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Organo-f-Element Thermochemistry. Thorium vs. Uranium and Ancillary Ligand Effects on Metal-Ligand Bond Disruption Enthalpies in Bis(pentamethylcyclopentadienyl)actinide Bis(hydrocarbyls) and Bis(pentamethylcyclopentadienyl)alkoxyactinide Hydrides and Hydrocarbyls

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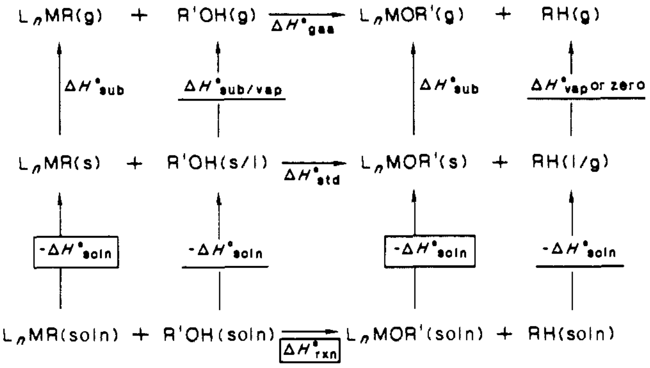
Abstract: Thorium- and uranium-ligand bond disruption enthalpies (D(M-R)) have been determined for a series of complexes of the type $Cp'_2M(R)X$, where M = Th or U, $Cp' = \eta^5\text{-}(CH_3)_5C_5$, R = alkyl, aryl, or hydride, and X = alkyl, chloride, or alkoxide. The thermodynamic data were obtained by anaerobic, batch-titration, solution calorimetry from the enthalpies of solution of the organo-f-element complexes in toluene and from the subsequent enthalpies of alcoholysis with *tert*-butyl alcohol or methanol. Average (of $Cp'_2U(R)\text{-}R$ and $Cp'_2U(OR')\text{-}R$) values for the nonstepwise alcoholysis of the Cp'_2UR_2 series (gas phase, solution phase, in kcal/mol, quantity in parentheses = 2σ) are as follows: 67.8 (3.5), 71.8 (3.3) (R = CH_3), 61.8 (2.7), 58.3 (2.1) (R = benzyl), and 73.3 (3.3), 73.3 (3.1) (R = $CH_2Si(CH_3)_3$). For the $Cp'_2U(Cl)R$ series, D(U-R) = 70.1 (1.7), 74.6 (1.6) (R = CH_3), 66.1 (2.8), 63.0 (2.7) (R = benzyl), 86.7 (2.6), 85.5 (2.6) (R = phenyl), and 90.5 (2.3), 89.2 (2.2) for $Cp'_2Th(C_6H_5)Cl$. Data for hydride/alkyl pairs include $Cp'_2U(R)\text{-}OR'$ ($R' = Si[C(CH_3)_3](CH_3)_2$) where D(U-R) = 76.4 (1.1), 82.4 (7) (R = H) and 72.4 (1.4), 76.0 (1.2) (R = CH_3) as well as $Cp'_2Th(R)\text{-}OR'$ ($R' = CH[C(CH_3)_3]_2$) where D(Th-R) = 87.8 (1.5), 93.3 (1.2) (R = H) and 81.5 (3.1), 81.2 (3.1) (R = $n\text{-}C_4H_9$). For $Cp'_2Th(H)\{O\text{-}2,6\text{-}[C(CH_3)_3]C_6H_3\}$, D(Th-H) = 84.9 (1.2), 92.1 (1.0). For corresponding Th/U pairs, $D(\text{Th-R}) - D(\text{U-R}) \approx 10$ kcal/mol. Alkoxide ancillary ligands appear to strengthen the M-R bond by several kcal/mol and to depress $D(\text{M-H})_{gas} - D(\text{M-R})_{gas}$ to $\lesssim 5$ kcal/mol. Chloride coligands have a smaller effect on D(M-R). These results show that ancillary ligands should significantly affect the thermodynamics of important M-H/M-C transposition processes such as β-H elimination.

Scheme I. Thermodynamic Cycle for the Measurement of M-R Bond Disruption Enthalpies[a]



[a] Boxed entries—measured in this research. Underlined entries—literature values.

There is a growing awareness of the unique insight that metal-ligand bond energy data can provide into the pathways of numerous organometallic chemical transformations (stoichiometric, catalytic, and biological).[2-4] Consequently, increasing efforts are being devoted to the measurement of these parameters, with one major focus being on middle and late first-row transition elements.[2,5-22] Our interest in understanding the driving force for a number of nonclassical reaction patterns involving organoactinides[23] (and by extension, analogous processes involving early

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transition metals and lanthanides) has motivated a detailed study of actinide–ligand bonding energetics.[24,25]

In earlier reports, we discussed thermodynamic trends within the Cp'_2ThR_2 ($Cp' = \eta^5\text{-}(CH_3)_5$; R = hydrocarbyl, hydride, or amide)[24a] and Cp_3ThR ($Cp = \eta^5\text{-}C_5H_5$; R = hydrocarbyl)[24b] series of molecules. Several interesting bond energy patterns were found which, in turn, raised questions about the generality of such trends among the acinitides and the sensitivity of these trends to various ancillary ligands. Furthermore, it would be of great interest to learn whether perceived differences in chemical reactivity[23] and/or metal–ligand bond covalency[23,26–30] between thorium and uranium organometallic compounds have any basis in metal–ligand bonding energetics, and whether the effects of coligands, which have major influences on chemical and structural properties, are similar for thorium and uranium.

