substantial differences between benzene and borazine π complexes, a mechanistic rationale for correlated motion of two ethyl groups in 2 is far from obvious. A variety of other schemes were therefore tried in an attempt to find alternatives to the above conclusions. A site-exchange process involving borazine-metal bond dissociation was ruled out by the observations of separate resonances in an equimolar mixture of hexaethylborazine and 2 in CD_2Cl_2 at the fast exchange limit of 2.[10] Random exchange, which requires that all rate constants should be equal for a given temperature, did not give satisfactory fit of simulated on experimental spectra over the observed temperature range even when large changes with temperature were allowed in the relative intensities of lines within a subspectrum. However, by allowing large changes in relative intensities, it was possible to obtain reasonably satisfactory fits of simulated on observed spectra (though noticeably poorer than those obtained by using the k's in Table II) by fixing the sets of rate constants k_{II} and k_{III} equal to zero. In consequence, we cannot rigorously exclude the possibility that both topomerization and conformational interconversion can be achieved by successive single (uncorrelated) ethyl group rotations. For this mechanism, the calculated $\Delta G^{\ddagger}_{220}$ is 10.1 ± 0.2 kcal mol^{-1}.

Attempts at line-shape fitting by including conformers **2a** and **2h** in an exchange scheme, along with **2c** and **2e**, proved unsuccessful. This evidence, though of a negative kind, tends to support our initial assumption that **2c** and **2e** are the only significant components in the conformational mixture.

Experimental Section

A sample of tricarbonyl(hexaethylborazine)chromium(0) (2),[11] prepared by Dr. M. Scotti, was supplied to us through the courtesy of Professor H. Werner. The sample contained about 10% of tricarbonyl(hexa*methyl*borazine)chromium(0). The 90.56-MHz $^{13}C\{^1H\}$ and 115.55-MHz $^{11}B\{^1H\}$ NMR spectra were obtained by using a Bruker WH360 spectrometer operating in the Fourier transform mode. The temperature of the probe was measured by a thermocouple inserted in an NMR tube filled with toluene to the same depth as the solution in the sample tube. Temperatures were considered accurate to ± 2 °C. The single frequency off-resonance decoupling experiments were performed at 15.08 MHz and ambient temperature by using a Bruker WP60 NMR spectrometer.

The sample solution, approximately 70 mM in CD_2Cl_2, was filtered under N_2 through a Grade 3 glass sinter, degassed by several freeze-pump-thaw cycles and sealed under vacuum.

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(9) Similarly, the rotation of the neopentyl groups in 1,2-dineopentyl-3,4,5,6-tetramethylbenzene is a stepwise process (Iverson, D. J.; Mislow, K. *Organometallics* **1982**, *1*, 3).

(10) In the 15.08-MHz ^{13}C NMR spectrum, the methyl absorptions of hexaethylborazine and 2 are almost isochronous, but the NCH_2 absorptions are well separated at 40.3 ppm (hexaethylborazine) and 44.1 ppm (2).

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Enthalpies of Formation of Bis(η^5-cyclopentadienyl)diphenyltitanium and Bis(η^5-cyclopentadienyl)diferrocenyltitanium

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The standard enthalpies of formation of the title crystalline complexes at 298.15 K were determined by reaction-solution calorimetry. The results gave $\Delta H_f°$ [$Ti(\eta^5\text{-}C_5H_5)_2Ph_2(c)$] = 294.4 ± 8.8 and $\Delta H_f°$ [$Ti(\eta^5\text{-}C_5H_5)_2Fc_2(c)$] = 520.4 ± 12.0 kJ mol^{-1} (Ph = phenyl and Fc = ferrocenyl). The titanium-carbon mean bond disruption enthalpies ($\bar{D}$) and mean bond enthalpy terms ($\bar{E}$) were also derived.

Introduction

Metal-ligand bond distances are commonly considered as measurements of metal-ligand bond strengths, which in turn are used to explain patterns of reactivity and stability of organometallic complexes. For example, Razuvaev et al.[1] explained some reactivity features of $Ti(\eta^5\text{-}C_5H_5)_2Ph_2$ and $Ti(\eta^5\text{-}C_5H_5)_2Fc_2$ (Ph = C_6H_5 and Fc = $(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)$) by assuming that the Ti-Fc bond strength is greater than the Ti-Ph bond strength (Ti-C bond distances are 219 and 227 pm, respectively).[2,3] As this hypothesis can be analyzed if reliable thermochemical data are available, we decided to study the thermochemistry of both complexes, by use of a reaction-solution calorimeter.

