

for partial support of this research.

Registry No. NH₃, 7664-41-7; H₂O, 7732-18-5; C₂H₆, 74-84-0; C₃H₈, 74-98-6; C₄H₁₀, 106-97-8; C₅H₁₂, 109-66-0; C₆H₁₄, 110-54-3; *iso*-C₄H₁₀, 75-28-5; *neo*-C₅H₁₂, 463-82-1; H₂, 1333-74-0; N₂, 7727-37-9; O₂, 7782-44-7; Ne, 7440-01-9; Ar, 7440-37-1; NO, 10102-43-9; HF, 7664-39-3;

CO, 630-08-0; PH₃, 7803-51-2; F₂, 7782-41-4; CO₂, 124-38-9; SO₂, 7446-09-5; NO₂, 10024-97-2; HCN, 74-90-8; HCP, 6829-52-3; HCl, 7647-01-0; C₄H₈, 287-23-0; C₆H₁₂, 110-82-7; CH₃⁺, 14531-53-4; C₄H₉⁺, 25453-90-1; C₂H₄, 74-85-1; C₂H₂, 74-86-2; C, 7440-44-0; cyclopropane, 75-19-4; cyclohexane, 110-82-7; methane, 74-82-8; bicyclo[1.1.0]butane, 157-33-5; [1.1.1]-propellane, 311-75-1.

Metal, Bond Energy, and Ancillary Ligand Effects on Actinide–Carbon σ -Bond Hydrogenolysis. A Kinetic and Mechanistic Study

Zerong Lin and Tobin J. Marks*

Contribution from the Department of Chemistry, Northwestern University, Evanston, Illinois 60201. Received January 20, 1987

Abstract: A kinetic/mechanistic study of actinide hydrocarbyl ligand hydrogenolysis ($\text{An-R} + \text{H}_2 \rightarrow \text{An-H} + \text{RH}$) is reported. For the complex $\text{Cp}'_2\text{Th}(\text{CH}_2\text{-}t\text{-Bu})(\text{O-}t\text{-Bu})$ ($\text{Cp}' = \eta^5\text{-Me}_5\text{C}_5$), the rate law is first-order in organoactinide and first-order in H₂, with $k_{\text{H}_2}/k_{\text{D}_2} = 2.5$ (4) and $k_{\text{THF}}/k_{\text{toluene}} = 2.9$ (4). For a series of complexes, hydrogenolysis rates span a range of ca. 10^5 with $\text{Cp}'_2\text{ThCH}_2\text{C}(\text{CH}_3)_2\text{CH}_2 \approx \text{Cp}'_2\text{U}(\text{CH}_2\text{-}t\text{-Bu})(\text{O-}t\text{-Bu})$ (too rapid to measure accurately) $>$ $\text{Cp}'_2\text{Th}(\text{CH}_2\text{-}t\text{-Bu})[\text{OCH}(t\text{-Bu})_2] = \text{Cp}'_2\text{Th}(\text{CH}_2\text{-}t\text{-Bu})(\text{O-}t\text{-Bu}) >$ $\text{Cp}'_2\text{Th}(\text{CH}_2\text{-}t\text{-Bu})(\text{Cl}) >$ $\text{Me}_2\text{Si}(\text{Me}_4\text{C}_5)_2\text{Th}(n\text{-Bu})_2 >$ $\text{Cp}'_2\text{Th}(n\text{-Bu})_2 \approx \text{Cp}'_2\text{ThMe}_2 >$ $\text{Cp}'_2\text{Th}(\text{Me})(\text{O}_3\text{SCF}_3) >$ $\text{Cp}'_2\text{Th}(n\text{-Bu})[\text{OCH}(t\text{-Bu})_2] \approx \text{Cp}'_2\text{Th}(\text{Me})[\text{OSiMe}_2(t\text{-Bu})] >$ $\text{Cp}'_2\text{ZrMe}_2 = \text{Cp}'_2\text{Th}(p\text{-C}_6\text{H}_4\text{NMe}_2)(\text{O-}t\text{-Bu}) >$ $\text{Cp}'_2\text{Th}(\text{Ph})(\text{O-}t\text{-Bu}) >$ $\text{Cp}'_2\text{U}(\text{Me})[\text{OCH}(t\text{-Bu})_2] >$ $\text{Cp}'_2\text{Th}(\text{Me})[\text{OCH}(t\text{-Bu})_2]$. In the majority of cases, the rate law is cleanly first-order in organoactinide over 3 or more half-lives. However, for $\text{Cp}'_2\text{ThMe}_2 \rightarrow (\text{Cp}'_2\text{ThH}_2)_2$, an intermediate is observed by NMR that is probably $[\text{Cp}'_2\text{Th}(\text{Me})(\mu\text{-H})_2]$. For $\text{Cp}'_2\text{Th}(\text{Me})(\text{O}_3\text{SCF}_3)$, a follow-up reaction, which consumes $\text{Cp}'_2\text{Th}(\text{H})(\text{O}_3\text{SCF}_3)$, is detected. Variable-temperature kinetic studies yield $\Delta H^\ddagger = 3.7$ (2) kcal/mol and $\Delta S^\ddagger = -50.8$ (7) eu for $\text{Cp}'_2\text{Th}(\text{CH}_2\text{-}t\text{-Bu})(\text{O-}t\text{-Bu})$ and $\Delta H^\ddagger = 9$ (2) kcal/mol and $\Delta S^\ddagger = -45$ (5) eu for $\text{Cp}'_2\text{U}(\text{Me})[\text{OCH}(t\text{-Bu})_2]$. The present results are in accord with a polar "heterolytic" four-center transition state involving significant H–H bond cleavage. There is no chemical shift or spin–lattice relaxation time NMR spectroscopic evidence for an H₂ complex in preequilibrium. There are approximate correlations between the hydrogenolysis rate and An–R bond disruption enthalpy, ancillary ligand electron-donor capacity, and An–R migratory CO insertion rate. Possible parallels between the present results and the activities of supported organoactinide catalysts, as well as the mechanism of molecular weight control by hydrogen in Ziegler–Natta catalysis, can be drawn.

Processes by which metal–carbon σ bonds suffer hydrogenolysis are essential components of numerous catalytic cycles.¹ For early-transition-metal, lanthanide, and actinide systems, many mechanistic aspects of the hydrogenolysis process remain obscure, despite the importance of such transformations in olefin and alkyne hydrogenation catalysis,^{2–4} as well as in molecular weight control during coordination polymerization.⁵ Additional motivation to

better understand H–H activation processes in d^0/f^0 systems is provided by the possibility of more effectively modulating analogous C–H functionalization processes.^{6–8} Mechanistically, the absence of energetically accessible metal oxidation states for oxidative addition/reductive elimination processes,^{1,9} the presence of relatively low-lying empty metal σ -bonding orbitals, and the

(1) For examples in homogeneous solution, see: (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; Chapter 10. (b) James, B. R. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Chapter 51. (c) Masters, C. *Homogeneous Transition-metal Catalysis*; Chapman and Hall: London, 1981; Chapter 2.1. (d) Parshall, G. W. *Homogeneous Catalysis*; Wiley-Interscience: New York, 1980; Chapter 3. (e) Crabtree, R. *Acc. Chem. Res.* 1979, 12, 331–338, and references therein.

(2) Early transition metals: (a) Couturier, S.; Tainturier, G.; Gautheron, G. *J. Organomet. Chem.* 1980, 195, 291–306. (b) Wailes, P. C.; Weigold, H.; Bell, A. P. *J. Organomet. Chem.* 1972, 43, C32–C34.

(3) Lanthanides: (a) Jeske, G.; Lauke, H.; Mauermann, H.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* 1985, 107, 8111–8118. (b) Mauermann, H.; Swepston, P. N.; Marks, T. J. *Organometallics* 1985, 4, 200–202. (c) Evans, W. J.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* 1983, 105, 1401–1403.

(4) Actinides: (a) Marks, T. J. In *The Chemistry of the Actinide Elements*; 2nd ed.; Katz, J. J., Seaborg, G. T., Morss, L. R., Eds.; Chapman and Hall: London, 1986; Chapter 23. (b) Marks, T. J.; Day, V. W. In *Fundamental and Technological Aspects of Organo-f-Element Chemistry*; Marks, T. J., Fragalá, I. L., Eds.; Reidel: Dordrecht, 1985; Chapter 4. (c) Fagan, P. J.; Manriquez, J. M.; Maata, E. A.; Seyam, A. M.; Marks, T. J. *J. Am. Chem. Soc.* 1981, 103, 6650–6667. (d) Duttera, M. R.; Mauermann, H.; Marks, T. J., unpublished results quoted in ref 3a.

(5) (a) Quirk, R. P.; Hsieh, H. L.; Klingensmith, G. B.; Tait, P. J., Eds. *Transition Metal Catalyzed Polymerization. Alkenes and Dienes*; Harwood Publishers for MMI Press: New York, 1983. (b) Gavens, P. D.; Bottrill, M.; Kelland, J. W.; McMeeking, J. In reference 1a, Chapter 22.5. (c) Boor, J., Jr. *Ziegler–Natta Catalysts and Polymerizations*; Academic: New York, 1979; pp 251–256.

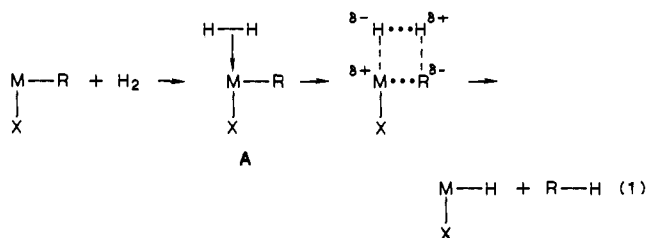
(6) Early transition metals: (a) Rothwell, I. P. *Polyhedron* 1985, 4, 177–200. (b) Thompson, M. E.; Bercaw, J. E. *Pure Appl. Chem.* 1984, 56, 1–11. (c) Thompson, M. E.; Baxter, S. M.; Bulls, A. R.; Burger, B. J.; Nolan, M. C.; Santarsiero, B. D.; Schaefer, W. P.; Bercaw, J. E. *J. Am. Chem. Soc.* 1987, 109, 203–219.