In this contribution, we extend our organoactinide thermochemical investigations to uranium in a study of U–R bonding energetics in the series $Cp'_2U(R)X$. Here, R = hydrocarbyl or hydride, and X = a variety of ancillary ligands (hydrocarbyl, chloride, and alkoxide). We also report ancillary ligand effects on $D(\text{Th–R})$ in the thorium alkoxide series $Cp'_2Th(R)OR'$, R = hydrocarbyl or hydride. As in our previous studies,[24] the metal–ligand bond disruption enthalpy[2a] is formally expressed as in eq 1 for the homolytic process depicted in eq 2. The experimental

$$D(\text{M–R}) = \Delta H_f{}^\circ[L_nM(g)] + \Delta H_f{}^\circ[R^\bullet(g)] - \Delta H_f{}^\circ[L_nMR(g)] \quad (1)$$

$$L_nM\text{–}R(g) \rightarrow L_nM(g) + R^\bullet(g) \quad (2)$$

technique employed is the measurement of M–R alcoholysis (eq 3) enthalpies by titration calorimetry.[31] The derived thermochemical data are related to bond disruption enthalpies as shown in eq 4 and in Scheme I.

$$L_nM\text{–}R + R'OH \rightarrow L_nM\text{–}OR' + RH \quad (3)$$

$$-\Delta H^\circ{}_{gas} = D(L_nM\text{–}OR') + D(\text{R–H}) - D(L_nM\text{–}R) - D(\text{R'O–H}) \quad (4)$$

Experimental Section

Synthetic Methods. All organoactinide compounds were handled in Schlenk-type glassware on a dual manifold Schlenk line or interfaced to a high vacuum (10^{-5} torr) system. Solid transfers were performed in a glovebox (Vacuum Atmospheres Corporation) equipped with an atmosphere purification system, maintained under a nitrogen atmosphere. Argon (Matheson, prepurified), deuterium (Air Products), and hydrogen (Linde) were purified by passage through sequential columns of MnO[32] and Davison 4-Å molecular sieves. The reactions with gases were carried out on the high vacuum system with use of a mercury-filled manometer.

Toluene, heptane, pentane, tetrahydrofuran (THF), benzene, and diethyl ether (Mallinckrodt) were dried over sodium and Davison 4-Å molecular sieves, distilled from Na/K–benzophenone under a nitrogen atmosphere, and condensed into evacuated storage bulbs on the vacuum line. For the calorimetric studies, toluene was further purified by an additional distillation on the vacuum system from Na/K alloy. The *tert*-butyl alcohol was distilled on the vacuum system first from activated Davison 4-Å molecular sieves and then from calcium hydride. The methanol was distilled from magnesium turnings under a nitrogen atmosphere. Both of these alcohols were deoxygenated by four freeze–thaw degassing cycles.

The complexes $Cp'_2U(CH_3)_2$[33] (**1**), $Cp'_2U(CH_3)Cl$[33] (**2**), $Cp'_2U(CH_2C_6H_5)_2$[33] (**3**), $Cp'_2U(CH_2C_6H_5)Cl$[33] (**4**), $Cp'_2U[CH_2Si(CH_3)_3]_2$[33] (**5**), $Cp'_2U(C_6H_5)Cl$[33] (**6**), $Cp'_2Th(C_6H_5)Cl$[33] (**7**), $Cp'_2Th(H)\{O\text{-}2,6[C(CH_3)_3]_2C_6H_3\}$,[3b] (**8**), $Cp'_2Th(H)\{OCH[C(CH_3)_3]_2\}$[3b] (**9**), $Cp'_2Th\{OCH[C(CH_3)_3]_2\}(OCH_3)$[3b] (**10**), and $Cp'_2Th(n\text{-}C_4H_9)\{OCH[C(CH_3)_3]_2\}$[3b] (**11**) were prepared and purified as previously described.

Analytical Methods. Proton NMR spectra were recorded on either a JEOL FX-90 (FT, 90 MHz) or Varian EM-360 (CW, 60 MHz) spectrometer. Infrared spectra were recorded on a Perkin-Elmer 599A spectrophotometer by using Nujol or Fluorolube mulls, sandwiched between KBr plates in an O-ring sealed airtight holder. Spectra were calibrated with polystyrene film. Elemental analyses were performed by Dornis and Kolbe Mikroanalytisches Laboratorium, Mülheim, West Germany. Cryoscopic molecular weight determinations were carried out in benzene solution by using a modified Knauer Type 24.00 instrument.

Synthesis of $Cp'_2U[OC(CH_3)_3]_2$ (12). To 0.35 g (0.51 mmol) of $Cp'_2U[CH_2Si(CH_3)_3]_2$ dissolved in ca. 20 mL of diethyl ether at −78 °C was added 0.08 g (1 mmol) of *tert*-butyl alcohol. After stirring for 10 min, the solution was allowed to warm to room temperature and stirred for an additional hour. The solvent was then removed, in vacuo, and heptane (ca. 10 mL) was distilled on to the green residue. The resulting solution was filtered, the filtrate volume was reduced (ca. 2 mL), and slow cooling of the solution to −78 °C produced greenish-yellow crystals: yield 0.21 g (62%); ^1H NMR (C_6D_6) δ 6.47 (s, 18 H), −0.30 (s, 30 H); IR (Nujol mull, cm^{-1}) 1350 (vs), 1220 (s), 1175 (sh), 1170 (vs), 1012 (m), 960 (vs), 940 (vs), 770 (s), 512 (m), 480 (m). Anal. Calcd for $C_{28}H_{48}UO_2$: C, 51.38; H, 7.34. Found: C, 51.44; H, 7.13.

$Cp'_2U[OC(CH_3)_3]Cl$ (13). By using a procedure similar to that employed in the synthesis of $Cp'_2Th[OC(CH_3)_3]Cl$,[3b] 0.87 g (1.5 mmol) of Cp'_2UCl_2 and 0.17 g (1.5 mmol) of potassium *tert*-butoxide were dissolved in ca. 60 mL of diethyl ether at room temperature, and the solution

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was stirred for 3 h. After removal of the solvent (in vacuo), heptane (ca. 15 mL) was distilled onto the reddish-brown residue, and the resulting solution was filtered. The filtrate volume was reduced to ca. 2 mL, and the solution was slowly cooled to 0 °C, yielding 0.46 g (50% yield) of the red crystalline product: ^{1}H NMR (C_6D_6) δ 33.5 (s, 9 H), 1.63 (s, 30 H), IR (Nujol mull, cm^{-1}) 1360 (s), 1230 (m), 1170 (s), 1015 (m), 942 (vs), 775 (m), 522 (m), 475 (m). Anal. Calcd for $C_{24}H_{39}UOCl$: C, 45.97; H, 6.23; Cl, 5.67. Found: C, 45.99; H, 6.26; Cl, 6.09.