Experimental Section

The reaction and solution enthalpies were measured in the reaction-solution calorimeter previously described.[4] The ther-

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Table I. Thermochemical Results (kJ mol^{-1}) for Reactions 1 and 2

complex	ΔH_r	ΔH_{d1}	ΔH_{d2}
$Ti(\eta^5\text{-}C_5H_5)_2Ph_2$	−210.7 ± 4.2	17.2 ± 1.3	3.27 ± 0.17
$Ti(\eta^5\text{-}C_5H_5)_2Fc_2$	−189.4 ± 3.8	17.2 ± 1.3	21.09 ± 0.48

Table II. Standard Enthalpies of Formation $\Delta H_f°(c)$ and $\Delta H_f°(g)$ (kJ mol^{-1})

complex	$\Delta H_f°(c)$	$\Delta H_s°$[a]	$\Delta H_f°(g)$
$Ti(\eta^5\text{-}C_5H_5)_2Ph_2$	294.4 ± 8.8	(88 ± 8)	382.4 ± 11.9
$Ti(\eta^5\text{-}C_5H_5)_2Fc_2$	520.4 ± 12.0	(150 ± 15)	670.4 ± 19.2

[a] Estimated values (see ref 17).

mochemical measurements were not made under a nitrogen atmosphere, as both complexes are fairly air stable for short periods.

The complexes $Ti(\eta^5\text{-}C_5H_5)_2Ph_2$ and $Ti(\eta^5\text{-}C_5H_5)_2Fc_2$ were prepared, purified, and characterized as described in the literature.[5,6] The reaction solutions were prepared from Merk p.a. hydrochloric acid and acetone which were used without further purification. Resublimed ferrocene and spectroscopically pure BDH benzene were also used.

The solution used in the thermochemical studies of reactions 1 and 2 was a 1:4 mixture of 10.0 mol dm^{-3} aqueous hydrochloric acid and acetone. The thermochemical disadvantages of this mixture were discussed in a previous paper.[7]

$$Ti(\eta^5\text{-}C_5H_5)_2Ph_2(c) + 2HCl(soln) \rightarrow Ti(\eta^5\text{-}C_5H_5)_2Cl_2(soln) + 2C_6H_6(soln) \quad (1)$$

$$Ti(\eta^5\text{-}C_5H_5)_2Fc_2(c) + 2HCl(soln) \rightarrow Ti(\eta^5\text{-}C_5H_5)_2Cl_2(soln) + 2Fe(\eta^5\text{-}C_5H_5)_2(soln) \quad (2)$$

Both reactions were found to be fast and quantitative, in agreement with the observations by Siegert and Liefde Meijer[8] and Razuvaev et al.[6]

All the reaction and solution enthalpies presented are mean values from at least five independent experiments and refer to 298.15 K. The associated uncertainties are twice the standard deviations of those means.

The following standard enthalpies of formation and enthalpies of vaporization at 298 K were used in evaluating the thermochemical results (values in kJ mol^{-1}): $\Delta H_f°(HCl(soln)) = -172.59 \pm 0.51$;[7] $\Delta H_f°(C_6H_6(\ell)) = 49.0 \pm 0.3$;[9] $\Delta H_f°[Ti(\eta^5\text{-}C_5H_5)_2Cl_2(c)] = -383.2 \pm 7.5$;[10] $\Delta H_v°(C_6H_6) = 33.85 \pm 0.04$;[9] $\Delta H_s°[Ti(\eta^5\text{-}C_5H_5)_2Cl_2] = 118.8 \pm 2.1$;[10] $\Delta H_f°(Cl(g)) = 121.302 \pm 0.008$;[11] $\Delta H_f°(H(g)) = 217.997 \pm 0.006$;[11] $\Delta H_s°[Fe(\eta^5\text{-}C_5H_5)_2] = 72.77 \pm 0.42$. The value for the enthalpy of sublimation of ferrocene is the average of four results obtained by different authors.[12-14]

Results

The thermochemical results are summarized in Table I. ΔH_r stands for the enthalpy of reactions 1 or 2, ΔH_{d1} refers to the enthalpy of solution of $Ti(\eta^5\text{-}C_5H_5)_2Cl_2(c)$ in the solution of aqueous HCl and acetone, and ΔH_{d2} represents the enthalpy of solution of the ligand (benzene or ferrocene) in the solution containing stoichiometric amounts of $Ti(\eta^5\text{-}C_5H_5)_2Cl_2$.

