# Enthalpies of Formation of Complexes $[Ti(\eta\text{-}C_5H_5)_2(N_3)_2]$ and $[Ti(\eta\text{-}C_5H_5)_2(NC_8H_6)_2]$ †

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The standard enthalpies of formation of the title crystalline solids at 298.15 K have been determined by reaction–solution calorimetry as $\Delta H_f^\ominus\{[Ti(\eta\text{-}C_5H_5)_2(N_3)_2], c\} = 436.4 \pm 10.4$ kJ mol$^{-1}$ and $\Delta H_f^\ominus\{[Ti(\eta\text{-}C_5H_5)_2(NC_8H_6)_2], c\} = 219.9 \pm 12.0$ kJ mol$^{-1}$. The titanium–nitrogen mean bond-enthalpy terms have been derived from the thermochemical data obtained, used together with extended-Hückel molecular-orbital calculations.

The standard enthalpies of formation for many organic compounds in the gaseous state can be accurately estimated by using several methods described in the literature.[1] In one of these methods, the Laidler scheme,[2] the enthalpy of atomization of a molecule is considered as the sum of all bond-enthalpy terms, each of which means the ' bond strength ' of the respective pair of atoms. As mentioned previously [3,4] there is a fair agreement between Laidler terms and bond-enthalpy values derived from bond enthalpy–bond length curves for molecules free from angular strain effects.

The scarcity of thermodynamic data and the difficulty of evaluating meaningful bond-enthalpy terms from thermochemical results explain why similar bond schemes are not available for most organometallic compounds and therefore why it is not possible to predict their enthalpies of formation.

The evaluation of mean bond-enthalpy terms for complexes of the type $[M(\eta\text{-}C_5H_5)_2L_2]$ (M = transition metal atom; L = mono- or poly-atomic ligand) was discussed in previous papers.[3,4] It involves calculation of the reorganization enthalpies of the fragments $M(\eta\text{-}C_5H_5)_2$ and in some cases it also implies knowledge of the enthalpy difference between the fragment L in $[M(\eta\text{-}C_5H_5)_2L_2]$ and HL. The M–L bond terms so obtained may be correlated with structural data, yielding a bond enthalpy–bond length scheme. The agreement between the Laidler terms and values from bond enthalpy–bond length curves for organic compounds may eventually enable us to regard the above procedure as an extension of the Laidler scheme for those complexes, although it is recognized that the curves give less reliable values than the Laidler method because in most cases a bond enthalpy–bond length correlation is an oversimplification of the problem.

In the present paper we suggest mean bond-enthalpy terms $\bar{E}$(Ti–N) for the complexes $[Ti(\eta\text{-}C_5H_5)_2(N_3)_2]$ and $[Ti(\eta\text{-}C_5H_5)_2(NC_8H_6)_2]$ ($NC_8H_6$ = indolate). The values were obtained from thermochemical data and corrected by using extended-Hückel molecular-orbital calculations to evaluate $Ti(\eta\text{-}C_5H_5)_2$ reorganization enthalpies.

## Experimental

*Calorimeter.*—The reaction and solution enthalpies were measured in the reaction–solution calorimeter previously described.[5] There was no need to make the thermochemical measurements under nitrogen because both complexes are fairly air-stable.

*Compounds.*—Complexes $[Ti(\eta\text{-}C_5H_5)_2(N_3)_2]$ and $[Ti(\eta\text{-}C_5H_5)_2(NC_8H_6)_2]$ were prepared and purified as described in the literature.[6,7] The reaction solutions were prepared from Merck *p.a.* hydrochloric acid and Carlo Erba *r.p.e.* dimethyl sulphoxide, which were used without any further treatment. Aldrich 99% pure indole was purified as described by Perrin *et al.*[8] Merck 99% pure $NaN_3$ and *p.a.* NaCl were used without further purification.

