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Organo-f-Element Thermochemistry. Metal–Ligand Bond Disruption Enthalpies in (Pentamethylcyclopentadienyl)thorium Hydrocarbyls, Metallacycles, Hydrides, and Dialkylamides

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Abstract: Thorium–ligand bond disruption enthalpies (D) have been determined in the series Cp'_2ThR_2 ($Cp' = \eta^5\text{-}(CH_3)_5C_5$) for a range of R groups including R = alkyl, aryl, metallacycle, hydride, and dialkylamide. Enthalpy data were obtained in an anaerobic batch-titration isoperibol reaction calorimeter from heats of solution in toluene followed by heats of alcoholysis with *tert*-butyl alcohol. Calculated Th–hydrocarbyl bond disruption enthalpies fall in the range 60–90 kcal/mol, with $C_6H_5 > CH_3 \approx CH_2Si(CH_3)_3 > CH_2CH_3 \gtrsim CH_2C_6H_5 \approx n\text{-}C_4H_9 \approx CH_2C(CH_3)_3$. Th–C bonds appear to be strengthened by ThOR coligands and possibly weakened by Th–Cl coligands. The strain energies in thoracyclobutanes $Cp'_2Th(CH_2)_2C(CH_3)_2$ and $Cp'_2Th(CH_2)_2Si(CH_3)_2$ are estimated to be ca. 16 and 8 kcal/mol, respectively. A Th–H bond is ca. 20 kcal/mol stronger than a Th–alkyl bond, while a $Th\text{–}NR_2$ bond is ca. 18 kcal/mol stronger. These data afford a considerably expanded understanding of organoactinide reaction patterns involving C–H activation, β-hydride elimination, and CO insertion as well as why they sometimes differ from those of middle and late first-row transition elements.

An indispensable prerequisite for understanding the course of known organometallic reactions and for predicting new ones is a detailed description of the reaction thermodynamics. Significantly, an accurate accounting of the strengths of chemical bonds being made and broken is usually impossible for a myriad of important organometallic/catalytic transformations. This point has recently been emphasized by Halpern, Whitesides, and others.[2-4] Although more information is gradually becoming available[2,4-10] (mostly for middle and late first-row transition metals), the paucity of reliable, systematic bond energy data for f-element[11] and many early transition-metal organometallic systems stimulated our interest in this problem. In particular, an emerging number of unusual organoactinide reaction patterns[12] suggested to us that important differences in bond dissociation enthalpy trends vis-à-vis the middle and late first-row transition elements might be operative.

Common techniques for acquiring metal–ligand bond dissociation energy data[4] include combustion[4a,b,11a,b] and solution calorimetry,[5-8] ion cyclotron resonance,[9] and electron-impact mass spectroscopy,[4a,b,11c] ion beam techniques,[10] kinetic and equilibrium measurements,[2,13] and photochemical threshold determinations.[14] The strengths and limitations of these various methods are discussed elsewhere.[2,4a,b] In the present investigation, we capitalize upon the tendency of organoactinide compounds of the type Cp'_2ThR_2 ($Cp' = \eta^5\text{-}(CH_3)_5C_5$, R = hydrocarbyl, hydride, or other ligand) to undergo rapid, sequential, quantitative, and highly exothermic protolysis[8] with alcohols such as *tert*-butyl alcohol (eq 1 and 2[12,15]). It is therefore possible to selectively and sequentially

$$Cp'_2ThR_2 + t\text{-}C_4H_9OH \rightarrow Cp'_2Th(R)(O\text{-}t\text{-}C_4H_9) + RH \quad (1)$$

$$Cp'_2Th(R)(O\text{-}t\text{-}C_4H_9) + t\text{-}C_4H_9OH \rightarrow Cp'_2Th(O\text{-}t\text{-}C_4H_9)_2 + RH \quad (2)$$

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(1) (a) Northwestern University. (b) Thesis parts appointee, Argonne National Laboratory. (c) Argonne National Laboratory.

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probe metal–ligand bonds of interest. Since all needed thermodynamic data are available for *tert*-butyl alchol and RH and the final thorium-containing product is the same in all cases, measurement of the enthalpies of these reactions by titration calorimetry[16] combined with several physically reasonable assumptions (vide infra) leads to a relative scale of Th–R bond disruption enthalpies, D,[17] formally defined as in eq 3 for the gas-phase process of eq 4. Here L_n represents various coligands. Furthermore, a plausible estimate of the Th–OR bond disruption enthalpy affords a series of absolute Th–R bond energies. This approach plausibly assumes that the bonding energetics of the Cp'_2Th fragment remain essentially constant throughout the series, which is supported by extensive metrical data.[12,18] In the present contribution, we describe such studies with a number of organothorium alkyls, aryls, metallacycles, hydrides, and dialkylamides (NR_2). It will be seen that such information provides a new and informative perspective on such important processes in organoactinide chemistry as intra- and intermolecular C–H activation, chemistry influenced by strain energies in metallacycles, β-hydride elimination and its microscopic reverse, olefin insertion into metal–carbon bonds, metal–carbon bond hydrogenolysis, CO insertion into metal–hydrogen bonds, and others. By extrapolation, these data are likely relevant to understanding certain reaction patterns in early transition-metal and lanthanide organometallic chemistry.

$$D(L_nTh\text{–}R) = \Delta H_f^\circ(L_nTh)(g) + \Delta H_f^\circ(R\cdot)(g) - \Delta H_f^\circ(L_nTh\text{–}R)(g) \quad (3)$$

$$L_nTh\text{–}R(g) \rightarrow L_nTh(g) + R\cdot(g) \quad (4)$$

We also describe in this contribution apparatus and methodology for carrying out batch-titration calorimetry under strictly anaerobic, anhydrous conditions. For the problem at hand, this method allows, for a suitably discriminating probe reaction, sequential and independent determinations of the reactant enthalpy of solution and of the enthalpy of protolysis of one metal–ligand bond (followed in some cases by the enthalpy of protolysis of the second metal–ligand bond).

Experimental Section

Synthetic Methods. All organoactinides were handled in Schlenk glassware on a dual manifold Schlenk line or interfaced to a high vacuum (10^{-5} torr) system. Solid transfers were accomplished in a Vacuum Atmospheres Corp. glovebox equipped with an atmosphere purification system, maintained under a nitrogen atmosphere. Argon (Matheson, prepurified), nitrogen (Matheson, prepurified), and hydrogen (Linde) were purified by passage through sequential columns of MnO and Davison 4A molecular sieves. Reactions with gases were carried out on the high vacuum line using a mercury-filled manometer. The complexes $Cp'_2Th(CH_3)_2$,[15a] $Cp'_2Th(C_2H_5)_2$,[15a] $Cp'_2Th(C_6H_5)_2$,[15a] $Cp'_2Th[CH_2C(CH_3)_3]_2$,[15a] $Cp'_2Th(CH_2)_2C(CH_3)_2$,[18b,c] $Cp'_2Th[CH_2Si(CH_3)_3]_2$,[15a] $Cp'_2Th(CH_2)_2Si(CH_3)_2$,[18b,c] $Cp'_2Th(Cl)CH_2CH_3$,[15a] $Cp'_2Th(Cl)CH_2C_6H_5$,[15a] $Cp'_2Th(Cl)N(CH_3)_2$,[18] $Cp'_2Th(Cl)N(CH_3)Si(CH_3)_3$,[19] and $(Cp'_2ThH_2)_2$[15a] were prepared and purified as described elsewhere. The new compound $Cp'_2Th(n\text{-}C_4H_9)_2$ was synthesized as described below.

Toluene, heptane, and diethyl ether (Mallinckrodt) were dried over sodium and molecular sieves, distilled from Na/K–benzophenone under a nitrogen atmosphere, and condensed into evacuated storage bulbs on the vacuum line. For calorimetric studies, toluene was further purified by an additional distillation on the vacuum line from Na/K alloy. *tert*-butyl alcohol was distilled on the vacuum line first from activated Davison 4A molecular sieves and then from CaH_2.

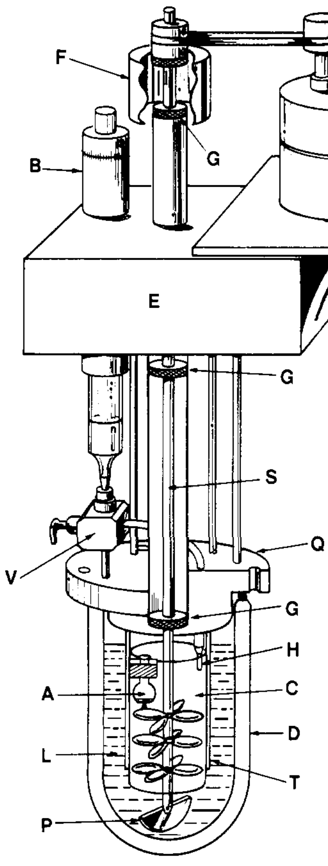

Figure 1. Diagram of the anaerobic batch-titration isoperibol reaction calorimeter employed in the present investigation. Components indicated by capital letters are identified in the Experimental Section.

Analytical Methods. Proton and carbon NMR spectra were obtained on either a JEOL FX 270 (FT, 270 MHz, ^{13}C 69.80 MHz), JEOL FX 90 (FT, 90 MHz), or Varian EM-360 (CW, 60 MHz) instrument. Infrared spectra were recorded on a Perkin-Elmer 599 spectrophotometer using Nujol 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.

