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## Thermochemistry of the complexes $\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)(\text{C}_5\text{Me}_4\text{CH}_2)$ and $\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)[\text{C}_5\text{Me}_3(\text{CH}_2)_2]$

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### Abstract

Reaction-solution calorimetric studies of the crystalline complexes  $\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)\text{L}$  ( $\text{L} = \text{C}_5\text{Me}_4\text{CH}_2$  or  $\text{C}_5\text{Me}_3(\text{CH}_2)_2$ ) led to relative values of their standard enthalpies of formation. These data, together with early results obtained for several analogous  $\text{Ti}^{\text{III}}$  complexes, enabled to discuss the energetics of two reactions of synthetic interest. The results are also used to analyse the possible bonding modes of ligands L to the titanium atom.

### Introduction

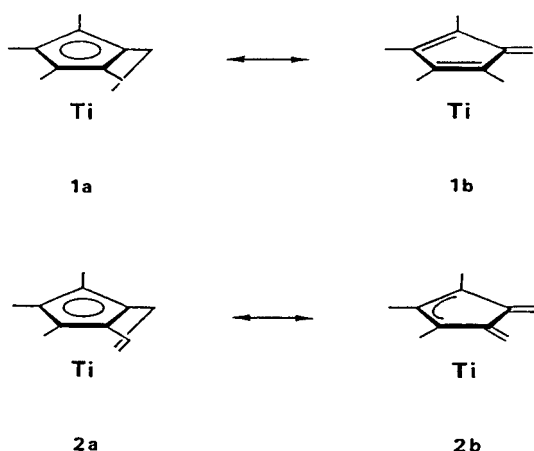
Previous thermochemical studies involving several complexes of the type  $\text{Ti}(\text{Cp}^\star)_2\text{L}$  and  $\text{Ti}(\text{Cp}^\star)_2\text{L}_2$  ( $\text{Cp}^\star = \eta^5\text{-C}_5\text{Me}_5$ ;  $\text{L} = \text{Cl}, \text{Me}, \text{Ph}$ ) enabled to derive the enthalpies of the reactions



viz.  $400 \pm 6$ ,  $281 \pm 8$ , and  $279 \pm 19$   $\text{kJ mol}^{-1}$  for  $\text{L} = \text{Cl}, \text{Me},$  and  $\text{Ph}$ , respectively [1]. These results, together with estimated enthalpies of sublimation of the complexes, led to the gas-phase enthalpies of reactions 1, which are identified with Ti-L first bond dissociation enthalpies in the  $\text{Ti}^{\text{IV}}$  molecules.

Additional thermochemical studies on two other  $\text{Ti}^{\text{III}}$  complexes,  $\text{Ti}(\text{Cp}^\star)\text{Fv}$  and  $\text{Ti}(\text{Cp}^\star)\text{Ad}$  ( $\text{Fv} = \text{C}_5\text{Me}_4\text{CH}_2$ ,  $\text{Ad} = \text{C}_5\text{Me}_3(\text{CH}_2)_2$ ), with the aim of obtaining information of the energetics of reactions 2 and 3, are now reported.





The thermolysis reaction 2 is a good synthetic method for the fulvene complex and occurs both in solution and in the solid state for a variety of ligands R (H, alkyl, vinyl, allyl, and aryl) [2-4]. The hydrogen extrusion reaction 3, on the other hand, is a convenient route to the allyldiene complex [2].

Another interesting feature of the title complexes relates to the bonding modes of the Fv and Ad moieties, which can be considered in terms of the two resonance structures shown below for each case. In **1a** and **2a** the  $sp^3$ -hybridized carbon atoms of the methylene groups are  $\sigma$ -bonded to the metal atom, whereas in **1b** and **2b** the  $sp^2$  hybridizations of the same carbon atoms correspond to  $\pi, \eta^6$ - and  $\pi, \eta^7$ -coordination of Fv and Ad, respectively.

The close resemblance of ESR and  $^1\text{H}$  NMR spectra of the fulvene complex to those of the compounds  $\text{Ti}(\text{Cp}^*)_2\text{R}$  suggested that structure **1a** was the most likely [5]. A similar conclusion was recently reported for the molecule  $\text{Zr}(\text{Cp}^*)(\text{Fv})\text{Ph}$  [6]. In the case of the allyldiene compound, the spectral data favour structure **2b** [2,5]. While a thermochemical analysis does not permit unambiguous conclusions about the best description of the bonding in those complexes, since many factors (bond enthalpies) are involved, it may give useful information for discussion of the problem.