$Cp'_2U(CH_3)\{OSi[C(CH_3)_3](CH_3)_2\}$ (14). $Cp'_2U(CH_3)_2$ (0.60 g, 1.1 mmol) was dissolved in ca. 20 mL of toluene, and the solution was cooled to −78 °C. To this solution was added dropwise over a period of 1 h a solution containing 0.175 mL (1.11 mmol) of $[C(CH_3)_3](CH_3)_2SiOH$ (Petrarch, dried as described previously[34,35]) in ca. 20 mL of toluene. Upon the completion of the addition of the silanol, the reaction solution was stirred for an additional hour at −78 °C and then allowed to slowly warm to room temperature. At this point, the solvent was evaporated, and the resulting solids were dried in vacuo overnight. Heptane (ca. 10 mL) was distilled onto the solids, and the solution was filtered, yielding a yellowish-green filtrate. The solution volume was reduced to ca. 1 mL and slowly cooled to −20 °C, resulting in the formation of yellow-green crystals: yield 0.35 g (48%); ^{1}H NMR (C_6D_6) δ 16.0 (s, 6 H), 8.52 (s, 9 H), 1.25 (s, 30 H), −183.2 (s, 3 H); IR (Nujol mull, cm^{-1}) 1245 (m), 1015 (w), 880 (s), 825 (m), 790 (w), 765 (m), 710 (m), 665 (m). Anal. Calcd for $C_{27}H_{48}UOSi$: C, 49.52; H, 7.39; Si, 4.29. Found: C, 49.39; H, 7.40; Si, 4.37.

$Cp'_2U(H)\{OSi[C(CH_3)_3](CH_3)_2\}$ (15). A flask containing 0.52 g (0.97 mmol) of $Cp_2'U\{OSi[C(CH_3)_3](CH_3)_2\}(CH_3)$ and ca. 20 mL of heptane was charged with ca. 740 torr of hydrogen. The reaction solution was stirred for 1 day, the system was recharged with hydrogen, and stirring was continued for a second day. The solution was next filtered, the volume was reduced to ca. 1 mL, and slow cooling to −20 °C afforded yellow crystals: yield 0.31 g (61%); ^{1}H NMR (C_6D_6) δ 17.1 (s, 6 H), 6.38 (s, 9 H), 0.22 (s, 30 H); IR (Nujol mull, cm^{-1}) 1240 (s), 1005 (w), 995 (sh), 870 (vs), 815 (s), 785 (m), 755 (s), 658 (m); IR (Fluorolube mull, cm^{-1}) 1475 (w), 1465 (w), 1395 (m), 1375 (m). Anal. Calcd for $C_{26}H_{46}UOSi$: C, 48.75; H, 7.03; Si, 4.38; mol wt, 640.8. Found: C, 49.04; H, 7.13; Si, 4.21; mol wt 652 (cryoscopic in benzene).

$Cp'_2U(D)\{OSi[C(CH_3)_3](CH_3)_2\}$ (16). This compound was prepared in a manner identical with that of the analogous hydride, except by using deuterium in the place of hydrogen: IR (Nujol mull, cm^{-1}) ν_{U-D} = 988.

$Cp'_2U\{OSi[C(CH_3)_3](CH_3)_2\}(OCH_3)$ (17). $Cp'_2U\{OSi[C(CH_3)_3](CH_3)_2\}(CH_3)$ (0.27 g, 0.41 mmol) was dissolved in ca. 20 mL of toluene, and the solution was cooled to −78 °C. To this solution was slowly added, with rapid stirring, over a period of 20 min a solution containing 17 μL (0.42 mmol) of methanol in ca. 20 mL of toluene. After the completion of the addition, the solution was allowed to warm to room temperature and stirred for an additional hour. Upon removal of the solvent (in vacuo), heptane (ca. 10 mL) was distilled onto the brown residue, and this solution was filtered. Concentration of the filtrate volume to ca. 2 mL, followed by slow cooling to −30 °C, produced 0.15 g (54% yield) of the greenish-brown crystalline solid: ^{1}H NMR (C_6D_6) δ 0.54 (s, 30 H), −0.70 (s, 3 H), −3.11 (s, 9 H), −3.49 (s, 6 H); IR (Nujol mull, cm^{-1}) 1240 (m), 1100 (s), 1018 (w, br), 890 (s), 824 (m), 795 (w), 762 (m), 662 (w). Anal. Calcd for $C_{27}H_{48}UO_2Si$: C, 48.34; H, 7.22; Si, 4.19. Found: C, 48.23; H, 7.36; Si, 4.31.

Titration Calorimetry. The anaerobic, isoperibol, solution batch-titration calorimeter has been previously described.[24] The procedures were similar to those employed for the Cp'_2ThR_2 series, with the additional use of methanol as a titrant.