Synthesis of $Th[(CH_3)_5C_5]_2(n\text{-}C_4H_9)_2$. A 1.55 M solution (3.6 mL, 5.58 mmol) of *n*-butyllithium in hexane was syringed into an argon-flushed flask, and after the solvent was removed in vacuo, ca. 6 mL of Et_2O was condensed in. In the glovebox, a frit apparatus was charged with 1.5 g (2.6 mmol) of Cp'_2ThCl_2. On the vacuum line, 20 mL of Et_2O was condensed onto the Cp'_2ThCl_2 at −78 °C and, under an argon flush, the *n*-BuLi/Et_2O solution was syringed in. The mixture was stirred at −78 °C for 20 min, then allowed to warm to room temperature, and stirred for 1.5 h. The solvent was then removed under high vacuum and 20 mL of heptane condensed in. The mixture was filtered, and the solids were washed with condensed solvent. The resulting solution was cooled to −78 °C and the colorless, microcrystalline product filtered, washed with condensed heptane, and dried: yield 56%; ^1H NMR (C_6D_6) δ 1.954 (30 H, s), 1.490 (8 H, m), 1.084 (6 H, t), 0.190 (4 H, t); IR (Nujol mull, cm^{-1}) 1019 (s), 938 (m), 721 (m). Anal. Calcd for $C_{28}H_{48}Th$: C, 54.53; H, 7.84. Found: C, 54.63; H, 7.54. This compound is stable for weeks in solution at room temperature.

Titration Calorimetry. The isoperibol calorimeter employed was designed specifically for this study, to deal with the extreme air and moisture sensitivity of the compounds of interest as well as to permit use of relatively small sample sizes. The external electronic circuitry is an adaptation of that described previously,[20] while the reaction cell (modified from an earlier design[21]) is shown in Figure 1. It is constructed from

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(17) We follow the recommendation of Pilcher and Skinner[4a] in referring to ΔH for eq 3 as D, the "bond disruption enthalpy". We note that the terminology used by various authors is not uniform and that "bond enthalpy contribution", "bond dissociation enthalpy contribution", "bond dissociation enthalpy", "bond dissociation energy", and other names have been employed for this parameter.[2,4–8]

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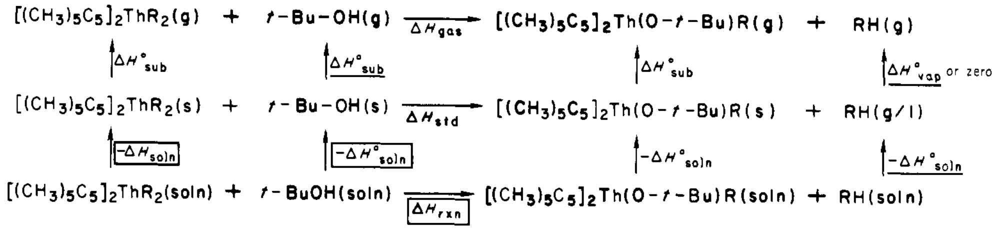
Scheme I. Cycle for Measurement of Th-R Bond Disruption Enthalpies[a]



[a] Entries in boxes: measured in this research. Underlined entries: experimental; from literature. In Table II, $-\Delta H_{gas} = D(\text{Th-O}) + D(\text{R-H}) - D(\text{Th-R}) - D(\text{O-H})$.

a thin-walled glass Dewar flask D (capacity 150 mL), the inside of which is Teflon coated. The assembly cover Q is Teflon, and all tubes that pass through the cover are sealed with counter-sunk nuts that tighten down on Viton O rings. The cover is sealed to the Dewar, which has a flat upper rim, with a Viton O ring. Four ampules A are placed in polypropylene holders that are mounted at the top of the Teflon-coated stirring baffle C. The baffle is attached to four Teflon-coated thin-walled stainless steel tubes, two on the inside and two on the outside of the baffle. The inner tubes each contain one series-wired 250 Ω resistor (TRW-IRC AS-1/2) used in heating the system for calibrations. The outer tubes T each contain a pair of series-wired 10^5 Ω thermistors (Fenwal GA51P8); the two pairs are wired in parallel. The thermistor circuit comprises part of a Wheatstone bridge; the temperature is monitored by recording the voltage (amplified by a Keithley microvoltmeter) of the slightly off-balance bridge as a function of time on a strip-chart recorder. The stainless-steel stirring shaft S is held in place by three spring-tightened Teflon bearings G contained inside a copper tube (shown cut away in Figure 1). These bearings (manufactured by Bal-Seal, Inc.) allow nearly frictionless stirring while remaining nearly gas tight. As an added precaution, the copper tube is flushed with argon during all calorimetric runs. Titrant is introduced into the reaction cell via a Gilmont precision 2.50-mL digital syringe B, readable to ±0.0001 mL. The syringe is mounted so as to be immersed in the constant temperature bath. Titrant solution flows through a Hamilton Precision valve V, through 0.50-mm i.d. Teflon tubing, and finally through a small diameter glass tube fitted through the calorimeter cover. To avoid inaccuracies due to droplet formation, the tip of the glass tube H through which titrant flows is immersed in the reactant solution L inside the calorimeter. To avoid the possibility of reactant mixing prior to addition, the tube tip has an inner diameter less than 0.2 mm. The calorimeter sensitivity is $\pm 10^{-5}$ °C (7×10^{-4} cal where toluene filled), and the instrument has an overall accuracy of ±1% for a heat of 0.1 cal.

In a typical experiment, flat-bottomed thin-walled glass ampules are loaded with 50–100 mg of compound and weighed in the inert-atmosphere box to ±0.01 mg on a Cahn GRAM electrobalance. A piece of glass rod is inserted into the neck of the ampule and sealed with melted Apiezon W wax inside the glovebox. These ampules are then mounted on the stirring baffle, and the entire calorimeter and syringe apparatus are loaded and sealed inside the glovebox. The apparatus is removed from the glovebox, and electrical connections made at control box E; it is then immersed in a water bath thermostatically controlled to ±0.001 °C. After temperature equilibration, a precise electrical calibration is initiated to determine the calorimeter energy equivalent. This calibration is repeated several times during the course of the experiment, because the energy equivalent changes slightly due to titrant addition. Additionally, calibration was occasionally checked (in separate experiments) by measuring the enthalpy of solution of KCl in water. Sample ampules are broken by means of a SiC breaker mounted on the uppermost stirrer propeller. The breaker is aligned under the desired ampule with the use of index marks on the pulley assembly F. The stir shaft is stopped, raised 5 mm to break the ampule, and stirring is resumed with clutch-brake motor M. A paddle P mixes any solid that has fallen to the bottom of the Dewar. Titrant solution (0.138 M *tert*-butyl alcohol in toluene) is added in 0.05–0.10-mL increments and all heats recorded on a strip-chart recorder. The system temperature is allowed to equilibrate between all heatings. A typical run results in 2–4 batch reactions (ΔH_{soln}) and 15–20 titrations (a ΔH_{rxn} values is calculated from each) and never exceeds a system temperature range of 24.85–25.15 °C.

Results

Experiment Design. The apparatus employed in this study was a Teflon and glass-lined isoperibol titration calorimeter designed for studying highly air-sensitive compounds. The chemical reactions of interest are given in eq 1 and 2, while Scheme I illustrates how the measured heat of alcoholysis (ΔH_{rxn}) is related to important thermodynamic parameters. An analogous scheme can be generated for the process $Cp'_2Th(R)(O\text{-}t\text{-}C_4H_9) \rightarrow Cp'_2Th(O\text{-}t\text{-}C_4H_9)_2$. In particular, $\Delta H°_{gas}$ is related to the bond disruption enthalpy contribution for gas-phase homolytic Th–R dissociation (D(Th–R)), eq 4) via eq 5. To be meaningful,

$$-\Delta H°_{gas} = D(\text{Th-O}) + D(\text{R-H}) - D(\text{Th-R}) - D(\text{O-H}) \quad (5)$$

experiments and analyses leading to such information must fulfill certain chemical requirements and must be provided with certain ancillary data.

Toluene was chosen as a solvent for the present study because all reactants and products are soluble in it and do not significantly react with it on the timescale of the experiments. Furthermore, the vapor pressure of toluene is sufficiently low to preclude significant solvent loss during various transfer operations. *tert*-Butyl alcohol was selected as the protolytic reactant because of low vapor pressure (again ensuring negligible evaporative losses) and protolytic chemoselectivity. Specifically, it does not attack η^5-$(CH_3)_5C_5$ functionalities under the reaction conditions and, with the exception of $(Cp'_2ThH_2)_2$ (vide infra), rapidly and quantitatively cleaves hydrocarbyl and dialkylamide residues in the selective, stepwise sequence indicated in eq 1 and 2.[15a,22] The protolytic rapidity ensures that reaction velocity is controlled by the rate of titrant addition and that thermal leakage from the calorimeter can be minimized. The clean, quantitative character of the chemistry with *tert*-butyl alcohol as limiting reagent means that thermochemical data need not be extracted from complex reaction mixtures and equilibria. The stepwise character of the reactions of course ensures that both Cp'_2ThR_2 and $Cp'_2Th(R)(O\text{-}t\text{-}C_4H_9)$ systems can be probed. The nature of these alcoholysis reactions was verified by NMR titrations carried out under the same conditions as the titration calorimetry. Only in the case of $(Cp'_2ThH_2)_2$ was the rapid alcoholysis reaction not stepwise. In this case, it appears that the second protolysis (eq 7) is more rapid than the first (eq 6), since only traces of the

$$\tfrac{1}{2}(Cp'_2ThH_2)_2 + t\text{-}C_4H_9OH \rightarrow \underset{\mathbf{1}}{Cp'_2Th(H)(O\text{-}t\text{-}C_4H_9)} + H_2 \quad (6)$$

$$Cp'_2Th(H)(O\text{-}t\text{-}C_4H_9) + t\text{-}C_4H_9OH \rightarrow Cp'_2Th(O\text{-}t\text{-}C_4H_9)_2 + H_2 \quad (7)$$

intermediate alkoxy hydride **1** could be observed during the course of the reaction. Since an independently prepared sample of **1** is stable with respect to disproportionation,[15a] it appears that **1** is more reactive, presumably a consequence of decreased steric hindrance or greater Th–H "hydridic" character. For these reasons, ΔH_{rxn} for $(Cp'_2ThH_2)_2$ represents an average of the first and second reaction enthalpies, and only a single, average bond disruption enthalpy can be derived.

