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Organo-f-element thermochemistry. Thorium–ligand bond disruption enthalpies in $\{(CH_3)_3SiC_9H_6\}_3ThX$ (X = H or D) and in $\{(CH_3)_3SiC_5H_4\}_3ThH$ complexes *

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Abstract

The bond disruption enthalpies [D(Th–X)] have been determined in the complexes $Ind^*_3Th{-}X$ and $Cp^*_3Th{-}H$ with $Ind^* = (CH_3)_3SiC_9H_6$, $Cp^* = (CH_3)_3SiC_5H_4$ and X = H or D. The thermodynamic data were obtained by iodinolysis batch-titration calorimetry. The calculated $D(Ind^*_3Th{-}H)$, $D(Ind^*_3Th{-}D)$ and $D(Cp^*_3Th{-}H)$ values in toluene are, respectively, 264 ± 8 kJ mol^{-1}, 276 ± 5 kJ mol^{-1} and 274 ± 6 kJ mol^{-1}.

1. Introduction

Knowledge of metal–ligand bond disruption enthalpies is of fundamental importance because it allows prediction of catalytic processes and organometallic reaction pathways. That is why such study is an active and important research area in modern chemistry [1–6]. Although the number of metal–hydrogen bond disruption enthalpies for middle and first row transition metals is steadily expanding [1] only a few publications deal with metal–hydrogen bonds in actinide compounds [6,7]. We report here the thermochemically derived bond disruption enthalpy data [D(Th–H)] for $Ind^*_3Th{-}H$ and $Cp^*_3Th{-}H$ and [D(Th–D)] for $Ind^*_3Th{-}D$.

2. Experimental section

All the organoactinide compounds were handled in Schlenk-type glassware, and solid or solution transfers were performed in a glovebox under purified nitrogen or argon. Solvents were purified by standard methods and distilled immediately prior to use.

2.1. *Synthesis of Ind^*_3ThCl*

To a tetrahydrofuran solution of 0.036 mol of $ThCl_4$ at −78°C was added a solution of 0.108 mol of Ind^*K [8] in a pentane (100 ml)/tetrahydrofuran (15 ml) mixture. The solution was allowed to warm to room temperature and stirred for 5 days. The solvents were then removed *in vacuo* and the yellow residue was extracted with pentane for 4 days (yield 80%). ^1H NMR (C_6D_6 in ppm from C_6D_5H, 7.28 ppm): δ 7.95

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(d, 3H); 7.50 (d, 3H); 7.22 (q, 3H); 7.12 (q, 3H); 5.60 (d, 3H); 5.04 (d, 3H); 0.60 (s, 27H). IR (hexachlorobutadiene, Nujol, polyethylene): 2950s, 2895m, 1245s, 275s, 245s cm^{-1}.

Anal. Found: C, 51.86; H, 5.55; Si, 9.67; Th, 28.26; Cl, 4.39. Calc.: C, 52.13; H, 5.47; Si, 10.16; Th, 27.97; Cl, 4.27%.

2.2. Synthesis of $\mathrm{Ind}^*_3\mathrm{ThH}$

For the synthesis of this compound we modified the method recently described by Ephritikhine [5,9]. The tris(trimethylsilyl)indenylthorium chloride was treated with an excess (5%) of $\mathrm{KEt_3BH}$ in toluene for 24 h at 60°C to give the hydride. The solvent was removed *in vacuo* and the yellow residue extracted with pentane for 4 days (yield 30%). ^{1}H NMR ($\mathrm{C_6D_5CD_3}$ in ppm from $\mathrm{C_6D_5CD_2H}$, 2.3 ppm): δ 14.73 (s, 1H); 7.85 (m, 6H); 7.15 (m, 6H); 6.53 (d, 2H); 5.76 (s, 1H); 4.46 (d, 2H); 4.19 (s, 1H); 0.80 (s, 9H); 0.65 (s, 9H); 0.64 (s, 9H). IR (hexachlorobutadiene, Nujol, polyethylene): 2960s, 2895m, 1485m, 1245s, 245s cm^{-1}. Anal. Found: C, 53.18; H, 5.76; Th, 29.98. Calc.: C, 54.39. H, 5.83; Th, 29.18. Molecular weight by osmometry in benzene (mean of three measurements): 817 (theoretical 796).