*Reactions.*—The solution used in the thermochemical studies of reactions (1) and (2) was a 1 : 3 mixture of 10.4 mol dm$^{-3}$ aqueous hydrochloric acid and dimethyl sulphoxide. The products of these reactions were confirmed by i.r. spectroscopic analysis.

$$[Ti(\eta\text{-}C_5H_5)_2(N_3)_2](c) + 2HCl(\text{soln } 1) \longrightarrow [Ti(\eta\text{-}C_5H_5)_2Cl_2](\text{soln } 2) + 2HN_3(\text{soln } 2) \quad (1)$$

$$[Ti(\eta\text{-}C_5H_5)_2(NC_8H_6)_2](c) + 2HCl(\text{soln } 1) \longrightarrow [Ti(\eta\text{-}C_5H_5)_2Cl_2](\text{soln } 3) + 2C_8H_6NH(\text{soln } 3) \quad (2)$$

All reaction and solution enthalpies presented are mean values from at least five independent experiments and refer to 298.15 K. The uncertainties are twice the standard deviation of the mean in each case.

*Auxiliary Data.*—The following standard enthalpies of formation and sublimation at 298 K were used in evaluating the thermochemical results (values in kJ mol$^{-1}$): $\Delta H_f^\ominus$[HCl, aq(10.4 mol dm$^{-3}$)] = −153.408 ± 0.004;[9] $\Delta H_f^\ominus(HN_3,g)$ = 294.2 ± 2.1;[10] $\Delta H_f^\ominus$(NaCl,c) = −411.15 ± 0.04;[11] $\Delta H_f^\ominus(C_8H_6NH,c)$ = 87.3 ± 4.4;[12] $\Delta H_f^\ominus\{[Ti(\eta\text{-}C_5H_5)_2Cl_2],c\}$ = −383.2 ± 7.5;[13] $\Delta H_f^\ominus$(Cl,g) = 121.302 ± 0.008;[14] $\Delta H_f^\ominus$(H,g) = 217.997 ± 0.006;[14] $\Delta H_s^\ominus\{[Ti(\eta\text{-}C_5H_5)_2Cl_2]\}$ = 118.8 ± 2.1;[13] $\Delta H_s^\ominus(C_8H_6NH)$ = 69.9 ± 0.8.[12] The value for $\Delta H_f^\ominus(NaN_3,c)$ = 21.58 ± 0.47 kJ mol$^{-1}$ was recalculated from the enthalpy of reaction (3), $\Delta H$ = 13.26 ± 0.21 kJ mol$^{-1}$,[15] and from $\Delta H_f^\ominus(N_3^-$, aq) = 275.14 ± 0.42 kJ mol$^{-1}$ (ref. 10) and $\Delta H_f^\ominus(Na^+$, aq) = −240.300 ± 0.065 kJ mol$^{-1}$.[14]

$$NaN_3(c) + \infty H_2O \longrightarrow Na^+(aq) + N_3^-(aq) \quad (3)$$

*Calculations.*—The extended-Hückel molecular-orbital calculations were made by using the ICON8 program, developed by Hoffmann and co-workers.[16,17] The basis set for the titanium atom consisted of 3*d*, 4*s*, and 4*p* orbitals. The *s* and *p* orbitals were described by single Slater-type wave functions and the *d* orbitals were taken as contracted linear combinations of two Slater-type wave functions. The orbital exponents and the parameters for the extended-Hückel calculations are collected in Table 1.

All calculations were performed by using the modified Wolfsberg–Helmholz method.[18] The model fragment Ti(η-

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† Diazidobis(η-cyclopentadienyl)- and bis(η-cyclopentadienyl)-bis(indolato)-titanium(IV).

**Table 1.** Orbital exponents and parameters used for the extended-Hückel molecular-orbital calculations

| Orbital | Slater exponent | $-H_{ii}$/eV [a] | Ref. |
|---|---|---|---|
| H 1*s* | 1.300 | 13.60 | 16 |
| C 2*s* | 1.625 | 21.40 | 16 |
| C 2*p* | 1.625 | 11.40 | 16 |
| N 2*s* | 1.950 | 26.00 | 16 |
| N 2*p* | 1.950 | 13.40 | 16 |
| Ti 4*s* | 1.075 | 8.97 | 24 |
| Ti 4*p* | 0.675 | 5.44 | 24 |
| Ti 3*d* | *b* | 10.81 | 24,[c] |

[a] 1 eV = 96.4845 kJ $mol^{-1}$. [b] $\zeta_1 = 4.55$, $\zeta_2 = 1.40$, $C_1 = 0.4206$, and $C_2 = 0.7839$. [c] J. W. Richardson, W. C. Nieuwpoort, R. R. Powell, and W. E. Edgell, *J. Chem. Phys.*, 1962, **36**, 1057.