Reference to eq 5 and Scheme I indicates that other thermodynamic data in addition to ΔH_{rxn} are required before a formal, gas-phase D(Th–R) can be calculated; these are set out in eq 8.

$$\begin{aligned}\Delta H°_{gas} = {} & \Delta H_{rxn} + \Delta H°_{sub}(L_nTh\text{-}O\text{-}t\text{-}C_4H_9) + \Delta H_{vap}(RH) - \\ & \Delta H°_{sub}(L_nThR) - \Delta H°_{vap}(t\text{-}C_4H_9OH) - \\ & \Delta H°_{soln}(L_nTh\text{-}O\text{-}t\text{-}C_4H_9) - \Delta H°_{soln}(RH) + \\ & \Delta H°_{soln}(L_nThR) + \Delta H°_{soln}(t\text{-}C_4H_9OH) \quad (8)\end{aligned}$$

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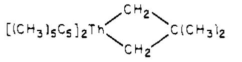
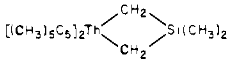
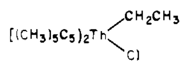
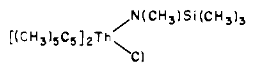
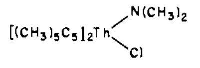
[22] Bruno, J. W.; Seyam, A. M.; Marks, T. J., unpublished results.

Table I. Experimental Heat of Solution Data (ΔH°_{soln}) for Organoactinides and *tert*-Butyl Alcohol

compd	ΔH°_{soln}, kcal/mol
$[(CH_3)_5C_5]_2Th(CH_3)_2$	4.23, 4.56
$[(CH_3)_5C_5]_2Th(C_6H_5)_2$	3.0
$[(CH_3)_5C_5]_2Th[CH_2C(CH_3)_3]_2$	3.75
	3.06
$[(CH_3)_5C_5]_2Th[CH_2Si(CH_3)_3]_2$	3.92, 3.97
	3.44
	3.60
	4.15, 4.38
	4.5
$[(CH_3)_5C_5]_2Th(O\text{-}t\text{-}C_4H_9)_2$	3.23, 3.58, 3.67
$(CH_3)_3COH$	5.41

Here ΔH°_{sub} refers to enthalpy of sublimation, ΔH°_{vap} to enthalpy of vaporization, and ΔH°_{soln} to enthalpy of solution. The $\Delta H_{soln}(L_nThR)$ values for the Cp'_2ThR_2 compounds are obtained when sample ampules are broken within the calorimeter prior to the titration process. We do not measure ΔH°_{soln} (i.e., at infinite dilution), but the dilution corrections should be very small and negligible in any case since they cancel on opposite sides of Scheme I. In addition, ΔH_{soln} has been measured for $Cp'_2Th(O\text{-}t\text{-}C_4H_9)_2$ in a separate experiment. These data are set out in Table I. Not unexpectedly,[6] the enthalpies of solution are small and fall within a narrow range, 2.9–4.3 kcal/mol; it will also be seen (vide infra) that they are very small compared to ΔH_{rxn}. For this reason, we have not measured ΔH°_{soln} values for individual $Cp'_2Th(R)(O\text{-}t\text{-}C_4H_9)$ complexes and have reasonably assumed them to be on the order of 3.7 kcal/mol.

The present analysis also requires information about the RH and $t\text{-}C_4H_9OH$ components of the reaction system. First, most of the reactions produce RH species that are gaseous at 25 °C. In these cases $\Delta H^\circ_{vap}(RH)$ is zero. The only exceptions are benzene, toluene, and tetramethylsilane, for which the heats of vaporization are 8.08, 9.07, and 5.85 kcal/mol, respectively.[23] The heat of sublimation of reactant *tert*-butyl alcohol is also available, 11.1 kcal/mol.[23] The heats of solution in toluene are not known for all the organic species involved in this study. However, enough data are known to approximate these numbers, and all are relatively small.[24] Nonetheless, the measured values, which range from −6.7 to +5.3 kcal/mol, or reasonable estimates thereof, are included in the computation of ΔH_{rxn}.[25] The bond disruption enthalpies $D(R\text{-}H)$ and $D(O\text{-}H)$ are available for all organic species in this study or are estimated from nearly identical functional groups.[26]

Also required in the present treatment are the organothorium quantities $\Delta H^\circ_{sub}(L_nTh\text{-}R)$, $\Delta H^\circ_{sub}(L_nTh\text{-}O\text{-}t\text{-}C_4H_9)$, and $D(Th\text{-}O)$. In regard to enthalpies of sublimation, we make the reasonable assumption, which is generally well supported,[5,6,27] that all $\Delta H^\circ_{sub}(L_nTh\text{-}R)$ values are approximately the same and are approximately equal to $\Delta H^\circ_{sub}(L_nTh\text{-}O\text{-}t\text{-}C_4H_9)$. Under this assumption, the ΔH°_{sub} terms cancel in eq 8. Alternatively, but less conventionally, it is possible to eliminate the uncertainty in the organometallic ΔH°_{sub} values and avoid ΔH°_{vap} corrections by defining solution-phase bond disruption enthalpies, related to ΔH_{rxn} as shown in eq 9. Such a scheme is workable if the

$$-\Delta H_{rxn} = D(Th\text{-}O)_{soln} + D(R\text{-}H)_{soln} - D(Th\text{-}R)_{soln} - D(O\text{-}H)_{soln} \quad (9)$$

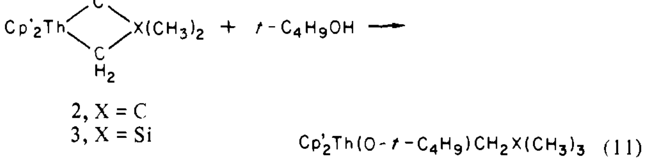
reasonable assumption is made that for relatively nonpolar RH and $t\text{-}C_4H_9OH$ molecules in dilute solutions of a nonpolar solvent such as toluene, $D(R\text{-}H) \approx D(R\text{-}H)_{soln}$ and $D(O\text{-}H) \approx D(O\text{-}H)_{soln}$. Since all organothorium chemistry of interest occurs in solutions of relatively nonpolar solvents, it could also be argued that solution bond disruption enthalpies are more meaningful. Both gas-phase and solution-phase D parameters will be reported—it will be seen that there are only minor differences, reflecting primarily differences in ΔH°_{vap} for different RH species.

Although a scale of *relative* Th–R bond disruption enthalpies would be satisfactory for understanding most aspects of organothorium chemistry, absolute $D(Th\text{-}R)$ values would allow comparisons with thermochemical data for other elements. Such absolute data require $D(Th\text{-}O)$, which has not been directly measured. To estimate $D(Th\text{-}O)$, we employ $M(OR)_4$ mean bond disruption enthalpy data ($R = i\text{-}C_3H_7$) from the closely analogous M = Ti, Zr, and Hf series[8] and make the pragmatic approximations of eq 10 where X = Cl or F. Within the M = Ti, Zr, and Hf series, eq 10a holds,[4b] and furthermore, the $\bar{D}(M\text{-}OR)$ parameters are relatively insensitive to R.[4b,28] Extensive bond disruption enthalpy data are available for all relevant tetrahalides.[8,29] Application of this proportionality to all M and X combinations yields a Th–OR $\bar{D}$ of 124 kcal/mol with a scatter in the estimation of $D(Th\text{-}O)$ of only 4 kcal/mol.[25] Support for the approximation of eq 10b derives from ThF_4 thermochemical data[29a] which reveal $\bar{D}(Th\text{-}F) = 159.1$ kcal/mol whereas $D_1(Th\text{-}F) = 154.4$ kcal/mol. Nevertheless, the derived absolute $D(Th\text{-}O)$ is probably not accurate to better than 10 kcal/mol.[25]

$$\bar{D}(Th\text{-}OR)/\bar{D}(M\text{-}OR) \approx \bar{D}(Th\text{-}X)/\bar{D}(M\text{-}X) \quad (10a)$$

$$D(Th\text{-}OR) \approx \bar{D}(Th\text{-}OR) \quad (10b)$$

Thermochemical Data. In Table II are compiled the results of the calorimetric titrations. The two values of ΔH_{rxn} reported for most compounds refer to the enthalpies associated with the two processes in eqs 1 and 2. Standard deviations reported are 2σ for 6–12 determinations. The ΔH_{rxn} data contain some useful internal checks. Thus, as can be seen in eq 11–14, the second heat



2, X = C
3, X = Si

$$\rightarrow Cp'_2Th(O\text{-}t\text{-}C_4H_9)CH_2X(CH_3)_3 \quad (11)$$

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[23] (a) Thermodynamic Research Center Data Tables, Texas A&M University, College Station, TX. (b) Wagman, D. D.; Evans, W. H.; Parker, V. B.; Halow, I.; Bailey, S. M.; Schumm, R. H. *NBS Tech. Note (U.S.)* **1968**, *No. 270-3*.