## Experimental

### Compounds

Analytically pure samples of the fulvene and allyldiene complexes were synthesized and purified as described in the literature [2,5]. The reaction solutions for the calorimetric experiments were  $1.34 \text{ mol dm}^{-3}$  (solution A) and  $3.02 \text{ mol dm}^{-3}$  (solution B) HCl in isopropyl ether solutions for the Fv and Ad complexes, respectively. These solutions were prepared by bubbling the moisture-free gas into a specific volume of the freshly distilled, dry solvent (Merck, p.a.).

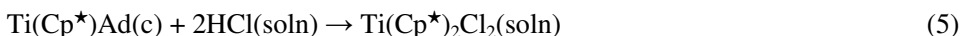
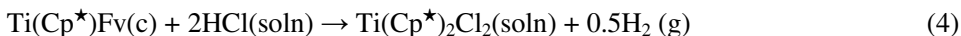
### Calorimeter

The reaction and solution enthalpies were measured in the calorimeter previously described [7]. All the experiments were carried out under pure argon. A known

volume (125 ml) of oxygen- and moisture-free calorimetric solvent was transferred to the Dewar vessel (previously flushed with argon) prior to each run. The glass bulbs containing the samples were also sealed under an inert atmosphere.

### Reactions

Thermochemical measurements on reactions 4 and 5 were used to derive the standard enthalpies of formation of the complexes relative to  $\Delta H_f^0[\text{Ti}(\text{Cp}^*)_2\text{Cl}_2, \text{c}]$ . Both reactions are rapid and quantitative, as described elsewhere [5].



All the reaction and solution enthalpies presented are mean values from five independent experiments and refer to 298 K. The associated uncertainties are twice the standard deviations of these mean values.

### Auxiliary data

The following enthalpies of formation were used in evaluating the thermochemical results (values in  $\text{kJ mol}^{-1}$ ):  $\Delta H_f^0(\text{CH}_4, \text{g}) = -74.5 \pm 0.4$  [8];  $\Delta H_f^0(\text{C}_6\text{H}_6, \text{l}) = 49.0 \pm 0.3$  [8];  $\Delta H_f^0(\text{C}_6\text{H}_6, \text{g}) = 82.9 \pm 0.3$  [8];  $\Delta H_f^0(\text{Me}, \text{g}) = 146.9 \pm 0.6$  [9];  $\Delta H_f^0(\text{Ph}, \text{g}) = 330 \pm 8$  [9-11];  $\Delta H_f^0(\text{H}, \text{g}) = 217.997 \pm 0.006$  [12].

### Results

The thermochemical results are summarized in Table 1. The enthalpies of reactions 4 or 5,  $\Delta H_r$ , used together with the enthalpies of solution of  $\text{Ti}(\text{Cp}^*)_2\text{Cl}_2$  in the calorimetric solutions,  $\Delta H_{\text{d1}}$ , and a correction term that takes account of the HCl dilution effect,  $\Delta H_{\text{d4}}$ , led to  $\Delta H_f^0[\text{Ti}(\text{Cp}^*)\text{L}, \text{c}] - \Delta H_f^0[\text{Ti}(\text{Cp}^*)_2\text{Cl}_2, \text{c}]$  (L = Fv, Ad), according to eq. 6:

$$\Delta H_f^0[\text{Ti}(\text{Cp}^*)\text{L}, \text{c}] - \Delta H_f^0[\text{Ti}(\text{Cp}^*)_2\text{Cl}_2, \text{c}] = -\Delta H_r + \Delta H_{\text{d1}} + 2m\Delta H_{\text{d4}} - 2\Delta H_f^0(\text{HCl}, \text{soln}) \quad (6)$$

This equation assumes a negligible heat effect associated with a partial solution of  $\text{H}_2$  in the case of reaction 4. The quantity  $m$  represents the molar ratios isopropyl ether/HCl in the calorimetric solutions before the reaction ( $m = 5.11$  and  $2.15$  for solutions A and B, respectively).  $\Delta H_{\text{d4}}$  was therefore measured by breaking bulbs containing stoichiometric amounts of ether in the calorimetric solutions. Finally,  $\Delta H_f^0(\text{HCl}, \text{soln})$  were taken as  $-144.1 \pm 0.7$  and  $-143.8 \pm 0.6$   $\text{kJ mol}^{-1}$  [13], respectively for solutions A and B.

