Preliminary communication

Stepwise Ti–Cl, Ti–CH$_3$, and Ti–C$_6$H$_5$ bond dissociation enthalpies in bis(pentamethylcyclopentadienyl)titanium complexes

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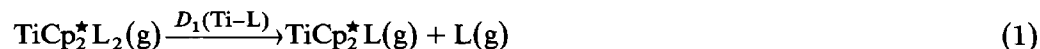**Johannes W. Pattiasina and Jan H. Teuben***

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Abstract

Reaction-solution calorimetric studies involving the complexes Ti[η^5-C$_5$(CH$_3$)$_5$]$_2$-(CH$_3$)$_2$, Ti[η^5-C$_5$(CH$_3$)$_5$]$_2$(CH$_3$), Ti[η^5-C$_5$(CH$_3$)$_5$]$_2$(C$_6$H$_5$), Ti[η^5-C$_5$(CH$_3$)$_5$]$_2$Cl$_2$, and Ti[η^5-C$_5$(CH$_3$)$_5$]$_2$Cl, have enabled derivation of titanium–carbon and titanium––chlorine stepwise bond dissociation enthalpies in these species.

The abundance of thermochemical data for neutral organometallic complexes, including metal-ligand bond enthalpy terms, E(M–L), and mean bond dissociation enthalpies, $\overline{D}$(M–L) [1], contrasts with the paucity of stepwise bond dissociation enthalpies, D_i(M–L), which are more appropriate quantities for dealing with reactivity problems. This led us to devise a simple method, involving both experimental data and extended Hückel molecular orbital calculations, for estimating the first and the second metal–ligand bond dissociation enthalpies for MCp$_2$L$_2$ complexes (Cp = η^5-C$_5$H$_5$) [2], i.e. the enthalpy changes associated with processes 1 and 2.

$$TiCp_2^\star L_2(g) \xrightarrow{D_1(Ti-L)} TiCp_2^\star L(g) + L(g) \tag{1}$$

$$TiCp_2^\star L(g) \xrightarrow{D_2(Ti-L)} TiCp_2^\star(g) + L(g) \tag{2}$$

We now present the results of thermochemical studies involving several TiCp$_2^\star$L$_n$ complexes (Cp* = η^5-C$_5$(CH$_3$)$_5$; n = 1 or 2) that have given experimental data for D_1(Ti–L) and thus can be used to assess our approach. To our knowledge, this is the first reported information on the energetics of Ti^{III} organotitanium compounds.
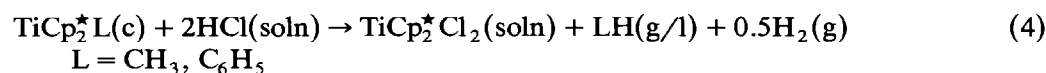
Table 1

Thermochemical data for $TiCp_2^* L_n$ complexes ($kJ\ mol^{-1}$)

Complex	ΔH_f^0(Complex, c) $-\Delta H_f^0$($TiCp_2^* Cl_2$, c)	ΔH_f^0(Complex, c) $-\Delta H_f^0$($TiCp_2^* Cl$, c)	D_1(Ti–L)	D_2(Ti–L)
$TiCp_2^*(CH_3)_2$	381.9 ± 4.5		271 ± 21	300 ± 29
$TiCp_2^* CH_3$	516.0 ± 5.5	237.4 ± 6.2	300 ± 29 [a]	
$TiCp_2^*(C_6H_5)_2$	671 ± 15 [b]		269 ± 28	366 ± 31
$TiCp_2^* C_6H_5$	621.0 ± 7.8	342.4 ± 8.3	366 ± 31 [a]	
$TiCp_2^* Cl_2$	0		380 ± 20	481 ± 21
$TiCp_2^* Cl$	278.6 ± 3.9	0	481 ± 21 [a]	

[a] D_1(Ti–L) in the Ti^{III} complex, equal to D_2(Ti–L) in the Ti^{IV} complex. [b] Value estimated from $\Delta H_f^0[TiCp_2(C_6H_5)_2$, c] 262.2 ± 8.9 kJ mol^{-1} [1b].