2.3. Synthesis of $\mathrm{Ind}^*_3\mathrm{ThD}$

In a procedure similar to that employed for $\mathrm{Ind}^*_3\mathrm{ThH}$, 2.7 ml of $\mathrm{LiEt_3BD}$ (1 mol dm^{-1} in THF) was added to a THF solution (*ca.* 100 ml) of 0.0025 mol of $\mathrm{Ind}^*_3\mathrm{ThCl}$. The solution was heated at 60°C for 1 day. The solvent was removed *in vacuo* and the yellow residue extracted with pentane for 4 days (yield 40%). ^{1}H NMR ($\mathrm{C_6D_5CD_3}$ in ppm from $\mathrm{C_6D_5CD_2H}$, 2.3 ppm): δ 7.85 (m, 6H); 7.15 (m, 6H); 6.53 (d, 2H); 5.76 (s, 1H); 4.45 (d, 2H); 4.19 (s, 1H); 0.80 (s, 9H); 0.65 (s, 9H); 0.64 (s, 9H). IR (hexachlorobutadiene, Nujol, polyethylene): 2950s, 2895m, 1245s, 1055m, 245s cm^{-1}. Anal. Found: C, 54.41; H(D), 6.1; Si, 11.22; Th, 28.31. Calc.: C, 54.32; H(D), 5.95; Si, 10.58; Th, 29.15.

2.4. Synthesis of $\mathrm{Cp}^*_3\mathrm{ThH}$

Tris(trimethylsilyl)cyclopentadienylthorium chloride was treated at room temperature with an excess (5%) of $\mathrm{KEt_3BH}$ in toluene to give the hydride. The solvent was removed *in vacuo* and the white residue extracted with pentane for 1 day (yield 85%). ^{1}H NMR ($\mathrm{C_6D_6}$ in ppm from $\mathrm{C_6D_5H}$, 7.28 ppm): δ 12.94 (s, 1H); 6.49 (t, 6H); 5.84 (t, 6H); 0.58 (s, 27H). IR (hexachlorobutadiene, Nujol, polyethylene): 3072w, 2952vs, 1042s, 834vs, 780vs, 243m cm^{-1}. Anal. Found: C, 45.06; H, 6.45; Si, 13.07; Th, 35.98. Calc.: C, 44.70; H, 6.25; Si, 13.07; Th, 35.98. Molecular weight by osmometry in benzene: 732 (theoretical 644).

2.5. Analytical methods

Proton NMR spectra were recorded on a Bruker AM400 (FT, 400.1 MHz) instrument and IR spectra on a Bruker IFS66 spectrophotometer. Elemental analysis and molecular weight determinations were carried out by Dornis and Kolbe Mikroanalytisches Laboratorium, Mülheim, Germany.

2.6. Titration calorimetry

The isoperibol calorimeter employed in this study and the general experimental procedure have been described previously [10].

3. Results and discussion

Two important differences can be seen between the IR spectrum of $\mathrm{Ind}^*_3\mathrm{ThCl}$ and $\mathrm{Ind}^*_3\mathrm{ThX}$ where X = H or D. The vibration at 275 cm^{-1} assigned to the Th–Cl stretching vibration [11] is absent for the $\mathrm{Ind}^*_3\mathrm{ThX}$ compounds but an additional band appears at 1485 cm^{-1} in the hydride compound. This band, assigned to the Th–H stretching vibration, is shifted to 1055 cm^{-1} in the deuteride (ν(Th–H)/ν(Th–D) = 1.4). The vibration frequency Th–H in $\mathrm{Cp}^*_3\mathrm{ThH}$ is at 1460 cm^{-1}. The relatively low frequency of the Th–H stretching vibration is consistent with data for early transition-metal hydrides and the reported actinide hydrides [5,9,12].