(7) Lanthanides: (a) Watson, P. J.; Parshall, G. W. *Acc. Chem. Res.* 1985, 18, 51–56. (b) Jeske, G.; Lauke, H.; Mauermann, H.; Swepston, P. J.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* 1985, 107, 8091–8103. (c) Jeske, G.; Schock, L. E.; Swepston, P. J.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* 1985, 107, 8103–8110.

(8) Actinides: (a) Simpson, S. J.; Andersen, R. A. *J. Am. Chem. Soc.* 1981, 103, 4064–4066. (b) Bruno, J. W.; Marks, T. J.; Day, V. W. *J. Am. Chem. Soc.* 1982, 104, 7357–7360. (c) Bruno, J. W.; Smith, G. M.; Marks, T. J.; Fair, C. K.; Schultz, A. J.; Williams, J. M. *J. Am. Chem. Soc.* 1986, 108, 40–56. (d) Fendrick, C. M.; Marks, T. J. *J. Am. Chem. Soc.* 1984, 106, 2214–2216. (e) Fendrick, C. M.; Marks, T. J. *J. Am. Chem. Soc.* 1986, 108, 425–437. (f) Smith, G. M.; Carpenter, J. D.; Marks, T. J. *J. Am. Chem. Soc.* 1986, 108, 6805–6807.

(9) (a) Saillard, J.-Y.; Hoffmann, R. *J. Am. Chem. Soc.* 1984, 106, 2006–2026. (b) Reamey, R. H.; Whitesides, G. M. *J. Am. Chem. Soc.* 1984, 106, 81–85. (c) Crabtree, R. H.; Hlatky, G. *Inorg. Chem.* 1980, 19, 572–574.

relatively polar metal–ligand bonding have implicated a “four-center” heterolytic picture for metal–carbon bond cleavage (eq 1).^{3a,4a,7,10,11} Nevertheless, the constraints under which such



processes operate have not been investigated systematically. In the present organoactinide contribution, we examine in detail the kinetics and mechanism of this process in the $\text{Cp}'_2\text{M}(\text{X})\text{R}$ series ($\text{Cp}' = \eta^5\text{-Me}_5\text{C}_5$) as a function of metal (Th, U, Zr), hydrocarbyl ligand R, ancillary ligand X, temperature, and solvent polarity. We also inquire whether a preequilibrium with a dihydrogen complex (A) is detectable. It will be seen here that there are qualitative reactivity correlations with the experimental M–R bond disruption enthalpies, the electron-donation tendencies of X, and other reactivity patterns of the M–R bonds. Parallels to catalytic reactivities of organoactinides adsorbed on metal oxides¹² are also suggested.

Experimental Section

Materials and Methods. All organoactinide compounds are exceedingly air- and moisture-sensitive and hence were handled in Schlenk-type glassware interfaced to a high-vacuum line, on a Schlenk line, or in a N_2 -filled glovebox. Solvents were predried and distilled from Na/K benzophenone. The gases Ar, H_2 , N_2 , and D_2 were purified by passage through a supported MnO oxygen-removal column and a Davison 4-Å molecular sieve column.

The complexes $\text{Cp}'_2\text{Th}(\text{CH}_2\text{-}t\text{-Bu})[\text{OCH}(t\text{-Bu})_2]$,^{13a} $\text{Cp}'_2\text{Th}(\text{CH}_2\text{-}t\text{-Bu})(\text{O-}t\text{-Bu})$,^{13a} $\text{Cp}'_2\text{Th}(n\text{-Bu})[\text{OCH}(t\text{-Bu})_2]$,^{13a} $\text{Cp}'_2\text{Th}(\text{Me})[\text{OCH}(t\text{-Bu})_2]$,^{13a} $\text{Cp}'_2\text{Th}(\text{Cl})(\text{O-}t\text{-Bu})$,^{13a} $\text{Cp}'_2\text{ThMe}_2$,^{4c} $\text{Cp}'_2\text{Th}(\text{CH}_2\text{-}t\text{-Bu})(\text{Cl})$,^{4c} $\text{Cp}'_2\text{Th}(n\text{-Bu})_2$,^{4c} $\text{Me}_2\text{Si}(\text{Me}_4\text{C}_3)_2\text{Th}(n\text{-Bu})_2$,^{13b,c} $\text{Cp}'_2\text{UMe}_2$,^{4c} $\text{Cp}'_2\text{U}(\text{Cl})(\text{O-}t\text{-Bu})$,¹⁴ $\text{Cp}'_2\text{ThCH}_2\text{C}(\text{CH}_3)_2\text{CH}_2$,^{8c} $\text{Cp}'_2\text{Th}(\text{Me})(\text{O}_3\text{SCF}_3)$,^{12e} $\text{Cp}'_2\text{Th}(\text{Me})[\text{OSiMe}_2(t\text{-Bu})]$,^{12e} and $\text{Cp}'_2\text{ZrMe}_2$ ¹⁵ were prepared according to the literature procedures. All lithium reagents were commercially available (Aldrich) except $\text{LiCH}_2\text{C}(\text{CH}_3)_2$,^{16a} and $\text{Li}(p\text{-C}_6\text{H}_5\text{NMe}_2)$,^{16b} which were prepared as described in the literature. The alcohol $\text{HOCH}(t\text{-Bu})_2$ was synthesized as described elsewhere.¹³

Physical and Analytical Measurements. All proton NMR spectra were recorded on a JEOL FX-90Q (FT, 90-MHz) or a JEOL FX-270 (FT, 270-MHz) spectrometer. Chemical shifts are reported relative to TMS. Spin–lattice relaxation time measurements were carried out on a Varian XL-400 spectrometer using the Varian inversion–recovery subroutine

(10) (a) Brothers, P. J. *Prog. Inorg. Chem.* **1981**, *28*, 1–61. (b) Gell, K. I.; Posin, B.; Schwartz, J.; Williams, G. M. *J. Am. Chem. Soc.* **1982**, *104*, 1846–1855. (c) Wochner, F.; Brintzinger, H. H. *J. Organomet. Chem.* **1986**, *309*, 65–75.

(11) For relevant theoretical studies see: (a) Rabaã, H.; Saillard, J.-Y.; Hoffmann, R. *J. Am. Chem. Soc.* **1986**, *108*, 4327–4333, and references therein. (b) Steigerwald, M. L.; Goddard, W. A., III. *J. Am. Chem. Soc.* **1984**, *106*, 308–311. (c) Brintzinger, H. H. *J. Organomet. Chem.* **1979**, *171*, 337–348.

(12) (a) He, M.-Y.; Burwell, R. L., Jr.; Marks, T. J. *Organometallics* **1983**, *2*, 566–569. (b) He, M.-Y.; Xiong, G.; Toscano, P. J.; Burwell, R. L., Jr.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 641–652. (c) Toscano, P. J.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 653–659. (d) Burwell, R. L., Jr.; Marks, T. J. In *Catalysis of Organic Reactions*; Augustine, R. L., Ed.; Dekker: New York, 1985; pp 207–224. (e) Toscano, P. J.; Marks, T. J. *Langmuir*, **1986**, *2*, 820–823. (f) Xiong, G.; Burwell, R. L., Jr.; Marks, T. J., to be submitted for publication.

(13) (a) Moloy, K. G.; Marks, T. J. *J. Am. Chem. Soc.* **1984**, *106*, 7051–7064. (b) Fendrick, C. M.; Mintz, E. A.; Schertz, L. D.; Marks, T. J.; Day, V. W. *Organometallics* **1984**, *3*, 819–821. (c) Fendrick, C. M.; Schertz, L. D.; Day, V. W.; Marks, T. J., submitted for publication.

(14) Bruno, J. W.; Stecher, H. A.; Morss, L. R.; Sonnenberger, D. C.; Marks, T. J. *J. Am. Chem. Soc.* **1986**, *108*, 7275–7280.

(15) Manriquez, J. M.; McAlister, D. R.; Sanner, R. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 2716–2724.

(16) (a) Schrock, R. R.; Fellmann, J. D. *J. Am. Chem. Soc.* **1978**, *100*, 3359–3370. (b) Ladd, J. A.; Parker, J. J. *Chem. Soc., Dalton Trans.* **1972**, 930–934.

DOT1. Reported T_1 values are an average of two measurements. Elemental analyses were performed by Dornis and Kolbe Mikroanalytisches Laboratorium.

Synthesis of $\text{Cp}'_2\text{Th}(\text{Ph})(\text{O-}t\text{-Bu})$. A 25-mL two-neck flask was charged with 1.32 g (2.16 mmol) of $\text{Cp}'_2\text{Th}(\text{Cl})(\text{O-}t\text{-Bu})$ in the glovebox. On the vacuum line, 15 mL of Et_2O was condensed into the flask. Then, 1.5 mL (2.0 M, 3.0 mmol) of LiPh cyclohexane/diethyl ether solution was added via a syringe under an Ar flush at -78°C . The reaction mixture was next stirred for 2 h at -78°C and for 1 h at room temperature. The volatiles were then pumped off, and 15 mL of pentane was condensed in. The mixture was filtered, and the solids were washed twice by condensing 3 mL of pentane from the solution into the upper portion of the frit. Following this, the volume of the filtrate was reduced to 10 mL. Slow cooling to -78°C followed by cold filtration afforded a colorless, crystalline solid. Yield: 71%. $^1\text{H NMR}$ (C_6D_6): δ 7.85 (d, 2 H), 7.48 (t, 2 H), 7.21 (t, 1 H), 1.95 (s, 30 H), 1.35 (s, 9 H). Anal. Calcd for $\text{C}_{30}\text{H}_{44}\text{OTh}$: C, 55.21; H, 6.80; Th, 35.55. Found: C, 55.16; H, 7.20; Th, 35.17.

Synthesis of $\text{Cp}'_2\text{Th}(p\text{-C}_6\text{H}_4\text{NMe}_2)(\text{O-}t\text{-Bu})$. A 30-mL flask was charged with 0.66 g (1.08 mmol) of $\text{Cp}'_2\text{Th}(\text{Cl})(\text{O-}t\text{-Bu})$ and 0.21 g (1.65 mmol) of $\text{Li}(p\text{-C}_6\text{H}_4\text{NMe}_2)$, and 15 mL of Et_2O was condensed in. The mixture was stirred at -78°C for 10 min and then at room temperature for 12 h. The Et_2O was next replaced with 15 mL of pentane, and the mixture was filtered. Finally, the volume of pentane was reduced to ca. 8 mL. Cold filtration (-78°C) afforded a snow-white solid. Yield: 48.0%. $^1\text{H NMR}$ (C_6D_6): δ 7.82 (d, 2 H), 6.94 (d, 2 H), 2.69 (s, 6 H), 2.01 (s, 30 H), 1.41 (s, 9 H). Anal. Calcd for $\text{C}_{22}\text{H}_{49}\text{NOTh}$: C, 55.24; H, 7.10; N, 2.01. Found: C, 55.76; H, 7.10; N, 2.03.