Results

Synthesis. All alkyl and hydride complexes employed for thermochemical measurements have been described elsewhere[3b,33] except alkoxy alkyls and hydrides/deuterides **14**, **15**, and **16**. These were prepared as shown in eq 5–7, and were characterized by standard analytical techniques (see Experimental Section for details). Compound **15** was found to be monomeric in benzene by cryoscopy—a contrast to the associated structures of $[Cp'_2Th(\mu\text{-}H)H]_2$ and $(Cp'_2UH_2)_2$.[33,36] As is typical of early transition element, lanthanide, and actinide molecular hydrides,[23,33] the assigned U–H stretching frequency of **15**, confirmed by deuterium substitution (**16** ν_{U-D} = 988 cm^{-1}), is rather low in energy: 1395 cm^{-1} (1395/988 = 1.41). The similar spectroscopic properties of compounds **8** and **9** are also in accord with monomeric structures.

$$Cp'_2U(CH_3)_2 + ROH \xrightarrow[\text{toluene}]{-78\ ^\circ C} \underset{\mathbf{14}}{Cp'_2U(CH_3)OR} + CH_4 \quad (5)$$

$$Cp'_2U(CH_3)OR + H_2 \xrightarrow[\text{heptane}]{25\ ^\circ C} \underset{\mathbf{15}}{Cp'_2U(H)OR} + CH_4 \quad (6)$$

$$Cp'_2U(CH_3)OR + D_2 \xrightarrow[\text{heptane}]{25\ ^\circ C} \underset{\mathbf{16}}{Cp'_2U(D)OR} + CH_3D \quad (7)$$

$$R = Si[C(CH_3)_3](CH_3)_2$$

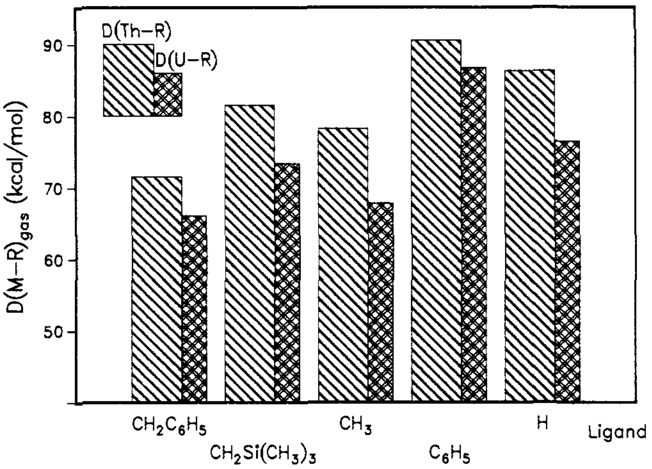

Figure 1. Comparison of gas-phase metal–ligand bond disruption enthalpies in analogous $Cp_2'Th(R)X$ and $Cp_2'U(R)X$ complexes.

For reference purposes, the expected products of the titration calorimetry, alkoxides **12**, **13**, and **17**, were synthesized on a preparative scale (eq 8–10). These were characterized by standard methodology (see Experimental Section for details),

$$Cp'_2U[CH_2Si(CH_3)_3]_2 + 2HOC(CH_3)_3 \xrightarrow[\text{ether}]{-78\ ^\circ C} \underset{\mathbf{12}}{Cp'_2U[OC(CH_3)_3]_2} + 2Si(CH_3)_4 \quad (8)$$

$$Cp'_2UCl_2 + KOC(CH_3)_3 \xrightarrow[\text{ether}]{25\ ^\circ C} \underset{\mathbf{13}}{Cp'_2U[OC(CH_3)_3]Cl} + KCl \quad (9)$$

$$Cp'_2U(CH_3)OR + CH_3OH \xrightarrow[\text{toluene}]{-78\ ^\circ C} \underset{\mathbf{17}}{Cp'_2U(OR)OCH_3} + CH_4 \quad (10)$$

$$R = Si[C(CH_3)_3](CH_3)_2$$

Thermochemistry. Essential to using titration calorimetry for determining metal–ligand bond disruption enthalpies via alcoholysis as in eq 3 is the requirement that such reactions be quantitative, rapid, and selective with respect to the M–R linkage. For the $Cp'_2U(R)X$ series, with X = Cl or R, ^{1}H NMR studies, conducted under conditions which simulate those of the calorimetric investigations, indicated that *tert*-butyl alcohol is an effective titrant. The alcoholyses were found to be rapid, quantitative, and selective for the U–R bond, although, in the case of the Cp'_2UR_2 complexes, the process was not stepwise (i.e., the rate of alcoholysis of the second hydrocarbyl group appeared to be greater than that of the first). For this reason, the enthalpy of reaction (ΔH_{rxn}) quantities measured and reported herein for the $Cp_2'UR_2$ compounds represents an average of the first and second U–R reaction enthalpies. The organouranium product at the completion of the titration was proven to be $Cp_2'U[OC(CH_3)_3]_2$ by comparison with an authentic sample.

In contrast to the above systems, the alcoholysis of $Cp_2'M(R)OR'$ compounds **8**, **9**, **11**, **14**, and **15** with *tert*-butyl alcohol

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Table I. Experimental Enthalpies of Solution (ΔH_{soln}) for Organoactinide Complexes in Toluene

complex	ΔH_{soln} (kcal/mol)
$Cp'_2U(CH_3)_2$	5.3
$Cp'_2U(CH_3)Cl$	3.5
$Cp'_2U(CH_2C_6H_5)_2$	4.5
$Cp'_2U(CH_2C_6H_5)Cl$	3.2
$Cp'_2U[CH_2Si(CH_3)_3]_2$	3.9
$Cp'_2U(C_6H_5)Cl$	2.4
$Cp'_2U[OC(CH_3)_3]_2$	4.1
$Cp'_2U[OC(CH_3)_3]Cl$	3.4
$Cp'_2U(CH_3)\{OSi[C(CH_3)_3](CH_3)_2\}$	5.6
$Cp'_2U(H)\{OSi[C(CH_3)_3](CH_3)_2\}$	5.6
$Cp'_2Th(C_6H_5)Cl$	2.8
$Cp'_2Th(H)\{O\text{-}2,6[C(CH_3)_3]_2C_6H_3\}$	3.6
$Cp'_2Th(n\text{-}C_4H_9)\{OCH[C(CH_3)_3]_2\}$	4.5
$Cp_2'Th(H)\{OCH[C(CH_3)_3]_2\}$	6.1
$Cp'_2Th\{OCH[C(CH_3)_3]_2\}(OCH_3)$	4.2

was found to be slow and to yield a mixture of products. With methanol as the protolytic reagent, however, NMR studies indicated that a clean, quantitative, selective, and rapid reaction occurred. The reaction of $Cp_2'Th(C_6H_5)Cl$ with both *tert*-butyl alcohol and methanol was investigated to provide a cross-comparison of the bond disruption enthalpy values obtained from the two alcoholic titrants (vide infra). The identity of the organoactinide titration products was verified by comparison to authentic samples.

