021 (w), 983 (m), 888 (w), 840 (w), 804 (s), 739 (s), 697 (s) cm^{-1}. Anal. Calcd for $C_{27}H_{37}ClU$: C, 51.06; H, 5.87; Cl, 5.58. Found: C, 50.15; H, 5.80; Cl, 5.75.

$Th[\eta^5\text{-}(CH_3)_5C_5]_2(C_6H_5)_2$. A 25-mL round-bottom flask was charged with 2.00 g (3.49 mmol) of $Th[\eta^5\text{-}(CH_3)_5C_5]_2Cl_2$ and 0.61 g (7.3 mmol) of LiC_6H_5. Diethyl ether (20 mL) was condensed into the flask in vacuo at −78 °C. The reaction mixture was stirred at this temperature for 5 h. Diethyl ether was then removed in vacuo while the flask was allowed to warm. Benzene (10 mL) was condensed into the flask, and the solution was filtered. The residual solids were washed by condensing benzene from the filtrate into the upper portion of the filtration apparatus. The washings were combined with the filtrate. Benzene was then removed in vacuo, and pentane (10 mL) was condensed into the flask at −78 °C. The precipitate was dislodged from the sides of the flask with the magnetic stirring bar by using an external magnet. The colorless to light brown crystalline product was isolated by cold filtration and was dried in vacuo. Yield: 32–40%. Recrystallization of this complex was accomplished from cold (−78 °C) pentane with an insignificant amount of decomposition (indicated by the very light brown tint of the product).

IR (Nujol mull): 3045 (s), 1566 (w), 1552 (w), 1414 (s), 1286 (w), 1233 (m), 1191 (w), 1164 (w), 1153 (w), 1049 (s), 1021 (m), 1014 (m), 991 (m), 801 (w), 717 (s), 704 (s), and 634 (m) cm^{-1}. Anal. Calcd for $C_{32}H_{40}Th$: C, 58.53; H, 6.14. Found: C, 58.68; H, 5.93.

$U[\eta^5\text{-}(CH_3)_5C_5]_2(C_6H_5)_2$. Dark orange $U[\eta^5\text{-}(CH_3)_5C_5]_2(C_6H_5)_2$ was synthesized in a manner identical with that for $Th[\eta^5\text{-}(CH_3)_5C_5]_2(C_6H_5)_2$ (described above) by using 2.00 g (3.45 mmol) of $U[\eta^5\text{-}(CH_3)_5C_5]_2Cl_2$ and 0.61 g (7.3 mmol) of LiC_6H_5. Yield: 34%. This complex is moderately stable in the solid state and is stable indefinitely if it is stored cold. It is stable indefinitely in benzene solution, but pentane or toluene solutions are not stable for long periods of time at room temperature (see Results and Discussion).

IR (Nujol mull): 3047 (s), 1566 (w), 1556 (w), 1414 (s), 1287 (w), 1236 (m), 1193 (w), 1160 (w), 1153 (w), 1051 (s), 1021 (m), 1013 (m), 990 (m), 802 (w), 719 (s), 705 (s), and 635 (m) cm^{-1}. Anal. Calcd for $C_{32}H_{40}U$: C, 58.00; H, 6.08. Found: C, 57.89; H, 6.05.

Thermolysis of the Complexes $M[\eta^5\text{-}(CH_3)_5C_5]_2(C_6H_5)_2$ (M = Th, U) in C_6D_6. Kinetic studies of the thermolyses of the diphenyl complexes in C_6D_6 solution were carried out in sealed ^1H NMR tubes under an argon atmosphere, and the reactions were monitored via ^1H NMR spectroscopy.

Thermolysis of $Th[\eta^5\text{-}(CH_3)_5C_5]_2[CH_2C(CH_3)_3]_2$ in Benzene and Perdeuteriobenzene. A small quantity (ca. 50 mg) of $Th[\eta^5\text{-}(CH_3)_5C_5]_2[CH_2C(CH_3)_3]_2$ in benzene was sealed in a ^1H NMR tube under argon. The tube was heated at 100 °C for 4 h. The tube was then opened and attached to a vacuum adapter. The solvent was then removed in vacuo, leaving a crystalline white solid, and then, C_6D_6 was condensed into the tube. The ^1H NMR spectrum of the product revealed it to be $Th[\eta^5\text{-}(CH_3)_5C_5]_2(C_6H_5)_2$ and indicated that the reaction proceeded essentially quantitatively. A similar experiment was carried out in C_6D_6 solution. The resulting ^1H NMR spectrum of this solution was consistent with the production of 2 equiv of neopentane and the perdeuteriophenyl derivative, $Th[\eta^5\text{-}(CH_3)_5C_5]_2(C_6D_5)_2$.

Reaction of $U[\eta^5\text{-}(CH_3)_5C_5]_2(C_6H_5)_2$ and $U[\eta^5\text{-}(CH_3)_5C_5]_2(C_6D_5)_2$ with Diphenylacetylene. A 25-mL round-bottom flask was charged with 0.28 g (0.42 mmol) of $U[\eta^5\text{-}(CH_3)_5C_5]_2(C_6H_5)_2$ and 0.09 g (0.50 mmol) of diphenylacetylene. Benzene (3 mL) was condensed into the flask in vacuo. The solution was stirred for 3 h at 25 °C during which time the color changed from dark orange-brown to dark maroon. The benzene was then removed in vacuo leaving a dark maroon-brown glassy solid. Pentane (5 mL) was condensed into the flask dissolving the product. The solution was filtered, and the filtrate was cooled to −78 °C. A small amount of a dark brown crystalline solid was observed, and this was isolated by cold filtration. While being warmed to room temperature and drying in vacuo, the brown crystalline solid was observed to "melt" and bubble forming a dark maroon glassy solid. On the basis of ^1H NMR spectral analysis, the complex was essentially >95% pure $U[\eta^5\text{-}(CH_3)_5C_5]_2C_2(C_6H_5)_2C_6H_4$.

In an NMR tube, $U[\eta^5\text{-}(CH_3)_5C_5]_2(C_6H_5)_2$ in C_6D_6 solution was converted to $U[\eta^5\text{-}(CH_3)_5C_5]_2(C_6D_5)_2$ by heating under argon at 60 °C for 6 h. The tube was opened, and diphenylacetylene was then added to the dark orange-brown solution at 25 °C. After several hours, the solution color became dark maroon. The ^1H NMR spectrum was recorded and was identical with the spectrum of the product isolated above except the resonances at −53.8, −6.36, and 3.40 ppm were not present. The resonance at 4.02 ppm became less complex and decreased in intensity (equivalent to 1 equiv of H/1 equiv of U as determined by peak integration). The reaction was essentially quantitative. Kinetic studies were performed by monitoring the appropriate ^1H resonances in the NMR spectrum.

$Th[\eta^5\text{-}(CH_3)_5C_5]_2(C_6H_5)Cl$. A 25-mL round-bottom flask was charged with 2.00 g (3.49 mmol) of $Th[\eta^5\text{-}(CH_3)_5C_5]_2Cl_2$ and 0.30 g (3.6 mmol) of LiC_6H_5. Diethyl ether (12 mL) was condensed into the flask in vacuo at −78 °C. The reaction mixture was stirred at −78 °C for 3 h and was then allowed to stir at room temperature for 1 h. Diethyl ether was then removed in vacuo. Pentane (10 mL) was condensed into the flask, and the solution was filtered. The remaining solids were washed by condensing pentane from the filtrate into the upper portion of the filtration apparatus. The washing was combined with the filtrate which was then cooled to −78 °C. The white crystalline precipitate was isolated by cold filtration and was dried in vacuo. Yield: 42%. Recrystallization of this complex was accomplished from cold (−78 °C) pentane.

IR (Nujol mull): 3040 (w), 1412 (m), 1238 (w), 1190 (w), 1161 (w), 1152 (w), 1060 (w), 1040 (m), 1021 (m), 1013 (m), 987 (m), 852 (w), 800 (w), 715 (s), 702 (s), 673 (w), and 634 (w) cm^{-1}. Anal. Calcd for $C_{26}H_{35}ClTh$: C, 50.77; H, 5.60; Cl, 5.76. Found: C, 49.96; H, 5.74; Cl, 5.82.

$U[\eta^5\text{-}(CH_3)_5C_5]_2(C_6H_5)Cl$. Orange crystalline $U[\eta^5\text{-}(CH_3)_5C_5]_2(C_6H_5)Cl$ was synthesized in a manner identical with that for $Th[\eta^5\text{-}(CH_3)_5C_5]_2(C_6H_5)Cl$ (described above) using 2.00 g (3.45 mmol) of $U[\eta^5\text{-}(CH_3)_5C_5]_2Cl_2$ and 0.30 g (3.6 mmol) of LiC_6H_5. Yield: 50%.

IR (Nujol mull): 3042 (w), 1420 (m), 1411 (m), 1238 (w), 1162 (w), 1151 (w), 1060 (w), 1040 (m), 1021 (m), 1014 (m), 987 (m), 851 (w), 801 (w), 717 (s), 702 (s), 672 (w), and 636 (w) cm^{-1}. Anal. Calcd for $C_{26}H_{35}ClU$: C, 50.28; H, 5.68; Cl, 5.71. Found: C, 50.13; H, 5.64; Cl, 5.89.

Preparation of 1,4-Dilithio-1,2,3,4-tetraphenylbutadiene, $Li_2C_4(C_6H_5)_4$. A modification of the literature procedure was used for the preparation of $Li_2C_4(C_6H_5)_4$.[18] A 100-mL two-necked round-bottom flask was charged with 10.0 g (56.1 mmol) of diphenylacetylene and 3.34 g (4.81 mmol) of lithium wire (3.2-mm diameter, 0.02% Na) cut into pieces of ca. 3 mm in length. Diethyl ether (25 mL) was added to the flask via

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[18] Braye, E. H.; Hubel, W.; Capilier, I. *J. Am. Chem. Soc.* **1961**, *83*, 4406–4413.

syringe under a flush of argon, and vigorous stirring was then commenced. The solution became red after ca. 50 s, and the flask was cooled in a water bath maintained at 25 °C. After 15 min, a yellow precipitate was observed, and after the mixture was stirred for an additional 12 min, diethyl ether was removed quickly in vacuo. Toluene (50 mL) was then added to the flask via syringe, and the yellow solid and the excess lithium were slurried in the toluene. The mixture was placed atop the glass frit of a filtration apparatus. The yellow solid settled onto the glass frit, and the excess lithium floated on top of the toluene. Suction was applied to the receiving flask effecting the filtration. The product was washed with two 20-mL portions of toluene and was then dried in vacuo. The excess lithium was removed mechanically from the surface of the product to yield 9.0 g (86%) of the air-sensitive yellow product. The product is moderately stable in the solid state but should be used immediately as decomposition occurs over long periods of time (even during cold storage).

$\overline{U[\eta^5\text{-}(CH_3)_5C_5]_2[C(C_6H_5)=C(C_6H_5)C(C_6H_5)=C}(C_6H_5)]$. A 200-mL round-bottom flask was charged with 2.00 g (3.45 mmol) of $U[\eta^5\text{-}(CH_3)_5C_5]_2Cl_2$ and 1.28 g (3.46 mmol) of $Li_2C_4(C_6H_5)_4$. Diethyl ether (120 mL) was added to the flask via syringe under a flush of argon, and the reaction mixture was stirred for 2.2 h at 25 °C. The diethyl ether was then removed in vacuo. Hexane (150 mL) was added to the flask, and after the mixture was stirred, the crude brown product was isolated by filtration and was dried in vacuo. The crude product was transferred to another flask to which benzene (40 mL) was added. The brown solution was filtered, and the benzene was then removed in vacuo. Hexane (40 mL) was added to the filtrate residue, and the brown-red crystalline product was isolated by filtration and was dried in vacuo. Yield: 30–40%.

IR (Nujol mull): 1586 (m), 1232 (m), 1173 (w), 1157 (m), 1070 (m), 1020 (m), 950 (w), 903 (w), 852 (w), 795 (w), 780 (w), 761 (m), 753 (m), 697 (s), and 672 (m) cm^{-1}. Anal. Calcd for $C_{48}H_{50}U$: C, 66.65; H, 5.83. Found: C, 66.56; H, 6.10.

Competition Reactions of $M[\eta^5\text{-}(CH_3)_5C_5]_2(CH_3)_2$ Compounds with *tert*-Butyl Alcohol, Acetone, and Iodine. Mixtures containing weighed quantities of $Th[\eta^5\text{-}(CH_3)_5C_5]_2(CH_3)_2$ and $U[\eta^5\text{-}(CH_3)_5C_5]_2(CH_3)_2$ were dissolved in toluene-d_8 in NMR tubes equipped with screw caps having Teflon-faced rubber septa. At −78 °C, 10% toluene-d_8 solutions of *tert*-butyl alcohol (distilled from magnesium under nitrogen), acetone (distilled from 4A molecular sieves under nitrogen), or iodine (triply sublimed) were added in small increments by syringe. After each addition, the samples were immediately mixed by vigorous agitation and were then transferred to an NMR spectrometer with the probe maintained at −70 °C. Spectra were recorded repetitively (and integrated) until it was certain that the reactions were complete. The samples were then removed to the −78 °C bath, and the addition/agitation process was repeated. That the product ratios were representative of kinetic competition for reactants and not subsequent equilibration of products was established by measuring the rates of equilibration among the various products, prepared separately. In all cases, this equilibration was not rapid enough to affect the observed product ratios at −70 °C.

$\{Th[\eta^5\text{-}(CH_3)_5C_5]_2(\mu\text{-}H)H\}_2$ and $\{Th[\eta^5\text{-}(CH_3)_5C_5]_2(\mu\text{-}D)D\}_2$. A 50-mL round-bottom flask was charged with 2.00 g (2.95 mmol) of $Th[\eta^5\text{-}(CH_3)_5C_5]_2[CH_2Si(CH_3)_3]_2$ (alternatively, the complex $Th[\eta^5\text{-}(CH_3)_5C_5]_2(CH_3)_2$ may be used). Toluene (10–20 mL) was condensed into the flask in vacuo. The solution was filtered, and dihydrogen (700–740 torr in an enclosed total volume of ca. 300 mL) was then introduced. Uptake of dihydrogen began immediately and continued for ca. 6 h at room temperature. After the solution was stirred for an additional 6 h, a white to pale-yellow precipitate was observed. The toluene was concentrated in vacuo to ca. 1 mL, and pentane (10–20 mL) was then condensed into the flask. The crystalline pale yellow product was isolated by filtration and was dried in vacuo overnight. Yield: 85–92%. Recrystallization was accomplished from hot toluene.

See Table II for IR data. Anal. Calcd for $C_{40}H_{64}Th_2$: C, 47.61; H, 6.39; mol wt, 1009 g/mol. Found: C, 48.63; H, 6.63; mol wt (cryoscopic in benzene), 1210 ± 10% g/mol.

The complex $\{Th[\eta^5\text{-}(CH_3)_5C_5]_2(\mu\text{-}D)D\}_2$ was prepared in a manner similar to that for $\{Th[\eta^5\text{-}(CH_3)_5C_5]_2(\mu\text{-}H)H\}_2$ by using deuterium gas.

See Table II for IR data.

In a separate experiment, a 10-mL round-bottom flask was charged with 0.220 g (0.413 mmol) (weighed by difference) of $Th[\eta^5\text{-}(CH_3)_5C_5]_2(CH_3)_2$. The flask was attached to a calibrated gas addition bulb (33.96 mL) which was then attached to a high vacuum line. Toluene (4 mL) was condensed into the flask in vacuo, and the stopcock leading to the flask was closed. After residual solvent vapor was removed from the gas addition bulb, dihydrogen gas (716.0 torr, 1.318 mmol) was introduced. The addition bulb stopcock was closed, and the gas was then admitted to the flask. After 15 h, the flask was cooled to −78 °C. The gases were then passed through a series of three liquid-nitrogen-cooled traps and were collected into a calibrated volume via a Toepler pump. The pressure was measured, and the gases which were collected amounted to a total of 1.326 mmol. The dihydrogen was oxidized to water by cycling the gases over a CuO catalyst at 285 °C, while simultaneously condensing the water formed into a liquid-nitrogen-cooled trap. The remaining gas was recollected and amounted to 0.744 mmol. This gas was determined to be methane by mass spectral analysis. Thus 1.82 equiv of CH_4 was produced and 1.78 equiv of dihydrogen was consumed/1 equiv of $Th[\eta^5\text{-}(CH_3)_5C_5]_2(CH_3)_2$. Solvent was removed in vacuo from the reaction flask, and the remaining white crystalline solid was determined to be ≥95% $\{Th[\eta^5\text{-}(CH_3)_5C_5]_2(\mu\text{-}H)H\}_2$ by ^1H NMR spectral analysis.

A similar experiment was performed by using deuterium gas and 0.2906 g (0.546 mmol) of $Th[\eta^5\text{-}(CH_3)_5C_5]_2(CH_3)_2$. In this case, 1.86 equiv of CH_3D (>90% deuterated as determined by mass spectral analysis)/1 equiv of $Th[\eta^5\text{-}(CH_3)_5C_5]_2(CH_3)_2$ was produced.