[24] (a) Clever, H. L.; Hsu, K.-Y. *Sel. Data Mixtures, Ser. A* **1975**, 163. (b) Clever, H. L.; Hsu, K.-Y. *Ibid.* **1975**, 14. (c) Harsted, B. S.; Thomsen, E. S. *J. Chem. Thermodn.* **1975**, *7*, 369–376. (d) Cone, J.; Smith, L. E. S.; Van Hook, W. A. *Ibid.* **1979**, *11*, 277–285. (e) Battino, R.; Marsh, K. *Aust. J. Chem.* **1980**, *33*, 1997–2003.

[25] A full tabulation of parameters employed in the thermochemical calculations is given as supplementary material. See paragraph at end of paper regarding this material.

[26] (a) Chamberlain, G. A.; Whittle, E. *Trans. Faraday Soc.* **1971**, *67*, 2077–2084. (b) Doncaster, A. M.; Walsh, R. *J. Chem. Soc., Faraday Trans. 1* **1976**, *72*, 2908–2916. (c) Golden, D. M.; Benson, S. W. *Chem. Rev.* **1969**, *69*, 125–134. (d) Golden, D. M.; Solly, R. K.; Gac, N. A.; Benson, S. W. *J. Am. Chem. Soc.* **1972**, *94*, 363–369. (e) Larson, C. W.; Hardwidge, E. A.; Rabinovitch, B. S. *J. Chem. Phys.* **1969**, *50*, 2769–2770. (f) Reed, K. J.; Brauman, J. I. *J. Am. Chem. Soc.* **1976**, *97*, 1625–1626. (g) McMillen, D. F., Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493–532.

[27] (a) For example, in the $Mn(CO)_5R$ series, where R includes such greatly differing ligands as CF_3, $Mn(CO)_5$, C_6H_5, and I, ΔH_{sub} falls within the range 18.3–22.4 kcal/mol for all compounds where thermal decomposition is not significant.[5] For $R = CH_3$, $\Delta H_{sub} = 14$ kcal/mol as measured by a technique[26b] other than that employed in ref 5. (b) Hieber, W.; Wagner, G. *Justus Liebigs Ann. Chem.* **1958**, *618*, 24–30.

[28] (a) Bradley, D. C.; Hillyer, M. J. *Trans. Faraday Soc.* **1966**, *62*, 2367–2373, 2374–2381. (b) Shaulov, U. K.; Genchel, V. G.; Aizatullova, R. M.; Petrova, N. N. *Russ. J. Phys. Chem. (Engl. Transl.)* **1972**, *46*, 1360–1361. (c) Genchel, V. G.; Volchkova, E. A.; Aizatullova, R. M.; Shaulov, Y. K. *Ibid.* **1973**, *47*, 643–644.

[29] (a) Wagman, D. D.; Evans, W. H.; Parker, V. B.; Schumm, R. H.; Nuttall, R. L. *NBS Tech. Note (U.S.)* **1981**, *No.* 270-8. (b) Huheey, J. E. "Inorganic Chemistry", 2nd ed.; Harper and Row: New York, 1978; Appendix F.

$$Cp'_2Th(O\text{-}t\text{-}C_4H_9)CH_2X(CH_3)_3 + t\text{-}C_4H_9OH \rightarrow Cp'_2Th(O\text{-}t\text{-}C_4H_9)_2 + X(CH_3)_4 \quad (12)$$

$$\underset{\mathbf{4},\ X = C;\ \mathbf{5},\ X = Si}{Cp'_2Th[CH_2X(CH_3)_3]_2} + t\text{-}C_4H_9OH \rightarrow Cp'_2Th(O\text{-}t\text{-}C_4H_9)CH_2X(CH_3)_3 + X(CH_3)_4 \quad (13)$$

$$Cp'_2Th(O\text{-}t\text{-}C_4H_9)CH_2X(CH_3)_3 + t\text{-}C_4H_9OH \rightarrow Cp'_2Th(O\text{-}t\text{-}C_4H_9)_2 + X(CH_3)_4 \quad (14)$$

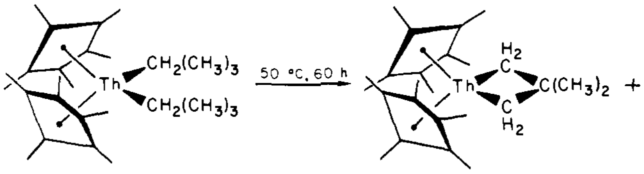
of alcoholysis for metallacycle **2** or **3** should be identical to the second heat for dialkyl **4** or **5**, respectively; i.e., eq 12 and 14 are identical. It can be seen in Table II that, within experimental error, the data are self-consistent. As already noted, only a single, average ΔH_{rxn} value is available for $(Cp'_2ThH_2)_2$. Also reported in Table II are the corresponding $D(Th\text{-}R)_{gas}$ and $D(Th\text{-}R)_{soln}$ values calculated from the ΔH_{gas} and ΔH_{rxn} data, respectively. Again, it can be seen that appropriate pairs of dialkyl/metallacycle data are self-consistent and that only a single type of $D(Th\text{-}H)$ value is available for $(Cp'_2ThH_2)_2$.

Discussion

Hydrocarbyls. It is immediately apparent on inspecting the data in Table II that Th-alkyl bonds are rather strong. Bond disruption enthalpies on the order of ca. 70 kcal/mol can be compared with values closer to ca. 30 kcal/mol or less for a great many $Mn(CO)_5R$ (e.g., R = CH_3, 37 kcal/mol; R = C_6H_5, 41 kcal/mol; R = $CH_2C_6H_5$, 21 kcal/mol; R = CF_3, 41 kcal/mol; R = $COCH_3$, 31 kcal/mol[2,5] and Co(Schiff's base)(L)R′ (R′ = $CH_2CH_2CH_3$, 25 kcal/mol; R′ = $CH_2C_6H_5$, 22 kcal/mol; R′ = $CH_2C(CH_3)_3$, 18 kcal/mol)[2] compounds. Higher values to the left of the periodic table are suggested by mean metal-carbon σ bond D values in $Cp_2M(CH_3)_2$ compounds, 30 kcal/mol (M = Mo) and 43 kcal/mol (M = W),[7c] by estimated[4b] mean D data for homoleptic $M(CH_3)_4$ compounds, 62 kcal/mol (M = Ti), 74 kcal/mol (M = Zr), and 79 kcal/mol (M = Hf), and by data for $Cp_2Ti(C_6H_5)_2$, 65 kcal/mol (mean D).[7a] One explanation for the relatively high thorium D result resides in the redox chemistry expressed in eq 4. The standard Th(IV) → Th(III) reduction potential has been estimated to be below −3.7 V,[30] and indeed, it has so far proven impossible to reduce Cp'_2ThCl_2 electrochemically, in contrast to the Ti, Zr, and U analogues.[31] Another interesting generalization that can be made about the Th-hydrocarbyl D parameters is that the Th-R bond in $Cp'_2Th(O\text{-}t\text{-}C_4H_9)R$ compounds appears invariably to be stronger than that in the related Cp'_2ThR_2 compounds. Although relief of severe nonbonded R···R interactions or ring strain may be an important factor in several specific cases (vide infra), the general trend is more convincingly explained in terms of redox arguments: the tendency of hard alkoxide ligands to stabilize high metal oxidation states is well established.[32] Further destabilization of Th(III) relative to Th(IV) should increase the bond disruption enthalpy. Likewise, the result for the alkyl $Cp'_2Th(Cl)CH_2CH_3$ suggests that the softer chloride ligand may slightly increase the stability of Th(III) relative to Th(IV).

Among the various hydrocarbyl moieties, several interesting bond disruption enthalpy trends can be discerned. There is a significant difference between R = CH_3 and R = $n\text{-}C_4H_9$ which is presumably steric in origin; D for the R = C_2H_5 compound falls somewhat in-between. In the $Ir[P(CH_3)_3]_2(CO)(Cl)(I)R$ series, the $D(Ir\text{-}CH_3)$ is reported to be ca. 4 ± 3 kcal/mol greater than $D(Ir\text{-}n\text{-}C_3H_7)$.[6c] Also apparent in Table II is the greater strength of the Th-C_6H_5 bond vs. R = CH_3, C_2H_5, and $n\text{-}C_4H_9$. A similar trend may be operative in the aforementioned titanium data although the supporting ligation differs in the two compounds and in the above $Mn(CO)_5R$ series.[5] The C-H D for benzene is approximately 7 kcal/mol greater than for methane.[26g,33] The data in Table II also indicate that the effect of the *tert*-butoxy substituent on $D(Th\text{-}R)$ is rather similar for R = CH_3, C_2H_5, $n\text{-}C_4H_9$, and C_6H_5.