Synthesis of $\text{Cp}'_2\text{U}(\text{Me})[\text{OCH}(t\text{-Bu})_2]$. A 30-mL flask was charged with 0.33 g (0.61 mmol) of $\text{Cp}'_2\text{UMe}_2$ and 0.13 g (0.90 mmol) of $\text{HOCH}(t\text{-Bu})_2$. The flask was next evacuated while cooling the contents with dry ice–acetone to prevent the sublimation of the alcohol. Then, 15 mL of toluene was condensed into the flask with use of liquid nitrogen. The mixture was subsequently stirred for 10 min at -78°C and then for 1 h at room temperature and was filtered. Toluene was replaced by 15 mL of pentane, and the solid residue was washed once with pentane. The solvent was then replaced by 15 mL of fresh pentane and the solution slowly cooled to -78°C . Cold filtration (-78°C) afforded a green crystalline solid. Yield: 71%. $^1\text{H NMR}$ (C_6D_6): δ 124.9 (s, 1 H), 19.4 (s, 9 H), 11.5 (s, 9 H), 3.06 (s, 15 H), -1.30 (s, 15 H), -188.2 (s, 3 H). Anal. Calcd for $\text{C}_{30}\text{H}_{52}\text{OU}$: C, 54.04; H, 7.86. Found: C, 54.03; H, 7.55.

Identification of $\text{Cp}'_2\text{U}(\text{H})[\text{OCH}(t\text{-Bu})_2]$. The reaction of H_2 with $\text{Cp}'_2\text{U}(\text{Me})[\text{OCH}(t\text{-Bu})_2]$ gave $\text{Cp}'_2\text{U}(\text{H})[\text{OCH}(t\text{-Bu})_2]$, which was identified by the similarity of the $^1\text{H NMR}$ spectrum to that of other $\text{Cp}'_2\text{U}(\text{H})\text{OR}^{\text{4a,13}}$ complexes. NMR (C_6D_6): δ 276.7 (s, 1 H), 135.3 (s, 1 H), 17.4 (s, 9 H), 11.7 (s, 9 H), 0.88 (s, 15 H), -3.07 (s, 15 H).

Synthesis of $\text{Cp}'_2\text{U}(\text{CH}_2\text{-}t\text{-Bu})(\text{O-}t\text{-Bu})$. A 30-mL flask was charged with 0.45 g (0.73 mmol) of $\text{Cp}'_2\text{U}(\text{Cl})(\text{O-}t\text{-Bu})$ and 0.060 g (0.77 mmol) of $\text{LiCH}_2\text{-}t\text{-Bu}$, and 20 mL of Et_2O was condensed in. The mixture was stirred at -78°C for 2 h and then at room temperature for 1.5 h. Et_2O was then replaced by 15 mL of pentane. The solution was next filtered, and the residual solids were washed once with pentane. The pentane was then pumped off, and a red-brown crystalline solid was obtained. Yield: 63%. $^1\text{H NMR}$ (C_6D_6): δ 34.3 (s, 9 H), 1.02 (s, 30 H), -17.4 (s, 9 H), -172.5 (s, 2 H). Anal. Calcd for $\text{C}_{29}\text{H}_{50}\text{OU}$: C, 53.36; H, 7.72; U, 36.47. Found: C, 52.49; H, 7.31; U, 37.29.

Identification of $\text{Cp}'_2\text{U}(\text{H})(\text{O-}t\text{-Bu})$. The reaction of H_2 with $\text{Cp}'_2\text{U}(\text{CH}_2\text{-}t\text{-Bu})(\text{O-}t\text{-Bu})$ gave $\text{Cp}'_2\text{U}(\text{H})(\text{O-}t\text{-Bu})$, which was identified by the characteristic $^1\text{H NMR}$ spectrum. NMR (C_6D_6): δ 267.1 (s, 1 H), 29.8 (s, 9 H), -1.35 (s, 30 H).

Identification of $\text{Cp}'_2\text{Th}(\text{H})[\text{OSiMe}_2(t\text{-Bu})]$. The reaction of H_2 with $\text{Cp}'_2\text{Th}(\text{Me})[\text{OSiMe}_2(t\text{-Bu})]$ gave $\text{Cp}'_2\text{Th}(\text{H})[\text{OSiMe}_2(t\text{-Bu})]$, which was identified by $^1\text{H NMR}$. NMR (C_6D_6): δ 18.0 (s, 1 H), 2.10 (s, 30 H), 1.05 (s, 9 H), 0.15 (s, 6 H).

Kinetic Studies of $\text{Cp}'_2\text{M}(\text{R})(\text{X}) + \text{H}_2$ Reactions. In a typical experiment, the NMR kinetics vessel described elsewhere¹⁷ was charged in the glovebox with a carefully weighed quantity (ca. 50 mg, 0.08 mmol) of the actinide complex dissolved in 3.0 mL of toluene- d_8 or other appropriate solvent. On the vacuum line, the solution was freeze–pump–thaw degassed three times. Then, H_2 of the desired pressure was introduced while the sample portion of the vessel was kept at -78°C . The amount of H_2 introduced was at least 20 times in molar excess that required to maintain pseudo-zero-order reaction conditions for H_2 . Then the vessel was immediately immersed in a constant-temperature bath, which was usually set to $30.0 \pm 0.1^\circ\text{C}$ and the solution stirred vigorously with a magnetic stirring bar. Control experiments established that the

(17) Katahira, D. A.; Moloy, K. G.; Marks, T. J. *Organometallics* **1982**, *1*, 1723–1726.

kinetics are not influenced by mass-transport effects under these conditions. After a measured time interval, the vessel was removed from the constant-temperature bath, and the stirring bar was lifted to a side chamber with the help of an external magnet. Then the vessel was placed in the probe of the JEOL FX-90Q NMR spectrometer, which was maintained at -40 °C. Before spectral data acquisition, the spectrometer was shimmed in the nonspinning mode. A long pulse delay was used to avoid saturation. No observable reaction was noticed during the data accumulation period at -40 °C. The kinetics were usually monitored from the intensity of the metal hydride (Th complexes) or Cp' (U complexes) signal over approximately 3 half-lives.

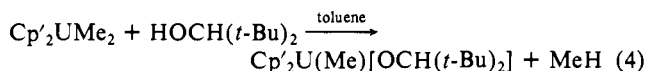
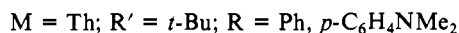
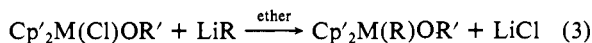
The concentration of the hydride, C, was measured by the hydride peak area A_H standardized to the residual solvent peak area A_S ($C = A_H/A_S$) by using a cutting and weighing procedure. All data collected for the hydrogenolysis reactions could be fit by least-squares to eq 2,

$$\ln [(C_\infty - C_0)/(C_\infty - C)] = k't \quad (2)$$

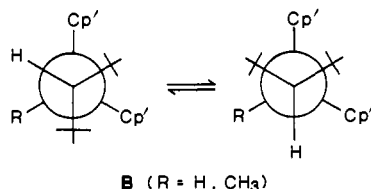
where C_0 is the initial concentration of the hydride and C_∞ is the final concentration. Standard deviations in the rate constants are derived from the fitting procedure. For the hydrogenolysis of $\text{Cp}'_2\text{Th}(\text{CH}_2-t\text{-Bu})(\text{O}-t\text{-Bu})$ and $\text{Cp}'_2\text{Th}(\text{Cl})(\text{CH}_2-t\text{-Bu})$, there is a good agreement between rate constants obtained by monitoring the methylene peak and those obtained by monitoring the hydride peak (i.e., there is no evidence of hydride exchange with solvent deuterons). H_2 solubilities were taken from the literature.¹⁸

Results

Synthesis. All hydrocarbyl complexes employed in this study were prepared as described elsewhere^{4a,12e,13-15} except for the alkoxyhydrocarbyls shown in eq 3 and 4. These were prepared



by straightforward approaches and were characterized by standard methodology (see the Experimental Section for details). One interesting structural/spectroscopic feature of both $\text{Cp}'_2\text{U}(\text{Me})[\text{OCH}(t\text{-Bu})_2]$ and $\text{Cp}'_2\text{U}(\text{H})[\text{OCH}(t\text{-Bu})_2]$ is magnetic nonequivalence of Cp' and $t\text{-Bu}$ protons in the isotropically shifted ^1H NMR at room temperature. This can be understood in terms of conformer **B** and restricted rotation of the alkoxy ligand. In



each case, raising the temperature results in reversible broadening, collapse, and finally coalescence of the separate Cp' and $t\text{-Bu}$ signals. At 270 MHz, the coalescence temperature of the Cp' signals (having nearly identical chemical shift separations at 30 °C) is ca. 100 °C for R = CH₃ and ca. 140 °C for R = H.