$\{U[\eta^5\text{-}(CH_3)_5C_5]_2(\mu\text{-}H)H\}_2$. Black-green crystalline $\{U[\eta^5\text{-}(CH_3)_5C_5]_2(\mu\text{-}H)H\}_2$ was synthesized in a manner identical with that for $\{Th[\eta^5\text{-}(CH_3)_5C_5]_2(\mu\text{-}H)H\}_2$ described above by using 2.00 g (2.93 mmol) of $U[\eta^5\text{-}(CH_3)_5C_5]_2[CH_2Si(CH_3)_3]_2$ (or, alternatively, $U[\eta^5\text{-}(CH_3)_5C_5]_2(CH_3)_2$). The complex loses dihydrogen readily in solution in vacuo at room temperature. Therefore, the presence of a dihydrogen atmosphere was maintained and solutions were kept cold as much as possible during workup. The complex was more stable in the solid state, losing dihydrogen only slowly in vacuo at room temperature. The complex was dinitrogen sensitive and was maintained at −20 °C under an argon atmosphere during prolonged storage. Yield: 70%.

IR (Nujol mull): 1355 (s(br)), 1190 (s(br)), 1021 (m), and 801 (w) cm^{-1}.

In a separate experiment, a 25-mL round-bottom flask was charged with 0.1376 g (0.255 mmol) of $U[\eta^5\text{-}(CH_3)_5C_5]_2(CH_3)_2$, and the flask was attached to a gas addition bulb. Toluene (20 mL) was then condensed to the flask in vacuo. Dihydrogen (1.763 mmol) was first admitted into the gas addition bulb and was then added to the reaction flask. The reaction was allowed to proceed for 12 h at room temperature. The flask was then cooled to −78 °C. The gases were admitted to the vacuum line, passed through a series of three liquid-nitrogen-cooled traps and were collected via Toepler pump into a calibrated volume. The total gas collected amounted to 1.745 mmol. The gas was then cycled through a liquid-nitrogen-cooled trap in series with a CuO catalyst maintained at 280 °C to convert the dihydrogen to H_2O. The remaining gas was then recollected into the calibrated volume and amounted to 0.489 mmol. This gas was retained and was later determined to be CH_4 by mass spectral analysis. Thus, 1.92 equiv of CH_4 was produced and 1.97 equiv of H_2 reacted/1 equiv of $U[\eta^5\text{-}(CH_3)_5C_5]_2(CH_3)_2$.

The solution of $\{U[\eta^5\text{-}(CH_3)_5C_5]_2H_2\}_2$ was allowed to warm to room temperature, and the gas addition bulb stopcock was opened periodically to release any evolved gases which were then collected into the calibrated volume and measured. Over a period of 3 h, 0.48 equiv of H_2 (identity of gas verified by CuO oxidation)/1 equiv of U was collected. This loss was determined to be reversible by adding a known amount of dihydrogen to the reaction flask, cooling the solution to −78 °C, and then determining the amount of absorbed dihydrogen (which amounted to 0.40 equiv of H_2/1 equiv of U).

A similar experiment was carried out by using deuterium gas. In this case, 1.91 equiv of deuterium was reacted, and 1.93 equiv of CH_3D (>85% deuterated as determined by mass spectral analysis) was produced/1 equiv of $U[\eta^5\text{-}(CH_3)_5C_5]_2(CH_3)_2$.

Homogeneous Hydrogenation of 1-Hexene Catalyzed by the Complexes $\{M[\eta^5\text{-}(CH_3)_5C_5]_2(\mu\text{-}H)H\}_2$ (M = Th, U). Hydrogenation experiments were performed on a high vacuum line, and dihydrogen uptake was monitored manometrically.[10] An accurately weighed amount of $\{Th[\eta^5\text{-}(CH_3)_5C_5]_2(\mu\text{-}H)H\}_2$ (0.2261 g, 0.224 mmol) was added to the reaction vessel. The vessel was evacuated, and 1-hexene (0.41 ± 0.02 mL, 3.2 mmol) was then condensed in. The hexene was allowed to react with the hydride complex for several minutes at room temperature, and toluene (9.90 ± 0.02 mL) was then condensed into the flask at −78 °C. The solution was warmed, and a thermostated water bath was used to maintain the temperature at 24 ± 1 °C. As soon as all the solids were dissolved, the reaction tube was opened to the enclosed vacuum line volume. When the solvent vapor pressure had come to equilibrium (total vapor pressure = 30.4 torr), vigorous stirring was initiated and dihydrogen gas was admitted (total initial dihydrogen partial pressure = 702.9 torr). The dihydrogen uptake was measured with an Hg manometer. (The volume above the solution had been calibrated previously.) The reaction was followed quantitatively for a total of 4.7 turnovers/Th and was then allowed to progress to completion overnight.

At 13 h after the initiation of the reaction, dihydrogen uptake was observed to have ceased and a total dihydrogen pressure drop of 200.0

torr was recorded. This corresponded to 3.40 mmol of H_2 consumed. This was (within experimental error) equivalent to the amount of 1-hexene originally added, indicating an essentially quantitative reaction. The solvents were then removed in vacuo and retained. Gas chromatographic analysis (20% SF-96 on Chromosorb P) indicated the product of the reaction to be >95% hexane. The white crystalline solid remaining in the reaction vessel was shown to be ≥95% pure $\{Th[\eta^5\text{-}(CH_3)_5C_5]_2(\mu\text{-}H)H\}_2$ by ^1H NMR spectral analysis.

An experiment using the uranium catalyst $\{U[\eta^5\text{-}(CH_3)_5C_5]_2(\mu\text{-}H)H\}_2$ was performed under identical concentration, pressure, and temperature conditions. The catalyst was generated in situ first by hydrogenation of an accurately weighed amount (0.2516 g, 0.467 mmol) of $U[\eta^5\text{-}(CH_3)_5C_5]_2(CH_3)_2$ in 10.32 ± 0.02 mL of toluene. The methane gas was removed in vacuo at −78 °C before condensing in the 1-hexene (0.43 ± 0.02 mL). The remainder of the experiment was carried out as described above for $\{Th[\eta^5\text{-}(CH_3)_5C_5]_2(\mu\text{-}H)H\}_2$. Dihydrogen uptake was quite rapid and was essentially complete after 11 min. The solution was stirred for another 10 min, and the final dihydrogen uptake was 3.39 mmol, which compares favorably with the amount of 1-hexene added (3.4 mmol). The product was verified to be >94% hexane by gas chromatographic analysis (20% SF-96 on Chromosorb P). A preparative scale reaction was carried out with 48 mL of 1-hexene by using a larger reaction vessel; in this case, multiple H_2 additions were necessary.

$Th[\eta^5\text{-}(CH_3)_5C_5]_2[OC(CH_3)_3]Cl$. A 50-mL round-bottom flask was charged with 2.01 g (3.51 mmol) of $Th[\eta^5\text{-}(CH_3)_5C_5]_2Cl_2$ and 1.80 g (3.38 mmol) of $Th[\eta^5\text{-}(CH_3)_5C_5]_2(CH_3)_2$. Toluene (20 mL) was condensed into the flask in vacuo. The solution was then stirred under argon at 50 °C for 1.5 h followed by 2 h at room temperature. The flask was next cooled to −78 °C, and argon was removed in vacuo. Acetone (0.58 mL, 7.9 mmol) was then condensed into the flask, and the solution was allowed to warm to room temperature. The toluene was then removed in vacuo, and the residue was dried overnight. Pentane (10 mL) was then condensed into the flask, and the solution was filtered. After the upper portion of the filtration apparatus was washed by Soxhlet extraction, the filtrate was cooled to −78 °C. The resulting white precipitate was isolated by cold filtration and was dried in vacuo. Yield: 48%.

$Th[\eta^5\text{-}(CH_3)_5C_5]_2[OC(CH_3)_3]CH_3$. The complex $Th[\eta^5\text{-}(CH_3)_5C_5]_2[OC(CH_3)_3]Cl$ was prepared (but not isolated) as described above in a 50-mL round-bottom flask with a stopcock-side arm. After the residue was dried overnight, diethyl ether (20 mL) was condensed into the flask at −78 °C. Under a flush of argon, 4.0 mL of $CH_3Li{\cdot}LiBr$ (1.75 M in diethyl ether) was syringed into the flask. The reaction mixture was allowed to warm to room temperature and was then stirred for 1 h. The diethyl ether was removed in vacuo, and pentane (15 mL) was condensed into the flask. The solution was filtered, and the residual solids in the upper portion of the filtration apparatus were washed twice by Soxhlet extraction. Each washing was combined with the filtrate which was then concentrated to ca. 8 mL. The solution was cooled to −78 °C. The resulting white precipitate was then isolated by cold filtration and was dried in vacuo. Yield: 54%. Recrystallization of this complex may be accomplished from cold (−78 °C) pentane.

IR (Nujol mull): 1359 (m), 1231 (m), 1183 (s), 1021 (m), 972 (s), 802 (w), and 779 (m) cm^{-1}. Anal. Calcd for $C_{25}H_{42}OTh$: C, 50.84; H, 7.17. Found: C, 50.76; H, 7.02.

$Th[\eta^5\text{-}(CH_3)_5C_5]_2[OC(CH_3)_3]H$. A 75-mL thick-walled glass tube with a Teflon needle valve was charged with 2.00 g (3.39 mmol) of $Th[\eta^5\text{-}(CH_3)_5C_5]_2[OC(CH_3)_3]CH_3$. Toluene (8 mL) was condensed into the tube in vacuo. An atmosphere of dihydrogen was then introduced. The tube was cooled with liquid nitrogen, and the needle valve was then closed. (The maximum possible pressure upon warming to 100 °C was ca. 5 atm). The tube was placed behind a safety shield while still cold and was then allowed to warm to room temperature. The tube was next lowered into an oil bath maintained at 100 °C such that the level of the oil bath was coincident with the solution level. The solution was stirred at 100 °C for 10 h. The tube was then cooled to −196 °C and was recharged with dihydrogen as before. After being stirred for another 12 h at 100 °C, the solution was cooled and gases and toluene were removed in vacuo. The reaction vessel was then connected to a filtration apparatus. Pentane (10 mL) was condensed into the tube, and the resulting solution was filtered. The filtrate was cooled to −78 °C and the white precipitate was isolated by cold filtration and was dried in vacuo. Yield: 20%. Recrystallization of this complex was accomplished from cold (−78 °C) pentane.

IR (Nujol mull): 1359 (s) (overlaps with 1357 (m) band of *tert*-butoxy ligand), 1232 (m), 1186 (s), 1022 (m), 970 (s), 802 (w), and 782 (m) cm^{-1}. Anal. Calcd for $C_{24}H_{40}OTh$: C, 49.99; H, 6.99. Found: C, 49.88; H, 6.91.

In a separate experiment, the above reaction was carried out in a sealed ^1H NMR tube (C_6D_6 solution) at 100 °C (1 atm of H_2) and was monitored periodically. The reaction was observed to proceed slowly and essentially quantitatively over a period of ca. 15 h.

$Th[\eta^5\text{-}(CH_3)_5C_5]_2[OC(CH_3)_3]D$. The complex $Th[\eta^5\text{-}(CH_3)_5C_5]_2[OC(CH_3)_3]H$ was dissolved in toluene solution and heated at 100 °C under an atmosphere of deuterium gas (1 atm of D_2) for 30 min. The product, $Th[\eta^5\text{-}(CH_3)_5C_5]_2[OC(CH_3)_3]D$, was then isolated in a manner similar to that described above for the corresponding hydride complex.

IR (Nujol mull): 1357 (m), 1231 (m), 1186 (s), 1021 (m), 981 (s), 965 (s), 802 (w), and 781 (s) cm^{-1}.

$Th[\eta^5\text{-}(CH_3)_5C_5]_2(C_2H_5)_2$. A 25-mL round-bottom flask was charged with 0.50 g (0.50 mmol) of $\{Th[\eta^5\text{-}(CH_3)_5C_5]_2(\mu\text{-}H)H\}_2$. Pentane (10 mL) was condensed into the flask in vacuo. An atmosphere of ethylene was admitted to the flask, and the reaction mixture was stirred at room temperature for 10 min. The starting material was observed to dissolve in the pentane, and the resulting solution was then filtered. The filtrate was cooled to −78 °C, and the white crystalline precipitate was isolated by cold filtration and was dried in vacuo. Yield: 70%.

Attempts to record an infrared spectrum of this compound as a Nujol mull led to decomposition in the infrared beam with bubbles of gas being observed in the Nujol. The spectrum exhibited strong, broadened bands at 1216, 1132, 827, and 674 cm^{-1} assignable to bridging M-H-M stretching modes as well as medium bands at 1021 (m) and 800 (w) cm^{-1} due to $\eta^5\text{-}(CH_3)_5C_5$. Anal. Calcd for $C_{24}H_{40}Th$: C, 51.42; H, 7.19. Found: C, 51.33; H, 6.93.

$\{Th[\eta^5\text{-}(CH_3)_5C_5]_2(\mu\text{-}H)Cl\}_2$. A 100-mL round-bottom flask was charged with 1.00 g (1.74 mmol) of $Th[\eta^5\text{-}(CH_3)_5C_5]_2Cl_2$ and 0.88 g (0.87 mmol) of $\{Th[\eta^5\text{-}(CH_3)_5C_5]_2(\mu\text{-}H)H\}_2$. Toluene (25 mL) was condensed into the flask, and the solution was stirred under argon for 30 min at 50 °C, followed by 12 h at room temperature. The solution was then warmed, dissolving as much solid as possible, and the solution was then filtered while warm. Any remaining solids were dissolved and combined with the filtrate by repeated Soxhlet extraction in vacuo with toluene from the filtrate. The filtrate was then concentrated to ca. 10 mL, and the white crystalline solid was isolated by filtration, was washed with 0.5 mL of toluene, and was dried in vacuo. Yield: 80%.

IR (Nujol mull): 1229 (s), 1152 (m), 1021 (m), 829 (s), 801 (w), and 672 (m) cm^{-1}.

Hydrogenolysis of the chloroalkyl complex $Th[\eta^5\text{-}(CH_3)_5C_5]_2[CH_2Si(CH_3)_3]Cl$ in C_6D_6 solution in a sealed NMR tube resulted in the production of 1 equiv of $Si(CH_3)_4$ and the complex $\{Th[\eta^5\text{-}(CH_3)_5C_5]_2(\mu\text{-}H)Cl\}_2$ in quantitative yield as determined from the ^1H NMR spectrum.

Reaction of the Complexes $\{M[\eta^5\text{-}(CH_3)_5C_5]_2(\mu\text{-}H)H\}_2$ (M = Th, U) with CH_3Cl. A 25-mL round-bottom flask was charged with 0.2476 g (0.245 mmol) of $\{Th[\eta^5\text{-}(CH_3)_5C_5]_2(\mu\text{-}H)H\}_2$. Toluene (10 mL) was condensed into the flask in vacuo. Excess methyl chloride was added to the flask from a gas addition bulb, and the reaction was allowed to stir at room temperature for 48 h. The gas evolved was then passed through a series of three liquid-nitrogen-cooled traps and was transferred via Toepler pump into a calibrated volume. A total of 3.76 equiv of CH_4 (identified by mass spectral analyses)/1 equiv of $\{Th[\eta^5\text{-}(CH_3)_5C_5]_2(\mu\text{-}H)H\}_2$ was produced. The white crystalline product of the reaction was dried in vacuo and was determined to be ≥95% $Th[\eta^5\text{-}(CH_3)_5C_5]_2Cl_2$ by ^1H NMR spectral analysis.

A similar reaction was carried out by using $\{U[\eta^5\text{-}(CH_3)_5C_5]_2H_2\}_2$ generated in situ by hydrogenation of $U[\eta^5\text{-}(CH_3)_5C_5]_2(CH_3)_2$ (0.1379 g, 0.256 mmol) in 10 mL of toluene. In this case 3.14 equiv of CH_4 and 0.10 equiv of H_2/1 equiv of $\{U[\eta^5\text{-}(CH_3)_5C_5]_2(\mu\text{-}H)H\}_2$ was produced. It was determined from an analysis of the ^1H NMR spectrum that the maroon crystalline product of the reaction consisted of a ca. 5:1 ratio of $U[\eta^5\text{-}(CH_3)_5C_5]_2Cl_2{:}U[\eta^5\text{-}(CH_3)_5C_5]_2(CH_3)Cl$.

Results

Synthetic Approaches to $M[\eta^5\text{-}(CH_3)_5C_5]_2X_2$ Precursors. The most straightforward approach to bis(pentamethylcyclopentadienyl) actinide dihalides, reacting $Li(CH_3)_5C_5$[19] with the metal tetrahalides, was only marginally successful, and poor yields were obtained under a variety of conditions (eq 1). Since cyclopentadienyl Grignard and thallium reagents have been used

$$2Li(CH_3)_5C_5 + MCl_4 \xrightarrow[\text{toluene or THF}]{80\text{-}100\ °C} M[\eta^5\text{-}(CH_3)_5C_5]_2Cl_2 + 2LiCl \quad (1)$$

$$M = U,\ 15\%\ \text{maximum yield}$$

$$M = Th,\ 0\%\ \text{yield}$$

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[19] Threlkel, R. S.; Bercaw, J. E. *J. Organomet. Chem.* **1977**, *136*, 1–5 and references therein.