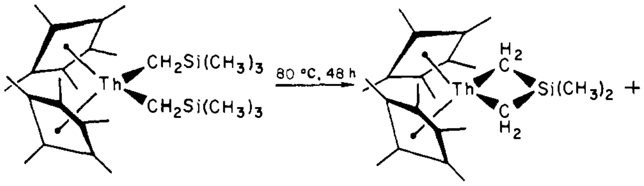
The R = $CH_2C(CH_3)_3$ and $CH_2Si(CH_3)_3$ complexes are of particular interest both because the origin of the stabilization these ligands generally impart to metal hydrocarbyls has not been completely resolved and because these particular organothorium complexes undergo facile, intramolecular cyclometalation to yield the first thoracyclobutanes (eq 15 and 16).[18b,c] This process involves an unusual C-H scission process on a saturated hydrocarbon substrate, which apparently proceeds via a pathway not involving oxidative addition or reductive elimination. Importantly, the driving force for such reactions[3] cannot be entirely clear without some quantitation of precursor stability and product ring strain. The bond distruption enthalpy data in Table II indicate that the first Th-C bond in **4** is somewhat weaker than in **5** and in $Cp'_2Th(CH_3)_2$. This effect can be reasonably attributed to the greater steric demands of a neopentyl ligand,[2,5] and, indeed, the molecular structure of **4** (and also **5**, but to a lesser degree) exhibits severe nonbonded interactions.[18c,f] For example, one Th-C-C-$(CH_3)_3$ angle is distorted to 160°.[18f] In the homoleptic MR_4 series, mean bond dissociation enthalpies for R = $CH_2Si(CH_3)_3$ are greater than those for R = $CH_2C(CH_3)_3$ by 20 kcal/mol (M = Ti) and 21 kcal/mol (M = Zr).[8] These differences have been attributed largely to steric effects, although silicon electronic effects may also be important.[34]



4 2

C(CH3)4 (15)

$$\Delta H^{\ddagger} = 20.6\ (6)\ \text{kcal/mol}$$
$$\Delta S^{\ddagger} = -17(2)\ \text{cal mol}^{-1}\ \text{K}^{-1}$$



5 3

Si(CH3)4 (16)

$$\Delta H^{\ddagger} = 25.2\ (9)\ \text{kcal/mol}$$
$$\Delta S^{\ddagger} = -9(1)\ \text{cal mol}^{-1}\text{K}^{-1}$$

The weakest bis(hydrocarbyl) Th-C σ bond detected in this study is for the first Th-C homolysis in metallacycle **2**; the corresponding bond in metallacycle **3** also appears to be somewhat weakened. As already noted, the second D's are experimentally indistinguishable from those in the corresponding dialkyl complexes. Structural data[18b,c,35] (vibrational, ^1H and ^{13}C NMR, diffraction on **3**) indicate that there is nothing geometrically unusual[35] about these metallacycles. Thus, the diminished Th-C

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(30) Nugent, L. J. *Int. Rev. Sci.: Inorg. Chem., Ser. Two* **1975**, *7*, Chapter 6.

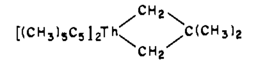
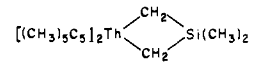
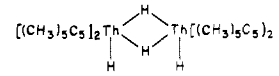
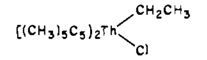
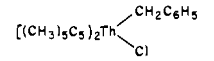
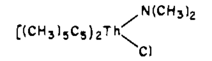
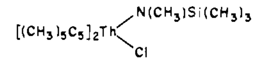
(31) Finke, R. G.; Gaughan, G.; Voegeli, R. *J. Organomet. Chem.* **1982**, *229*, 179–183.

(32) (a) Reference 29b, pp 275–288, and references therein. (b) Chisholm, M. H.; Folting, K.; Huffman, J. C.; Rothwell, I. P. *J. Am. Chem. Soc.* **1982**, *104*, 4389–4399 and references therein. (c) Huffman, J. C.; Moloy, K. G.; Marsella, J. A.; Caulton, K. G. *Ibid.* **1980**, *102*, 3009–3014 and references therein. (d) Marsella, J. A.; Moloy, K. G.; Caulton, K. G. *J. Organomet. Chem.* **1980**, *201*, 389–398.

(33) Benson, S. W. "Thermochemical Kinetics"; Wiley: New York, 1976; p 309.

(34) (a) Armitage, D. A. In ref 12a, Chapter 9.1, and references therein. (b) Chan, T.-H. *Acc. Chem. Res.* **1977**, *10*, 442–448. (c) Cook, M. A.; Eaborn, C.; Jukes, A. E.; Walton, D. R. M. *J. Organomet. Chem.* **1970**, *24*, 529–535. (d) Eaborn, C.; Retta, N.; Smith, J. D. *Ibid.* **1980**, *190*, 101–106.

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

compd	ΔH_{rxn}[b]	ΔH_{gas}[c]	D^c (Th–R)$_{gas}$	D^c (Th–R)$_{soln}$
$[(CH_3)_5C_5]_2Th(CH_3)_2$	−42.8 (0.8)	−46.8 (1.1)	77.2 (1.1)	81.2 (0.8)
	−40.4 (0.9)	−44.7 (1.2)	79.3 (1.2)	83.6 (0.9)
$[(CH_3)_5C_5]_2Th(C_2H_5)_2$	−43.4 (1.2)	−44.9 (1.7)	70.4 (2.0)	73.5 (1.6)
	−40.6 (1.2)	−42.4 (1.7)	72.9 (2.0)	76.3 (1.6)
$[(CH_3)_5C_5]_2Th(n\text{-}C_4H_9)_2$	−45.3 (0.7)	−45.3 (1.5)	71.6 (1.7)	71.6 (1.0)
	−43.3 (3.0)	−43.0 (3.5)	73.9 (3.7)	73.6 (3.4)
$[(CH_3)_5C_5]_2Th(C_6H_5)_2$	−41.0 (1.3)	−39.6 (1.5)	90.3 (2.5)	88.9 (2.4)
	−37.5 (0.7)	−34.8 (1.1)	95.1 (2.3)	92.4 (2.1)
$[(CH_3)_5C_5]_2Th[CH_2C(CH_3)_3]_2$	−46.5 (3.2)	−46.7 (3.4)	72.2 (3.9)	72.3 (3.8)
	−42.0 (3.1)	−41.9 (3.3)	77.0 (3.9)	76.9 (3.7)
	−53.3 (1.1)	−59.8 (1.4)	59.1 (2.4)	65.3 (2.3)
	−40.3 (1.7)	−40.2 (2.1)	78.7 (2.9)	78.6 (2.6)
$[(CH_3)_5C_5]_2Th[CH_2Si(CH_3)_3]_2$	−37.9 (0.8)	−37.6 (1.5)	80.3 (3.4)	80.0 (3.1)
	−35.6 (0.6)	−35.2 (1.4)	82.7 (3.3)	82.2 (3.1)
	−42.0 (1.2)	−48.1 (1.4)	69.8 (3.3)	75.5 (3.2)
	−34.9 (1.7)	−34.6 (2.1)	83.3 (3.7)	83.0 (3.4)
	−25.6 (0.7)	−32.6 (1.3)	90.5 (1.3)	97.5 (0.7)
 $[(CH_3)_5C_5]_2Th(CH_2CH_3)Cl$	−44.7 (1.5)	−48.6 (1.7)	68.3 (2.0)	72.2 (1.8)
 $[(CH_3)_5C_5]_2Th(CH_2C_6H_5)Cl$	−38.7 (1.0)	−35.4 (1.6)	71.5 (1.9)	68.2 (1.4)
 $[(CH_3)_5C_5]_2Th[N(CH_3)_2]Cl$	−21.2 (0.3)	−19.6 (1.3)	90.8 (2.4)	89.2 (2.0)
 $[(CH_3)_5C_5]_2Th[N(CH_3)Si(CH_3)_3]Cl$	−14.9 (0.6)	−10.2 (1.4)	100.2 (2.5)	95.5 (2.1)

[a] Terms as defined in Scheme I and eq 5, 8, and 9. For most compounds two entries appear in each column. The upper entry refers to breaking the first Th–R bond (eq 1 in text), and the lower entry refers to breaking the second Th–R bond (eq 2 in text). [b] Quantities in parentheses refer to 2σ for 6–12 determinations. [c] Error limits do not include uncertainties that are constant throughout the series (see supplementary material).