Hydrogenolysis Studies. All of the hydrocarbyl complexes investigated undergo metal-carbon bond cleavage (eq 1) to form the corresponding hydrides. In all cases, the hydrides are known compounds^{4a,13-15} or can be readily identified by ^1H NMR spectra, which are closely analogous to those of known hydrides. Kinetic measurements were carried out in a pseudo-constant-pressure reaction vessel, which incorporates a 10-mm NMR tube, a 600-mL gas reservoir, high-vacuum connections, and a means of efficient stirring.¹⁷ As monitored by the appearance of the product Th-H or Cp'₂U signal in the ^1H NMR, the majority of the reactions were found to be first-order in metal complex over 3 or more half-lives. The only complications encountered were in systems

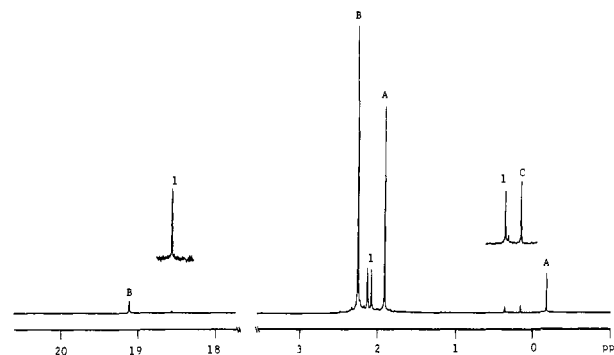
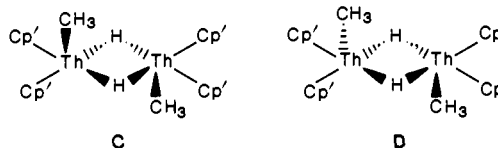


Figure 1. ^1H NMR spectrum (270 MHz, toluene- d_8 , 25 °C) taken during the $\text{Cp}'_2\text{ThMe}_2$ hydrogenolysis process. Resonances marked A denote $\text{Cp}'_2\text{ThMe}_2$, B denote $(\text{Cp}'_2\text{ThH}_2)_2$, C denote CH_4 , and I denote an intermediate species.

where rates were too rapid or too slow to be measured accurately or where additional follow-up chemistry or hydride precipitation occurred (vide infra). In the cases of $\text{Cp}'_2\text{Th}(\text{CH}_2-t\text{-Bu})(\text{O}-t\text{-Bu})$ and $\text{Cp}'_2\text{Th}(\text{Cl})(\text{CH}_2-t\text{-Bu})$, the reaction rates determined by the disappearance of the neopentyl methylene signals were indistinguishable from those determined from the appearance of the Th-H signals.

The reaction of $\text{Cp}'_2\text{ThMe}(\text{O}_3\text{SCF}_3)$ with hydrogen initially follows good first-order kinetics, and a hydride, presumed to be $\text{Cp}'_2\text{Th}(\text{H})(\text{O}_3\text{SCF}_3)$, is observed in the ^1H NMR (δ 20.0 (s, 1 H, ThH), 2.16 (s, 30 H, Cp')). However, these spectral features slowly begin to decay, and new resonances, which lack a Th-H signal, grow in. This observation suggests reduction of the trifluoromethanesulfonate anion by the hydridic thorium hydride.¹⁹ In the case of $\text{Cp}'_2\text{ThMe}_2$, a species other than the ultimate $(\text{Cp}'_2\text{ThH}_2)_2$ ^{4a,20} product is observed by ^1H NMR to grow in and to remain in low, approximately steady-state concentrations throughout most of the reaction. The disappearance of $\text{Cp}'_2\text{ThMe}_2$ and the formation of $(\text{Cp}'_2\text{ThH}_2)_2$ obey first-order kinetics. The ^1H NMR spectrum of the intermediate species (Figure 1) exhibits Th-H (δ 18.6), nonequivalent Cp' (δ 2.14, 2.09), and Th-CH₃ (δ 0.35) signals in an intensity ratio of 1:15:15:3. The simplest molecular structures that accommodate the Cp' nonequivalence are dimers analogous to $(\text{Cp}'_2\text{ThH}_2)_2$ ²⁰ (C) and $[(\text{CH}_3\text{C}_5\text{H}_4)\text{-ZrH}_2]_2$ ²¹ (D). The C₂ structure C is only compatible with the



NMR data if the $\mu\text{-H}$ atoms are magnetically degenerate or rapidly interconverting. Structure **D** is compatible as long as the symmetry is only C₂ or C_i (the $(\text{CH}_3)\text{Th}(\mu\text{-H})_2\text{Th}(\text{CH}_3)$ fragment does not lie in a mirror plane). Although not investigated in great detail, analogous, but somewhat weaker, intermediate signals are observed in the hydrogenolysis of $\text{Cp}'_2\text{Th}(n\text{-Bu})_2$. In the case of $\text{Me}_2\text{Si}(\text{Me}_4\text{C}_5)_2\text{Th}(n\text{-Bu})_2$, an accurate kinetic analysis was complicated by precipitation of the sparingly soluble hydride, $[\text{Me}_2\text{Si}(\text{Me}_4\text{C}_5)_2\text{ThH}_2]_2$,^{13bc} after ca. 1.5–2 half-lives. There was no evidence of an intermediate in the 400-MHz ^1H NMR spectrum.

As already noted, the hydrogenolysis of most complexes obeys first-order kinetics at constant H_2 pressure. In the case of $\text{Cp}'_2\text{Th}(\text{CH}_2-t\text{-Bu})(\text{O}-t\text{-Bu})$, the reaction kinetics were investigated as a function of H_2 pressure. Representative first-order kinetic plots are shown in Figure 2, and the dependence of the observed

(19) Andersen, K. K. In *Comprehensive Organic Chemistry*; Jones, D. N., Ed.; Pergamon: Oxford, 1979; Vol. 3, Chapter 11.19.

(18) (a) Cook, M. W.; Hanson, D. N.; Alder, B. J. *J. Chem. Phys.* **1957**, *26*, 748–751. (b) Young, C. L., Ed. *Solubility Data Series: Hydrogen and Deuterium*; Pergamon: Oxford, 1981; Vol. 5/6, p 219.

(20) 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.

(21) Jones, S. B.; Petersen, J. L. *Inorg. Chem.* **1981**, *20*, 2889–2894.

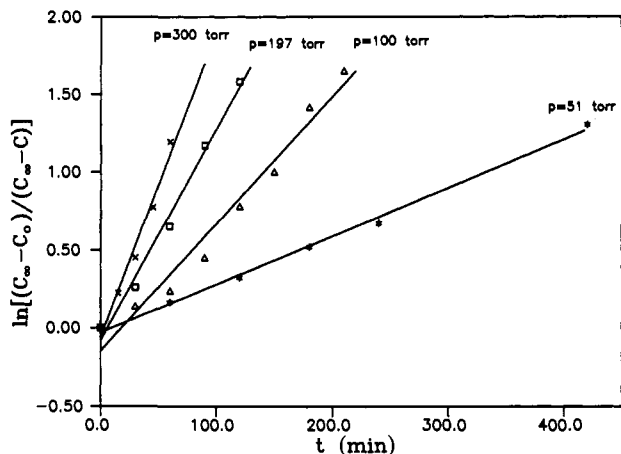


Figure 2. Kinetic plots for the hydrogenolysis of $\text{Cp}'_2\text{Th}(\text{CH}_2\text{-}t\text{-Bu})(\text{O-}t\text{-Bu})$ at various hydrogen pressures at 30.0 °C.

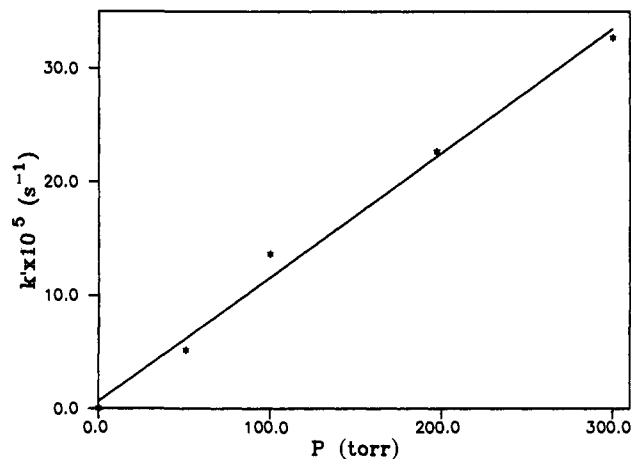


Figure 3. Plot of the pseudo-first-order rate constant k' versus hydrogen pressure P for the hydrogenolysis of $\text{Cp}'_2\text{Th}(\text{CH}_2\text{-}t\text{-Bu})(\text{O-}t\text{-Bu})$.

Table I. Second-Order Rate Constant Data for Hydrogenolysis of $\text{Cp}'_2\text{M}(\text{R})\text{X}$ Complexes in Toluene

compound	k , Torr ⁻¹ s ⁻¹	k , M ⁻¹ s ⁻¹	T , °C
$\text{Cp}'_2\text{ThCH}_2\text{C}(\text{CH}_3)_2\text{CH}_2$	$>10^{-5}$	>1	30.0
$\text{Cp}'_2\text{U}(\text{CH}_2\text{-}t\text{-Bu})(\text{O-}t\text{-Bu})$	$>10^{-5}$	>1	30.0
$\text{Cp}'_2\text{Th}(\text{CH}_2\text{-}t\text{-Bu})[\text{OCH}(t\text{-Bu})_2]$	$1.1(1) \times 10^{-6}$	$2.9(3) \times 10^{-1}$	30.0
$\text{Cp}'_2\text{Th}(\text{CH}_2\text{-}t\text{-Bu})(\text{O-}t\text{-Bu})$	$1.1(1) \times 10^{-6}$	$2.7(2) \times 10^{-1}$	30.0
$\text{Cp}'_2\text{Th}(\text{CH}_2\text{-}t\text{-Bu})(\text{O-}t\text{-Bu}) + \text{D}_2$	$4.5(4) \times 10^{-7}$	$1.1(1) \times 10^{-1}$	30.0
$\text{Cp}'_2\text{Th}(\text{CH}_2\text{-}t\text{-Bu})(\text{Cl})$	$8.2(6) \times 10^{-7}$	$2.0(1) \times 10^{-1}$	30.0
$\text{Me}_2\text{Si}(\text{Me}_2\text{C}_5)_2\text{Th}(\eta\text{-Bu})_2^a$	$\sim 4 \times 10^{-7}$	$\sim 1.0 \times 10^{-1}$	30.0
$\text{Cp}'_2\text{Th}(\eta\text{-Bu})_2$	$1.5(1) \times 10^{-7}$	$3.8(3) \times 10^{-2}$	30.0
$\text{Cp}'_2\text{ThMe}_2$	$1.4(2) \times 10^{-7}$	$3.6(6) \times 10^{-2}$	30.0
$\text{Cp}'_2\text{Th}(\text{Me})(\text{O}_3\text{SCF}_3)^b$	$\sim 1 \times 10^{-8}$	$\sim 2 \times 10^{-3}$	30.0
1	$4.5(3) \times 10^{-9}$	$1.1(1) \times 10^{-3}$	30.0
$\text{Cp}'_2\text{Th}(\text{Me})[\text{OSiMe}_2(t\text{-Bu})]$	$3.0(4) \times 10^{-8}$	$6.3(8) \times 10^{-3}$	60.0
$\text{Cp}'_2\text{ZrMe}_2$	$2.2(2) \times 10^{-8}$	$4.8(3) \times 10^{-3}$	60.0
$\text{Cp}'_2\text{Th}(\rho\text{-C}_6\text{H}_4\text{NMe}_2)(\text{O-}t\text{-Bu})$	$2.2(2) \times 10^{-8}$	$4.8(4) \times 10^{-3}$	60.0
$\text{Cp}'_2\text{Th}(\text{Ph})(\text{O-}t\text{-Bu})$	$4.5(5) \times 10^{-9}$	$9.5(11) \times 10^{-4}$	60.0
$\text{Cp}'_2\text{U}(\text{Me})[\text{OCH}(t\text{-Bu})_2]$	$3.5(1) \times 10^{-9}$	$7.5(3) \times 10^{-4}$	60.0
$\text{Cp}'_2\text{Th}(\text{Me})[\text{OCH}(t\text{-Bu})_2]^c$	$\sim 3 \times 10^{-10}$	$\sim 5 \times 10^{-5}$	100.0