Table I. ^{1}H NMR Spectral Data for Bis(pentamethylcyclopentadienyl)thorium and -uranium Complexes[a,b]

complex	η^5-$(CH_3)_5C_5$	other
$Th[\eta^5\text{-}(CH_3)_5C_5]_2Cl_2$ (1)	1.98 (30 H, s)	
$U[\eta^5\text{-}(CH_3)_5C_5]_2Cl_2$ (2)	13.1 (30 H, s, line width = 65 Hz)	
$Th[\eta^5\text{-}(CH_3)_5C_5]_2(CH_3)_2$ (3)	1.92 (30 H, s)	−0.19 (6 H, s, Th–CH_3)
$U[\eta^5\text{-}(CH_3)_5C_5]_2(CH_3)_2$ (4)	5.03 (30 H, s)	−124 (6 H, s, U–CH_3)
$Th[\eta^5\text{-}(CH_3)_5C_5]_2(CH_3)Cl$ (21)	2.01 (30 H, s)	0.41 (3 H, s, Th–CH_3)
$U[\eta^5\text{-}(CH_3)_5C_5]_2(CH_3)Cl$ (22)	8.96 (30 H, s)	−154 (3 H, s, U–CH_3)
$Th[\eta^5\text{-}(CH_3)_5C_5]_2[CH_2Si(CH_3)_3]_2$ (5)	1.98 (30 H, s)	0.31 (18 H, s, -$Si(CH_3)_3$), -0.43 (4 H, s, Th–CH_2)
$U[\eta^5\text{-}(CH_3)_5C_5]_2[CH_2Si(CH_3)_3]_2$ (6)	5.04 (30 H, s)	−6.14 (18 H, s, $Si(CH_3)_3$), −89 (4 H, s, U–CH_2)
$Th[\eta^5\text{-}(CH_3)_5C_5]_2[CH_2Si(CH_3)_3]Cl$ (13)	2.04 (30 H, s)	0.45 (9 H, s, $Si(CH_3)_3$), 0.24 (2 H, s, Th–CH_2)
$U[\eta^5\text{-}(CH_3)_5C_5]_2[CH_2Si(CH_3)_3]Cl$ (14)	9.48 (30 H, s)	−11.52 (9 H, s, $Si(CH_3)_3$), −124 (2 H, s, U–CH_2)
$Th[\eta^5\text{-}(CH_3)_5C_5]_2[CH_2C(CH_3)_3]_2$ (7)	2.05 (30 H, s)	1.30 (18 H, s $C(CH_3)_3$), 0.15 (4 H, s, Th–CH_2)
$Th[\eta^5\text{-}(CH_3)_5C_5]_2[CH_2C(CH_3)_3]Cl$ (19)	1.99 (30 H, s)	1.30 (9 H, s, $C(CH_3)_3$), 0.55 (2 H, s, Th–CH_2)
$U[\eta^5\text{-}(CH_3)_5C_5]_2[CH_2C(CH_3)_3]Cl$ (20)	8.77 (30 H, s)	−7.17 (9 H, s, $C(CH_3)_3$), −83 (2 H, s, U–CH_2)
$Th[\eta^5\text{-}(CH_3)_5C_5]_2[CH_2C_6H_5]_2$ (8)	1.87 (30 H, s)	1.40 (4 H, s, Th–CH_2), 6.74–7.33 (10 H, complex m, C_6H_5)
$U[\eta^5\text{-}(CH_3)_5C_5]_2[CH_2C_6H_5]_2$ (9)	7.62 (30 H, s)	2.56 (4 H, t, meta H), −1.09 (2 H, t, para H), −16.2 (4 H, m, ortho H), −98.1 (4 H, s, U–CH_2)
$Th[\eta^5\text{-}(CH_3)_5C_5]_2[CH_2C_6H_5]Cl$ (15)	1.91 (30 H, s)	1.86 (2 H, s, Th–CH_2), 6.59–7.21 (5 H, complex m, C_6H_5)
$U[\eta^5\text{-}(CH_3)_5C_5]_2[CH_2C_6H_5]Cl$ (16)	9.62 (30 H, s)	−2.74 (2 H, t, meta H), −5.15 (1 H, t, para H), −44.7 (2 H, complex m, ortho H), −110 (2 H, s, U–CH_2)
$Th[\eta^5\text{-}(CH_3)_5C_5]_2(C_6H_5)_2$ (10)	1.77 (30 H, s)	7.02–7.82 (10 H, complex m, C_6H_5)
$U[\eta^5\text{-}(CH_3)_5C_5]_2(C_6H_5)_2$[c] (11)	4.81 (30 H, s)	13.0 (2 H, t, para H)
$Th[\eta^5\text{-}(CH_3)_5C_5]_2(C_6H_5)Cl$ (17)	1.90 (30 H, s)	7.05–7.74 (5 H, complex m, C_6H_5)
$U[\eta^5\text{-}(CH_3)_5C_5]_2(C_6H_5)Cl$ (18)	9.93 (30 H, s)	1.26 (2 H, complex m, meta H), 0.90 (1 H, complex m, para H)
	13.42 (30 H, s)[d]	−4.18 (1 H, s, para H), −14.16 (1 H, s, meta H), −24.06 (1 H, s, meta H), −66.6 (1 H, s, ortho H), −185.9 (1 H, s, ortho H)[d]
$Th[\eta^5\text{-}(CH_3)_5C_5]_2(C_2H_5)_2$ (31)	1.93 (30 H, s)	0.21 (4 H, q, J = 7.8 Hz, Th–CH_2), 1.26 (6 H, t, J = 7.8 Hz, CH_3)
$Th[\eta^5\text{-}(CH_3)_5C_5]_2[OC(CH_3)_3]Cl$ (28)	2.01 (30 H, s)	1.22 (9 H, s, $MOC(CH_3)_3$)
$Th[\eta^5\text{-}(CH_3)_5C_5]_2[OC(CH_3)_3]CH_3$ (29)	1.98 (30 H, s)	1.20 (9 H, s, $OC(CH_3)_3$), 0.26 (3 H, s, Th–CH_3)
$U[\eta^5\text{-}(CH_3)_5C_5]_2C_4(C_6H_5)_4$[e] (12)	6.02 (30 H, s)	5.72 (4 H, complex m), 4.52 (4 H, complex m), −0.27 (2 H, t), −1.25 (4 H, t), −33.0 (4 H, complex m)
$U[\eta^5\text{-}(CH_3)_5C_5]_2C_2(C_6H_5)_2C_4H_6$[f] (23)	6.14 (30 H, s)	4.02 (3 H, m), 3.40 (1 H, t), 1.04 (2 H, m), −4.46 (2 H, t); −6.36 (1 H, t), −6.72 (2 H, t), −4.81 (2 H, m), −53.8 (1 H, m)
$\{Th[\eta^5\text{-}(CH_3)_5C_5]_2H_2\}_2$ (24)	2.20 (30 H, s)	19.2 (2 H, s, Th-H)
$\{U[\eta^5\text{-}(CH_3)_5C_5]_2H_2\}_2$ (25)	−2.27 (30 H, s)	316.8 (4 H, s, U-H)
$\{Th[\eta^5\text{-}(CH_3)_5C_5]_2(\mu\text{-}H)Cl\}_2$ (27)	2.27 (30 H, s)	19.03 (1 H, s, Th-H)
$\{Th[\eta^5\text{-}(CH_3)_5C_5]_2[OC(CH_3)_3]H$ (30)	2.12 (30 H, s)	1.24 (9 H, s, $OC(CH_3)_3$), 17.4 (1 H, s, Th–H)

[a] Recorded in C_6D_6 at 35 °C. Chemical shifts are reported in parts per million from Me_4Si. [b] s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet. [c] See Figure 2 for low-temperature spectrum. [d] Recorded in toluene-d_8 at −44 °C. [e] See Figure 1B for assignments. [f] See Figure 3 for assignments.

successfully in other d- and f-element organometallic syntheses,[20] reagents for the present targets were prepared via eq 2 and 3. The

$$(CH_3)_5C_5H + i\text{-}PrMgCl \xrightarrow[\text{(2)THF}]{\text{(1)toluene, 120 °C, 2 h}} Mg[(CH_3)_5C_5]Cl\cdot THF + \text{propane} \quad (2)$$

85–90%, colorless prisms

$$Mg[(CH_3)_5C_5]Cl\cdot THF + TlCl \xrightarrow[Et_2O]{25\ °C} Tl[(CH_3)_5C_5] + MgCl_2\cdot THF \quad (3)$$

ca. 20%, yellow needles

pentamethylcyclopentadienyl Grignard reagent is an air-sensitive, thermally stable, crystalline solid which can be stored indefinitely at room temperature. It is only slightly soluble in toluene and moderately soluble in tetrahydrofuran. The formulation $Mg[(CH_3)_5C_5]Cl\cdot THF$ is based on the ^{1}H NMR spectrum which is indicative of a 1:1 ratio of coordinated tetrahydrofuran to pentamethylcyclopentadienide (see Experimental Section). The yellow thallium reagent, $Tl[(CH_3)_5C_5]$,[10] was obtained in low yield (unoptimized) by sublimation from the residue of the reaction of the Grignard salt with TlCl (eq 3). In contrast to the known, air-stable TlC_5H_5, the pentamethylcyclopentadienyl compound is pyrophoric. It is very soluble and thermally stable in toluene solution at room temperature; it is, however, unstable at elevated temperatures and proved to be unsuitable for the present syntheses.

The reaction of the Grignard reagent with the actinide tetrahalides provides an effective, high yield synthesis of the desired complexes (eq 4). An excess of the Grignard reagent is employed

$$2Mg[(CH_3)_5C_5]Cl\cdot THF + MCl_4 \xrightarrow[\text{toluene, 80–90\% yield}]{100\ °C} M[\eta^5\text{-}(CH_3)_5C_5]_2Cl_2 + MgCl_2\cdot THF \quad (4)$$

1, M = U (maroon prisms)
2, M = Th (colorless prisms)

to prevent contamination by the single-ring products $M[\eta^5\text{-}(CH_3)_5C_5]Cl_3\cdot 2S$ (S = THF).[2a,21] Interestingly, and in marked contrast to cyclopentadienyl actinide(IV) chemistry,[20] it proved impossible under all conditions tried to introduce a third pentamethylcyclopentadienyl ring. The air-sensitive bis(pentamethylcyclopentadienyl) actinide dichlorides were characterized by ^{1}H NMR and IR spectroscopy, elemental analysis, and cryoscopic molecular weight determinations. Both compounds are slightly to moderately soluble in toluene at 25 °C but only slightly soluble in diethyl ether or pentane. The infrared spectra as Nujol mulls exhibit medium to weak bands at ca. 1020 and 800 cm^{-1} which are characteristic of η^5-bound pentamethylcyclopentadienyl ligands.[2,19] The ^{1}H NMR spectrum of the diamagnetic thorium complex exhibits a single resonance at δ 1.98 (Table I), whereas the paramagnetic uranium complex exhibits an isotropically shifted singlet at δ 13.1 with a rather large line width (ca. 65 Hz) for a U(IV) organometallic (typical values are 4–10 Hz).[2,22] The origin of the line-width effect, which is in-

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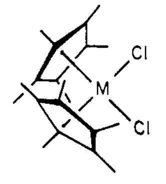
[20] Marks, T. J.; Seyam, A. M.; Wachter, W. A. *Inorg. Synth.* **1976**, *16*, 147–151 and references therein.

[21] Mintz, E. A.; Marks, T. J., manuscript in preparation.

dependent of concentration, solvent, and temperature, will be discussed elsewhere.[23] On the basis of spectroscopic and analytical data, the monomeric pseudotetrahedral solution structure A is



A, M = Th, U

entirely reasonable.[5] This has now been confirmed by single-crystal X-ray diffraction studies.[24] Shortly after our initial report on the bis(pentamethylcyclopentadienyl) actinide dichloride complexes,[10] Green and Watts[25] reported the synthesis of the related complex, bis(ethyltetramethylcyclopentadienyl)uranium dichloride by using a tin reagent to introduce the substituted cyclopentadienyl ligand.

Metalation of cyclopentadiene with the uranium dialkylamide, $U[N(C_2H_5)_2]_4$, has provided another route to $U(C_5H_5)_2X_2$ compounds (eq 5).[26] However, with pentamethylcyclopentadiene,

$$2C_5H_6 + U[N(C_2H_5)_2]_4 \rightarrow U(\eta^5\text{-}C_5H_5)_2[N(C_2H_5)_2]_2 + 2HN(C_2H_5)_2 \quad (5)$$

only a single ring could be introduced, even with excess $(CH_3)_5C_5H$ in refluxing toluene (eq 6).[10] The desired bis(pentamethyl-

$$(CH_3)_5C_5H + U[N(C_2H_5)_2]_4 \rightarrow U[\eta^5\text{-}(CH_3)_5C_5][N(C_2H_5)_2]_3 + HN(C_2H_5)_2 \quad (6)$$

cyclopentadienyl) $U[\eta^5\text{-}(CH_3)_5C_5]_2[N(C_2H_5)_2]_2$ complex has been prepared by another route,[27] and the failure of $U[\eta^5\text{-}(CH_3)_5C_5][N(C_2H_5)_2]_3$ to react with additional $(CH_3)_5C_5H$ moiety appears to reflect unfavorable steric interactions.

Bis(hydrocarbyl) and Chlorohydrocarbyl Complexes. Alkylation of the actinide dichlorides **1** and **2** can be accomplished readily with a wide variety of alkyl- and aryllithium reagents to form dialkyl and diaryl complexes (eq 7). All of these very air-sensitive

$$M[\eta^5\text{-}(CH_3)_5C_5]_2Cl_2 + 2LiR \xrightarrow[-78\ °C]{Et_2O} \underset{\textbf{3-11}}{M[\eta^5\text{-}(CH_3)_5C_5]_2R_2} + 2LiCl \quad (7)$$

3, M = Th, R = CH_3 (colorless needles)

4, M = U, R = CH_3 (orange needles)

5, M = Th, R = $CH_2Si(CH_3)_3$ (colorless needles)

6, M = U, R = $CH_2Si(CH_3)_3$ (orange needles)

7, M = Th, R = $CH_2C(CH_3)_3$ (colorless needles)

8, M = Th, R = $CH_2C_6H_5$ (pale yellow crystals)

9, M = U, R = $CH_2C_6H_5$ (black-green crystals)

10, M = Th, R = C_6H_5 (colorless plates)

11, M = U, R = C_6H_5 (orange-brown crystals)

new complexes were characterized by infrared and ^1H NMR spectroscopy, elemental analysis, and in many cases, by cryoscopic molecular weight measurements (see Experimental Section). The bis(neopentyl) and bis((trimethylsilyl)methyl) complexes are very soluble in toluene and pentane at room temperature, while the dimethyl complexes are moderately soluble in pentane and toluene. The dibenzyl complexes are very soluble in toluene but insoluble in pentane and diethyl ether. As will be discussed subsequently, the diphenyl complexes are soluble in toluene, benzene, and pentane but decompose in toluene and pentane solution. The thorium hydrocarbyls are invariably less soluble than the analogous uranium complexes; the same relationship has previously been observed in the $M(C_5H_5)_3R^3$ and $M(C_8H_8)_2$[28] series.

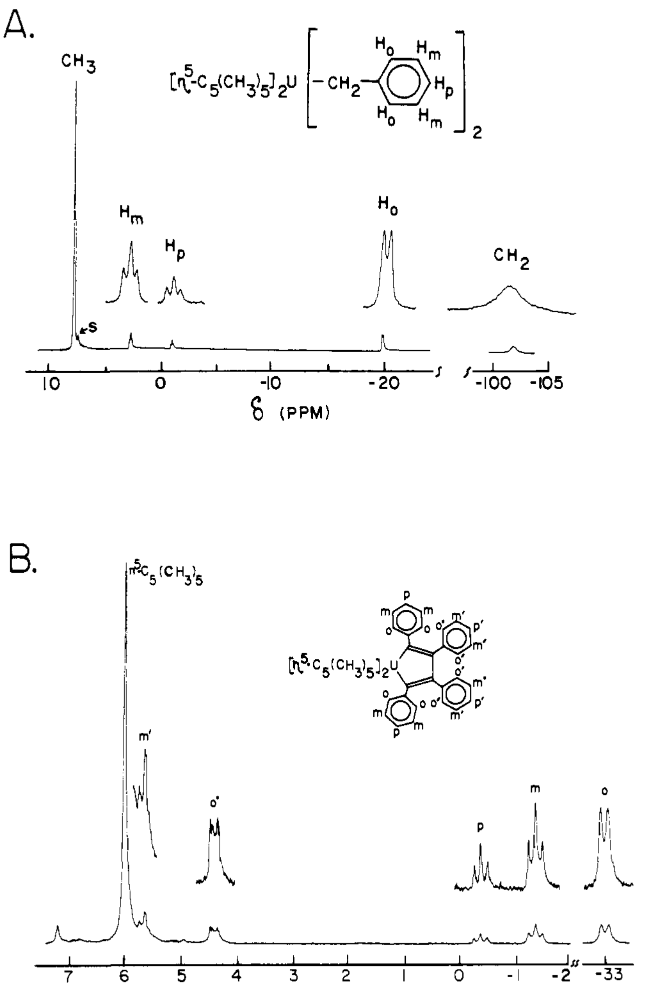
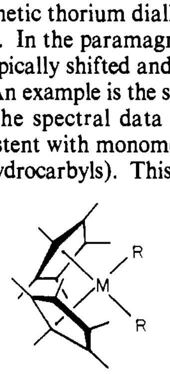


Figure 1. Proton NMR spectra (CW, 60 MHz) of A, $U[\eta^5\text{-}(CH_3)_5C_5]_2(CH_2C_6H_5)_2$, and B, $U[\eta^5\text{-}(CH_3)_5C_5]C_4(C_6H_5)_4$ as solutions in C_6D_6. Signal p′ in B is obscured by the $\eta^5\text{-}(CH_3)_5C_5$ resonance (s = benzene-d_5).