bond enthalpies are logically measures of metallacycle ring strain. If this quantity is defined[36] as the gas-phase enthalpic destabilization incurred when the normal acyclic hydrocarbyl ligand is forced into a metallacyclobutane and if averaged $Cp'_2Th(CH_3)_2$ and $Cp'_2Th(n\text{-}C_4H_9)_2$ data are taken as reference points of "normality", strain energies of ca. 15 and 5 kcal/mol are calculated for **2** and **3**, respectively. The former value can be compared with the only other existing data of this kind: using differential scanning calorimetry (DSC) in the solid state, Puddephatt[35e] has estimated strain energies in Pt(IV) metallacyclobutanes ($\overline{PtCH_2CH_2CH_2}$) on the order of 9–13 kcal/mol, with the DSC-determined Pt–CH_3 bond energy in $Pt[P(CH_3)_2(C_6H_5)]_2(I)(CH_3)_3$ taken as a reference point. In the present case it might be argued that $Cp'_2Th(CH_3)_2$ and $Cp'_2Th(n\text{-}C_4H_9)_2$ are invalid reference points because they lack multiple methyl substituents in the β position and do not incorporate electronic effects that may be imparted by the Si atom. However, the evidence for significant steric destabilization in **4** (vide supra) and a similar possibility in **5** argues that the metallacycle precursors are not entirely valid reference points for estimating strain energy. One approach to correcting for at least part of the steric destabilization and retaining the Si substituent would be to employ for a reference point the second homolysis *D*'s for **4** and **5** corrected by the average difference between the

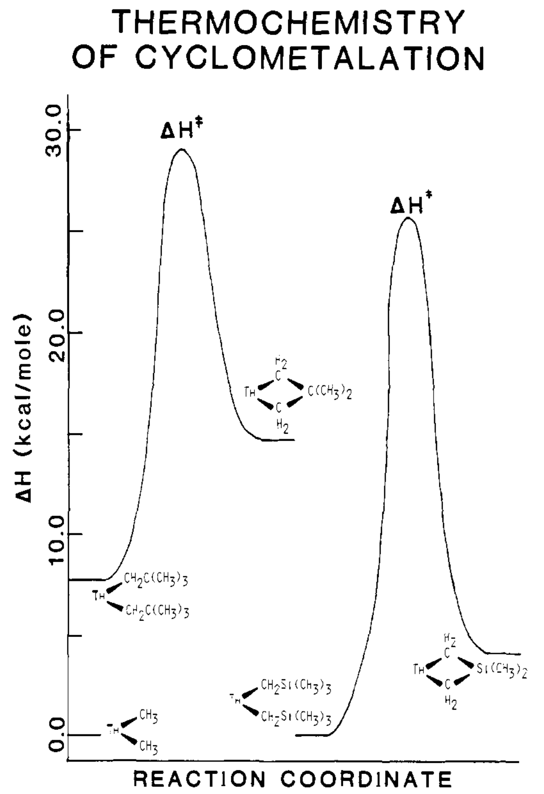


Figure 2. Approximate solution phase thermochemical relationships for the cyclometalation processes **4** → **2** and **5** → **3**. The first bond disruption of $Cp'_2Th(CH_3)_2$ is shown as a point of reference.

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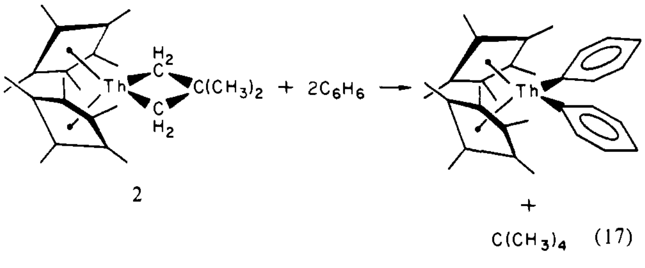
(35) For structural information on transition metal metallacyclobutanes, see ref 3 and: (a) Klinger, R. J.; Huffman, J. C.; Kochi, J. K. *J. Am. Chem. Soc.* **1982**, *104*, 2147–2157. (b) Ott, K. C.; Lee, J. B.; Grubbs, R. H. *Ibid.* **1982**, *104*, 2942–2944. (c) Tulip, T. H.; Thorn, D. L. *Ibid.* **1981**, *103*, 2448–2450. (d) Lee, J. B.; Gajda, G. L.; Schaefer, W. P.; Howard, T. R.; Ikariya, T.; Straus, D. A.; Grubbs, R. H. *Ibid.* **1981**, *103*, 7358–7361. (e) Puddephatt, R. J. *Coord. Chem. Rev.* **1980**, *33*, 149–194 and references therein.

(36) (a) See reference 33, pp 60–63. (b) Schleyer, P. von R.; Williams, J. E.; Blanchard, K. R. *J. Am. Chem. Soc.* **1970**, *92*, 2377–2386.

first and second D's in the dimethyl and dibutyl complexes (2.0 kcal/mol). The result of this analysis is a strain energy of ca. 16 kcal/mol in **2** and ca. 11 kcal/mol in **3**. Averaging the results of the two approaches yields strain energies of 16 and 8 kcal/mol for **2** and **3**, respectively.

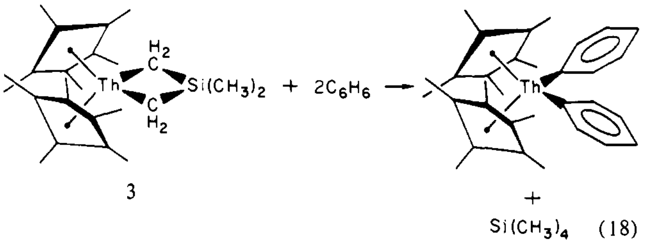
Figure 2 depicts what is now known about the enthalpic characteristics of cyclometalation reactions eq 15 and 16. Although there may be steric and/or electronic destabilization within the precursor molecules, it is apparent that *both* cyclometalation reactions are still calculated to be *endothermic* in the solution phase. The obvious driving force for cyclometalation, in the absence of unusual solvent effects or neopentane/tetramethylsilane loss (thermolyses were carried out on cyclohexane solutions in sealed containers), would then be entropic.[3] Indeed, it can be seen in Figure 2 that the translational and rotational $T\Delta S$ contribution to ΔG of one particle → two particles, ca. 10 kcal/mol under the cyclometalation conditions,[37] would render both reactions spontaneous.

The present thermochemical information also sheds some informative light on other thoracyclobutane chemistry. With use of these data and tabulated[26g,33] C–H D values, it is seen that the known[18] ring opening-metalation of **2** with benzene (eq 17) is calculated to be exothermic in solution.[38a,c] In contrast we have never observed (despite repeated attempts) an analogous reaction with less strained **3**, and the diminished calculated[33,38b,c] exothermicity in solution (eq 18) is in accord with this result. In regard to saturated hydrocarbon activation, the thermochemical data also rationalize the recently observed,[38d] stepwise metalation of **2** by tetramethylsilane to ultimately yield **3** (eq 19) and the ring-opening reaction of **2** with methane to yield **6** (eq 20).[38e]



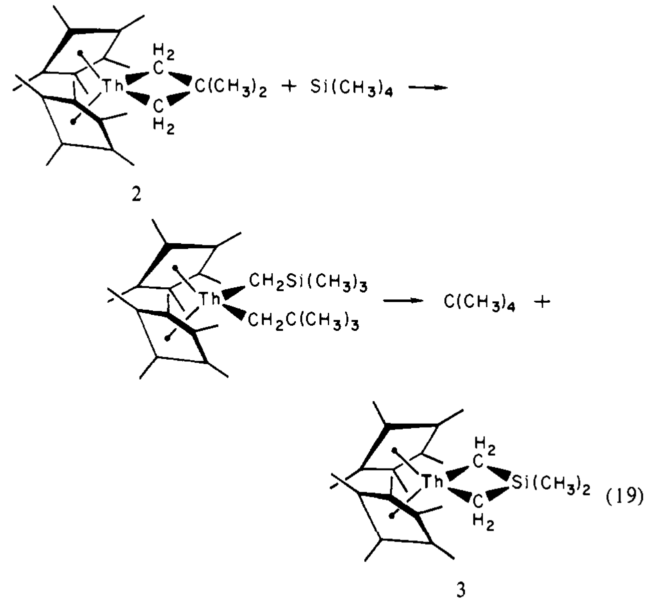
(17)

$\Delta H_{\mathrm{calcd}} \approx -19$ kcal/mol



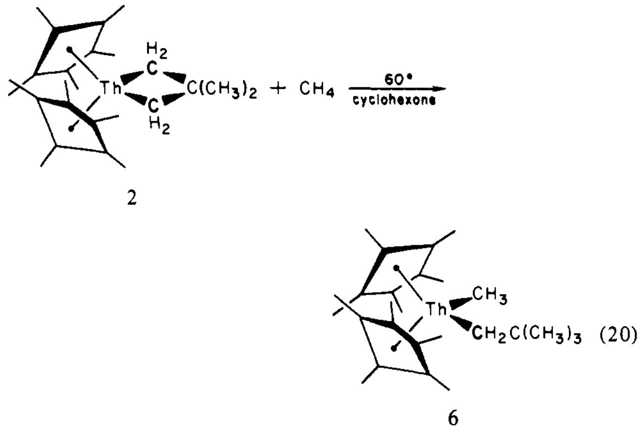
(18)

$\Delta H_{\mathrm{calcd}} \approx -1$ kcal/mol



(19)

$\Delta H_{\mathrm{calcd}} \approx -17$ kcal/mol



(20)

ΔH calcd ≈ -12 kcal/mol

Hydrides. The D(Th–H) given in Table II is an average value, and judging from the hydrocarbyl results, it is likely that the first Th–H homolysis enthalpy is several kilocalories per mole lower than the average value. The present Th–H bond enthalpy can be compared to the rather small number of available D(M–H) data for transition-metal complexes,[2] all of which fall remarkably near 60 kcal/mol, e.g., 51 kcal/mol ($Mn(CO)_5H$),[5] 60 kcal/mol ($Ir[P(C_6H_5)_3]_2(CO)(Cl)H_2$, mean),[2] 58 kcal/mol ($Co(CO)_4H$),[2] 60 kcal/mol (Cp_2MoH_2), and 58 kcal/mol ($Rh[P(p\text{-tolyl})_3]_2(Cl)(L)H_2$, L = $P(p\text{-tolyl})_3$, tetrahydrothiophene, mean).[13d] Surprisingly and in marked contrast to the middle and late transition metals, the quantity D(Th–H) minus D(Th–alkyl) is rather small, ca. 20 kcal/mol (taking D(Th–alkyl) as the average of D(Th–methyl), D(Th–ethyl), and D(Th–n-butyl)), as opposed to ca. 30 kcal/mol for the corresponding quantity among most d-element systems.[2] The actinide result has interesting consequences for reactions involving M–C → M–H or M–H → M–C transposition.