^a Kinetic analysis complicated by precipitation of hydride product. ^b Kinetic analysis complicated by follow-up reaction. ^c Kinetic analysis complicated by slowness of reaction.

pseudo-first-order rate constants on hydrogen pressure (Figure 3) indicates the rate law shown in eq 5. Making the reasonable

$$\nu = k[\text{Th}]P_{\text{H}_2} \quad (5)$$

assumption that the other hydrogenolysis reactions have similar kinetic dependence on P_{H_2} and using tabulated H_2 solubility¹⁸ and toluene density²² data yield the second-order rate constants in

(22) Riddick, J. A.; Bunger, W. B. *Techniques of Chemistry, Organic Solvents*; Wiley: New York, 1970; Vol. II, p 109 (toluene), p 220 (THF).

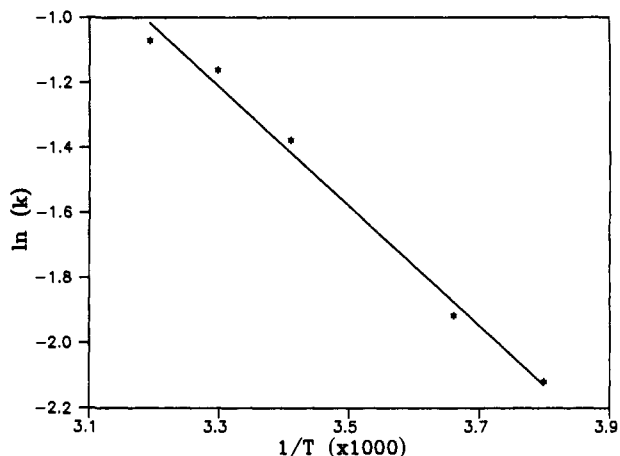


Figure 4. Arrhenius plot for the hydrogenolysis of $\text{Cp}'_2\text{Th}(\text{CH}_2\text{-}t\text{-Bu})(\text{O-}t\text{-Bu})$. Units: k , M⁻¹ s⁻¹; T , K.

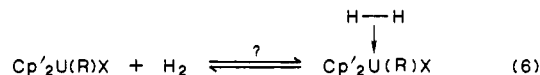
Table II. Activation Parameters for Hydrogenolysis of Two $\text{Cp}'_2\text{M}(\text{R})\text{X}$ Complexes in Toluene

compound	$\text{Cp}'_2\text{Th}(\text{CH}_2\text{-}t\text{-Bu})(\text{O-}t\text{-Bu})$	$\text{Cp}'_2\text{U}(\text{Me})[\text{OCH}(t\text{-Bu})_2]$
E_a , kcal/mol	3.7 (2)	10 (2)
$\log A$	2.1 (2)	3 (1)
ΔH^\ddagger , kcal/mol	3.1 (2)	9 (2)
ΔS^\ddagger , eu	-50.8 (7)	-45 (5)

Table I. In the case of $\text{Cp}'_2\text{ThCH}_2\text{C}(\text{CH}_3)_2\text{CH}_2$ and $\text{Cp}'_2\text{U}(\text{CH}_2\text{-}t\text{-Bu})(\text{O-}t\text{-Bu})$, the hydrogenolysis rate is too rapid to measure accurately at 30 °C, while in the case of $\text{Cp}'_2\text{Th}(\text{Me})[\text{OCH}(t\text{-Bu})_2]$ the half-life at 100 °C is on the order of several months.

The rate of $\text{Cp}'_2\text{Th}(\text{CH}_2\text{-}t\text{-Bu})(\text{O-}t\text{-Bu})$ hydrogenolysis was also investigated with D_2 .²³ The Th-C cleavage process is significantly slower, and a kinetic isotope effect (KIE) of $k_{\text{H}}/k_{\text{D}} = 2.5(4)$ is derived. The rate of $\text{Cp}'_2\text{Th}(\text{CH}_2\text{-}t\text{-Bu})(\text{O-}t\text{-Bu})$ hydrogenolysis was also examined in THF- d_8 , and a modest solvent effect of $k_{\text{THF}}/k_{\text{toluene}} = 2.9(4)$ is found to be operative. The temperature dependence of hydrogenolysis was also measured for representative thorium ($\text{Cp}'_2\text{Th}(\text{CH}_2\text{-}t\text{-Bu})(\text{O-}t\text{-Bu})$) and uranium ($\text{Cp}'_2\text{U}(\text{Me})[\text{OCH}(t\text{-Bu})_2]$) complexes. Satisfactory Arrhenius (e.g., Figure 4) and Eyring plots were obtained, and derived activation parameters are set out in Table II. Particularly noteworthy are the small enthalpies of activation and the rather large, negative entropies of activation.

Efforts were also made to detect interaction between dihydrogen and the coordinatively unsaturated actinide complexes prior to hydrogenolysis (e.g., a dihydrogen complex²⁴ as in eq 6). Because



of the large isotropic shifts expected for nuclei in close proximity to the paramagnetic U(IV) $5f^2$ ion,^{4a,14,25} studies were conducted with $\text{Cp}'_2\text{U}(\text{Me})[\text{OCH}(t\text{-Bu})_2] + \text{H}_2$ (1.1 atm) over the temperature range +25 to -90 °C. No shift in the dissolved H_2 peak versus the internal toluene- d_7 resonance was observed, no were new, isotropically shifted spectral features detected. Assuming

(23) (a) For D_2 solubilities in various solvents, see: Wilhelm, E.; Battino, R. *Chem. Rev.* **1973**, *73*, 1-9, and ref 18b. (b) Disappearance of the neopentyl methylene signals was monitored.

(24) (a) Kubas, G. J.; Ryan, R. R.; Wroblewski, G. A. *J. Am. Chem. Soc.* **1986**, *108*, 1339-1341. (b) Sweany, R. *J. Am. Chem. Soc.* **1985**, *107*, 2374-2379. (c) Upmacis, R. K.; Gadd, G. E.; Poliakov, M.; Simpson, M. B.; Turner, J. J.; Whyman, R.; Simpson, A. F. *J. Chem. Soc., Chem. Commun.* **1985**, 27-30. (d) Church, S. P.; Grevels, F.-W.; Hermann, H.; Schaffner, K. *J. Chem. Soc., Chem. Commun.* **1985**, 30-32. (e) Crabtree, R. H.; Lavin, M. *J. Chem. Soc., Chem. Commun.* **1985**, 794-797, 1661-1662. (f) Morris, R. H.; Sawyer, J. F.; Shiralioni, M.; Zubkowski, J. D. *J. Am. Chem. Soc.* **1985**, *107*, 5581-5582.

(25) Fischer, R. D. In reference 4b, Chapter 8.

a bound H_2 chemical shift of ca. 260 ppm¹⁴ and eq 6 at the fast exchange limit at room temperature, it can be estimated that less than ca. 0.001% of the uranium complex is present as a dihydrogen complex or, using published H_2 solubilities,¹⁸ that $K(\text{eq } 6) \lesssim 10^{-3} M^{-1}$ at room temperature.

The anticipated efficacy of paramagnetic U(IV) to serve as a spin-lattice relaxation (via dipolar and electron-nuclear hyperfine interactions) reagent²⁶ for bound H_2 offers an alternative means to probe for transitory η^2 - H_2 complexation. Furthermore, the effect should be describable, to a first approximation, by the classic Solomon-Bloembergen equations (e.g., eq 7).^{26,27} Here T_{1p} is

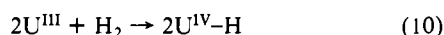
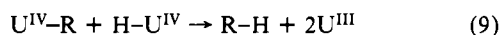
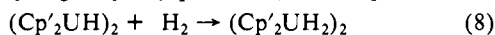
$$1/T_{1p} = f/(T_{1M} + \tau_M) \quad i = 1 \text{ or } 2 \quad (7)$$

the observed spin-lattice relaxation time for the exchanging ligand of interest, f is the fraction of ligand that is bound, T_{1M} is the bound-ligand relaxation time, and τ_M is the mean lifetime of the metal-ligand complex. Measurements on $Cp'_2U(H)(O-t-Bu)$ yield a U-H T_1 of 0.096 (8) s (ca. 10 mM in toluene- d_8) at 30 °C. For a mixture of H_2 (ca. 3 mM) and a presumably noncoordinating cyclohexane standard (ca. 1 mM) in toluene- d_8 at 30 °C, T_1 values of 1.39 (6) and 17.9 (5) s, respectively, are measured. For an identical toluene- d_8 solution (30 °C) also containing ca. 10 mM $Cp'_2U(CH_3)[OCH(t-Bu)_2]$, H_2 , and cyclohexane, T_1 values of 1.25 (7) and 17.5 (6) s, respectively, are determined. These results yield little evidence for significant preferential H_2 spin-lattice relaxation. Assuming $\tau_M < 10^{-4}$ s, $T_{1M} = 0.096$ s, and $T_{1p} \gtrsim 1.2$ s, it is estimated that $\lesssim 2\%$ of the $Cp'_2U(CH_3)[OCH(t-Bu)_2]$ is bound as an H_2 complex.