In all cases, the infrared spectra of analogous thorium and uranium dialkyl complexes are virtually superimposable (within 5 cm^{-1}). ^1H NMR data for the bis(hydrocarbyls) are collected in Table I. The diamagnetic thorium dialkyls exhibit resonances at the expected positions. In the paramagnetic U(IV) complexes, the resonances are isotropically shifted and have relatively narrow (4–10 Hz) line widths. An example is the spectrum of **9**, presented in Figure 1A. Thus, the spectral data and molecular weight measurements are consistent with monomeric, pseudotetrahedral structure B for the bis(hydrocarbyls). This proposal has now been



B

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[22] (a) Fischer, R. D. In ref 2a, Chapter 11 and references therein. (b) Marks, T. J.; Kolb, J. R. *J. Am. Chem. Soc.* **1975**, *97*, 27–33 and references therein.

[23] Fagan, P. J.; Marks, T. J., manuscript in preparation.

[24] Day, V. W., private communication.

[25] Green, J. C.; Watts, O. *J. Organomet. Chem.* **1978**, 153, C40.

[26] (a) Jamerson, J. D.; Takats, J. *J. Organomet. Chem.* **1974**, *78*, C23–C25. (b) Arduini, A. L.; Edelstein, N. M.; Jamerson, J. D.; Reynolds, J. G.; Schmid, K.; Takats, J. *Inorg. Chem.* **1981**, *20*, 2470–4.

[27] Fagan, P. J.; Manriquez, J. M.; Marks, T. J.; Vollmer, S. H.; Day, C. S.; Day, V. W. *J. Am. Chem. Soc.* **1981**, *103*, 2206–20.

[28] Streitwieser, A., Jr. In ref 2a, Chapter 5.

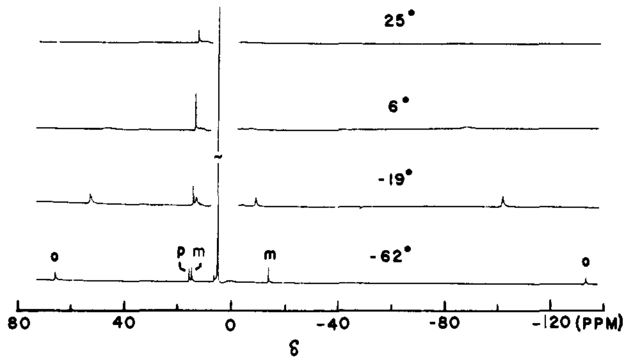
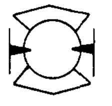
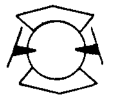


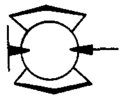
Figure 2. Variable-temperature ^{1}H NMR spectra (FT, 90 MHz) of $U[\eta^5\text{-}(CH_3)_5C_5]_2(C_6H_5)_2$ as a solution in $C_6D_5CD_3$. Labels indicate suggested assignments of phenyl resonances. Extensive decomposition occurs above 25 °C.

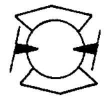
confirmed by single-crystal X-ray diffraction for $U[\eta^5\text{-}(CH_3)_5C_5]_2(CH_3)_2$.[29]

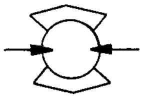
Important structural–dynamic information is also derivable from the ^{1}H NMR spectra. Thus, while at room temperature the ortho and meta resonances are not observable in the spectrum of $U[\eta^5\text{-}(CH)_3)_5C_5]_2(C_6H_5)_2$, variable-temperature studies reveal that hindered rotation takes place about the U–C σ bonds (Figure 2). The low-temperature spectra reveal magnetically equivalent $\eta^5\text{-}(CH_3)_5C_5$ ligands and two nonequivalent sets of ortho and meta protons in each phenyl ligand. This argues against the ground state phenyl plane orientations as shown in structures C, D, and E and in favor of those in structure F or G. Structure F is


C


D

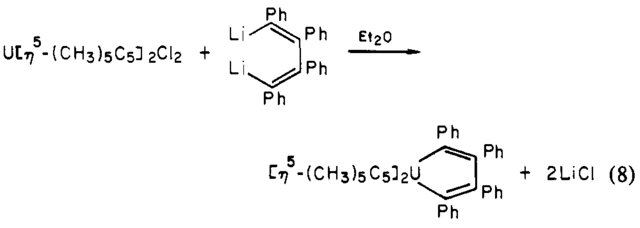

E


F


G

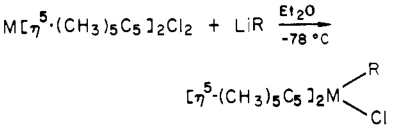
analogous to that found in actinide $M[\eta^5\text{-}(CH_3)_5C_5]_2(NR_2)_2$ complexes[27] as well as in the solid-state structure of $Ti(C_5H_5)_2(C_6H_5)_2$.[30] The free energy of activation for bond rotation in **11** can be estimated from the coalescence point modified Bloch line-shape formalism.[31] Correcting for the approximate Curie dependence of the resonance positions,[32] $\Delta G^\ddagger \approx 12.4 \pm 1.0$ kcal/mol at +40 °C.

A uranium metallacycle complex (**12**) could be prepared by the route of eq 8 by using 1,4-dilithiotetraphenylbutadiene.[33] This complex has been characterized by standard techniques; the ^{1}H NMR spectra are remarkable in that the chemical shift dispersion allows observation and assignment of nearly every resonance at 60 MHz (Figure 1B); all multiplets are well resolved. This complex can also be prepared by the reaction of $\{U[\eta^5\text{-}(CH_3)_5C_5]_2Cl\}_3$ with diphenylacetylene[34a] or by the sodium amalgam reduction of **1** in the presence of diphenylacetylene.[34b]



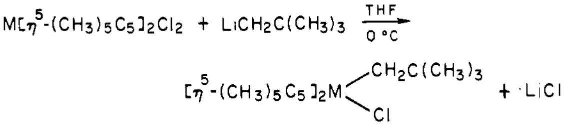
12, brown crystals

Monofunctionalized chlorohydrocarbyls are accessible via the approach of eq 9 and 10. For complexes **13–18**, hydrocarbylation



$$M[\eta^5\text{-}(CH_3)_5C_5]_2Cl_2 + LiR \xrightarrow[-78\ ^\circ C]{Et_2O} [\eta^5\text{-}(CH_3)_5C_5]_2M{\overset{R}{\underset{Cl}{<}}} + LiCl \qquad (9)$$

13, M = Th, R = $CH_2Si(CH_3)_3$ (colorless crystals)
14, M = U, R = $CH_2Si(CH_3)_3$ (maroon crystals)
15, M = Th, R = $CH_2C_6H_5$ (colorless crystals)
16, M = U, R = $CH_2C_6H_5$ (black-green crystals)
17, M = Th, R = C_6H_5 (colorless prisms)
18, M = U, R = C_6H_5 (orange-brown prisms)

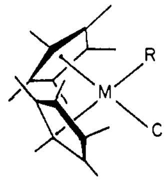


$$M[\eta^5\text{-}(CH_3)_5C_5]_2Cl_2 + LiCH_2C(CH_3)_3 \xrightarrow[0\ ^\circ C]{THF} [\eta^5\text{-}(CH_3)_5C_5]_2M{\overset{CH_2C(CH_3)_3}{\underset{Cl}{<}}} + LiCl \qquad (10)$$

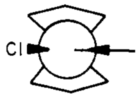
19, M = Th (colorless needles)
20, M = U (brown crystals)

proceeds smoothly and without complications in diethyl ether at −78 °C. However, the $M[\eta^5\text{-}(CH_3)_5C_5]_2[CH_2C(CH_3)_3]Cl$ complexes could only be prepared at 0 °C with rapid addition of freshly prepared neopentyllithium to a slurry of $M[\eta^5\text{-}(CH_3)_5C_5]_2Cl_2$ in THF. This reaction has been found to be critically dependent on both the purity of the starting materials and the conditions employed.

The thermally stable, air-sensitive chlorohydrocarbyls were characterized by infrared and ^{1}H NMR spectroscopy (Table I), by elemental analysis, and in some cases, by cryoscopic molecular weight measurements. On the basis of these results, we propose the monomeric[35] solution structure H. As in the case of **11**, the variable-temperature ^{1}H NMR spectrum of the chlorophenyluranium compound **18** indicates restricted rotation about the uranium–carbon σ bond. The limiting low-temperature spectrum (Table I) is consistent with conformation I for the plane of the phenyl ring. A similar, coplanar ground-state configuration was observed for actinide $M[\eta^5\text{-}(CH_3)_5C_5]_2(NR_2)Cl$ compounds.[27] Application of the appropriate line-shape relationship[31] and correcting for the temperature dependence of the chemical shifts[36]



H



I

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[29] Day, V. W., private communication.

[30] Kocman, V.; Rucklidge, J. C., O'Brien, R. J.; Santo, W. *J. Chem. Soc., Chem. Commun.* **1971**, 1340.

[31] (a) Binsch, G. In Jackman, L. M., Cotton, F. A., Eds. "Dynamic Nuclear Magnetic Resonance Spectroscopy"; Academic Press: New York, 1976; pp 45–81. (b) Binsch, G.; Kessler, H. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 411–428 and references therein.

[32] By least squares: $\delta_{meta} = 2.20 \times 10^3(1/T) + 4.92$; $\delta_{meta'} = -6.14 \times 10^3(1/T) + 5.83$.

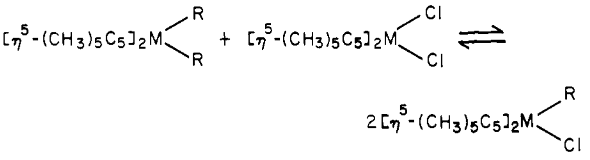
[33] For related group 4B compounds, see: Atwood, J. L.; Hunter, W. E.; Alt, H.; Rausch, M. D. *J. Am. Chem. Soc.* **1976**, *98*, 2454–2459 and references therein.

[34] (a) Manriquez, J. M.; Fagan, P. J.; Marks, T. J.; Vollmer, S. H.; Day, C. S.; Day, V. W. *J. Am. Chem. Soc.* **1979**, *101*, 5075–5078. (b) Fagan, P. J.; Manriquez, J. M.; Marks, T. J.; Vollmer, S. H.; Day, C. S.; Day, V. W. *Organometallics*, in press.

[35] In our preliminary communication,[5] we proposed a dimeric structure based upon an incorrect molecular weight, provided by a commercial laboratory.

yield $\Delta G^{\ddagger} = 13.5 \pm 0.3$ kcal/mol (at 65 °C) for rotation about the uranium-to-phenyl σ bond.

An alternate route to several of the chloro alkyl derivatives is afforded by a redistribution reaction between dialkyl and dichloride complexes (eq 11). This reaction is actually an equilibrium lying

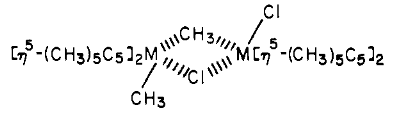


(11)

M = Th, U; R = CH_3, $CH_2Si(CH_3)_3$

21, M = Th, R = CH_3 (colorless crystals)
22, M = U, R = CH_3 (maroon crystals)

ca. 90–95% to the right as determined by ^{1}H NMR spectroscopy. This is the preferred method for synthesis of the complexes $M[\eta^5\text{-}(CH_3)_5C_5]_2(CH_3)Cl$ (M = Th (**21**), U (**22**)) because the procedure of eq 9 results in a mixture of $M[\eta^5\text{-}(CH_3)_5C_5]_2(CH_3)Cl$ and $M[\eta^5\text{-}(CH_3)_5C_5]_2(CH_3)Br$ owing to the presence of LiBr in the commercial methyllithium solutions employed. The rate of redistribution was observed by ^{1}H NMR spectroscopy to be considerably faster for R = CH_3 than for R = $CH_2Si(CH_3)_3$ at 35 °C. This result suggests that the increased steric bulk of the (trimethylsilyl)methyl groups hinders the intermolecular alkyl transfer. Presumably, a dimeric intermediate such as J is involved



J

in these exchange reactions. Such two-electron, three-center bonded alkyl intermediates are proposed for alkyl-exchange reactions involving, for example, group 3A metals,[37] and such bonding has been observed in the ground state of dimeric lanthanide complexes $[M(\eta^5\text{-}C_5H_5)_2(\mu\text{-}CH_3)]_2$.[38]

Bis(pentamethylcyclopentadienyl)thorium and -uranium Hydrocarbyls. Thermal Stability and Hydrocarbon Metathesis. Despite a rather low formal coordination number, the $M[\eta^5\text{-}(CH_3)_5C_5]_2R_2$ and $M[\eta^5\text{-}(CH_3)_5C_5]_2(R)Cl$ complexes as typified by **3–20** exhibit appreciable thermal stability. There are, however, several noteworthy exceptions (vide infra). As found in the $M(C_5H_5)_3R$ series,[3] the thorium complexes are more thermally stable in solution (benzene, toluene) than the uranium complexes. The dimethyl complexes are the most thermally stable of the bis(hydrocarbyls) with half-lives at 100 °C in toluene-d_8 solution of ca. 170 h (M = Th) and 16 h (M = U). These half-lives are still considerably lower than for the higher coordination number $M(C_5H_5)_3R$ derivatives[2,3] with a comparable R moiety (e.g., for M = Th, R = neopentyl, $t_{1/2}$ = 7500 h at 167 °C,[3b] for M = U, R = CH_3, $t_{1/2}$ = 6300 h at 97 °C[3a]). Among the bis(pentamethylcyclopentadienyl) complexes, the $CH_2Si(CH_3)_3$ and $CH_2C_6H_5$ compounds are roughly comparable to the methyl compounds in thermal stability, while the neopentyl compounds are markedly less stable. Indeed, all attempts to prepare $U[\eta^5\text{-}(CH_3)_5C_5]_2[CH_2C(CH_3)_3]_2$ failed, and $U[\eta^5\text{-}(CH_3)_5C_5]_2[CH_2C(CH_3)_3]Cl$ was found to be unstable at room temperature. For a given M and R functionality, the $M[\eta^5\text{-}(CH_3)_5C_5]_2(R)Cl$ derivative is more thermally stable than the $M[\eta^5\text{-}(CH_3)_5C_5]_2R_2$ derivative.

Although exhaustive studies of $M[\eta^5\text{-}(CH_3)_5C_5]_2$ compounds with alkyl groups containing β-hydrogen atoms have not been conducted, several informative observations have been made. When eq 9 is carried out with M = U and the bulky R = *tert*-butyl group, a trivalent uranium complex $(\{U[\eta^5\text{-}(CH_3)_5C_5]_2Cl\}_3)$[34,39] rapidly precipitates from solution. A plausible route for the formation of this product is via β-hydride elimination from an unstable *tert*-butyl uranium complex and subsequent decomposition of the resulting, unstable (vide infra) uranium chlorohydride.[34,39] On the other hand, it will be seen that a bis(pentamethylcyclopentadienyl)thorium ethyl derivative has appreciable thermal stability (vide infra).

The diphenyl derivatives of both uranium and thorium are indefinitely stable in the solid state at 10 °C, but the stability in solution is markedly solvent dependent. Both complexes are stable indefinitely in benzene solution at temperatures up to 80–100 °C. However, the uranium complex decomposes (as judged by changes in the ^{1}H NMR spectrum) within 3 h at room temperature in either pentane or toluene solution. The thorium diphenyl complex does not decompose as rapidly at 25 °C, but pentane solutions discolor upon standing. NMR spectra of $U[\eta^5\text{-}(CH_3)_5C_5]_2(C_6H_5)_2$ solutions freshly prepared in C_6D_6 at room temperature evidence rapid formation of $C_6H_{6-x}D_x$, $x = 0, 1, 2, \ldots$ (a sharp singlet at δ 7.1) and the concurrent disappearance of the metal-bound phenyl resonances; no new isotropically shifted resonances are observed. The process obeys pseudo-first-order kinetics with $k = (6.06 \pm 0.3) \times 10^{-2}$ min^{-1} at 45 °C and $\gtrsim 1.0 \times 10^{-1}$ min^{-1} at 70 °C.[40a] Integration studies indicate essentially quantitative ($\gtrsim$95%) conversion of the phenyl protons to benzene protons at the completion of the reaction; the intensity of the $(CH_3)_5C_5$ signal remains unchanged while the resonance position shifts ca. 0.02-ppm downfield. We ascribe these changes to a rapid hydrocarbon metathesis process (eq 12). That it is completely reversible is

$$\underset{M\,=\,U,\,Th}{M[\eta^5\text{-}(CH_3)_5C_5]_2(C_6H_5)_2} \underset{C_6H_6}{\overset{C_6D_6}{\rightleftharpoons}} M[\eta^5\text{-}(CH_3)_5C_5]_2(C_6D_5)_2 \qquad (12)$$

demonstrated by stripping the solvent from the above $U[\eta^5\text{-}(CH_3)_5C_5]_2(C_6D_5)_2$ sample, condensing in benzene, warming, stripping off the solvent, and redissolving the sample in C_6D_6. This procedure regenerates the spectrum of $U[\eta^5\text{-}(CH_3)C_5]_2(C_6H_5)_2$. The thorium analogue undergoes the same transformations; however temperatures of 100 °C are required to achieve rates comparable to the uranium system at room temperature.