The enthalpies of solution (ΔH_{soln}) of the $Cp_2'U(R)X$ and $Cp_2'M(R)OR'$ complexes in toluene are collected in Table I. The enthalpies of reaction (ΔH_{rxn}) of the former series with *tert*-butyl alcohol and the latter series with methanol are compiled in Table II. The relationship of these measured quantities to other important thermodynamic parameters is outlined in Scheme I. Through Scheme I, the experimentally measured ΔH_{rxn} can be equated to ΔH°_{gas} via eq 11. With respect to the enthalpy of

$$\Delta H^\circ_{gas} = \Delta H_{rxn} + \Delta H^\circ_{sub}(L_nMOR') + \Delta H^\circ_{vap}(RH) - \Delta H^\circ_{sub}(L_nMR) - \Delta H^\circ_{sub/vap}(R'OH) - \Delta H^\circ_{soln}(L_nMOR') - \Delta H^\circ_{soln}(R'OH) + \Delta H^\circ_{soln}(L_nMR) + \Delta H^\circ_{soln}(R'OH) \quad (11)$$

sublimation terms for the organoactinides, we make the reasonable, well-founded assumption[5b,24] that all enthalpies of sublimation values are of approximately the same magnitude. Under this approximation, the $\Delta H^\circ_{sub}(L_nMR)$ and $\Delta H^\circ_{sub}(L_nMOR')$ terms in eq 11 cancel. We did not measure ΔH°_{soln}, the enthalpy of solution at infinite dilution, but the dilution corrections are expected to be negligible, and, in addition, these corrections are expected to cancel on opposite sides of Scheme I.

Thermodynamic information concerning *tert*-butyl alcohol, methanol, and the RH components of the reaction system is also required. The enthalpies of solution for *tert*-butyl alcohol[24a] and methanol[37] in toluene have been determined. The ΔH°_{soln} values for all of the organic species, RH, in toluene are not known, but sufficient data do exist to approximate their values, and all are relatively small.[38] The enthalpies of vaporization of benzene, methanol, tetramethylsilane, and toluene have been reported, as has the enthalpy of sublimation of *tert*-butyl alcohol.[39] The other RH components of the system are gaseous at 25 °C so that $\Delta H^\circ_{vap}(RH)$ is zero in those cases. The values of ΔH°_{gas}, based on the above assumptions, are listed in Table II for the systems investigated.

The bond disruption enthalpies, $D(M\text{–}R)_{soln}$ and $D(M\text{–}R)_{gas}$, can be related to ΔH_{rxn} and ΔH°_{gas} through eq 12 and 4, respectively. The values of $D(R\text{–}H)$ and $D(O\text{–}H)$ for all the organic components of the system are available or can be estimated from similar compounds.[40] In regard to eq 12, we make the reasonable

$$-\Delta H_{rxn} = D(M\text{–}O)_{soln} + D(R\text{–}H)_{soln} - D(M\text{–}R)_{soln} - D(O\text{–}H)_{soln} \quad (12)$$

assumption that for the relatively nonpolar RH and alcohol components in dilute toluene solution, the values $D(R\text{–}H)_{soln}$ and $D(O\text{–}H)_{soln}$ are equal to $D(R\text{–}H)$ and $D(O\text{–}H)$, respectively. As seen in our previous investigations, the derived values of $D(M\text{–}R)_{soln}$ and $D(M\text{–}R)_{gas}$ are rather similar in magnitude.[24]

Within each particular series (Cp'_2UR_2, $Cp'_2U(R)X$, and $Cp'_2Th(R)X$) the organoactinide titration product and reactant alcohol are identical, so that relative values of $D(M\text{–}R)$ can be arrived at directly from the $D(R\text{–}H)$ and ΔH°_{gas} values. Equally desirable, however, are absolute $D(M\text{–}R)$ values, so that these results can be compared and contrasted with other observations on d- and f-element organometallic complexes. In order to achieve this objective, the quantity $D(M\text{–}O)$ must be estimated. As in our earlier studies,[24] we estimate a value of 124 kcal/mol for both $D(Th\text{–}OC(CH_3)_3)$ and $D(Th\text{–}OCH_3)$. We believe that the equality of these quantities is a reasonable approximation because thermochemical investigations on $Ti(OR)_4$,[41] $Nb(OR)_5$,[42] $Ta(OR)_5$,[42] and $M(NR_2)_4$[43] complexes where M = Ti, Zr, and Hf indicate that the strength of the metal–ligand interaction is relatively insensitive to the nature of the R = alkyl substituent. To further test this hypothesis with an organothorium complex, the alcoholysis reactions of $Cp'_2Th(C_6H_5)Cl$ with *tert*-butyl alcohol and methanol were examined independently, and the derived $D(Th\text{–}R)$ values, both gas- and solution-phase, are given in Table II. It can be seen that, within experimental error, $D(Th\text{–}R)$ is insensitive to the identity of the alcohol. Final values of $D(Th\text{–}R)_{soln}$ and $D(Th\text{–}R)_{gas}$ for the $Cp'_2Th(X)R$ complexes of this study are presented in Table II.