Discussion

In interpreting the present organoactinide hydrogenolysis results, we make primary reference to the heterolytic description of eq 1. The possibility of oxidative addition/reductive elimination processes involving Th(IV) seems unlikely on the basis of known redox properties⁴ as well as PES²⁸ and theoretical results.^{10a,29} In principle, U(IV) \rightarrow U(VI) processes are energetically more feasible;³⁰ however, such chemistry is, at present, unknown for organoactinide complexes.^{4,30} Although the present experiments do not explicitly address the possibility of a homolytic free-radical chain process^{1a,9a} (U(IV) \rightarrow U(III) is feasible,^{4,30b} Th(IV) \rightarrow Th(III) is less so^{4,31}), organoactinide^{4c} and organolanthanide^{3a,b} results presented elsewhere argue against the importance of such processes. Thus, hydrogen abstraction from solvents or radical dimerization/disproportionation products are not evident, not is the free radical-diagnostic inversion of 2-butenyl fragments observed.^{3a}

BinuclearU(III) \rightarrow U(IV) addition processes (e.g., known eq 8)^{4c} could, in principle, be coupled with binuclear eliminations to effect U-R hydrogenolysis (eq 9 and 10) In the present case,



(26) (a) Campbell, I. D.; Dwek, R. A. *Biological Spectroscopy*; Benjamin/Cummings: Menlo Park, CA, 1984; pp 127-177. (b) Jardetzky, O.; Roberts, G. C. K. *NMR in Molecular Biology*; Academic: New York, 1981; pp 83-114. (c) Marks, T. J.; Kolb, J. R. *J. Am. Chem. Soc.* **1975**, *97*, 27-33.

(27) (a) Toney, J. H.; Brock, C. P.; Marks, T. J. *J. Am. Chem. Soc.* **1986**, *108*, 7263-7274. (b) Granot, J.; Feigon, J.; Kearns, D. R. *Biopolymers* **1982**, *21*, 181-201. (c) Granot, J.; Kearns, D. R. *Biopolymers* **1982**, *21*, 203-218. (d) Carrington, J.; McLachlan, A. D. *Introduction to Magnetic Resonance*; Harper & Row: New York, 1967; Chapter 13.

(28) (a) Fragalà, I. L.; Gulino, A. In reference 4b, Chapter 9. (b) Ciliberto, E.; Condorelli, G.; Fagan, P. J.; Manriquez, J. M.; Fragalà, I. L.; Marks, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 4755-4759. (c) In accord with theoretical results,²⁹ the PES data indicate that the only electrons available for oxidative addition are largely Cp' centered.

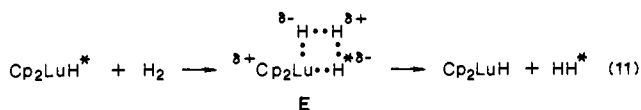
(29) Tatsumi, K.; Nakamura, A. *J. Am. Chem. Soc.* **1987**, *109*, 3195-3206.

(30) (a) PES²⁸ and theoretical results²⁹ reveal a uranium-centered HOMO containing two f electrons. (b) Weigel, F. In reference 4a, Chapter 5.

(31) (a) Bratsch, S. G.; Lagowski, J. J. *J. Phys. Chem.* **1986**, *90*, 307-312, and references therein. (b) Nugent, L. J. *MTP Int. Rev. Sci.: Inorg. Chem., Ser. Two* **1976**, *7*, Chapter 6. (c) Blake, P. C.; Lappert, M. F.; Atwood, J. L.; Zhang, H. *J. Chem. Soc., Chem. Commun.* **1986**, 1148-1149.

such chemistry would appear to require an induction period. For rate-limiting eq 9 and rapid eq 10 (the only scenario compatible with the NMR data and known properties of $Cp'_2U(H)(OR)$ complexes¹⁴), the kinetics would be autocatalytic³² and not obey the observed rate law. Furthermore, the prodigious steric requirements of eq 9 and 10 appear inhibitory, and it is not clear in such a situation why uranium substituent effects (vide infra) and activation parameters should so closely mirror those of the thorium analogues.

As already noted, the rate law for $Cp'_2Th(CH_2-t-Bu)(O-t-Bu)$ hydrogenolysis is first order in organoactinide and first order in H_2 (eq 5). Combined with a KIE of 2.5 (4), this result argues for a transition state in which H-H scission is rate-limiting. Evidence against a preequilibrium step involving an H_2 complex (an admittedly nonclassical one³³) is provided by the failure of NMR chemical shift and T_1 studies to detect such a species. Theoretical work at the EHMO level also fails to identify a structure of this type along the reaction coordinate.^{10a,34} The magnitude of the present KIE³⁵ can be compared to smaller values (ca. 1.06-1.22) reported for oxidative addition of dihydrogen to *trans*-Ir(Cl)(CO)(PPh₃)₂.³⁶ The latter result has been interpreted in terms of a reactant-like triangular transition state³⁶ with possibly as little as ca. 4% H-H stretching.³⁷ In contrast, EHMO studies of eq 11^{10a} reveal a substantial decrease in the H_2 H-H overlap



population on reaching the transition state (E).³⁸ Similar theoretical results have been obtained for the hydrogenolysis of Cp_2LuCH_3 .³⁴ In accord with our data and a heterolytic four-center picture is the larger reported KIE of 1.64 for the hydrogenolysis of *n*-octyllithium at 50 °C.³⁹

The solvent dependence of the hydrogenolysis rate and the activation parameters are also informative. Although these organoactinides are far too reactive to allow kinetic studies in solvents as polar as DMF, CH_2Cl_2 , and acetonitrile, the aforementioned observation that $k_{THF}/k_{toluene} = 2.9$ (4) also is in accord with some polarity in the transition state (eq 1). This sensitivity to solvent

(32) Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 2488-2489.

(33) (a) The current picture of bonding in transition-metal dihydrogen complexes^{9a,33b,c} involves both $H_2 \rightarrow M$ σ donation and $M \rightarrow H_2$ (σ^*) back-bonding. As drawn, an actinide- H_2 complex would be stabilized predominantly by the σ -bonding component, as in H_3^+ . The latter is bound by ca. 80 kcal/mol in the gas phase.^{33d} (b) Hay, P. J. *Chem. Phys. Lett.* **1984**, *103*, 466-471. (c) Jean, Y.; Eisenstein, O.; Volatron, F.; Maouche, B.; Sefta, F. *J. Am. Chem. Soc.* **1986**, *108*, 6587-6592. (d) Greenwood, N. N.; Earnshaw, A. *The Chemistry of the Elements*; Pergamon: Oxford, 1984; p 43.

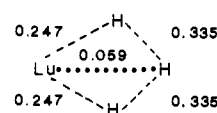
(34) Saillard, J.-Y., private communication.

(35) (a) The approximate relationship^{35b} $k_1/k_2 = e^{(0.7193(v_1-v_2)/T)}$ predicts a maximum H_2/D_2 KIE of ca. 16.8 for atom-transfer reactions at room temperature. For simple atom-transfer reactions in the gas phase, experimental H_2/D_2 KIE values in the range 1-6^{35c-e} are common near room temperature. (b) Buddenbaum, W. E.; Shiner, V. J., Jr. In *Isotope Effects on Enzyme-Catalyzed Reactions*; Cleland, W. W., O'Leary, M. H., Northrop, D. B., Eds.; University Park: Baltimore, 1977; Chapter 1. (c) Fitzcharles, M.; Schatz, G. C. *J. Phys. Chem.* **1986**, *90*, 3634-3644, and references therein. (d) Schatz, G. C. *J. Chem. Phys.* **1985**, *83*, 5677-5686, and references therein. We thank Professor G. C. Schatz for making us aware of ref 35c and d. (e) Cohen, N.; Westberg, K. R. *J. Phys. Chem. Ref. Data* **1983**, *12*, 531-590.

(36) (a) Zhou, P.; Vitale, A. A.; San Filippo, J., Jr.; Saunders, W. H., Jr. *J. Am. Chem. Soc.* **1985**, *107*, 8049-8054. (b) Chock, P. B.; Halpern, J. J. *J. Am. Chem. Soc.* **1966**, *88*, 3511-3514. (c) Reference 1a, p 298.

(37) Kitaura, K.; Obara, S.; Morokuma, K. *J. Am. Chem. Soc.* **1981**, *103*, 2891-2892.

(38) Reported^{10a} overlap populations:



(39) Vitale, A. A.; San Filippo, J., Jr. *J. Am. Chem. Soc.* **1982**, *104*, 7341-7343.

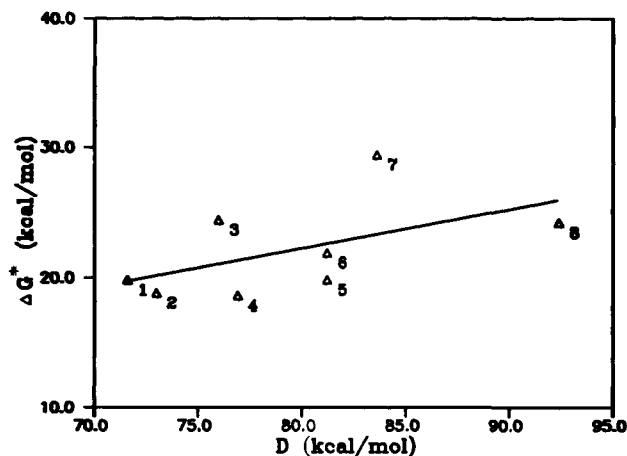
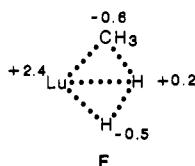


Figure 5. Relationship of the free energies of activation for $\text{Cp}'_2\text{M(R)X}$ hydrogenolysis versus experimental bond disruption enthalpies. Compound identification: (1) $\text{Cp}'_2\text{Th}(n\text{-Bu})_2$, (2) $\text{Cp}'_2\text{Th}(\text{CH}_2\text{-}t\text{-Bu})\text{Cl}$, (3) $\text{Cp}'_2\text{U}(\text{Me})[\text{OCH}(t\text{-Bu})_2]$, (4) $\text{Cp}'_2\text{Th}(\text{CH}_2\text{-}t\text{-Bu})(\text{O}-t\text{-Bu})$, (5) $\text{Cp}'_2\text{ThMe}_2$, (6) $\text{Cp}'_2\text{Th}(n\text{-Bu})[\text{OCH}(t\text{-Bu})_2]$, (7) $\text{Cp}'_2\text{Th}(\text{Me})[\text{OCH}(t\text{-Bu})_2]$, (8) $\text{Cp}'_2\text{Th}(\text{Ph})(\text{O}-t\text{-Bu})$.