An ortho-hydrogen-abstraction process to form an actinide benzyne complex (Scheme I), followed by the reverse reaction with benzene (or C_6D_6) explains the present observations. A similar mechanism has been proposed for the less clean and far slower (as compared to M = U) transarylation of $Zr(C_5H_5)_2(aryl)_2$ complexes ($k = (1.8 \pm 0.1) \times 10^{-3}$ min^{-1} at 70°);[41,42] furthermore, a mononuclear tantalum benzyne complex has recently been isolated.[43] Further mechanistic support in the present case is provided by trapping experiments[40b] with diphenylacetylene. Thus, decomposition of $U[\eta^5\text{-}(CH_3)_5C_5]_2(C_6H_5)_2$ (4.8×10^{-3} M) in the presence of a threefold molar excess of diphenylacetylene in C_6D_6 also obeys good first-order kinetics and proceeds at a rate indistinguishable ($(6.42 \pm 1.4) \times 10^{-2}$ min^{-1} at 45 °C) from that in the absence of diphenylacetylene.[40b] The product is the me-

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(36) By least squares: $\delta_{ortho} = -2.28 \times 10^4(1/T) + 33.0$; $\delta_{ortho'} = -5.70 \times 10^4(1/T) + 63.7$.

(37) (a) Mole, F.; Jeffrey, E. A. "Organoaluminum Compounds"; Elsevier: Amsterdam, 1972 and references therein. (b) Oliver, J. P. *Adv. Organomet. Chem.* **1970**, *8*, 167–209.

(38) (a) Holton, J.; Lappert, M. F.; Ballard, D. G. H.; Pearce, R.; Atwood, J. L.; Hunter, W. E. In ref 2a, Chapter 6 and references therein. (b) Holton, J.; Lappert, M. F.; Ballard, D. G. H.; Pearce, R.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Dalton, Trans.* **1979**, 54–61.

(39) Manriquez, J. M.; Fagan, P. J.; Marks, T. J., unpublished observations. An electron-transfer mechanism and/or the involvement of $U[(CH_3)_5C_5]_2Cl$ Lewis base adducts[34] cannot be rigorously ruled out.

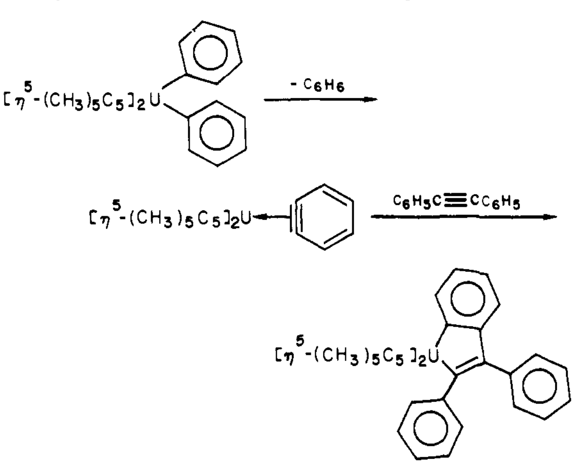
(40) (a) Kinetic plots were fit by standard linear regression techniques. (b) To rigorously prove that a reactive intermediate is being trapped, it is necessary to establish that the trapping agent has not entered into the chemistry prior to the formation of the intermediate.

(41) Erker, G. *J. Organomet. Chem.* **1977**, *134*, 189–202.

(42) For related work, see: (a) Erker, G.; Kropp, K. *J. Am. Chem. Soc.* **1979**, *101*, 3659–3660. (b) Boekel, C. P.; Teuben, J. H.; DeLiefde Meijer, H. J. *J. Organomet. Chem.* **1971**, *81*, 371–377. (c) Masai, H.; Sonogoshira, H.; Hagihara, N. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 750–751.

(43) McLain, S. J.; Schrock, R. R.; Sharp, P. R.; Churchill, M. R.; Youngs, W. J. *J. Am. Chem. Soc.* **1979**, *101*, 265–266.

tallacycle **23** shown in eq 13.[44] That trapping of the intermediate is efficient is confirmed by the fact that metallacycle formation also follows good first-order kinetics and occurs at essentially the same rate as the disappearance of the phenyl protons of **11** (k = (6.78 ± 0.6) × 10^{-2} min^{-1} at 45 °C). The ^1H NMR spectrum of the product supplemented by that of the material prepared from $U[\eta^5\text{-}(CH_3)_5C_5]_2(C_6D_5)_2$ (Figure 3) supports the structural assignment, and integration also indicates that the back-reaction with C_6D_6 does not favorably compete with the trapping reaction under the conditions employed.



(13)

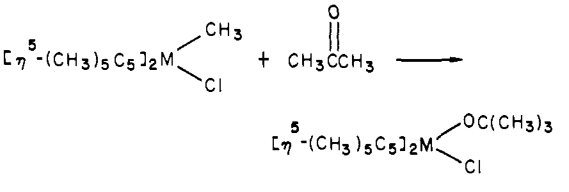
23

The instability of several neopentyl complexes (vide supra) prompted a brief investigation of $Th[\eta^5\text{-}(CH_3)_5C_5]_2[CH_2C(CH_3)_3]_2$ thermolysis. In benzene solution, metathesis occurs to quantitatively produce the corresponding diphenyl compound (eq 14) and neopentane (detected by ^1H NMR). In C_6D_6 solution,

$$[\eta^5\text{-}(CH_3)_5C_5]_2Th[CH_2C(CH_3)_3]_2 \xrightarrow[100\ °C,\ 4\ h]{C_6H_6} [\eta^5\text{-}(CH_3)_5C_5]_2Th(C_6H_5)_2 + 2C(CH_3)_4 \quad (14)$$

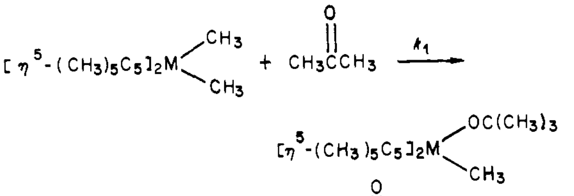
$Th[\eta^5\text{-}(CH_3)_5C_5]_2(C_6D_5)_2$ is formed. More detailed studies of the scope and mechanism of this interesting C–H activation process will be discussed elsewhere.[7]

Bis(pentamethylcyclopentadienyl)thorium and -uranium Hydrocarbyls. Addition to Ketones, Alcoholysis, and Halogenolysis. The polarity as well as steric accessibility of the actinide–carbon σ bonds in the bis(pentamethylcyclopentadienyls) was probed with ketones, alcohols, and halogens. For acetone (eq 15), insertion is complete in a few seconds at room temperature. Competition experiments using dimethyl compounds revealed that at −78 °C acetone addition to Th–CH_3 is more rapid than to U–CH_3 by a factor of ca. 30 but that the second addition to thorium is far slower than the first addition to uranium, i.e., $k_1(Th) \approx 30k_1(U) >> k_2(Th) \approx 20k_2(U)$ (eq 16, 17).[45]

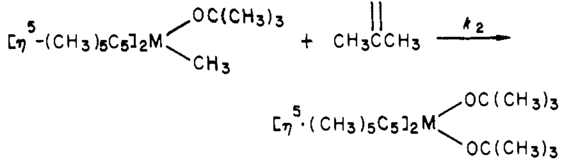


$$[\eta^5\text{-}(CH_3)_5C_5]_2M(CH_3)(Cl) + CH_3C(O)CH_3 \longrightarrow [\eta^5\text{-}(CH_3)_5C_5]_2M(OC(CH_3)_3)(Cl) \quad (15)$$

The actinide-to-carbon σ bonds also undergo rapid protolysis with alcohols. Thus, the dimethyl compounds react rapidly with methanol at all temperatures (as monitored by ^1H NMR) to produce methoxide compounds and methane (eq 18, 19).

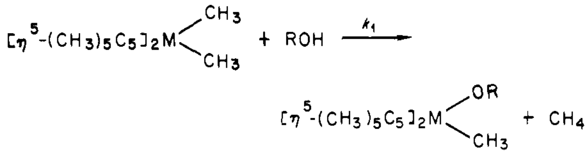


$$[\eta^5\text{-}(CH_3)_5C_5]_2M(CH_3)_2 + CH_3C(O)CH_3 \xrightarrow{k_1} [\eta^5\text{-}(CH_3)_5C_5]_2M(OC(CH_3)_3)(CH_3) \quad (16)$$

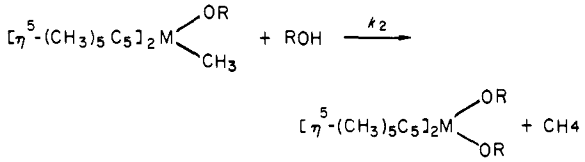


$$[\eta^5\text{-}(CH_3)_5C_5]_2M(OC(CH_3)_3)(CH_3) + CH_3C(O)CH_3 \xrightarrow{k_2} [\eta^5\text{-}(CH_3)_5C_5]_2M(OC(CH_3)_3)_2 \quad (17)$$

M = Th, U



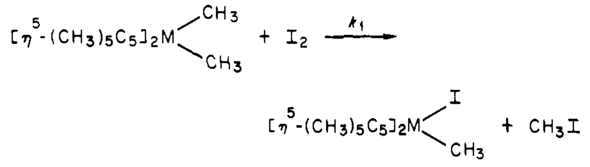
$$[\eta^5\text{-}(CH_3)_5C_5]_2M(CH_3)_2 + ROH \xrightarrow{k_1} [\eta^5\text{-}(CH_3)_5C_5]_2M(OR)(CH_3) + CH_4 \quad (18)$$



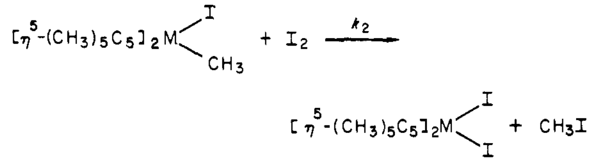
$$[\eta^5\text{-}(CH_3)_5C_5]_2M(OR)(CH_3) + ROH \xrightarrow{k_2} [\eta^5\text{-}(CH_3)_5C_5]_2M(OR)_2 + CH_4 \quad (19)$$

Cleavage of the metal–ring bonds also occurred but was not competitive with attack on the σ bonds. Competition experiments at −78 °C using *tert*-butyl alcohol revealed that $k_1(Th) \approx 1.5k_1(U) >> k_2(Th) \approx 4k_2(U)$;[45] with this alcohol, cleavage of the $\eta^5\text{-}(CH_3)_5C_5$ ligands is imperceptible in the course of several hours at room temperature. Intermediate alkoxy alkyl compounds, $M(OR)CH_3$, could be detected during the course of the *tert*-butyl alcohol reactions, but with methanol under all conditions examined, only dialkyls and dimethoxides were evident.

Halogenolysis experiments using iodine revealed facile cleavage of the actinide-to-carbon bonds (eq 20, 21) to yield the known[45] iodo complexes and methyl iodide (94% yield by NMR integration). At −78 °C, $k_1(Th) \approx 3k_1(U) >> k_2(U) \approx 2k_2(Th)$. Displacement of the pentamethylcyclopentadienyl ring was also found to occur, but the rate was far slower and not competitive with cleavage of the actinide-to-carbon σ bonds. Detailed experiments with other halogens were also conducted. These reactions are more complex and will be discussed elsewhere.[46]



$$[\eta^5\text{-}(CH_3)_5C_5]_2M(CH_3)_2 + I_2 \xrightarrow{k_1} [\eta^5\text{-}(CH_3)_5C_5]_2M(I)(CH_3) + CH_3I \quad (20)$$



$$[\eta^5\text{-}(CH_3)_5C_5]_2M(I)(CH_3) + I_2 \xrightarrow{k_2} [\eta^5\text{-}(CH_3)_5C_5]_2MI_2 + CH_3I \quad (21)$$

Metal–Carbon σ Bond Hydrogenolysis. The Synthesis of Organoactinide Hydrides. Hydrogenolysis of the thorium and uranium dialkyls in toluene solution at 25 °C (1 atm of H_2) results in the rapid formation of molecular hydrides (eq 22). In ex-

$$2M[\eta^5\text{-}(CH_3)_5C_5]_2R_2 + 4\ H_2 \xrightarrow[toluene]{25\ °C} \{M[\eta^5\text{-}(CH_3)_5C_5]_2(\mu\text{-}H)H\}_2 + 4RH \quad (22)$$

24, M = Th (pale-yellow prisms)
25, M = U (green-black crystals)

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[44] For analogous transition-metal compounds, see: (a) Boekel, C. P.; Teuben, J. H.; DeLiefde Meijer, H. J. *J. Organometal. Chem.* **1974**, *81*, 371–377 and references therein. (b) Rausch, M. D.; Mintz, E. A. *Ibid.* **1980**, *190*, 65–72.

[45] The synthesis and characterization of the individual products will be discussed elsewhere. Seyam, A. M.; Marks, T. J., manuscript in preparation.

[46] Seyam, A. M.; Marks, T. J., manuscript in preparation.

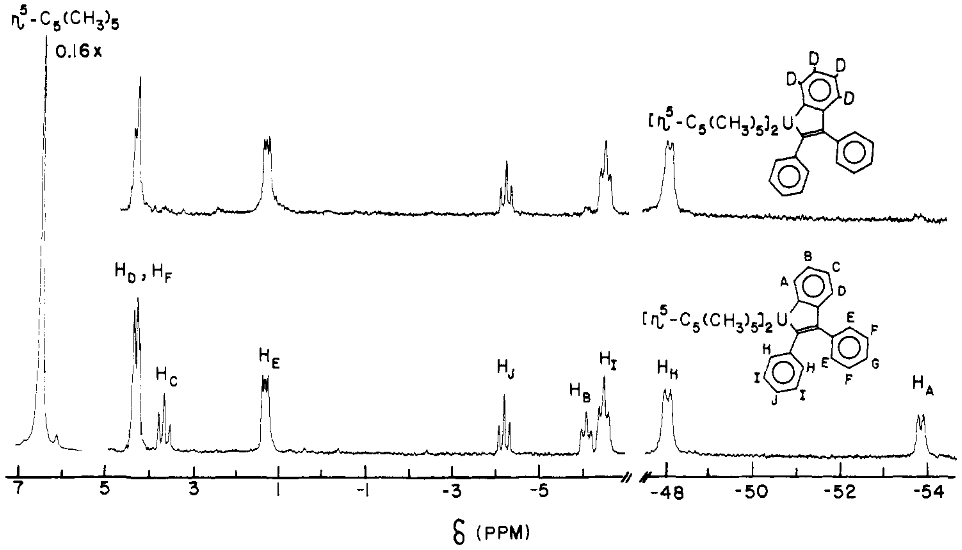
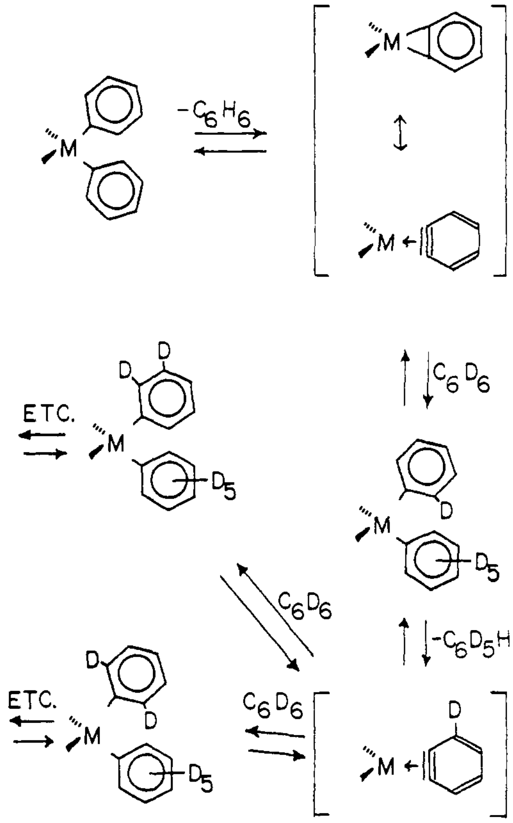


Figure 3. Proton NMR spectra (CW, 60 MHz) of the result of thermolyzing $U[\eta^5\text{-}(CH_3)_5C_5]_2(C_6D_5)_2$ (ca. 95% D, top) and $U[\eta^5\text{-}(CH_3)_5C_5]_2(C_6H_5)_2$ (bottom) in the presence of diphenylacetylene.

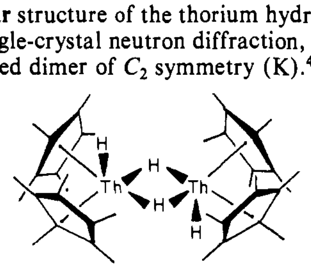
Scheme I



periments with the $M[\eta^5\text{-}(CH_3)_5C_5]_2(CH_3)_2$ complexes, gas measurements indicated the production of 2 equiv of methane and the absorption of 2 equiv of H_2/1 equiv of the actinide dialkyl, as predicted by eq 22. If deuterium gas is used, CH_3D is produced quantitatively, and in the case of thorium, $\{Th[\eta^5\text{-}(CH_3)_5C_5]_2(\mu\text{-}D)D\}_2$ is the product. In the case of uranium, because of relatively rapid interchange of protons of the $\eta^5\text{-}(CH_3)_3C_5$ group with the U-D bonds,[47] the complex $\{U[\eta^5\text{-}(CH_3)_5C_5]_2(\mu\text{-}D)D\}$ cannot be isolated without extensive isotopic scrambling (vide infra).