Methodology similar to that used to estimate $D(Th\text{–}O)$[24a] was utilized in approximating the value of $D(U\text{–}O)$.[44] Again, we employ mean bond disruption enthalpy data from the complexes $M(O\text{-}i\text{-}C_3H_7)_4$ with M = Ti, Zr, and Hf[43] and make the pragmatic approximations of eq 13 and 14 where X = a halogen. Within

$$\bar{D}(U\text{–}OR)/\bar{D}(M\text{–}OR) \approx \bar{D}(U\text{–}X)/\bar{D}(M\text{–}X) \quad (13)$$

$$D(U\text{–}OR) \approx \bar{D}(U\text{–}OR) \quad (14)$$

the Group 4 metals,[2b] a relationship analogous to eq 13 holds, and extensive bond disruption enthalpy data on the actinide tetrahalide compounds of interest are also available (Table III).[45] The application of eq 13 to uranium yields a value for $\bar{D}(U\text{–}OR)$ of 115 kcal/mol.[44] Further support for these approximations derives

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Table II. Experimental Enthalpies of Alcoholysis and Derived Bond Disruption Enthalpies (D) for Organoactinides (kcal/mol)[a]

complex	ΔH_{rxn}[b]	$\Delta H°_{gas}$[c]	$D(M-R)_{soln}$[c]	$D(M-R)_{gas}$[c]
$Cp'_2U(CH_3)_2$	-43.2 (3.3)	-47.2 (3.5)	71.8 (3.3)	67.8 (3.5)
$Cp'_2U(CH_3)Cl$	-40.4 (1.6)	-44.9 (1.7)	74.6 (1.6)	70.1 (1.7)
$Cp'_2UnCH_2C_6H_5)_2$	-39.6 (1.9)	-36.1 (2.5)	58.3 (2.1)	61.8 (2.7)
$Cp'_2U(CH_2C_6H_5)Cl$	-34.9 (2.5)	-31.8 (2.6)	63.0 (2.7)	66.1 (2.8)
$Cp'_2U[CH_2Si(CH_3)_3]_2$	-35.6 (0.8)	-35.6 (1.4)	73.3 (3.1)	73.3 (3.3)
$Cp'_2U(C_6H_5)Cl$	-35.4 (1.6)	-34.2 (1.7)	85.5 (2.6)	86.7 (2.6)
$Cp'_2U(CH_3)\{OSi[C(CH_3)_3](CH_3)_2\}$	-39.7 (1.2)	-43.3 (1.4)	76.0 (1.2)	72.4 (1.4)
$Cp'_2U(H)\{OSi[C(CH_3)_3](CH_3)_2\}$	-32.7 (0.7)	-38.4 (1.1)	82.4 (0.7)	76.4 (1.1)
$Cp'_2Th(C_6H_5)Cl$	-40.7 (0.9)[d]	-39.4 (1.1)	89.2 (2.2)	90.5 (2.3)
	-39.7 (3.2)[e]	-38.8 (3.3)	90.9 (3.8)	91.8 (3.8)
$Cp'_2Th(H)\{O\text{-}2,6[C(CH_3)_3]C_6H_3\}$	-31.7 (1.0)	-38.9 (1.2)	92.1 (1.0)	84.9 (1.2)
$Cp'_2Th(H)\{OCH[C(CH_3)_3]_2\}$	-30.5 (1.2)	-36.0 (1.5)	93.3 (1.2)	87.8 (1.5)
$Cp'_2Th(n\text{-}C_4H_9)\{OCH[C(CH_3)_3]_2\}$	-36.4 (2.9)	-36.1 (2.9)	81.2 (3.1)	81.5 (3.1)

[a] The values reported for the Cp'_2UR_2 complexes refer to an average of the breaking of the first ($Cp'_2U(R)-R$) and second ($Cp'_2U(OR')-R$) U-R bonds. [b] Quantities in parentheses refer to 2σ for 10-30 determinations. [c] Error limits do not include uncertainties that are constant throughout the series (see Supplementary Material). [d] With *tert*-butyl alcohol as the titrant. [e] With methanol as the titrant.

Table III. Comparison of Bond Disruption Enthalpies in Actinide Tetrahalides[a] (kcal/mol)

	$\bar{D}(M-X)$[b]		$D_1(M-X)$[c]	
halide	Th	U	Th	U
F	159.0	146.3	154	148
Cl	122.5	109.4		86
Br	108.0	94.7		77
I	88.7	75.5		

[a] Calculated from the thermodynamic data of ref 45. [b] $\bar{D}(M-X)$ is the average M-X bond disruption enthalpy. [c] $D_1(M-X)$ is the first bond disruption enthalpy (X_3M-X).

from UF_4 thermochemical data[45] which indicate that $\bar{D}(U-F)$ is 146.3 kcal/mol and $D_1(U-F)$ is 147.9 kcal/mol, whereas our method, using UCl_4 or UBr_4 data, places $D(U-F)$ at 146 kcal/mol.[46] Nevertheless, we emphasize the the derived, *absolute* $D(U-O)$ value is probably not accurate to better than 10 kcal/mol (in contrast to the high expected reliability of *relative* $D(U-R)$ values). The final values of $D(U-R)_{soln}$ and $D(U-R)_{gas}$ for the complexes studied are compiled in Table II.

Discussion

As already noted, the kinetic nature of the *tert*-butyl alcohol titrations is such that the derived $D(U-R)$ values for $Cp_2'UR_2$ compounds are actually averages of the corresponding $Cp_2'U(R)-R$ and $Cp_2'U[OC(CH_3)_3]-R$ disruption enthalpies. This is not the case for $Cp_2'U(R)X$ compounds, and it will be seen that the above "averaging" presents no serious interpretive problems. From the $D(U-R)$ data set out in Table II, it is evident that uranium-hydrocarbyl and uranium-hydride bonds in the tetravalent bis(pentamethylcyclopentadienyl) series are rather "strong". The observed D(U-hydrocarbyl) values of 60-85 kcal/mol are considerably in excess of values in the 30 kcal/mol range reported for a number of classes of middle and late transition-metal complexes.[2,5,6,8,10] The present $D(U-R)$ values are also somewhat in excess of analogous $\bar{D}(M-R)$ values reported for Cp_2MR_2 complexes of Group 4, i.e., 60.0 ($M = Ti$, $R = CH_3$),[47a] 66.4 ($M = Zr$, $R = CH_3$),[47b] 74.3 ($M = Ti$, $R = C_6H_5$),[8b] 69.8 ($M = Zr$, $R = C_6H_5$),[47b] and 51.3 ($M = Ti$, $R = CH_2C_6H_5$).[47a] Furthermore, as can be seen in Figure 1, uranium-hydrocarbyl and hydride bonds are "weaker" than those in analogous thorium complexes by 5-10 kcal/mol.