Table 1  
Thermochemical results ( $\text{kJ mol}^{-1}$ )

| Complex   | $\Delta H_r$     | $\Delta H_{\text{d1}}$ | $\Delta H_{\text{d4}}$ | $\Delta H_f^0(\text{complex}, \text{c}) - \Delta H_f^0[\text{Ti}(\text{Cp}^*)_2\text{Cl}_2, \text{c}]$ |
|-----------|------------------|------------------------|------------------------|--|
| Ti(Cp*)Fv | $-312.9 \pm 4.3$ | $21.7 \pm 1.5$         | $-0.27 \pm 0.08$       | $620.0 \pm 4.8$  |
| Ti(Cp*)Ad | $-233.9 \pm 3.9$ | $33.0 \pm 1.4$         | $-0.55 \pm 0.13^a$     | $552.1 \pm 4.3$  |

<sup>a</sup> Ref. 13.

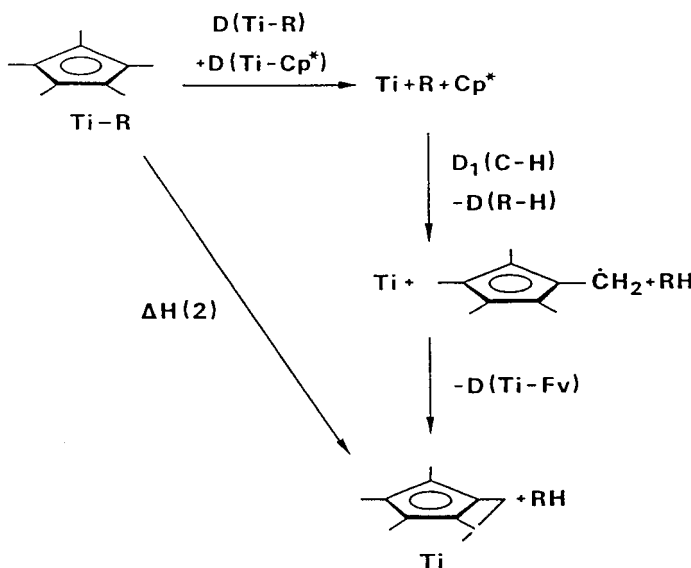
## Discussion

The enthalpies of formation in Table 1 and two early relative values,  $\Delta H_f^0[\text{Ti}(\text{Cp}^*)_2\text{Me},\text{c}] = (516.0 \pm 5.5) + \Delta H_f^0[\text{Ti}(\text{Cp}^*)_2\text{Cl}_2,\text{c}]$  and  $\Delta H_f^0[\text{Ti}(\text{Cp}^*)_2\text{-Ph},\text{c}] = (621.0 \pm 7.8) + \Delta H_f^0[\text{Ti}(\text{Cp}^*)_2\text{Cl}_2,\text{c}]$ , enable calculation of the enthalpy of reaction 2,  $\Delta H(2)$ , for R = Me and Ph, on the reasonable assumption that the solution enthalpies cancel within the experimental error. The results are shown in Table 2, and it can be seen that both reactions are endothermic. Nevertheless, estimated entropy changes for the same reactions (Table 2) indicate that these unfavourable enthalpies are offset by large positive entropic terms, both for R = Me and Ph, although this compensation is less marked in the case of the aryl ligand. An approximate temperature effect on  $\Delta G(2)$  can also be predicted by neglecting the heat capacity difference between the complexes  $\text{Ti}(\text{Cp}^*)_2\text{R}$  and  $\text{Ti}(\text{Cp}^*)\text{Fv}$  and by using data from [14]. It is observed that  $\Delta G(2)$  becomes more negative as the temperature is increased. For example, at 70 °C, a suitable temperature for reactions 2 and 3 [5],  $\Delta G(2)$  is ca. -34 kJ mol<sup>-1</sup> (R = Me) or -11 kJ mol<sup>-1</sup> (RH = C<sub>6</sub>H<sub>6</sub>,g).