Both actinide hydride complexes are only partially soluble in toluene and are virtually insoluble in pentane. Cryoscopic molecular weight measurements in benzene indicate that **24** is dimeric.

The molecular structure of the thorium hydride has been determined by single-crystal neutron diffraction, and the result is a hydride-bridged dimer of C_2 symmetry (K).[48] The infrared



K

Table II. Infrared Spectral Data for Actinide Hydrides and Several Early Transition-Metal Hydrides[a]

complex	ν_{M-H} (ν_{M-D}), cm^{-1}	ν_{M-H}/ν_{M-D}	ref
$\{Th[\eta^5\text{-}(CH_3)_5C_5]_2\text{-}(\mu\text{-}H)H\}_2$ (24)	1404 (1002)	1.40	this work
	1370 (979)	1.40	
	1215 (873)	1.39	
	1114 (803)	1.39	
	844 (609[b])		
	650 (465)	1.40	
$\{U[\eta^5\text{-}(CH_3)_5C_5]_2\text{-}(\mu\text{-}H)H\}_2$ (25)	1335		this work
	1180		
$\{Th[\eta^5\text{-}(CH_3)_5C_5(\mu\text{-}H)Cl\}_2$ (27)	1229		this work
	1152		
	829		
	672		
$Th[\eta^5\text{-}(CH_3)_5C_5]_2\text{-}[OC(CH_3)_3]H$ (30)	1359[c] (981)	1.39	this work
$Th\{N[Si(CH_3)_3]_2\}_3H$	1480 (1060)	1.40	53
$U\{N[Si(CH_3)_3]_2\}_3H$	1430 (1020)	1.40	53
$Ti[\eta^5\text{-}(CH_3)_5C_5]_2H_2$	1560		52a
$Zr[\eta^5\text{-}(CH_3)_5C_5]_2H_2$	1555 (1100)	1.41	52b
$\{Zr[\eta^5\text{-}C_5H_4(CH_2)_4]_2\text{-}(\mu\text{-}H)H\}_2$	1545 (1104)	1.40	52c
	1285 (932)	1.39	
$\{Zr(\eta^5\text{-}C_5H_5)_2H_2\}_x$	1520 (1100)	1.38	52d
	1300 (960)	1.35	
$\{Zr[\eta^5\text{-}(CH_3)_5C_5]_2H\}_2\text{-}$[*trans*-$OC(H)=C(H)O$]	1580 (1130)	1.40	52e
$Zr[\eta^5\text{-}(CH_3)_5C_5]_2(OCH_3)H$	1590 (1130)	1.41	52f

[a] Solid-state spectra recorded as Nujol mulls. [b] Overlapping band. [c] Overlapping with a band due to $OC(CH_3)_3$.

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

[48] Broach, R. W.; Schultz, A. J.; Williams, J. M.; Brown, G. M.; Manriquez, J. M.; Fagan, P. J.; Marks, T. J. *Science* (*Washington, D.C*) **1979**, *203*, 172-174.

spectrum of **24** (Table II) is consistent with this structure, and the assignment of normal modes which are predominantly terminal[49] (1404 and 1370 cm^{-1}) and bridging[50] (1215, 1114, 844, and 650 cm^{-1}) metal-hydrogen stretching in character[51] is supported by deuterium substitution. The observation of the four higher energy bands in solution spectra (the other two were masked by solvent absorption) argues that solid-state effects on the spectra are unimportant.

In the bridging region, the bands at 1215 and 1114 cm^{-1} can be assigned to antisymmetric Th–H–Th stretching modes and the bands at 844 and 650 cm^{-1} to symmetric stretching modes. The average of the antisymmetric modes divided by the average of the symmetric modes is 1.56. With use of the formalism of Howard et al.,[51b] the predicted tan $(\theta/2)$ is thus 1.83° or θ = 123°. This agrees favorably with the crystallographically observed average Th–H–Th angle of θ = 122 (4)°. The relatively low energies of the Th–H stretching frequencies are reminiscent of data for early transition-metal hydrides[52] and the recently reported tris(amido)actinide hydrides $M\{N[Si(CH_3)_3]_2\}_3H$, (M = Th, U);[53] some comparative data are set out in Table II.

The ^1H NMR spectrum of $\{Th[\eta^5\text{-}(CH_3)_5C_5]_2(\mu\text{-}H)H\}_2$ exhibits a singlet at δ 2.20 ($\eta^5\text{-}(CH_3)_5C_5$), and a singlet at δ 19.2. The latter resonance is not present in the spectrum of the complex $\{Th[\eta^5\text{-}(CH_3)_5C_5]_2(\mu\text{-}D)D\}_2$ and is assigned to the metal hydride resonance. These resonances remain sharp singlets at temperatures as low as −85 °C in $C_6H_5CD_3$ solution although, at this temperature, the hydride resonance does begin to broaden somewhat relative to other resonances. This result is indicative of rapid bridge–terminal hydrogen permutation, presumably analogous to fluxional processes in metal tetrahydroborate complexes;[22b,54] alternatively, rapid dimer–monomer equilibration is occurring (eq 23). An analogous, albeit slower, hydride-exchange process has

$$\{Th[\eta^5\text{-}(CH_3)_5C_5]_2H_2\}_2 \rightleftharpoons 2Th[\eta^5\text{-}(CH_3)_5C_5]_2H_2 \quad (23)$$

been reported for $[Zr(tetrahydroindenyl)_2(\mu\text{-}H)H]_2$.[52c] The position of δ 19.2 for the hydride resonance is the lowest field position ever observed for a diamagnetic metal hydride[55] but is in accord with the general trend observed for analogous d^0 cyclopentadienyl metal hydride complexes.[56a,b]

The thermal stability of the thorium hydride complex is remarkably high with little or no decomposition occurring over a period of hours at 80 °C in toluene solution.

The infrared spectrum of the uranium dihydride complex, **25**, is similar to that observed for the thorium dihydride complex; however, the infrared bands are much broader and less well resolved (Table II). The broad band centered at 1335 cm^{-1} is assigned to a terminal U–H stretching mode and the broad band at 1180 cm^{-1} is assigned to a bridging U–H–U stretching mode. In the room-temperature (34 °C) ^1H NMR spectrum, the paramagnetic uranium complex exhibits a sharp isotropically shifted singlet at δ −2.27 ($\eta^5\text{-}(CH_3)_5C_5$); the hydride resonance is observed at δ 316.8 and shifts with temperature according to an approximate Curie dependence.[56c] This result represents one of the few known examples where the resonance of a hydrogen atom bound directly to the metal in a paramagnetic complex has been observed.[22] It is the largest proton isotropic shift observed to date. The resonance remains a sharp singlet down to −85 °C, again indicating very rapid bridge–terminal hydrogen interchange based on the proposed dimeric structure. On the basis of the similarity of the solubility and spectroscopic properties of the uranium hydride to those of the thorium hydride, a structure of type K is also assigned for this complex. Further structural studies are in progress.

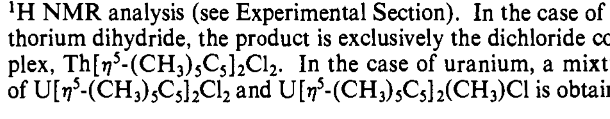
In contrast to the high thermal stability of the thorium dihydride in toluene solution, the uranium complex loses dihydrogen (0.48 mol of H_2/1 mol of U) at room temperature in vacuo over a period of 3 h. This loss is reversed if a dihydrogen atmosphere is again introduced. If a sample of **25** dissolved in C_6D_6 is sealed in an NMR tube in vacuo (or under argon), the sharp singlet due to the $\eta^5\text{-}(CH_3)_5C_5$ ligands of the uranium(IV) hydride at δ −2.27 (line width = 4 Hz) is observed along with another broad (line width = 18 Hz) singlet at δ −9.37. If the sample is sealed under a dihydrogen atmosphere, the resonance at δ −9.37 is significantly decreased in relative intensity. The above results are consistent with an equilibrium between the uranium(IV) hydride with uranium(III) hydride complex **26** (eq 24). The broad singlet at

$$\underset{\mathbf{25}}{\{[\eta^5\text{-}(CH_3)_5C_5]_2UH_2\}_2} \rightleftharpoons (2/x)\underset{\mathbf{26}}{\{[\eta^5\text{-}(CH_3)_5C_5]_2UH\}_x} + H_2 \quad (24)$$

δ −9.37 is assigned to the $\eta^5\text{-}(CH_3)_5C_5$ resonance of the uranium(III) hydride species. The breadth and position of this resonance are typical of what has been observed for other uranium(III) pentamethylcyclopentadienyl complexes;[34] the metal-bound hydride resonance could not be located. Further studies of this interesting compound are in progress. The facility of eq 24 in contrast to the stability of the thorium hydride **24** is understandable in terms of the ready accessibility of the trivalent uranium oxidation state.[2,6,57]

Organoactinide Hydrides. Reactions. In view of the pronounced hydridic character of early transition-metal hydrides (in contrast to those of the later transition metals),[55,58] it was of interest to explore the hydridic nature of the organoactinide hydrides. Reaction of methyl chloride with **24** and **25** in toluene solution proceeds as shown in eq 25 and 26. The reactions are essentially

$$\{Th[\eta^5\text{-}(CH_3)_5C_5]_2H_2\}_2 + 4CH_3Cl \rightarrow 2Th[\eta^5\text{-}(CH_3)_5C_5]_2Cl_2 + 4\ CH_4 \quad (25)$$



$$\{U[\eta^5\text{-}(CH_3)_5C_5]_2H_2\}_2 + 4CH_3Cl \rightarrow 0.80U[\eta^5\text{-}(CH_3)_5C_5]_2Cl_2 + 0.20[\eta^5\text{-}(CH_3)_5C_5]_2U(CH_3)(Cl) + 3.2CH_4 + 0.10H_2 \quad (26)$$

quantitative as indicated by accurate gasometric studies and by ^1H NMR analysis (see Experimental Section). In the case of the thorium dihydride, the product is exclusively the dichloride complex, $Th[\eta^5\text{-}(CH_3)_5C_5]_2Cl_2$. In the case of uranium, a mixture of $U[\eta^5\text{-}(CH_3)_5C_5]_2Cl_2$ and $U[\eta^5\text{-}(CH_3)_5C_5]_2(CH_3)Cl$ is obtained

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(49) Irreducible representations A and B under C_2 symmetry.

(50) Irreducible representations A and B under C_2 symmetry.

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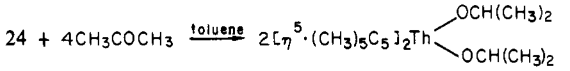
(56) (a) Some examples are $Ti[\eta^5\text{-}(CH_3)_5C_5]_2H_2$, δ 0.28,[52a] $Zr[\eta^5\text{-}(CH_3)_5C_5]_2H_2$, δ 7.46,[52b] $Hf[\eta^5\text{-}(CH_3)_5C_5]_2H_2$, δ 15.6,[52b] $\{Zr[\eta^5\text{-}C_5H_4\text{-}(CH_2)_4]_2(\mu\text{-}H)H\}_2$, δ −1.56(H_{bridge}), 4.59($H_{terminal}$),[52c] $Hf[\eta^5\text{-}(CH_3)_3CC_5H_4]_2(\mu\text{-}H)H\}_2$, δ 1.25(H_{bridge}), 9.45($H_{terminal}$),[56b] $Zr[\eta^5\text{-}(CH_3)_5C_5]_2(OCH_3)H$, δ 5.70.[52f] (b) Couturier, S.; Fointurier, G.; Gautheron, B. *J. Organomet. Chem.* **1980**, *196*, 291–306. (c) By least squares: $\delta_{U-H} = 3.03 \times 10^4(1/T) + 218$.

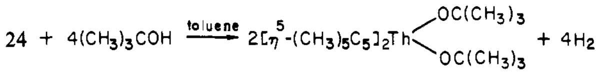
(57) Nujent, L. J. *Int. Rev. Sci.: Inorg. Chem., Ser. Two* **1976**, *7*, 195–219.

(58) (a) Labinger, J. A. In ref 55b, Chapter 11. (b) Labinger, J. A.; Komadina, K. H. *J. Organomet. Chem.* **1978**, *155*, C25–C28. (c) The possible importance of free radical pathways in such processes has only been appreciated recently: Ashby, E. C.; Goel, A. B.; DePriest, R. B. *J. Am. Chem. Soc.* **1980**, *102*, 7779–7780.

in a ratio of 5:1. The presence of the latter complex can most reasonably be attributed to the formation of U[η^5-$(CH_3)_5C_5]_2$-(H)Cl, which is known to lose H_2 to form {U[η^5-$(CH_3)_5C_5]_2Cl\}_3$ (vide infra). The trivalent monochloride has been found to react rapidly with alkyl halides (via a free radical mechanism) to yield **2** and the corresponding U(R)Cl compound.[10,34b,59] Other evidence for the hydridic character of the organoactinide hydrides derives from the rapid addition to ketones (eq 27) and the rapid reaction with alcohols (eq 28) to produce, in both cases, alkoxides.



$$24 + 4CH_3COCH_3 \xrightarrow{\text{toluene}} 2[\eta^5\text{-}(CH_3)_5C_5]_2Th\begin{smallmatrix}OCH(CH_3)_2\\ OCH(CH_3)_2\end{smallmatrix} \tag{27}$$



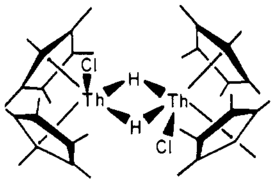
$$24 + 4(CH_3)_3COH \xrightarrow{\text{toluene}} 2[\eta^5\text{-}(CH_3)_5C_5]_2Th\begin{smallmatrix}OC(CH_3)_3\\ OC(CH_3)_3\end{smallmatrix} + 4H_2 \tag{28}$$

Under the reaction conditions employed, an intermediate hydridoalkoxide could not be detected. It will be seen (vide infra) that this result reflects kinetic rather than thermodynamic aspects of the chemistry; i.e., the alkoxyhydrides are not intrinsically unstable.

In a reaction analogous to the alkyl exchange reaction of eq 11, the thorium dihydride, {Th[η^5-$(CH_3)_5C_5]_2(\mu\text{-}H)H\}_2$, undergoes metathesis with Th[η^5-$(CH_3)_5C_5]_2Cl_2$ to form the new chlorohydride complex {Th[η^5-$(CH_3)_5C_5]_2(\mu\text{-}H)Cl\}_2$ (**27**) (eq 29). From

$$\tfrac{1}{2}\{Th[\eta^5\text{-}(CH_3)_5C_5]_2(\mu\text{-}H)H\}_2 + Th[\eta^5\text{-}(CH_3)_5C_5]_2Cl_2 \rightleftharpoons \underset{\mathbf{27}}{\{Th[\eta^5\text{-}(CH_3)_5C_5]_2(\mu\text{-}H)Cl\}_2} \tag{29}$$

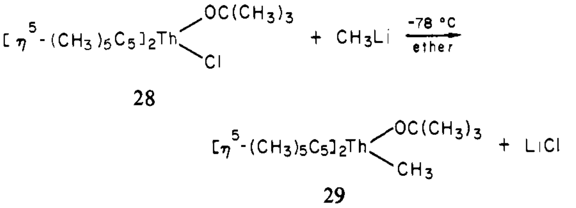
the ^1H NMR spectrum, it can be surmised that the equilibrium shown in eq 29 lies mainly (>95%) to the right. An alternate route to **27** is by hydrogenolysis of a chloroalkyl complex, e.g., Th-[η^5-$(CH_3)_5C_5]_2[CH_2Si(CH_3)_3]Cl$. In the ^1H NMR spectrum of **27**, the resonance due to η^5-$(CH_3)_5C_5$ appears at δ 2.27, and the hydride resonance is at δ 19.0. In the infrared spectrum, strong, broad bands attributable to bridging metal hydride stretching modes are observable at 1229, 1152, 829, and 672 cm^{-1}. The structure of {Th[η^5-$(CH_3)_5C_5]_2(\mu\text{-}H)Cl\}_2$ is thus probably analogous to that of (K) with terminal chloride ligands in place of the terminal hydride ligands (L).



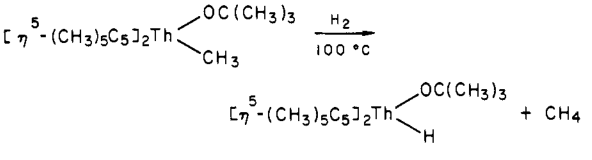
L

In contrast to the above thorium chemistry, hydrogenolysis of uranium chloroalkyl complexes or metathesis of {U[η^5-$(CH_3)_5C_5]_2H_2\}_2$ with U[η^5-$(CH_3)_5C_5]_2Cl_2$ has been found *not* to proceed in a manner analogous to eq 29. Rather, reduction occurs to form the known[34] uranium(III) complex, {U[η^5-$(CH_3)_5C_5]_2Cl\}_3$. The ease of reducing U(IV) to U(III) vis-à-vis the Th(IV) to Th(III) reduction[57] logically explains the comparative instability of {U[η^5-$(CH_3)_5C_5]_2(H)Cl\}_2$.