At the most qualitative level, the overall trend of rather high metal-ligand bond disruption enthalpies for actinides (and, it would appear, early transition elements) can be explained on the basis of simple Pauling bond ionicity/bond energy concepts.[48a,b] The highly electropositive character of the actinide metals, modulated of course by supporting ligands,[48c,d] would be expected, a priori, to give rise to relatively large bond energies—eq 2 should be highly endothermic. The highly polar character of actinide-to-carbon and actinide-to-hydrogen σ bonds is evident in their chemistry[23,33] and has also been invoked in rationalizing bond length/coordination number relationships.[23,49] In regard to overall $D(Th-R)/D(U-R)$ trends, it should be noted that eq 2 implies a formal M(IV) → M(III) reduction process. The trend for actinides of an increasingly stable trivalent state with increasing Z is well-established.[50] Especially relevant to the present case is the observation that while the U(IV)/U(III) $E_{1/2}$ value in THF for $Cp_2'UCl_2$ is -1.22 V vs. SCE, that for $Cp_2'ThCl_2$ under the same conditions is beyond -2.7 V.[51a] Indeed, theoretical estimates[50] place the $E°$ value for Th(IV)/Th(III) in the -3.0 to -3.7 V range vs. SCE.

The variation in $D(U-R)$ for various hydrocarbyl ligands is found to be $C_6H_5 > CH_2Si(CH_3)_3 > CH_3 > CH_2C_6H_5$. This trend closely parallels that in the Cp'_2ThR_2 series[24a] (Figure 1) and in d-element complexes.[2] In the present case, it presumably reflects R-R and Cp'-R nonbonded repulsions within the hydrocarbyl complex (which can be severe in the Cp'_2MR_2 series[52]) as well as the stability of the R• radical ($\Delta H°_f[R^\bullet(g)]$ in eq 1. The effect on $D(M-R)$ of an ancillary alkoxide ligand was first noted in the $Cp_2'ThR_2$, $Cp_2'Th(R)OR'$ series, where $D(Th-R)$ was invaraibly ca. 2-4 kcal/mol greater for the alkoxide-substituted molecules.[24] Since $D(U-CH_3)$ for $Cp_2'U(CH_3)_2$ in Table II is an average value for $Cp_2'U(CH_3)-CH_3$ and $Cp_2'U[OC(CH_3)_3]-CH_3$, it appears (Table II) that the same effect is operative in $Cp_2'U(CH_3)_2$ and $Cp_2'U(CH_3)\{OSi[C(CH_3)_3](CH_3)_2\}$. The average solution-phase $D(Th-C)$ in $Cp_2'Th(n\text{-}C_4H_9)_2$ is 72.6 (3.4) kcal/mol,[24a] and the result in Table II for $Cp_2'Th(n\text{-}C_4H_9)\{OCH[C(CH_3)_3]_2\}$ adheres to the same trend. The most plausible explanation for the stabilizing effect of alkoxide coligands is again the reductive process expressed in eq 2. "Hard" ligands such as alkoxides should stabilize higher actinide oxidation states and thereby render eq 2 more endothermic.[51b] An alternative (or contributing) explanation for the effect would be that $D(M-O)$ is greater in $Cp_2'M(R)OR'$

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[46] That $D_1 \approx \bar{D}$ for a first-row ligand is, of course, crucial to our $D(M-OR)$ derivation. That the validity of this approximation deteriorates with heavier halogen ligands (Table III) may be an ancillary ligand effect (see ref 51b).

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[49] Raymond, K. N. in ref 23d, pp 249-280.

[50] (a) Bratsch, S. G.; Lagowski, J. J. *J. Phys. Chem.* **1986**, *90*, 307-312, and references therein. (b) Nugent, L. J. In *MTP Int. Rev. Sci., Inorg. Chem. Series Two*; Bagnall, K. W., Ed.; University Park Press: Baltimore, 1976; Vol. 7, Chapter 6.

[51] (a) Finke, R. G.; Gaughan, G.; Voegeli, R. *J. Organomet. Chem.* **1982**, *229*, 179-184. (b) The increase of $\bar{D}(U-X) - D_1(U-X)$ with heavier X (Table III) could be explained by an analogous ancillary ligand effect.

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complexes than in $Cp_2'M(OR')_2$ complexes for either steric or electronic reasons. Since the effect is fairly uniform for a wide variety of R ligands, steric effects appear to be of secondary importance. As regards electronic factors, it is difficult to judge whether the effect of the π-donor character[53] of a single alkoxide ligand on the M–R bond would be greater than an M–OR weakening saturation of the actinide π-acceptor power by two alkoxide ligands. Since ancillary alkoxide ligands are known to have a dramatic effect on actinide-to-carbon σ bond reactivity,[13,54] and since there is at present no spectroscopic or structural data to support the weakened M–OR argument, we favor the strengthening of M–R.

The effect of a chloride coligand on D(M–R) appears to be smaller than that of an alkoxide coligand. For solution phase data in the thorium series, $D(Cp_2'Th(R)–R) - D(Cp_2'Th(Cl)–R) \approx 3$ ($R = C_2H_5$) and 0 ($R = C_6H_5$) kcal/mol.[24a] In the present uranium series, the corresponding values are ca. −2 ($R = CH_3$) and −4 ($R = CH_2C_6H_5$) kcal/mol.