polarity is roughly the same as for some Menshutkin reactions (e.g., $\text{Et}_3\text{N} + \text{EtI}$).⁴⁰ Interestingly, the addition of H_2 to $\text{trans-Ir}(\text{Cl})(\text{CO})(\text{PPh}_3)_2$ is accelerated by polar media as well.^{36b}

A reactivity mode that is not observed (or at least is not dominant) in $\text{Cp}'_2\text{Th}(\text{CH}_2\text{-}t\text{-Bu})(\text{O}-t\text{-Bu})$ chemistry is inhibition of hydrogenolysis by THF. This could arise if THF coordination sterically or electronically depressed H_2 activation at the metal center. Such behavior is suggested by results with less saturated/congested $\text{Cp}'_2\text{LnR}$ ($\text{Ln} = \text{lanthanide}$)^{7c} and $\text{Cp}'_2\text{ScR}$ complexes.^{6c} Also observed for the present actinide systems are small enthalpies of activation and large negative entropies of activation. The former parameters suggest a concerted process having significant bond making in the transition state to compensate for the bond breaking. This agrees well with the aforementioned mechanistic and theoretical (E)³⁸ results. The very negative entropies of activation are also in accord with highly organized transition states having significant polar character.^{36b,40} Furthermore, recent EHMO calculations³⁴ on the $\text{Cp}'_2\text{LuCH}_3 + \text{H}_2$ reaction yield the approximate, rather polar, transition-state charge distributions shown in F. Similar patterns in ΔS^\ddagger are observed



for both intra- and intermolecular heterolytic C–H activation processes at actinide centers.^{8c,f} Corresponding trends in both ΔH^\ddagger and ΔS^\ddagger have also been reported for H_2 addition to a number of group VIIIA (9)⁵⁴ complexes,³⁶ as well as for the hydrogenolysis of *n*-octyllithium.³⁹

As can be seen in Table I, $\text{Cp}'_2\text{M(X)(R)}$ hydrogenolysis rates are highly sensitive to the nature of the hydrocarbyl ligand, the metal, and ancillary ligands. For fixed metal (Th) and ancillary ligand (alkoxide), the order $\text{CH}_2\text{-}t\text{-Bu} > n\text{-Bu} > \text{Ph} > \text{Me}$ argues that H_2 attack is not impeded by steric factors. For both alkyl and aryl ligands, the rate constant data correlate qualitatively with the experimental Th–R bond disruption enthalpies.^{13,41} This can be seen in Figure 5. A comparison of $\text{Cp}'_2\text{Th}(\text{Ph})(\text{O}-t\text{-Bu})$ and $\text{Cp}'_2\text{Th}(p\text{-C}_6\text{H}_4\text{NMe}_2)(\text{O}-t\text{-Bu})$ hydrogenolysis rates also provides information on electronic aspects of the transition state. The

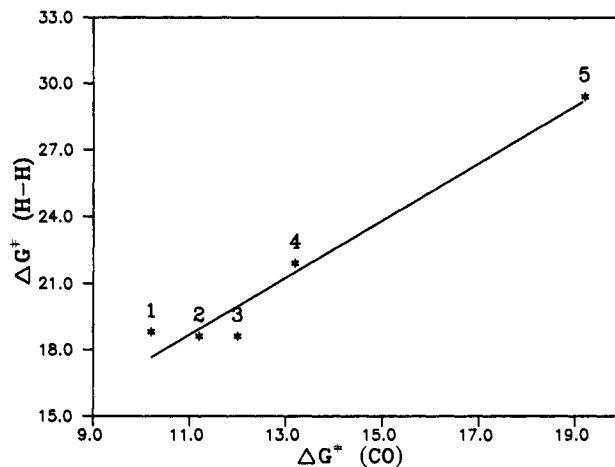
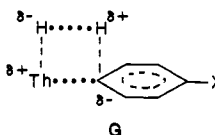


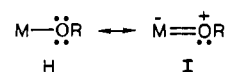
Figure 6. Relationship of the free energies of activation for hydrogenolysis versus CO insertion^{13a} in a series of $\text{Cp}'_2\text{Th(R)X}$ complexes. Compound identification: (1) $\text{Cp}'_2\text{Th}(\text{CH}_2\text{-}t\text{-Bu})\text{Cl}$, (2) $\text{Cp}'_2\text{Th}(\text{CH}_2\text{-}t\text{-Bu})(\text{O}-t\text{-Bu})$, (3) $\text{Cp}'_2\text{Th}(\text{CH}_2\text{-}t\text{-Bu})[\text{OCH}(t\text{-Bu})_2]$, (4) $\text{Cp}'_2\text{Th}(n\text{-Bu})[\text{OCH}(t\text{-Bu})_2]$, (5) $\text{Cp}'_2\text{Th}(\text{Me})[\text{OCH}(t\text{-Bu})_2]$.

electron-releasing NMe_2 group effects a 5.0 (1)-fold rate acceleration, in accord with an electrophilic attack on the aromatic ring (G). However, the derived Hammett $\rho \approx -0.4$ (based on



σ^+ values)⁴² evidences a rather modest (but not unprecedented) substituent sensitivity compared to that observed in typical electrophilic aromatic substitution reactions.⁴² Here ρ values in the range from -6 to -13 are common, although $\rho = -2.4$ has been reported for alkylation by $\text{EtBr}/\text{GaBr}_3$ and -2.9 for protodestannylation.⁴² An even smaller sensitivity has been reported for arene C–H activation processes at $\text{Sc}(\text{III})$ ^{6c} and $\text{Zr}(\text{IV})$ ⁴³ centers. For the same ligand array, uranium hydrogenolysis rates are more rapid than those for thorium. This trend can also be correlated with differences in bond-disruption enthalpy (Figure 5). Although the reaction mechanism was not investigated in great detail (the reaction is first order in zirconium, and no intermediates are perceptible in the ^1H NMR), it can be seen in Table I that $\text{Cp}'_2\text{ZrMe}_2$ hydrogenolysis is significantly slower than $\text{Cp}'_2\text{ThMe}_2$ hydrogenolysis.

In regard to ancillary ligand effects, the kinetic data reveal that alkoxide substitution greatly depresses the hydrogenolysis rate. For $\text{Cp}'_2\text{ThMe}_2 \rightarrow \text{Cp}'_2\text{Th}(\text{Me})(\text{OR})$, the rate falls by a factor of ca. 4×10^3 (Table I).⁴⁴ That the rate is insensitive to the bulk of the alkoxide ligand again suggests that H_2 attack is not sterically very sensitive. This alkoxide effect is explicable in terms of decreased metal electrophilicity, arising from the demonstrated^{4,45} π -donor character of alkoxide ligands in d^0, f^0 systems (H, I).



Closely connected and also possibly operative here may be the

(42) (a) Carey, F. A.; Sundberg, R. J. *Advanced Organic Chemistry*, 2nd ed.; Plenum: New York, 1984; Part A, pp 455–520. (b) Rys, P.; Skrabal, P.; Zollinger, H. *Angew. Chem., Int. Ed. Engl.* 1972, 11, 874–883.

(43) Latesky, S. L.; McMullen, A. K.; Rothwell, I. P.; Huffman, J. C. *J. Am. Chem. Soc.* 1985, 107, 5981–5987.

(44) The rate constant for $\text{Cp}'_2\text{Th}(\text{Me})[\text{OCH}(t\text{-Bu})_2]$ was adjusted to 30 °C by assuming $E_a = 7$ kcal/mol.

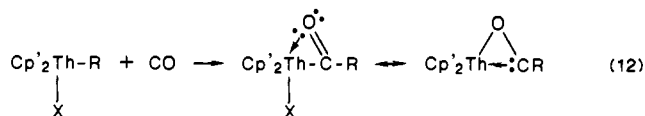
(45) (a) Bursten, B. E.; Casarin, M.; Ellis, D. E.; Fragalá, I.; Marks, T. J. *Inorg. Chem.* 1986, 25, 1257–1261. (b) Duttera, M. R.; Day, V. W.; Marks, T. J. *J. Am. Chem. Soc.* 1984, 106, 2907–2912. (c) Cotton, F. A.; Marler, D. O.; Schwotzer, W. *Inorg. Chim. Acta* 1984, 95, 207–209. (d) Cotton, F. A.; Marler, D. O.; Schwotzer, W. *Inorg. Chim. Acta* 1984, 85, L31–32.

(40) (a) Wiberg, K. B. *Physical Organic Chemistry*; Wiley: New York, 1964; pp 376–388. (b) Jones, R. A. Y. *Physical and Mechanistic Organic Chemistry*, 2nd ed.; Cambridge University: Cambridge, 1984; Chapter 5.

(41) (a) Bruno, J. W.; Marks, T. J.; Morss, L. R. *J. Am. Chem. Soc.* 1983, 105, 6824–6832. (b) Bruno, J. W.; Stecher, H. A.; Morss, L. R.; Sonnenberger, D. C.; Marks, T. J. *J. Am. Chem. Soc.* 1986, 108, 7275–7280.

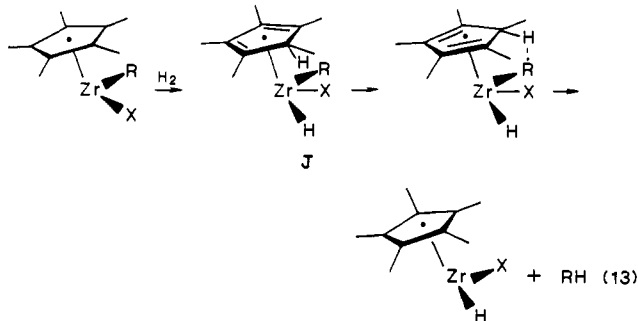
slight increase (ca. 2–4 kcal/mol) in $\text{Cp}'_2\text{MR}_2$ bond disruption enthalpies, which accompanies the introduction of alkoxide ancillary ligands.^{14,41} Not unexpectedly, more electron-withdrawing oxygenate ligands such as trifluoromethanesulfonate⁴⁶ and siloxide⁴⁷ do not depress the hydrogenolysis rate to as great an extent (Table I). Ancillary chloride ligation has a similar effect (Table I).