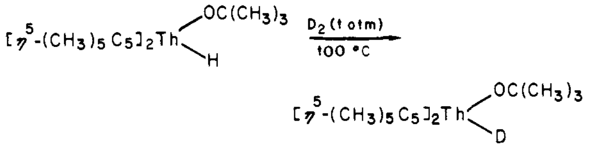
An efficient route to Th[η^5-$(CH_3)_5C_5]_2(OR)H$ complexes is via hydrogenolysis of the corresponding alkoxy alkyl complexes. Thus, the alkoxy chloride **28** can be straightforwardly alkylated with methyllithium (eq 30), and the resulting methyl complex reacted with hydrogen (eq 31) to yield the alkoxy hydride **30**. The hydrogenolysis reaction (31) is decidedly slow compared to M-[η^5-$(CH_3)_5C_5]_2R_2$ hydrogenolysis and requires ca. 15 h at 100 °C (monitored by ^1H NMR). In the infrared spectrum (Table II) of **30**, a strong band at 1359 cm^{-1} is observed, which shifts to 981 cm^{-1} in the corresponding deuteride (prepared according to eq 32); this band is assigned to a terminal Th–H stretching mode ($\nu_{M\text{-}H}/\nu_{M\text{-}D} = 1.39$). There is no evidence in the infrared spectrum for bands due to bridging Th–H–Th stretching modes, and the *tert*-butoxy hydride derivative is assigned the monomeric structure M. In the ^1H NMR spectrum of **30** the hydride resonance appears at δ 17.4 and is absent in the deuteride complex. The only other known monomeric hydrides of the 5f elements are the aforementioned M{N[Si$(CH_3)_3]_2\}_3H$ (M = Th, U) complexes.[53]



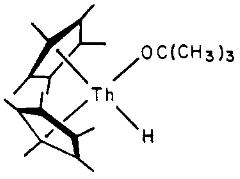
$$\underset{\mathbf{28}}{[\eta^5\text{-}(CH_3)_5C_5]_2Th\begin{smallmatrix}OC(CH_3)_3\\ Cl\end{smallmatrix}} + CH_3Li \xrightarrow[\text{ether}]{-78\ °C} \underset{\mathbf{29}}{[\eta^5\text{-}(CH_3)_5C_5]_2Th\begin{smallmatrix}OC(CH_3)_3\\ CH_3\end{smallmatrix}} + LiCl \tag{30}$$



$$[\eta^5\text{-}(CH_3)_5C_5]_2Th\begin{smallmatrix}OC(CH_3)_3\\ CH_3\end{smallmatrix} \xrightarrow[100\ °C]{H_2} \underset{\mathbf{30}}{[\eta^5\text{-}(CH_3)_5C_5]_2Th\begin{smallmatrix}OC(CH_3)_3\\ H\end{smallmatrix}} + CH_4 \tag{31}$$

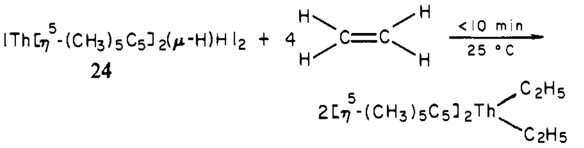


$$[\eta^5\text{-}(CH_3)_5C_5]_2Th\begin{smallmatrix}OC(CH_3)_3\\ H\end{smallmatrix} \xrightarrow[100\ °C]{D_2\ (1\ atm)} [\eta^5\text{-}(CH_3)_5C_5]_2Th\begin{smallmatrix}OC(CH_3)_3\\ D\end{smallmatrix} \tag{32}$$



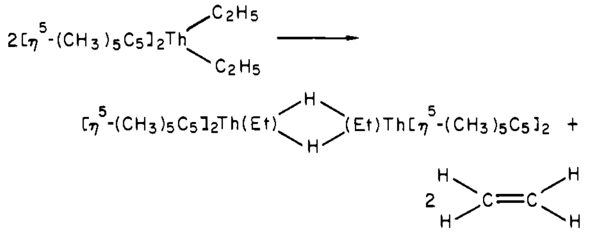
M

Organoactinide Hydrides. Olefin and Molecular Hydrogen Activation. The thorium hydride {Th[η^5-$(CH_3)_5C_5]_2(\mu\text{-}H)H\}_2$ was also found to activate ethylene. Thus **24** reacts rapidly and quantitatively with ethylene in toluene solution at room temperature to yield the corresponding diethyl complex **31** (eq 33).



$$\underset{\mathbf{24}}{\{Th[\eta^5\text{-}(CH_3)_5C_5]_2(\mu\text{-}H)H\}_2} + 4\,H_2C{=}CH_2 \xrightarrow[25\ °C]{<10\ min} \underset{\mathbf{31}}{2[\eta^5\text{-}(CH_3)_5C_5]_2Th\begin{smallmatrix}C_2H_5\\ C_2H_5\end{smallmatrix}} \tag{33}$$

This compound appears to be indefinitely stable with respect to β-hydride elimination at room temperature both in the solid state and in solution in the dark. Interestingly, however, the heat and/or light produced by the glowbar of an infrared spectrometer-induced decomposition of **31**. Thus, bubbles of gas were observed in a Nujol mull and strong, broad bands (increasing with time) were observed at 1216, 1132, 827, and 674 cm^{-1}. These transitions are characteristic of bridging hydride ligands, and we tentatively suggest the reaction of eq 34; we have previously demonstrated photoinduced β-hydride elimination in the Th(η^5-$C_5H_5)_3R$ and



$$2[\eta^5\text{-}(CH_3)_5C_5]_2Th\begin{smallmatrix}C_2H_5\\ C_2H_5\end{smallmatrix} \longrightarrow [\eta^5\text{-}(CH_3)_5C_5]_2Th(Et)\begin{smallmatrix}H\\ H\end{smallmatrix}(Et)Th[\eta^5\text{-}(CH_3)_5C_5]_2 + 2\,H_2C{=}CH_2 \tag{34}$$

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[59] (a) Finke, R. G.; Hirose, Y.; Gaughan, G. *J. Chem. Soc., Chem. Commun.* **1981**, 232–234. (b) Finke, R. G., Schiraldi, D. A.; Hirose, Y. *J. Am. Chem. Soc.* **1981**, *103*, 1875–1876. (c) Finke, R. G., private communication of electrochemical results on Th[$(CH_3)_5C_5]_2Cl_2$ and U[$(CH_3)_5$-$C_5]_2Cl_2$.

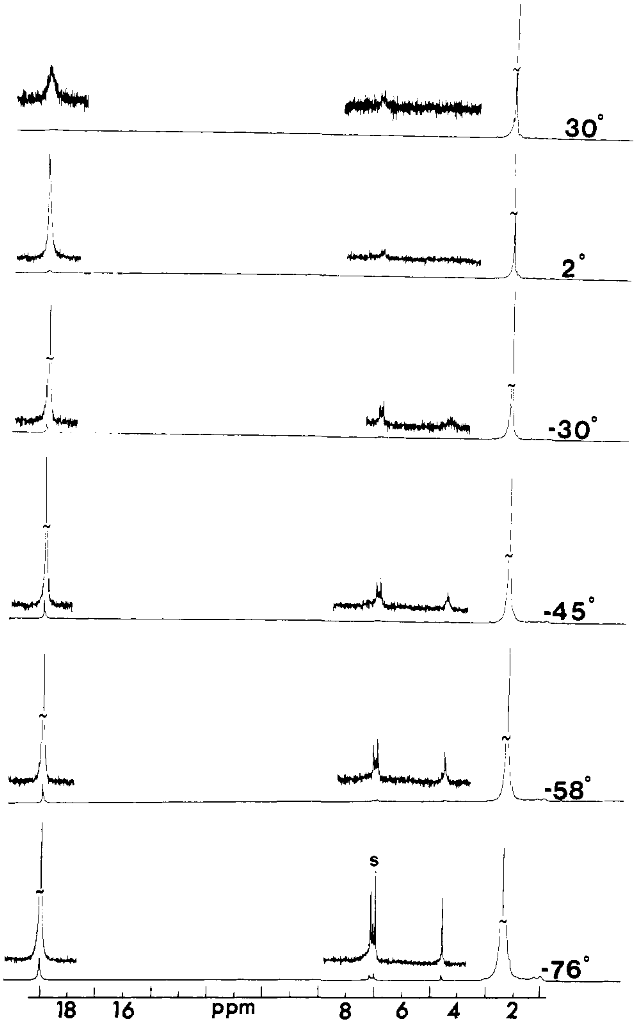

Figure 4. Variable-temperature ^1H NMR spectra (FT, 90 MHz) of a solution of $\{Th[\eta^5-(CH_3)_5C_5]_2(\mu-H)H\}_2$ (9.4×10^{-4} M) in $C_6D_5CD_3$ under 0.75 atm of H_2 (s = toluene-d_7).

$U(\eta^5-C_5H_5)_3R$ series.[60] Further studies of this process are in progress.

Exposure of a toluene solution of **24** to deuterium gas results in facile exchange of the hydride ligands for deuterium (eq 35).

$$\{Th[\eta^5-(CH_3)_5C_5]_2(\mu-H)H\}_2 \underset{H_2}{\overset{D_2}{\rightleftharpoons}} \{Th[\eta^5-(CH_3)_5C_5]_2(\mu-D)D\}_2 \quad (35)$$

That such processes are exceedingly rapid is quantified by dynamic ^1H NMR experiments (Figure 4). At -76 °C, a 9.4×10^{-4} M toluene-d_8 solution of **24** under 0.75 atm of H_2 gas (2.8×10^{-4} M)[61] exhibits sharp singlets for the hydride resonance (δ 19.2) and for dissolved H_2 (δ 4.65). As the temperature is raised, both resonances broaden, with the least populated site (H_2) broadening the most rapidly. In the absence of **24**, the variable-temperature spectrum of dissolved H_2 remains unchanged. Additional support for a hydride–H_2 site-exchange process is provided by magnetization transfer experiments[62] (Figure 5). These confirm that the hydride and H_2 resonances, and only these resonances, are involved in an exchange process. Application of the appropriate lineshape equations[31,63] to the sample of Figure 4 yields a preexchange lifetime for dissolved H_2 at -30 °C of 0.012 ± 0.001 s. The line width of the H_2 signal at this temperature is proportional to the concentration of **24** over an approximately threefold concentration range, consistent with a bimolecular process. These data yield a bimolecular rate constant for hydride–H_2 exchange at -30 °C of 7×10^4 L mol^{-1} s^{-1}.

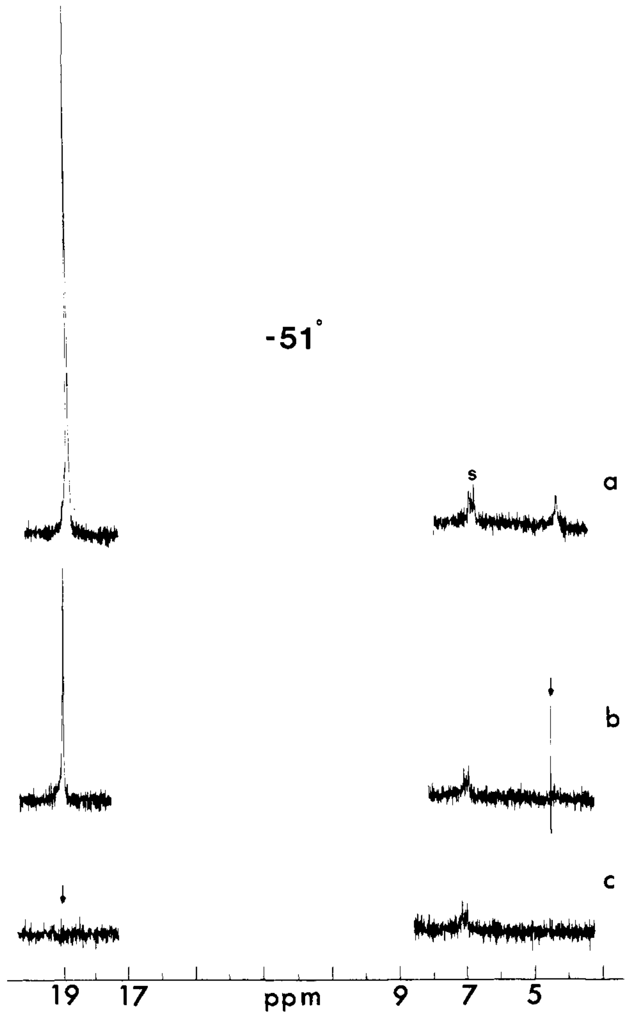

Figure 5. Magnetization transfer experiment on the sample of Figure 4 at -51 °C. Arrows in b and c indicate the position of the saturating radio frequency field (s = toluene-d_7).

Organoactinide Hydrides as Olefin Hydrogenation Catalysts. The relatively facile insertion of ethylene into actinide–hydride bonds and the ready hydrogenolysis of actinide–carbon bonds suggested a possible cycle for olefin hydrogenation. Experiments with **24**, **25**, and 1-hexene (see Experimental Section for details) verified that a sequence of such processes can indeed be made catalytic. Under the conditions shown in Figure 6, typical initial turnover frequencies for 1-hexene hydrogenation per MH_2 moiety at 25 °C, 0.9 atm of H_2, were 0.5 h^{-1} (M = Th) and 70 h^{-1} (M = U). The hydrides can also be recovered unchanged when the olefin is exhausted. In a preparative scale reaction, the uranium-1-hexene system functioned for 812 turnovers with no detectable decay in catalytic efficiency. In regard to other substrates, it was also found that diphenylacetylene could be hydrogenated under the same conditions to yield 1,2-diphenylethane. Further studies of the scope and mechanism of this reaction are in progress. On the basis of the information at hand, a plausible catalytic scenario for **24** (invoking either monomer or dimer) can be generated (Scheme II). For the more reactive uranium hydride, the involvement of the trivalent species $\{U[(CH_3)_5C_5]_2H\}_x$ seems likely,

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[60] (a) Kalina, D. G.; Marks, T. J.; Wachter, W. A. *J. Am. Chem. Soc.* **1977**, *99*, 3877–3879. (b) Kalina, D. G.; Mintz, E. A.; Marks, T. J. *J. Am. Chem. Soc.*, in press.

[61] Concentrations were determined by integration vs. the toluene-d_8 ^1H resonances and then calibration of the solvent intensities with weighed amounts of ferrocene.

[62] (a) McFarlane, W.; Rycroft, W. *Annu. Rep. NMR Spectrosc.* **1979**, *9*, 377–379. (b) Faller, J. W. In Nachod, F. C., Zuckerman, J. J., Eds. "Determination of Organic Structures by Physical Methods"; Academic Press: New York, 1973, Vol. 5, pp 75–106.

[63] Anet, F. A. L.; Basus, V. J. *J. Magn. Reson.* **1978**, *32*, 339–343.

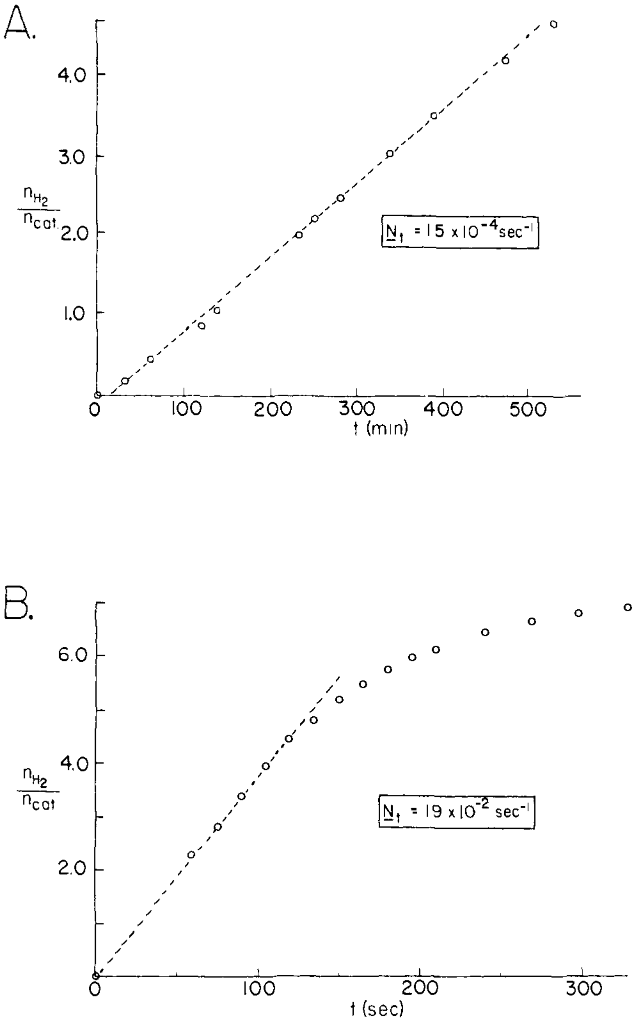
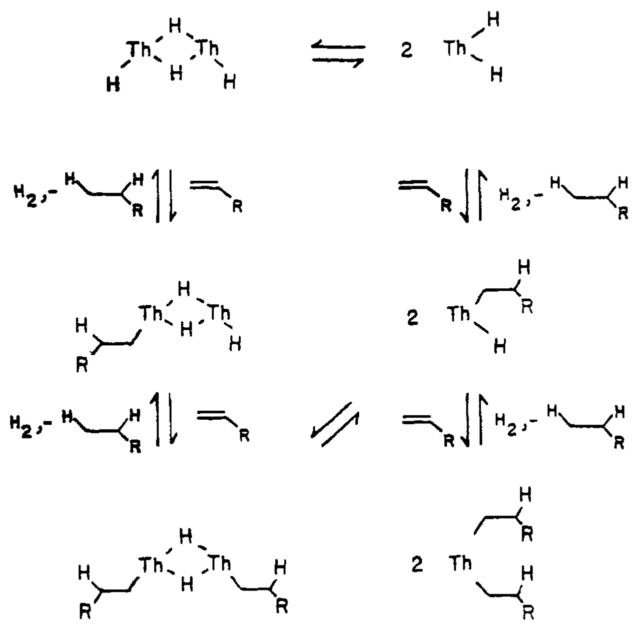


Figure 6. Plots of H_2 uptake per actinide equivalent as a function of time for the hydrogenation of 1-hexene by A, $\{Th[\eta^5\text{-}(CH_3)_5C_5]_2(\mu\text{-}H)H\}_2$, and B, $\{U[\eta^5\text{-}(CH_3)_5C_5]_2(\mu\text{-}H)H\}_2$. The solvent is toluene and the temperature is 24 °C. N_t is the turnover frequency during the initial part of the reaction, and is derived from the slope of the dashed lines.