Table III. Mean Bond Disruption Enthalpies and Mean Bond Enthalpy Terms (kJ mol^{-1})

complex	$\bar{D}$(Ti-C)	$\bar{E}$(Ti-C)[a]
$Ti(\eta^5\text{-}C_5H_5)_2Ph_2$	311 ± 10	(271 ± 9)[b]
$Ti(\eta^5\text{-}C_5H_5)_2Fc_2$	(311)	262 ± 11

[a] The uncertainties associated with the Laidler parameter or with the value obtained through the correlation curve was ±8 kJ mol^{-1}. [b] Uncorrected value (see text).

The standard enthalpies of formation of the crystalline complexes (Table II) were evaluated from the above results and the relevant auxiliary data. The enthalpy of formation of ferrocene was taken as $\Delta H_f°[Fe(\eta^5\text{-}C_5H_5)_2(c)] = 154.8 \pm 4.2$ kJ mol^{-1}. This value, recommended by Tel'noi and Rabinovich in 1977,[10] differs from another value obtained by Tel'noi et al. in 1975,[15] ca. 168.2 kJ mol^{-1}. It agrees, however, with a more recent result by Chipperfield, Sneyd, and Webster,[16] ca. 158 ± 4 kJ mol^{-1}, also obtained by static bomb combustion calorimetry.

Estimated values of the enthalpies of sublimation and results for $\Delta H_f°(g)$ are also collected in Table II.

Discussion

From the experimental results of Table I, from $\bar{E}$(Ti–Cl) = 430.5 ± 1.3 kJ mol^{-1} in $Ti(\eta^5\text{-}C_5H_5)_2Cl_2$,[10] and from other auxiliary data it was possible to obtain Ti–C mean bond disruption enthalpies, $\bar{D}$(Ti–Ph) and $\bar{D}$(Ti–Fc), and Ti–C mean bond enthalpy terms, $\bar{E}$(Ti–Ph) and $\bar{E}$(Ti–Fc), for the complexes studied (Table III). These calculations were based on several assumptions discussed in an early paper.[17]

The dissociation energy[18] D(Ph–H) = 460.2 ± 8.4 kJ mol^{-1} and the Laidler term[19] E(Ph–H) = 420.6 kJ mol^{-1} were used to evaluate $\bar{D}$(Ti–Ph) and $\bar{E}$(Ti–Ph), respectively.

In the case of $Ti(\eta^5\text{-}C_5H_5)_2Fc_2$ it was not possible to derive a reliable value for $\bar{D}$(Ti–Fc), as the dissociation energy D(Fc–H) has not been measured. However, if it is assumed that this value is similar to $D(C_5H_4\text{–}H)$ which in turn equals D(Ph–H), we are led to $\bar{D}$(Ti–Fc) ≈ 311 kJ mol^{-1}, matching $\bar{D}$(Ti–Ph).

The Laidler scheme does not provide a parameter E(Fc–H), necessary for the evaluation of $\bar{E}$(Ti–Fc). Therefore we had to use other methods to obtain E(Fc–H). As Sanderson's calculations[20,21] did not seem reliable for the present case, we decided to use a correlation between bond enthalpy terms and bond lengths.[17] The curve $\bar{E}$(C–H)/r(C–H), which can be regarded as a straight line, has a very small slope and so the $\bar{E}$ values obtained by interpolation are affected by small errors. On the other

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hand it can be noticed that the method yields $\bar{E}$(C–H) values that are very similar to those given by the Laidler scheme.[17]

A value of E(Fc–H) ≈ 411 kJ mol^{-1} was then obtained by a small extrapolation of the curve (r(Fc–H) = 110.4 pm)[2] and led to the final result of $\bar{E}$(Ti–Fc) (Table III).