The bonding mode of the fulvene complex can be discussed on the assumption that the experimental values for  $\Delta H(2)$  are close to the corresponding gas phase values. Scheme 1 (where the second Cp\* moiety is omitted and the methylene group is arbitrarily  $\sigma$ -bonded to the titanium atom) enables estimation of the difference:

$$D(\text{Ti-Fv}) - D(\text{Ti-Cp}^*) = -\Delta H(2) - D(\text{R-H}) + D(\text{Ti-R}) + D_1(\text{C-H}) \quad (7)$$

Assigning a value to  $D_1(\text{C-H})$  raises some difficulties. A typical C(*sp*<sup>3</sup>)-H bond dissociation enthalpy is about 410 kJ mol<sup>-1</sup> [9], but this is too high since the Fv fragment is resonance stabilized. Identifying  $D_1(\text{C-H})$  with  $D[\text{C}(\text{sp}^3)\text{-H}]$  in toluene, 368 kJ mol<sup>-1</sup> [9], is probably a much better choice. The effect of an *ortho* methyl group on this bond dissociation enthalpy must be rather small, as indicated



Scheme 1

Table 2  
Energetics of reactions 2 and 3 at 298 K (kJ mol<sup>-1</sup>)

| Reaction | $\Delta H$  | $T\Delta S^a$ | $\Delta G^a$ |
|----------|-------------|---------------|--------------|
| 2 R = Me | 29.5 ± 7.3  | 55.5          | -26          |
| R = Ph   | 48.0 ± 9.2  | 51.7          | -4           |
| 3        | -67.9 ± 6.4 | 19.5          | -87          |

<sup>a</sup> Estimated by assuming identical entropy values for the complexes.  $S^0(\text{H}_2, \text{g}) = 130.6$ ,  $S^0(\text{CH}_4, \text{g}) = 186.3$ , and  $S^0(\text{C}_6\text{H}_6, \text{l}) = 173.3 \text{ J mol}^{-1} \text{ K}^{-1}$  [14].

by a reported value for  $D(o\text{-MeC}_6\text{H}_4\text{CH}_2\text{-H})$  [15], which is only 3 kJ mol<sup>-1</sup> lower than the above value for  $D[\text{PhCH}_2\text{-H}]$ . The remaining terms in eq. 7,  $D(\text{R-H})$  and  $D(\text{Ti-R})$ , can be obtained from the auxiliary data above or from a previous paper [1]:  $D(\text{Ti-R}) \sim 300$  and  $366 \text{ kJ mol}^{-1}$  for R = Me and Ph, respectively. We obtain:

$$\text{R = Me} \quad D(\text{Ti-Fv}) - D(\text{Ti-Cp}^*) \sim 199 \text{ kJ mol}^{-1}$$

$$\text{R = Ph} \quad D(\text{Ti-Fv}) - D(\text{Ti-Cp}^*) \sim 221 \text{ kJ mol}^{-1}$$

Such a large difference, ca. 200 kJ mol<sup>-1</sup> [16\*], is likely to reflect the formation of a strained Ti-C  $\sigma$  bond in the fulvene complex (structure **1a**) rather than a change from a  $\pi, \eta^5$ - to a  $\pi, \eta^6$ -coordination, in keeping with the spectral evidence (see also the discussion below).

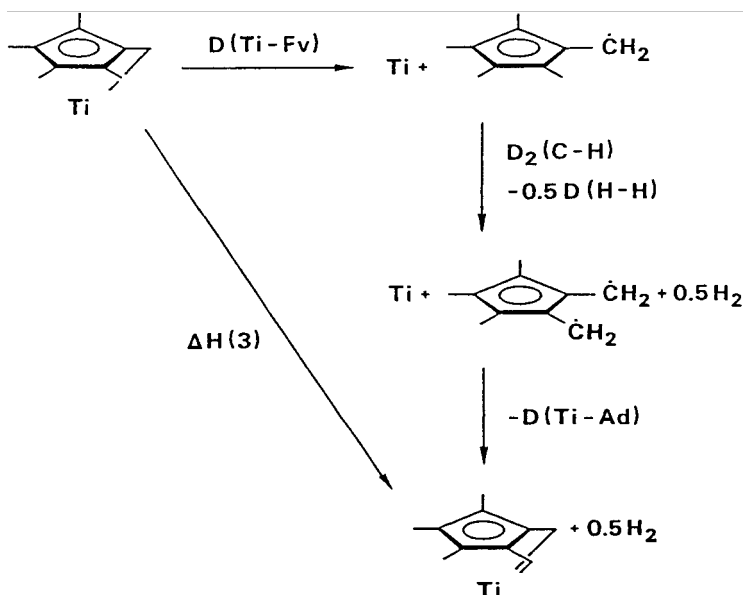
We now consider the energetics of reaction 3. The enthalpies of formation in Table 1 enable us to calculate the enthalpy of this reaction as  $\Delta H(3) = -67.9 \pm 6.4 \text{ kJ mol}^{-1}$  upon the assumption that the solution enthalpies of the fulvene and allyldiene complexes are similar. As observed in Table 2, the hydrogen extrusion reaction is also favoured by a positive entropic change. The stability of the fulvene complex relative to its thermolysis products thus is of kinetic origin.