Scheme II



and the possibility of binuclear oxidative addition/reductive elimination as well as more extensive free radical chemistry[34,59] cannot be dismissed.

We report elsewhere[64] that upon high area metal oxide supports, the $M[\eta^5\text{-}(CH_3)_5C_5]_2(CH_3)_2$ complexes are precursors for potent heterogeneous olefin hydrogenation catalysts. For example, turnover frequencies for propylene hydrogenation are comparable to those for supported platinum under the same conditions.

Discussion

The results of this study demonstrate that it is possible to achieve a degree of coordinative unsaturation in actinide hydrocarbyls which preserves pragmatically important thermal stability while still promoting high chemical reactivity. The $M[\eta^5\text{-}(CH_3)_5C_5]_2R_2$ and $M[\eta^5\text{-}(CH_3)_5C_5]_2R(Cl)$ complexes of thorium and uranium are the most reactive and chemically versatile actinide hydrocarbyls studied to date. They undergo a wide variety of previously unobserved reaction patterns and serve as important precursors for many new organoactinides, including molecular hydrides. In discussing the present results, the contrast between thorium and uranium provides information on the importance of 5f electron configuration in actinide hydrocarbyl chemistry (Th(IV) has a $5f^0$ configuration and U(IV), $5f^2$). An instructive perspective is also obtained by considering the characteristics of the more saturated $M(\eta^5\text{-}C_5H_5)_3R$ actinide species[2,3] as well as the (presumably) closest analogues among the d elements, the $M'(C_5H_5)_2R_2$ and $M'[\eta^5\text{-}(CH_3)_5C_5]_2R_2$ hydrocarbyls of group 4B.

Much of the chemistry of the bis(pentamethylcyclopentadienyl) actinide hydrocarbyls suggests significant polarity in the metal–carbon σ bonding. Thus, the rapid reactions with acetone and alcohols are typical of polar organometals.[1] The trend of thorium being more reactive than uranium was also observed in the $M(\eta^5\text{-}C_5H_5)_3R$ series[2,3] and suggests greater polarity in the thorium-to-ligand bonding. However, the metal–carbon σ bonds in the present case are far more reactive than in the tris(cyclopentadienyl) series, presumably reflecting the relatively high coordinative unsaturation (steric and/or electronic). As an illustration, $Th(\eta^5\text{-}C_5H_5)_3CH_3$ and $U(\eta^5\text{-}C_5H_5)_3CH_3$ react only slowly with *tert*-butyl alcohol and acetone under comparable conditions, although the rate trend Th > U is still preserved.[65] In regard to other ligand systems, the greater ionicity of thorium over uranium is also evident in chemical, He I and He II PES spectroscopic, and SCF-Xα results on the $M(\eta^8\text{-}C_8H_8)_2$ sandwich compounds.[2,66] Structurally and stoichiometrically similar group 4B hydrocarbyls also undergo alcoholysis to yield alkoxides,[67] however, from the limited data at hand, it appears that addition to ketones is not as facile.[68]

The iodinolysis of the $M[\eta^5\text{-}(CH_3)_5C_5]_2R_2$ complexes is consistent with but not necessarily indicative of polar bonding.[67b,69] Interestingly, the similarity in rates between thorium and uranium suggests that the higher oxidation states of uranium (the +5 and +6 states are accessible for uranium but not for thorium[2,57]) are not involved. We show elsewhere that stronger oxidizing agents may alter this situation.[46] The $M(\eta^5\text{-}C_5H_5)_3R$ complexes are far less reactive with iodine, again reflecting the greater saturation and congestion of the actinide coordination sphere.[65] The group 4B hydrocarbyls also undergo facile halogenolysis;[67] in the case of $Zr(C_5H_5)_2(R)X$ systems, retention of configuration at R has

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(64) Bowman, R. G.; Nakamura, R.; Burwell, R. L., Jr.,; Marks, T. J. *J. Chem. Soc., Chem. Commun.* **1981**, 257-8.

(65) Seyam, A. M.; Marks, T. J., unpublished results.

(66) (a) Streitwieser, A., Jr. In ref 2a, Chapter 5. (b) For PES studies of $M[(CH_3)_5C_5]_2X_2$ compounds, M = Zr, Th, U; X = CH_3, Cl, see: Ciliberto, E.; Condorelli, G.; Fagan, P. J.; Manriquez, J. M.; Fragalà, I.; Marks, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 4755-9.

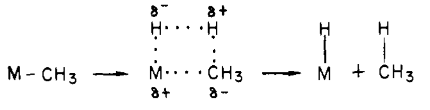
(67) (a) Wailes, P. C.; Coutts, R. S. P.; Weigold, H. "Organometallic Chemistry of Titanium, Zirconium, and Hafnium"; Academic Press: New York, 1974; Chapters III and IV. (b) Schwartz, J.; Labinger, J. A. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 333-34.

(68) (a) Gell, K. I.; Schwartz, J. *J. Chem. Soc., Chem. Commun.* **1979**, 244-246. (b) Carr, D. B.; Schwartz, J. *J. Am. Chem. Soc.* **1979**, *101*, 3521-31. (c) Yasuda, H.; Kajihara, Y.; Machima, K.; Nagasuma, K.; Nakamura, A. *Chem. Lett.* **1981**, 671-4.

(69) (a) Reference 1b, pp 532-542. (b) Matteson, D. S. "Organometallic Reaction Mechanisms"; Academic Press: New York, 1974; pp 109-120.

been interpreted in terms of a closed, four-center transition state.[67b]

The $M[\eta^5\text{-}(CH_3)_5C_5]_2R_2$ compounds undergo rapid metal–carbon σ bond hydrogenolysis to yield hydrides. That the rates for M = Th and U are qualitatively similar argues again that changes in formal oxidation state are not involved. Rather, the simplest plausible mechanism appears to be a closed, four-center transition state (eq 36). Hydrogenolysis via such a nonoxidative pathway is well documented in main-group chemistry,[30,70,71] the alkyls of lithium, magnesium, zinc, and aluminum being particularly relevant examples.[70] A transition state similar to N has also been proposed for bis(cyclopentadienyl)zirconium systems on the basis of extended Hückel molecular orbital calculations[72] and mechanistic studies.[73,74] Considering the polarity of the bonding in the present case, it is attractive to view eq 36 as an *intramolecular*, *heterolytic* H_2 cleavage. This nonoxidative hydrogen activation pathway has been previously discussed for several transition-metal systems,[75] although the requisite basic functionality is usually exomolecular (eq 37). Four-center processes



$$M{-}CH_3 \longrightarrow \begin{matrix} \overset{\delta-}{H} \cdots \overset{\delta+}{H} \\ \vdots \quad\quad \vdots \\ \underset{\delta+}{M} \cdots \underset{\delta-}{CH_3} \end{matrix} \longrightarrow \begin{matrix} H & & H \\ | & & | \\ M & + & CH_3 \end{matrix} \qquad (36)$$

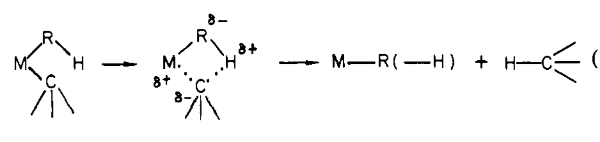
N

$$M + H_2 + B \rightarrow M\cdots\overset{\delta-}{H}\cdots\overset{\delta+}{H}\cdots B \rightarrow M\overset{-}{-H} + \overset{+}{H}{-}B \qquad (37)$$

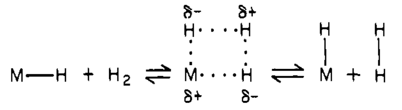
have also recently been proposed for H–D exchange reactions in $M\{N[Si(CH_3)_3]_2\}_3H$ actinide complexes.[76] The hydrogenolysis of the metal–carbon σ bond in $Th[\eta^5\text{-}(CH_3)_5C_5]_2[OC(CH_3)_3]CH_3$ (eq 31) is markedly slower than in the actinide dialkyls. It seems likely that the demonstrated tendency of alkoxide ligands to transfer appreciable electron density to oxophilic metal centers[77,78] deactivates the complex by reducing the positive character of the actinide ion. The mechanism of actinide-to-carbon σ bond hydrogenolysis is under further investigation.

It is noteworthy that the rate of hydrogenolysis of the actinide bis(hydrocarbyl) complexes appears to be considerably greater than in analogous group 4B systems.[52a,56b,67] The explanation for this reasonably lies in the greater polarity of the actinide-to-carbon bonds and in the relatively greater unsaturation of the larger metal center with an identical ligand array. The importance of relative bond polarity has been demonstrated in the rates of hydrogenolysis of alkali-metal alkyls, where reactivity trends can be roughly correlated with differences in Pauling electronegativity.[70c] In addition, the influence of the actinide ion coordination environment should not be minimized, and a particularly graphic example is found in the attempted hydrogenolysis of the more coordinatively saturated complex $Th(\eta^5\text{-}C_5H_5)_3CH_3$.[79] No reaction is observed in the course of days at room temperature (1 atm of H_2)![79] At higher temperatures, thermal decomposition of the complex competes with any hydrogenolysis which may be occurring.

The actinide–carbon bond polarity likely plays an important role in the C–H activation processes observed here. The rate-determining step in eq 12 and presumably eq 14 could be viewed as an intramolecular metallation (eq 38) to yield the corresponding benzyne, alkylidene, etc. Again, reaction rates appear to be considerably in excess of those in analogous group 4B systems, plausibly reflecting the enhanced polarity and coordinative unsaturation. We have previously shown that the thermolysis of the thorium and uranium $M(\eta^5\text{-}C_5H_5)_3R$ derivatives takes place via an intramolecular cyclopentadienyl hydrogen atom abstraction process analogous to eq 38; there is retention of configuration at the α carbon atom of R.[2b,3a,b,d]


(38)

The properties of the organoactinide hydrides also reflect significant metal–ligand bond polarity. Thus, rapid reactions with alcohols and ketones are indices of "hydridic" character.[58] Analogous Ti, Zr, and Hf complexes undergo similar reactions.[58,67] However, differences in preferred coordination numbers are evident in the dimeric structures of the actinide dihydride derivatives (formally nine-coordinate) and the monomeric structures of the Ti, Zr, and $M[\eta^5\text{-}(CH_3)_5C_5]_2H_2$ complexes (formally eight-coordinate).[52a,b] The organoactinide hydrides also activate molecular hydrogen. In the case of the dimeric thorium hydride **22**, the degenerate process is remarkable in terms of the rapidity. A nonoxidative, heterolytic cleavage process (eq 39) again appears plausible. That the related hydride $Th[\eta^5\text{-}(CH_3)_5C_5][OC(CH_3)_3]H$ exchanges more slowly (eq 32) may reflect the aforementioned electronic characteristics of the alkoxide ligand and/or that the presence of two metal ions, and available bridging hydride positions accelerates the activation and cleavage. The hydride and H_2 chemical shifts in the ^1H NMR give no indication of H_2 coordination prior to exchange. The contrast between **22** and **23** is one of the strongest divergences of thorium and uranium chemistry observed to date. It reflects the tendency of the latter element to shuttle between the +3 and +4 oxidation states; considerable evidence from this Laboratory[2,60] and elsewhere[57,59c] indicates that Th(III) is far less accessible than U(III).



$$M{-}H + H_2 \rightleftharpoons \begin{matrix} \overset{\delta-}{H} \cdots \overset{\delta+}{H} \\ \vdots \quad\quad \vdots \\ \underset{\delta+}{M} \cdots \underset{\delta-}{H} \end{matrix} \rightleftharpoons \begin{matrix} H & & H \\ | & & | \\ M & + & H \end{matrix} \qquad (39)$$

The organothorium hydrides (and presumably those of uranium) react readily with terminal olefins to form alkyls. This process can be coupled to the aforementioned hydrogenolysis reaction to effect catalytic hydrogenation of the olefin. An interesting contrast to the thorium hydride addition of ethylene to yield a diethyl compound (eq 33) is the behavior of $Zr[\eta^5\text{-}(CH_3)_5C_5]_2H_2$, which also adds ethylene, but ultimately forms a metallocycle (eq 40).[74b] This difference in behavior appears to reflect the greater instability of Zr(IV) relative to Th(IV) with respect to reductive elimination.[59c,74b,80]

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(71) A similar heterolytic cleavage has been proposed for the hydroxide-catalyzed exchange of deuterium gas with water

$$H_2O + D_2 + {}^-OH \rightarrow H{-}O\cdots H\cdots D\cdots D\cdots O{-}H^- \rightarrow HO^- + HD + HDO$$

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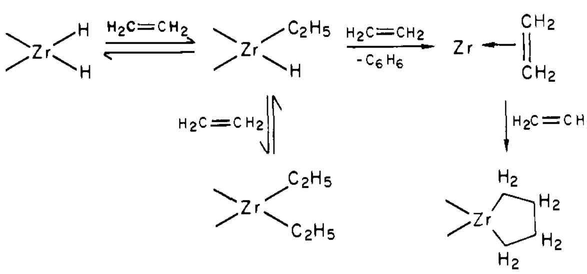

(40)

Conclusions

This work demonstrates that proper ligational adjustment can lead to thermally stable yet highly reactive actinide hydrocarbyls and hydrides. It is evident that such species have a rich and diverse chemistry. In placing this chemistry in perspective, there appear distinct similarities to main-group and early transition-metal[66b] reactivity patterns; there are also striking differences. In regard to the group 4B systems, differences in structure and reactivity appear to reflect the relative availability of metal formal oxidation states, the greater polarity of actinide-element bonds, the larger actinide ionic radii, and the commensurate increase in available coordination sites about the 5f ion. The actinide chemistry is by no means monolithic, and the observed chemical differences between the thorium and uranium arise from differences in accessible oxidation states as well as in metal-ligand bond polarity.

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Effects of Ligand Substituents on Excited-State Reactivity and Overall Photoredox Behavior for (Polypyridyl)ruthenium(II) Complexes. A Laser Flash Study with Potential Reductive Quenchers

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Abstract: This paper reports results of a study of the quenching of excited states of RuL_3^{2+} ruthenium complexes and subsequent reactions occurring with potential reductants—amines, aromatic ethers, *p*-hydroquinone, and water. The ligands, L, contain electron-withdrawing carboxy ester groups in the meta (5,5′) (**1**) or para (4,4′) (**2**) positions of the bipyridine ring; this substitution produces anodic shifts in both the 2+/+ and 3+/2+ electrochemical potentials for the complexes, rendering them easier to reduce but more difficult to oxidize. Both laser flash and conventional spectroscopic techniques have been used to monitor the primary quencher products. Thus the photoreduction of one complex (**1**) with triethylamine can be shown to consist of two components, a primary photoprocess and a subsequent dark reaction, while for **2** only the first process is observed. The reduced complexes, RuL_3^+, produced in the reaction are relatively stable in dry, deaerated solutions but can be observed to react rapidly with both oxygen and water. The reaction of reduced **1** with water produces a relatively stable product which appears to be a ligand (probably carboxy ester)-protonated species, RuL_3H^{2+}; this product yields hydrogen and the starting complex **1** upon treatment with colloidal platinum. Excited states of **1** are also quenched by aromatic ethers and hydroquinone in processes giving transients having spectra similar to that of reduced **1**; no permanent chemistry is observed with these quenchers and rapid first-order decay of the transient is observed. A reaction of excited **1** with water is also observed; this reaction ($k = 1 \times 10^7\ M^{-1}\ s^{-1}$) gives a short-lived transient ($\tau = 250$ ns) which is apparently not a redox product but more likely an adduct or ligand-protonated species.

Introduction

A large number of investigations with polypyridyl complexes of ruthenium(II), osmium(II), iridium(III), and chromium(III) have shown that excited states of these complexes can be both oxidized and reduced by a variety of reagents.[3-21] The well-characterized spectroscopic properties[22-26] of these complexes and their one-electron redox products have facilitated study of processes

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