The main conclusion that can be drawn from the values of Table III is that the titanium–carbon bond strengths are similar in both complexes. The fact that $\bar{E}$(Ti–Ph) ≈ $\bar{E}$(Ti–Fc) when the uncertainties are considered apparently conflicts with r(Ti–Ph) ≈ r(Ti–Fc) + 8 pm. However it is possible that some of the assumptions made in the calculation of $\bar{E}$(Ti–C) may not be entirely satisfactory.[17] One of those assumptions was that the structure of the fragment L should be similar in the molecule LH and in the complex $Ti(\eta^5\text{-}C_5H_5)_2L_2$. From the crystal structures of C_6H_6,[22] $Ti(\eta^5\text{-}C_5H_5)_2Ph_2$,[3] $Fe(\eta^5\text{-}C_5H_5)_2$,[23] and $Ti(\eta^5\text{-}C_5H_5)_2Fc_2$[2] it can be noticed that the average molecular parameters of L remain fairly constant, supporting the above assumption. Another hypothesis considered in the calculation procedure[17] was that the reorganization enthalpy of the fragments $Ti(\eta^5\text{-}C_5H_5)_2$ from the complexes $Ti(\eta^5\text{-}C_5H_5)_2Ph_2$, $Ti(\eta^5\text{-}C_5H_5)_2Fc_2$, and $Ti(\eta^5\text{-}C_5H_5)_2Cl_2$ have identical values. These reorganization enthalpies seem to depend strongly upon the ring centroid angles $(\eta^5\text{-}C_5H_5)\text{–}M\text{–}(\eta^5\text{-}C_5H_5)$. For example in the case of $(\eta^5\text{-}C_5H_5)_2Mo$ and $(\eta^5\text{-}C_5H_5)_2W$ fragments, a change of the centroid angle from 130 to 145° corresponds to −42 kJ mol^{-1}.[24] This angle is similar in $Ti(\eta^5\text{-}C_5H_5)_2Fc_2$ (131.2°)[2] and in $Ti(\eta^5\text{-}C_5H_5)_2Cl_2$ (130.97°),[25] but is slightly higher in $Ti(\eta^5\text{-}C_5H_5)_2Ph_2$ (135.9°).[26] Therefore the reorganization enthalpy of $Ti(\eta^5\text{-}C_5H_5)_2$ from the latter complex, ER_1, must be less negative than the reorganization enthalpy of the corresponding fragment from $Ti(\eta^5\text{-}C_5H_5)_2Cl_2$, ER_3, and so the obtained value for $\bar{E}$(Ti–Ph) (Table III) must be higher than the real value. The correction to be applied to the value of $\bar{E}$(Ti–Ph) in Table III, $(ER_3 - ER_1)/2$, should not be far from −7 kJ mol^{-1}, making $\bar{E}$(Ti–Ph) ≈ 264 kJ mol^{-1}.

The previous discussion confirms the main conclusion given above; i.e., the titanium–carbon bond strengths are similar in both complexes. We believe that a reevaluation of all those hypotheses and estimations (e.g., the enthalpies of sublimation) would not change dramatically the observed trend. Hence it is likely that the differences in reactivity between the complexes $Ti(\eta^5\text{-}C_5H_5)_2Ph_2$ and $Ti(\eta^5\text{-}C_5H_5)_2Fc_2$ are only a question of different labilities[27] of the titanium–carbon bonds.

A final comment to refer an early result of $\Delta H_f^\circ[Ti(\eta^5\text{-}C_5H_5)_2Ph_2(c)] = 71.1 \pm 12.6$ kJ mol^{-1},[28] obtained with a static bomb combustion calorimeter. This result would lead to $\bar{E}$(Ti–Ph) ≈ 383 kJ mol^{-1}, a value which is too high to be accepted.

On the other hand, our results for $\bar{E}$(Ti–Ph) and $\bar{E}$(Ti–Fc) are in good agreement with previous $\bar{E}$(Ti–R) values[29] for TiR_4 complexes, ca. 268 kJ mol^{-1} (R = CH_2SiMe_3) and 264 kJ mol^{-1} (R = CH_2Ph). This is consistent with the hypothesis of considering identical $\bar{E}$(Ti–Cl) values for the compounds $Ti(\eta^5\text{-}C_5H_5)_2Cl_2$ and $TiCl_4$.[10,17]

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