It is also of interest here to compare the present hydrocarbyl and ancillary ligand effects with those for a different Th-R disruption process: CO migratory insertion in the $\text{Cp}'_2\text{Th}(\text{X})\text{R}$ series (eq 12) where R is an alkyl group.¹³ Viewed in terms of



ΔG^\ddagger (Figure 6), it can be seen that there is some correlation in kinetic parameters. This result was by no means expected and indicates surprisingly similar electronic and bond energetic demands in the hydrogenolysis and carbonylation transition states.

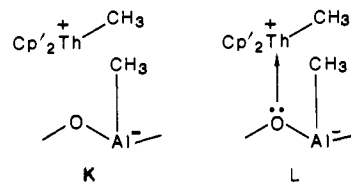
In studies of $\text{Cp}'_2\text{Zr}(\text{X})(\text{CH}_2-t\text{-Bu})/\text{C}_2\text{H}_4(\text{Me}_4\text{C}_5)_2\text{Zr}(\text{X})(\text{CH}_2-t\text{-Bu})$ hydrogenolysis processes (X = F, Cl, Br, H), Wochner and Brintzinger^{10c} observed a marked depression ($\geq 200\times$) in the reaction rate for the ring-bridged complexes having X = F, Cl, or Br and an inverse KIE ($k_{\text{H}_2}/k_{\text{D}_2} = 0.78$) for X = Cl. This result was interpreted in terms of Me_4C_5 ring involvement in the H-H scission process eq 13. Here, steric/electronic factors apparently



favor H_2 attack on the "X side", and the C_2H_4 bridge restricts the ring rotation required for RH elimination. For ancillary ligand X = H, Zr-R hydrogenolysis rates are far more rapid and insensitive to the presence of the C_2H_4 bridge. It was proposed^{10c} that the standard four-center mechanism is operative in this case. With regard to the importance of the ring-mediated pathway in organo-f-element hydrogenolysis processes, the absence in the present study both of an inverse KIE and of a large hydrogenolysis rate depression in $\text{Me}_2\text{Si}(\text{Me}_4\text{C}_5)_2\text{Th}(n\text{-Bu})_2$ versus $\text{Cp}'_2\text{Th}(n\text{-Bu})_2$ kinetics (Table I) argue against it. Furthermore, the stability of a "classical" diene complex as depicted in **J**^{10c} remains questionable for f-elements.^{4,49,50} It is conceivable, however, that the Wochner-Brintzinger mechanism is operative for $\text{Cp}'_2\text{ZrMe}_2$.

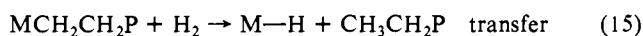
The present correlation between hydrogenolysis reactivity and the ancillary ligand-modulated electrophilic character at the metal

center finds a possible parallel in heterogeneous catalysis with organoactinides. On Lewis acidic dehydroxylated alumina, $\text{Cp}'_2\text{ThR}_2$ compounds are highly active catalysts for the hydrogenation of simple olefins,^{4b,d} and kinetic measurements indicate that Th-C hydrogenolysis is rate-limiting.⁵¹ Moreover, CPMAS NMR spectra reveal electron-deficient thorium adsorbate centers arising from methide transfer to surface aluminum sites (e.g., **K** and **L**).^{12c} In contrast, such Lewis acid sites are not available



on the surface of dehydroxylated silica, CPMAS spectra reveal more electron-rich $\text{Cp}'_2\text{Th}(\text{Me})(\text{OSi}\leftarrow)$ species, and the supported organoactinides do not exhibit significant catalytic activity.^{12f} From the present solution results, it is not surprising that electron-deficient thorium alkyls should be the most reactive with respect to hydrogenolysis.

As already mentioned, hydrogen is an important molecular weight control agent in Ziegler-Natta catalysis.⁵ To the extent that congruencies can be drawn between these complex, frequently heterogeneous early-transition-metal systems and "homogeneous" $\text{Cp}'_2\text{M}$ organo-f-element ethylene polymerization catalysts,^{3,7} it is interesting to note that H_2 -induced chain transfer (eq 15)



frequently obeys the same rate law as the present hydrogenolysis results (eq 5).⁵² We previously pointed out that the tendency in Ziegler-Natta catalysis of alkoxide ancillary ligands to depress chain-terminating β -hydride elimination processes⁵³ may have a thermodynamic basis in modifications of relative M-H/M-alkyl bond disruption enthalpies.¹⁴ The ancillary ligand effects on hydrogenolysis presented here now suggest that this thermodynamic advantage may well be counterbalanced by a depression in H_2 -induced chain-transfer rates caused by the same ancillary ligands.

Acknowledgment. We are grateful to the Department of Energy for support of this research under Contracts DEAC 02-81ER 10980 and DE F602 86ER 13511. We thank Prof. J.-Y. Saillard for information in advance of publication and V. P. Conticello for a sample of $\text{Me}_2\text{Si}(\text{Me}_4\text{C}_5)_2\text{Th}(n\text{-Bu})_2$.

Registry No. $\text{Cp}'_2\text{ThCH}_2\text{C}(\text{CH}_3)_2\text{CH}_2$, 83692-52-8; $\text{Cp}'_2\text{U}(\text{CH}_2-t\text{-Bu})(\text{O}-t\text{-Bu})$, 110487-75-7; $\text{Cp}'_2\text{Th}(\text{CH}_2-t\text{-Bu})[\text{OCH}(t\text{-Bu})_2]$, 91742-35-7; $\text{Cp}'_2\text{Th}(\text{CH}_2-t\text{-Bu})(\text{O}-t\text{-Bu})$, 91742-34-6; $\text{Cp}'_2\text{Th}(\text{CH}_2-t\text{-Bu})(\text{Cl})$, 74587-39-6; $\text{Me}_2\text{Si}(\text{Me}_4\text{C}_5)_2\text{Th}(n\text{-Bu})_2$, 89597-07-9; $\text{Cp}'_2\text{Th}(n\text{-Bu})_2$, 86727-40-4; $\text{Cp}'_2\text{ThMe}_2$, 67506-90-5; $\text{Cp}'_2\text{Th}(\text{Me})(\text{O}_3\text{SCF}_3)$, 110487-76-8; $\text{Cp}'_2\text{Th}(n\text{-Bu})[\text{OCH}(t\text{-Bu})_2]$, 91742-33-5; $\text{Cp}'_2\text{Th}(\text{Me})[\text{OSiMe}_2(t\text{-Bu})]$, 104835-35-0; $\text{Cp}'_2\text{ZrMe}_2$, 67108-80-9; $\text{Cp}'_2\text{Th}(\text{Ph})(\text{O}-t\text{-Bu})$, 110487-78-0; $\text{Cp}'_2\text{Th}(p\text{-C}_6\text{H}_4\text{NMe}_2)(\text{O}-t\text{-Bu})$, 110487-77-9; $\text{Cp}'_2\text{U}(\text{Me})[\text{OCH}(t\text{-Bu})_2]$, 110487-79-1; $\text{Cp}'_2\text{Th}(\text{Me})[\text{OCH}(t\text{-Bu})_2]$, 91742-32-4; $\text{Cp}'_2\text{U}(\text{Me}_2)$, 67605-92-9; $\text{Cp}'_2\text{U}(\text{Cl})(\text{O}-t\text{-Bu})$, 104489-79-4; $\text{HOCH}(t\text{-Bu})_2$, 14609-79-1.

(51) Gillespie, R. J.; Hedden, D.; Burwell, R. L., Jr.; Marks, T. J., to be submitted for publication.

(52) (a) Machon, J. A. In reference 5a, Part B, pp 639–649. (b) Böhm, L. L. *Polymer* **1978**, *19*, 562–569. (c) Doi, Y.; Neki, S.; Keii, T. *Polymer* **1980**, *21*, 1352–1355. (d) Cases also exist where H_2 appears to alter the nature of the catalyst: Mortimer, G. A.; Ort, M. R.; Mottus, E. H. *J. Polym. Sci., Polym. Chem. Ed.* **1978**, *16*, 1337–1342.

(53) (a) Reference 5c, pp 354–355. (b) Henrici-Olive, G.; Olive, S. *Adv. Polym. Sci.* **1974**, *15*, 1–30.

(54) In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III \rightarrow 3 and 13.)

(46) (a) Lawrance, G. A. *Chem. Rev.* **1986**, *86*, 17–33. (b) Although infrared spectroscopy indicates that the triflate ligand is coordinated,^{46c,d} exact details of the ligation mode are not yet known. (c) Dedert, P. L.; Sorrell, T.; Marks, T. J.; Ibers, J. A. *Inorg. Chem.* **1982**, *21*, 3506–3517. (d) Dedert, P. L.; Thompson, J. S.; Ibers, J. A.; Marks, T. J. *Inorg. Chem.* **1982**, *21*, 969–977, and references therein.

(47) Rochow, E. G. In *Comprehensive Inorganic Chemistry*; Bailar, J. C., Jr., Emeleus, H. J., Nyholm, R. S., Trotman-Dickenson, A. F., Eds.; Pergamon: Oxford, 1973; Vol. 1, p 1447.

(48) In $\text{Me}_2\text{Si}(\text{Me}_4\text{C}_5)_2\text{LnR}$ hydrogenolysis,^{3a} the bridging group effects a depression in rate of only ca. 3–7.

(49) (a) Marks, T. J.; Streitwieser, A. W., Jr. In reference 4a, Chapter 22. (b) Smith, G. M.; Suzuki, H.; Sonnenberger, D. C.; Day, V. W.; Marks, T. J. *Organometallics* **1986**, *5*, 549–561, and references therein.

(50) Indeed, the situation is by no means clear for group 4: (a) Yasuda, H.; Tatsumi, K.; Nakamura, A. *Acc. Chem. Res.* **1985**, *18*, 120–126. (b) Erker, G.; Krüger, C.; Müller, G. *Adv. Organomet. Chem.* **1985**, *24*, 1–39. (c) Schock, L. E.; Brock, C. P.; Marks, T. J. *Organometallics*, **1987**, *6*, 232–241.