The above value of  $-67.9 \text{ kJ mol}^{-1}$  can also be identified with the enthalpy of reaction 3 in the gas phase, since the enthalpies of sublimation of the complexes are likely to be rather similar. This allows us to estimate the difference between Ti-Fv and Ti-Ad bond dissociation enthalpies, by using Scheme 2. As in Scheme 1, the Cp\* ligand was omitted for sake of clarity and all the methylene groups are arbitrarily  $\sigma$ -bonded to the titanium atom, but obviously this option does not affect the difference:

$$\begin{aligned} D(\text{Ti-Ad}) - D(\text{Ti-Fv}) &= -\Delta H(3) - D(\text{H-H})/2 + D_2(\text{C-H}) \\ &= -(150.1 \pm 6.4) + D_2(\text{C-H}) \end{aligned} \quad (8)$$

Assigning a value to  $D_2(\text{C-H})$  is again a difficult exercise. Fortunately the *second* C(*sp*<sup>3</sup>)-H bond dissociation enthalpy in *o*-xylene can be calculated from the reported enthalpy of formation of *o*-C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>)<sub>2</sub>, 222 kJ mol<sup>-1</sup> [17], together with the above-mentioned value for  $D(o\text{-MeC}_6\text{H}_4\text{CH}_2\text{-H})$ , 365 kJ mol<sup>-1</sup> [15], and  $\Delta H_f^0(o\text{-C}_6\text{H}_4\text{Me}_2, \text{g}) = 18.0 \text{ kJ mol}^{-1}$  [8]. The result,  $D_2(\text{C-H}) \sim D[o\text{-C}_6\text{H}_4(\text{CH}_2)\text{CH}_2\text{-H}] = 274 \text{ kJ mol}^{-1}$ , leads to  $D(\text{Ti-Ad}) - D(\text{Ti-Fv}) \sim 124 \text{ kJ mol}^{-1}$ . Note that this difference is about 80 kJ mol<sup>-1</sup> smaller than that derived for

\* Reference number with asterisk indicates a note in the list of references.



Scheme 2

$D(\text{Ti-Fv}) - D(\text{Ti-Cp}^*)$ , and may suggest that a second Ti-C  $\sigma$ -bond is not formed in the allyldiene complex, in agreement with the spectral data mentioned in the Introduction. If structure **2b** is accepted, then  $D(\text{Ti-Ad}) - D(\text{Ti-Cp}^*) \sim 124 + 200 = 324 \text{ kJ mol}^{-1}$  will reflect the bond enthalpy difference between a  $\pi, \eta^7$ - and a  $\pi, \eta^5$ -coordinated ligand.

The enthalpy of reaction 3,  $\Delta H(3) = -67.9 \text{ kJ mol}^{-1}$ , or the constant in eq. 8,  $150.1 \text{ kJ mol}^{-1}$ , can be looked at from another angle. This value represents  $\text{Ti}(\text{Cp}^*)\text{C}_5\text{Me}_3(\text{CH}_2)\text{CH}_2\text{-H}$  bond dissociation enthalpy, which is considerably lower than the above value for  $D_2(\text{C-H})$  in the free organic molecule. The dehydrogenation of fulvene is therefore significantly easier when this ligand is coordinated to titanium.

Although the conclusions from the above discussions of bond dissociation enthalpies is not inconsistent with other experimental data, it must be emphasized that, at present the reliability of some of our estimates, in particular  $D_1(\text{C-H})$ ,  $D_2(\text{C-H})$ , and  $D(\text{Ti-R})$  can be questioned. We believe, however, that large changes in those estimates are unlikely, implying that the conclusions have at least a qualitative value.

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