The magnitude of D(M–H) − D(M–C)alkyl)) has profound consequences for the thermodynamic favorability of transformations such as β-H elimination (e.g., eq 15). In the bis(pentamethylcyclopentadienyl)thorium system, it was previously found

$$L_nM–CH_2CH_3 \rightleftharpoons L_nM–H + H_2C{=}CH_2 \qquad (15)$$

that D(Th–H) − D(Th–C(alkyl)) ≈ 20 kcal/mol,[24a] rendering β-H elimination substantially more endothermic ($\Delta H \approx +20$ kcal/mol) than for typical middle and late first-row transition-metal complexes where D(M–H) − D(M–C(alkyl)) ≈ 30 kcal/mol ($\Delta H \approx +10$ kcal/mol)[2]. However, the above D(Th–H) value (90.5 (1.3) kcal/mol in the gas phase, 97.5 (0.7) kcal/mol in solution) is an average result from the nonselective *tert*-butyl alcoholysis of $[Cp_2'Th(\mu\text{-}H)H]_2$,[24a] and the effect of bridging hydrogen atoms (if any) on D(Th–H) is unclear. From Table II it can be seen that thorium–hydrogen bond disruption enthalpies for two monomeric $Cp_2'Th(H)OR'$ complexes are somewhat smaller than for $[Cp_2'Th(\mu\text{-}H)H]_2$, implying possible stabilization of Th–H by bridge formation (not unprecedented[55]) and/or that the alkoxide coligand destabilizes Th–H (however, note that the $Cp_2'Th(OR')–R$ D value is invariably larger than $D(Th–R)_{average}$). The result for the $Cp_2'U(H)OR'$ complex (Table II) indicates that D(Th–H) − D(U–H) parallels the trend in the hydrocarbyl series. Finally, it can also be seen in Table II that for alkoxide ancillary ligands, D(M–H) − D(M–C(alkyl)) is in the range of only ca. 0–6 kcal/mol.[56]

We have suggested previously[3c,24a] that the reason for low organoactinide D(M–H) − D(M–C(alkyl)) values may reflect the aforementioned high polarity of the metal–ligand bonding and

$$\overset{\delta+}{M} - \overset{\delta-}{CH_3} \qquad \overset{\delta+}{M} - \overset{\delta-}{H} \qquad (16)$$

the comparatively poor ability of the (hydridic) hydride ligand in nonpolar environments to stabilize the attendant negative charge.[57,58] With reference to the present results, it may be that additional π donation from alkoxide supporting ligands places additional negative charge on the hydride ligand, further destabilizing the bonding interaction relative to that of more polarizable alkyl ligands. In regard to β-H elimination, alkoxide coligands render processes as in eq 17 very endothermic indeed. One important manifestation of this ancillary ligand effect may be in olefin polymerization catalysis. We have previously noted[24a] that ethylene polymerization centers with small D(M–H) − D(M–C(alkyl)) values (e.g., actinides,[23,59] probably early transition elements,[60] and lanthanides[61]) have a thermodynamic advantage over many metals with respect to polymerization efficacy in that chain termination by β-H elimination (e.g., eq 18) can be highly endothermic.

$$Cp_2'Th(OR')CH_2CH_3 \rightleftharpoons Cp_2'Th(OR')H + H_2C{=}CH_2 \qquad (17)$$

$$\Delta H \approx +35 \text{ kcal/mol}$$

$$L_nMCH_2CH_2(CH_2CH_2)_mCH_3 \rightleftharpoons L_nM–H + H_2C{=}CH(CH_2CH_2)_mCH_3 \qquad (18)$$

Interestingly, a considerably body of empirical data indicates that for soluble Ziegler–Natta catalysts, coordination of alkoxide ancillary greatly depresses chain termination via β-H elimination.[62] It is reasonable that the aforementioned ancillary alkoxide ligand effect is operative here. In the same vein, it is likely that many other processes which involve the transposition of M–H and M–C bonds can be similarly tuned by ancillary ligand effects.

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Registry No. 1, 67605-92-9; **2**, 67506-91-6; **3**, 79301-24-9; **4**, 79301-26-1; **5**, 68963-85-9; **6**, 79301-31-8; **7**, 79313-86-3; **8**, 79932-09-5; **9**, 79932-08-4; **10**, 83398-67-8; **11**, 91742-33-5; **12**, 104505-37-5; **13**, 104489-79-4; **14**, 104489-80-7; **15**, 104489-81-8; **16**, 104489-82-9; **17**, 104489-83-0; $Cp'UCl_2$, 67506-89-2; $[C(CH_3)_3](CH_3)_2SiOH$, 18173-64-3.

Supplementary Material Available: Tables of parameters employed in thermochemical calculations (2 pages). Ordering information is given on any current masthead page.

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[55] For a trinuclear iron–carbonyl cluster, Vites and Fehlner argue that μ_2 bridging stabilizes an Fe–H bond by 10–11 kcal/mol.[12]

[56] Since $D(Th–CH_3)$ is greater than $D(Th–CH_2CH_3)$ and $D(Th\text{–}n\text{-}C_4H_9)$ by ca. 6–10 kcal/mol,[24a] it is likely that D(U–H) − $D(U–CH_3)$ underestimates D(U–H) − D(U–C(alkyl)).

[57] Similar polarizability arguments have been invoked to explain $D°(M^+ - CH_3) > D°(M^+ - H)$ trends in gas-phase ion-molecule chemistry.[20h,i]

[58] The trend D(M–H) − D(M–C(alkyl)) ≤ 20 kcal/mol has precedent in main group organometallic chemistry. For example, D(Al–H) = 69.4 kcal/mol and $D(Al–CH_3)$ = 67.3 kcal/mol (Eisch, J. J. in ref 23b, Vol. 1, p 168.

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