The NMR spectra of $\mathrm{Ind}^*_3\mathrm{ThH}$ and $\mathrm{Cp}^*_3\mathrm{ThH}$ exhibit a low field signal at 14.73 ppm and at 12.94 ppm, respectively; these signals are absent from the spectra of the deuteride analogues and so are assigned to the metal hydride resonances. The NMR spectrum of $\mathrm{Cp}^*_3\mathrm{ThH}$ was foreseeable, but this was not the case for $\mathrm{Ind}^*_3\mathrm{ThH}$, and it seems that one trimethylsilylindenyl ligand in this case is probably placed differently around the metal relative to the other ligands; a similar arrangement was observed in the $\mathrm{Cp_3Sm}$ compound [13a]. It seems that the small size of hydrogen atom and the bulk of the substituted indenyl ligand play an important role in determining the molecular organization. The high temperature (331 K) ^{1}H NMR spectrum of $\mathrm{Ind}^*_3\mathrm{ThH}$ exhibits narrower peaks (δ 0.80 ppm; $T = 298$ K, $\nu_{1/2} = 8.2$ Hz; $T = 331$ K, $\nu_{1/2} = 2.1$ Hz). The same feature was noted in the NMR spectrum of $\mathrm{Cp_3UR}$ [13b] where R = $\mathrm{CN(C_6H_3Me_2\text{-}2,6)^tBu}$ and $[\mathrm{Cp}^*_3\mathrm{U}]_2[\mathrm{CS_2}]$ [13c] compounds, and was attributed to a non-equivalence of the sites in the auxiliary ligands. Unfortunately no crystal structure of a compound with a trimethylsilylindenyl ligand is available, but the NMR results imply important steric congestion around the thorium metal in the new compounds. In the crystal structure of $\mathrm{Cp}^*_3\mathrm{UH}$ [5], although Cp* is less bulky than Ind*, steric factors already cause bending of the Si–$\mathrm{C_5}$ plane axes and it is thus not surprising that one bulky trimethylsilylindenyl ligand is differently located in relation to the other two ligands around the thorium metal. On the other hand, the NMR spectrum of Ind$^*_3$ThCl indicates a high symmetrical molecule in spite of the presence of a chloride ligand, which is bulkier than a hydride ligand. So it appears that knowledge of the crystal structure (probably requires neutron diffraction studies) of the new compounds is necessary for interpretation of the NMR spectra.

After taking account of possible experimental uncertainty, the results of osmometry in benzene seem to indicate a slight association in the Cp* compound, which is absent for the Ind* compound probably because of the steric congestion in the latter.

The absolute bond disruption enthalpies [D(Th–X) where X = H or D] are given by [6]

$$D(L^*_3Th\text{–}X) = \Delta H_{rx} - \Delta H_{ox} + 1/2D(X\text{–}X) \qquad (1)$$

where L* = Ind* or Cp*. The absolute D(L$^*_3$Th–X) value requires knowledge of the thermochemical data corresponding to the oxidative addition reaction (ΔH_{ox}) which have not been directly measured. To estimate this value we employ the accepted parallelism between thorium-alkyl and uranium-alkyl bond disruption enthalpies. Indeed D(Th–R) (with R = hydrocarbyl and halide) is always about 40 kJ mol^{-1} [7b,10] higher than D(U–R) in the analogous compounds because the trivalent state is more stable for uranium than for thorium. It is then possible to estimate the oxidative addition enthalpy (ΔH_{ox}) by adding that difference to ΔH_{ox} from iodinolysis reaction of uranium(III) compounds [6,14].

$$Ind^*_3U + 1/2\ I_2 \longrightarrow Ind^*_3UI \qquad (2)$$

$$\Delta H^0_{ox} = -142.7 \pm 3.3\ \text{kJ mol}^{-1}\ \text{(per mol of complex)}$$

It is found that the value of the enthalpy of the oxidation reaction (Th^{III}/Th^{IV}) per mol of complex is −183 kJ mol^{-1}. If we use the same process for the cyclopentadienyl compound, the value of the enthalpy of oxidation reaction is −230 kJ mol^{-1}. This difference can be attributed to greater steric congestion in the case of the Ind* ligands, which would weaken the metal–halide bond [14]. The derived values are probably not accurate to better than 4 kJ mol^{-1}.