For a middle or late transition metal where $D(\mathrm{M{-}H}) \approx 60$ kcal/mol and $D(\mathrm{M{-}R}) \approx 30$ kcal/mol, β-hydride elimination (e.g., eq 21) is calculated to be slightly endothermic but still in a range

$$\mathrm{M{-}CH_2CH_3 \rightleftharpoons \overset{\overset{H_2C{=}CH_2}{\downarrow}}{M{-}H} \rightleftharpoons M{-}H + CH_2{=}CH_2} \quad (21)$$

$\Delta H_{\mathrm{calcd}} \approx +10$ kcal/mol

where entropic factors may render it spontaneous. In contrast, β-hydride elimination is calculated to be significantly more en-

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(37) (a) Page, M. I. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 449–459. (b) Page, M. I.; Jencks, W. P. *Proc. Natl. Acad. Sci. U.S.A.* **1971**, *68*, 1678–1683.

(38) (a) We take the Th–C bond disruption enthalpies in the metallacycle to be 65 and 77 (78.6–2.0; i.e., the second metallocycle bond dissociation minus the alkoxy coligand correction term) kcal/mol and those in the diphenyl compound to be 90 kcal/mol. D(R–H) terms are given in the supplementary material. (b) We take the Th–C bond enthalpies in the metallacycle to be 76 and 81 (83.0–2.0; i.e., the second metallocycle bond dissociation minus the alkoxy coligand correction) kcal/mol. D(R–H) terms are given in the supplementary material. (c) Gas-phase enthalpies must be corrected by $\Delta H^\circ_{\mathrm{vap}}(C_6H_6)$ and $\Delta H_{\mathrm{vap}}(\mathrm{Me_4Si})$. Then $\Delta H_{\mathrm{calcd}}$ becomes ca. –27 kcal/mol (eq 17) and ca. –10 kcal/mol (eq 18). Entropic contributions to ΔG° may be on the order of ca. +10 kcal/mol.[37] (d) Bruno, J. W.; Duttera, M. R.; Fendrick, C. M.; Smith, G. M.; Marks, T. J. *Inorg. Chim. Acta*, in press. (e) Fendrick, C. M.; Marks, T. J., submitted for publication.

dothermic (ca. +20 kcal/mol) for a thorium ethyl compound. This projection is in accord with the observation that to date organothorium β-hydride elimination has only been observed in cases where there is an ultimate thermodynamic sink[12,39] or where there is severe destabilization[40] (steric) of the hydrocarbyl. Although it can be cogently argued that kinetic factors alone (coordinative saturation) prevent β-hydride elimination in the Cp_3ThR series,[39a] the stability of the R = ethyl and *n*-butyl derivatives in the present coordinatively unsaturated Cp'_2 series, the reaction of $(Cp'_2ThH_2)_2$ with ethylene to yield $Cp'_2Th(C_2H_5)_2$,[15a] and our recent observations that attempts to prepare $Cp'_2Th(i\text{-}Pr)_2$ invariably result in recovery of the isomerization product (e.g., eq 22)[41] strongly

$$Cp'_2ThCl_2 + 2i\text{-}C_3H_7Li \xrightarrow{-78\ ^\circ C} Cp'_2Th(n\text{-}C_3H_7)_2 + 2LiCl \tag{22}$$

argue that thermodynamic rather than kinetic factors hinder eq 21 in the thorium bis(pentamethylcyclopentadienyl) series. We suspect that similar trends in early transition-metal[42] and organolanthanide chemistry[43] have an analogous basis. It should be noted that the related M–C → M–C′ olefin insertion reaction (e.g., eq 23) will be equally exothermic for transition metals and thorium. However, β-hydride elimination should be thermodynamically far less favorable for the M = Th insertion product. Hence, for systems kinetically suited (i.e., sufficiently coordinatively unsaturated, etc.) to undergo further ethylene insertion, resulting in chain growth, or competing β-hydride elimination, resulting in chain termination, it appears that situations where the quantity D(M–H) minus D(M–C) is relatively small (≲20 kcal/mol) will have a considerable thermodynamic advantage for ethylene polymerization. We suspect that the facility with which certain early transition-metal,[44] lanthanide,[43,45] and actinide[46] complexes efficiently polymerize ethylene is closely connected with such bond energy orderings.

$$M{-}CH_3 + CH_2{=}CH_2 \rightarrow MCH_2CH_2CH_3 \quad \Delta H_{calcd} \approx -25\ \text{kcal/mol} \tag{23}$$

In the Cp'_2ThR_2 series, metal–carbon bond hydrogenolysis (e.g., 24) is a rapid, quantitative reaction.[12,15a] Interestingly, however,

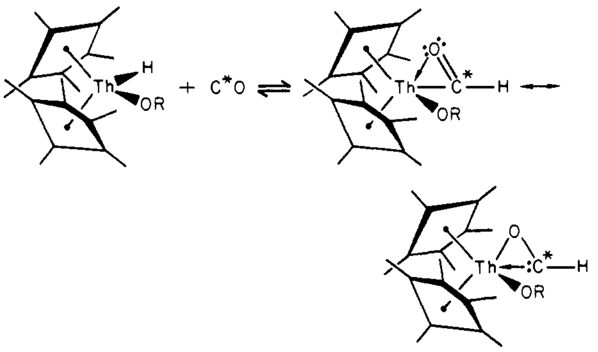
$$2Cp'_2Th(CH_3)_2 + 4H_2 \rightarrow (Cp'_2ThH_2)_2 + 4CH_4 \tag{24}$$

the present thermodynamic data indicate that it is not as exothermic ($\Delta H \approx -15$ kcal/mol of Th–C) as for a middle or late transition-metal methyl compound ($\Delta H \approx -30$ kcal/mol of M–C). Conversely, certain classes of Th–H → Th–C metalation reactions will be considerably more favorable.

Those factors limiting the favorability of CO insertion into metal–hydrogen bonds to yield formyls (eq 25) and how they differ

$$MH + CO \rightleftharpoons M(CHO) \tag{25}$$

from analogous metal alkyl reactions have been the topic of intense recent discussion.[2,5,47] For typical transition-metal hydrides, ΔH for this reaction has been estimated to be in the range +5 to +15 kcal/mol,[2,5] with the latter value for a D(M–H) = 60 kcal/mol and D(M–C) = 30 kcal/mol system. We recently demonstrated that several thorium alkoxyhydrides undergo rapid, reversible CO migratory insertion to yield η^2-formyls (eq 26).[48] By van't Hoff measurements, it was determined that $\Delta H \approx -5$ kcal/mol,[48a] so that the organoactinide environment has contributed ca. 10–20 kcal/mol to the exothermicity. It is difficult to rigorously partition this extra driving force into Th–H/Th–C and Th–O bond energy contributions since the bonding in a η^2-formyl, as assessed by spectroscopic[48] and analogue metrical data,[49] is likely to be much different than in a typical transition-metal η^1-formyl. However, assuming the bonding to be similar for the moment and the Th–H/Th–C contribution to ΔH to be −15 kcal/mol over that of a typical transition-metal system, it is concluded that the Th–O contribution to ΔH of eq 26 is only ca. −5 kcal/mol, which would seem to be an underestimate. For example, the Th–O distance in the dihaptoacyl η^2-$Cp'_2Th(Cl)[\eta^2\text{-}COCH_2C(CH_3)_3]$ is only 0.2 Å longer than in the enediolate $(Cp'_2Th)_2[\mu\text{-}O_2C_2(CH_3)_2]_2$.[49b]



(26)

Closely related to the above hydride carbonylation results are those for alkyls. As a consequence of the considerably weaker

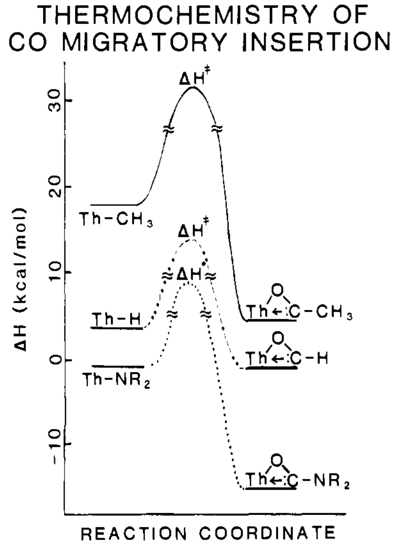


Figure 3. Approximate gas-phase thermochemical relationships in the migratory insertion of carbon monoxide into Th–CH_3, Th–H, and Th–NR_2 bonds.