The enthalpies of reactions 3, 4, and 5, ΔH_r, and several enthalpies of solution, ΔH_d, were measured in the reaction-solution calorimeter previously described [3]. The complexes were prepared and purified by published procedures [4*], and the calorimetric solution was a 1/4 mixture of 10.0 mol dm^{-3} aqueous HCl and acetone for reaction 3, and a 1.33 mol dm^{-3} solution of HCl in isopropyl ether for reactions 4 and 5.

$$TiCp_2^*(CH_3)_2(c) + 2HCl(soln) \rightarrow TiCp_2^* Cl_2(soln) + 2CH_4(g) \tag{3}$$

$$TiCp_2^* L(c) + 2HCl(soln) \rightarrow TiCp_2^* Cl_2(soln) + LH(g/l) + 0.5H_2(g) \tag{4}$$
$$L = CH_3, C_6H_5$$

$$TiCp_2^* Cl(c) + HCl(soln) \rightarrow TiCp_2^* Cl_2(soln) + 0.5H_2(g) \tag{5}$$

The standard enthalpies of formation of the crystalline complexes relative to the unknown standard enthalpies of formation of the related monochloride or dichloride molecules were derived from the values of ΔH_r, ΔH_d, and literature data [1a,5], and are listed in Table 1. Also included are D_1(Ti–L) and D_2(Ti–L), calculated as described below.

The enthalpies of reaction 1 (D_1(Ti–L), Table 1) were obtained from the results for the ΔH_f^0(Complex, c) $-\Delta H_f^0$($TiCp_2^* Cl_2$, c) (Table 1) and ΔH_f^0(L, g) [6]. It was also necessary to assume values for the differences between the standard enthalpies of sublimation of the Ti^{IV} and the analogous Ti^{III} complexes (10 ± 20 kJ mol^{-1} for $L = CH_3$ and C_6H_5, and 20 ± 20 kJ mol^{-1} for L = Cl). These conservative estimates are avoided if values of D_1(Ti–L) are defined for solutions. Since it can reasonably be assumed that the solution enthalpies of each pair of Ti^{III}, Ti^{IV} complexes cancel within ca. ± 4 kJ mol^{-1}, the following "solution" values can be obtained: D_1(Ti–Cl) 400 ± 6, D_1(Ti–CH_3) 281 ± 8, and D_1(Ti–C_6H_5) 279 ± 19 kJ mol^{-1}.

The enthalpy required to break the second Ti–L bond in $TiCp_2^* L_2$, D_2(Ti–L), i.e. the Ti–L bond in the Ti^{III} complex, was derived, according to reaction 6, from ΔH_f^0(Complex, c) $-\Delta H_f^0$($TiCp_2^* Cl$, c) (Table 1), ΔH_f^0(L, g) [6], ΔH_f^0(Cl, g) [5], and the estimates ΔH_s^0($TiCp_2^* Cl$) $-\Delta H_s^0$($TiCp_2^* L$), 30 ± 20 and 20 ± 20 kJ mol^{-1} for $L = CH_3$ and C_6H_5, respectively. In contrast to the values of D_1(Ti–L), the values D_2(Ti–L) presented in Table 1 cannot strictly be regarded as absolute values

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* A reference number with an asterisk indicates a note in the list of references.

because they depend on values of $D_2(\text{Ti–Cl})$, and this quantity was derived by subtracting $D_1(\text{Ti–Cl})$ from that estimated for $2\bar{D}(\text{Ti–Cl})$, namely 861 kJ mol^{-1} [1]. There is, however, experimental evidence supporting this value [1a,1c].

$$\text{TiCp}_2^{\star}\text{L(g)} + \text{Cl(g)} \rightarrow \text{TiCp}_2^{\star}\text{Cl(g)} + \text{L(g)} \qquad (6)$$
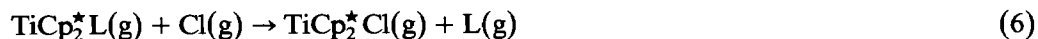
The results in Table 1 or the above values for the bond dissociation enthalpies in solution (for which estimates of sublimation enthalpies were not needed), are in fair agreement with the earlier predictions for the cyclopentadienyl complexes, viz. $D_1(\text{Ti–CH}_3)$ 285, $D_2(\text{Ti–CH}_3)$ 300, $D_1(\text{Ti–Cl})$ 390, and $D_2(\text{Ti–Cl})$ 460 kJ mol^{-1} [2]. The same method applied to the phenyl compound yields $D_1(\text{Ti–C}_6\text{H}_5)$ 290 and $D_2(\text{Ti–C}_6\text{H}_5)$ 372 kJ mol^{-1}, also close to the values in Table 1 [7].

As expected, Ti–L bond dissociation enthalpies are higher when the metal is in the lower oxidation state and coordinated to a smaller number of ligands.

We are extending our studies to related systems, e.g. $\text{TiCp}_2^{\star}\text{H}$, $\text{TiCp}_2^{\star}\text{C}_2\text{H}_5$, $\text{TiCp}_2^{\star}\text{C}_3\text{H}_5$, and complexes with fulvene and allyldiene ligands.

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