The thermochemical data corresponding to the ligand exchange reaction are presented in Table 1.

The values of D(H–H) and D(D–D) necessary for the derivation D(Th–H) and D(Th–D) have been taken from the literature [15]. The enthalpies of solution in toluene are quite small, and very similar to those of a vast variety of complexes [6]. Derivation of D(Th–X) values from solution data assumes that solvation effects in toluene can be cancelled out.

TABLE 1. Enthalpies of solution (ΔH_{soln}) in toluene, enthalpies of reaction with I_2 (per mol of complex) and the derived bond disruption enthalpies of Ind$^*_3$ThX and Cp$^*_3$Th–H complexes (kJ mol^{-1}) (95% confidence)

X	ΔH_{soln}	ΔH_{rx}	D(Ind$^*_3$Th–X)
H	12.7 ± 4.2	−134.2 ± 7.7	264 ± 8
D	14.9 ± 3.4	−123.8 ± 5.0	276 ± 5
			D(Cp$^*_3$Th–H)
H	14.5 ± 2.3	−171.4 ± 5.8	274 ± 6

In spite of a very different congestion around the metal, it is immediately apparent on inspecting the data in Table 1 that the D(Th–X) values are quite similar.

The Th–H bond enthalpy can be compared with the rather small number of available D(M–H) values for transition–metal complexes, all falling remarkably near 250 kJ mol^{-1} [1] and to the recently reported value of D(U–H) [6]. By alcoholytic isoperibol titration, Marks *et al.* [7] have determined the relative disruption enthalpies D(Th–H) in the complexes {Cp$^*_2$ThH$_2$}$_2$ (407.9 ± 2.9 kJ mol^{-1}), Cp$^*_2$Th(OCH^{t}Bu$_2$)H (390.3 ± 5.0 kJ mol^{-1}) and Cp$^*_2$Th(O2,6-^{t}Bu–C$_6$H$_3$)H (385.3 ± 4.8 kJ mol^{-1}) with Cp* = $(CH_3)_5C_5$. The origin of this disparity has been discussed in detail [1,4,16].

The D(Th–H) and D(Th–D) values for organometallic compounds (Table 1) agree very well with the value of $\bar{D}$(Th–H), 275.6 ± 1.2 kJ mol^{-1} in $ThH_{3.75}$ and of $\bar{D}$(Th–D), 278.5 ± 1.4 kJ mol^{-1}, in $ThD_{3.75}$ as defined by eqns. (3) and (4) calculated from available thermochemical data [15,17].

$$ThX_{3.75} \longrightarrow Th + 3.75X^{\cdot} \qquad (3)$$

$$\bar{D}(Th\text{–}H) = 1/3.75(3.75\ \Delta H^0_f X^{\cdot} - \Delta H^0_f ThX_{3.75}) \qquad (4)$$

It is noteworthy that the D(Th–H) values determined by Mark are similar in spite of the presence of different ancillary ligands. The slightly higher D(Th–H) value found for {Cp$^*_2$Th–H$_2$}$_2$ is in fact an average value, but the first Th–H bond disruption enthalpy is several kJ per mol lower than the average value [7a]. These observations and the aforementioned D($ThH_{3.75}$)/ D(L$^*_3$ThH) data suggest that ancillary ligands have a similar influence on D(Th–H). An identical conclusion was reached from the uranium hydride bond disruption enthalpy [6].

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