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(39) (a) Marks, T. J.; Wachter, W. A. *J. Am. Chem. Soc.* **1976**, *98*, 703–710 and references therein. (b) Marks, T. J.; Seyam, A. M.; Kolb, J. A. *Ibid.* **1973**, *95*, 5529–5539. (c) Bruno, J. W.; Kalina, D. G.; Mintz, E. A.; Marks, T. J. *Ibid.* **1982**, *104*, 1860–1869.

(40) (a) Maatta, E. A.; Marks, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 3576–3578. (b) Maatta, E. A.; Marks, T. J., manuscript in preparation.

(41) Bruno, J. W.; Marks, T. J., unpublished observations.

(42) (a) Schwartz, J.; Labinger, J. A. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 333–340. (b) McAlister, D. R.; Erwin, D. K.; Bercaw, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 5966–5968. (c) Guggenberger, L. J.; Meakin, P.; Tebbe, F. N. *Ibid.* **1974**, *96*, 5420–5427.

(43) Watson, P. L. *J. Am. Chem. Soc.* **1982**, *104*, 337–339.

(44) (a) Sinn, H.; Kaminsky, W. *Adv. Organomet. Chem.* **1980**, *18*, 99–149. (b) Pino, P. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 857–875. (c) Boor, J., Jr. "Ziegler-Natta Catalysts and Polymerizations"; Academic Press: New York, 1979. (d) Yamamoto, A.; Yamamoto, T. *Macromol. Rev.* **1978**, *13*, 161–218. (e) Chien, J. W. Ed. "Coordination Polymerization"; Academic Press: New York, 1975. Later transition-metal olefin polymerization systems not requiring a cocatalyst are rare: Keim, W.; Kowaldt, F. H.; Goddard, R.; Kruger, C. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 466–467 and references therein.

(45) (a) Ballard, D. G. H.; Courtis, A.; Holton, J.; McMeeking, J.; Pearce, R. *J. Chem. Soc., Chem. Commun.* **1978**, 994–995. (b) Mauermann, H.; Marks, T. J., submitted for publication.

(46) (a) Berlin, J. R.; Fagan, P. J.; Marks, T. J., unpublished results (1978). (b) Suzuki, H., Marks, T. J., manuscript in preparation.

(47) Gladysz, J. A. *Adv. Organomet. Chem.* **1982**, *20*, 1–47.

(48) (a) Fagan, P. J.; Moloy, K. G.; Marks, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 6959–6962. (b) Katahira, D. A.; Moloy, K. G.; Marks, T. J. "Advances in Catalytic Chemistry II", in press. (c) Katahira, D. A.; Moloy, K. G.; Marks, T. J. *Organometallics* **1982**, *1*, 1723–1726. (d) Moloy, K. G.; Marks, T. J., submitted for publication.

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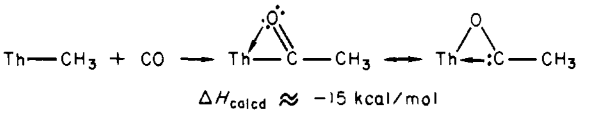
M–C bond, carbonylation of a typical transition-metal hydrocarbyl is predicted[2,5] to be appreciably more exothermic than for the hydride (eq 27). If it is assumed that D(C–H) − D(C–C) in

$$\text{M-CH}_3 + \text{CO} \rightarrow \text{M(COCH}_3) \quad \Delta H_{\text{calcd}} \approx -10 \text{ kcal/mol} \tag{27}$$

thorium η^2-formyls and -acetyls is the same as that in acetaldehyde and acetone, 6 kcal/mol,[33] then the present D(Th–H) vs. D(Th–C) results along with the experimental thermochemical data for eq 26[48a] predict that CO insertion into a thorium–methyl bond to yield a dihaptoacetyl (eq 28) is more exothermic than the analogous insertion for a thorium hydride. However, as a consequence of the more comparable Th–H and Th–C bond disruption enthalpies, the disparity (ca. 10 kcal/mol) is not as great as for the transition-metal systems (ca. 15–25 kcal/mol). Also, the exothermicities of the methyl compound insertions (eq 27 and 28) are rather comparable. The thermochemical results for organothorium carbonylation are summarized in Figure 3.



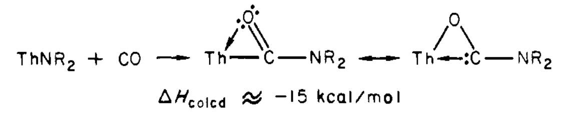
(28)

Dialkylamides. Bond disruption enthalpies for two thorium chloroamide compounds are given in Table II. If a "chloro correction" of ca. +2 kcal/mol is made, the $D(\text{Th–N})_{\text{gas}}$ values become 93 and 102 kcal/mol. These bond enthalpies are greater than those for any of the thorium hydrocarbyls. The increases of D over that for a Th–$CH_2Si(CH_3)_3$ bond of ca. 13 and 27 kcal/mol can be compared with increases in the $M[N(CH_3)_2]_4/M[CH_2Si(CH_3)_3]_4$ series of 17 kcal/mol (M = Ti) and 16 kcal/mol (M = Zr).[5] The present results readily explain known[49c,50] solution metalation reactions such as those shown in eq 29 and 30.

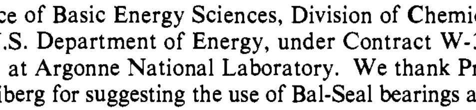
$$\text{Th-H} + \text{HNR}_2 \rightarrow \text{Th-NR}_2 + \text{H}_2 \quad \Delta H_{\text{calcd}} \approx -16 \text{ kcal/mol} \tag{29}$$

$$\text{Th-CH}_3 + \text{HNR}_2 \rightarrow \text{Th-NR}_2 + \text{CH}_4 \quad \Delta H_{\text{calcd}} \approx -30 \text{ kcal/mol} \tag{30}$$

We recently reported the carbonylation of thorium dialkylamides to yield η^2-carbamoyls (eq 31).[49c] From Table II and the foregoing discussion it is evident that the thorium–amide bond is stronger than the thorium–hydride bond; hence the thermochemical driving force for eq 31 vis-à-vis hydride migratory insertion must reside largely in the stabilization of the carbonyl product over the stabilization inherent in a formyl. To the extent that aldehyde and amide bond disruption enthalpies[33] can be transferred, the C–N bond formed in eq 31 is more stable than the C–H bond formed in eq 26 by ca. 14 kcal/mol, and eq 31 is calculated to be approximately as exothermic as eq 28. The strength of an organic amide CN bond no doubt reflects conjugation with the CO π system and resulting CN multiple-bond character. Similarly, the η^2-carbamoyl spectroscopic (ν_{CO}, δ-^{13}CO, DNMR studies of CN bond rotation) and metrical ($r_{\text{C–O}}$, $r_{\text{C–N}}$) data evidence a qualitatively analogous bonding pattern. Interestingly, however, the reversibility[49c] of the *second* insertion at the metal center (the first is irreversible) (eq 32) suggests that steric and electronic saturation effects also play a role in the carbonylation chemistry. The amide carbonylation thermochemical data have been incorporated in Figure 3.



(31)



(32)

Conclusions

This study demonstrates that it is possible to acquire meaningful metal–ligand bond disruption enthalpy data for a homologous series of organoactinide complexes spanning a rather broad range of metal–ligand bonds. The resulting data are instructive not only for understanding the driving force behind chemical transformations connecting various organoactinide reactants and products but also for understanding some of the reasons why organoactinide reactivity patterns differ from those of typical middle and late first-row transition metals. These results have clear implications for designing as well as testing interesting new stoichiometric and catalytic organoactinide reaction patterns. Furthermore, they raise a number of equally relevant questions about bond dissociation enthalpy trends in the organometallic compounds of the early transition elements and lanthanides.

Acknowledgment. This research was supported by the National Science Foundation under Grant CHE8009060 to T.J.M. and by the Office of Basic Energy Sciences, Division of Chemical Sciences, U.S. Department of Energy, under Contract W-31-109-ENG-38 at Argonne National Laboratory. We thank Professor K. B. Wiberg for suggesting the use of Bal-Seal bearings and Drs. D. C. Sonnenberger and P. J. Toscano for assistance with measurements on $Cp'_2Th(C_2H_5)_2$.

Registry No. 2, 83692-52-8; **3**, 83692-53-9; **4**, 79301-21-6; **5**, 69040-88-6; $Cp'_2Th(CH_3)_2$, 67506-90-5; $Cp'_2Th(C_6H_5)_2$, 79847-77-1; $Cp'_2Th(Cl)CH_2CH_3$, 86727-37-9; $Cp'_2Th(Cl)N(CH_3)Si(CH_3)_3$, 86727-38-0; $Cp'_2Th(Cl)N(CH_3)_2$, 77260-84-5; $Cp'_2Th(O\text{-}t\text{-}C_4H_9)_2$, 86727-39-1; $Cp'_2Th(CH_3)_2$, 86727-40-4; $(Cp'_2ThH_2)_2$, 67506-92-7; $Cp'_2Th(Cl)CH_2C_6H_5$, 79301-25-0; Cp'_2ThCl_2, 67506-88-1.

Supplementary Material Available: Tables of parameters employed in thermochemical calculations (5 pages). Ordering information is given on any current masthead page.

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(50) Fagan, P. J., Ph.D. Thesis, Northwestern University, 1981.