**Table 2.** Thermochemical results (kJ $mol^{-1}$) for the complexes $[Ti(\eta\text{-}C_5H_5)_2(N_3)_2]$ and $[Ti(\eta\text{-}C_5H_5)_2(NC_8H_6)_2]$

| | Complex | |
|---|---|---|
| | $[Ti(\eta\text{-}C_5H_5)_2(N_3)_2]$ | $[Ti(\eta\text{-}C_5H_5)_2(NC_8H_6)_2]$ |
| $\Delta H_r$ | 41.8 ± 1.5 | −40.18 ± 0.42 |
| $\Delta H_{d1}$ | 0 ± 3 | 3 ± 3 |
| $\Delta H_{d2}$ | −49.8 ± 2.3 | 6.42 ± 0.32 |
| $\Delta H_{d3}$ | −32.83 ± 0.52 | −32.83 ± 0.52 |
| $\Delta H_f^\circ$(c) | 436.4 ± 10.4 | 219.9 ± 12.0 |

$C_5H_5)_2$ was considered as having $C_{2v}$ symmetry. The bond lengths Ti–C 238.8, C–C 140, and C–H 109 pm were quoted from *X*-ray-determined structures of several $[Ti(\eta\text{-}C_5H_5)_2L_2]$ compounds. The bond lengths N–N and the bond angle N–N–N in the fragment $N_3$ were taken as 118, 110 pm,[19] and 180°, respectively.

## Results

$[Ti(\eta\text{-}C_5H_5)_2(N_3)_2]$.—The thermochemical results together with the enthalpy of formation of the crystalline complex are summarized in Table 2. $\Delta H_r$ represents the enthalpy of reaction (1) and $\Delta H_{d2}$ refers to the enthalpy of solution of stoicheiometric amounts of hydrogen azide in solution 1. As $HN_3$ is not a stable molecule, $\Delta H_{d2}$ had to be determined through the following cycle (4)—(7). A value of $\Delta H_c'$ was obtained by

$$NaN_3(c) + HCl(soln\ 1) \xrightarrow{\Delta H_a} HN_3(soln\ 4) + NaCl(soln\ 4) \quad (4)$$

$$NaN_3(c) + HCl(soln\ 1) \xrightarrow{\Delta H_b} HN_3(g) + NaCl(c) \quad (5)$$

$$NaCl(c) \xrightarrow{\Delta H_c} NaCl(soln\ 5) \quad (6)$$

$$HN_3(g) \xrightarrow{\Delta H_{d2}} HN_3(soln\ 1) \quad (7)$$

breaking ampoules of NaCl in solution 4. To check whether the presence of NaCl in the solution affects $\Delta H_c'$, supplementary amounts (0.4—2.0 mmol) of sodium chloride were added to solution 4 before each run. It was concluded that under our experimental conditions $\Delta H_c' \approx 0$, independently of the amount of NaCl present. Therefore this value can be taken as that of $\Delta H_c$. (Solution 5 is equivalent to solution 1 containing stoicheiometric amounts of hydrogen azide.)

From the value of $\Delta H_c$, from the experimental result for $\Delta H_a$, *ca.* −2.04 ± 0.61 kJ $mol^{-1}$, and by using auxiliary data for evaluating $\Delta H_b$ [$\Delta H_f^\circ$(HCl, soln 1) is given below] we arrive at $\Delta H_{d2} = \Delta H_a - \Delta H_b - \Delta H_c = -49.8 \pm 2.3$ kJ $mol^{-1}$.

$\Delta H_{d1}$ represents the enthalpy of solution of $[Ti(\eta\text{-}C_5H_5)_2Cl_2]$ in solution 5. As in the case of $\Delta H_{d2}$ it could not be obtained directly. A value of $\Delta H_{d2}'$ was then measured by breaking ampoules of this complex in solution 4 containing supplementary amounts of NaCl. $\Delta H_{d2}'$ does not seem to be affected by the amount of sodium chloride and therefore we consider $\Delta H_{d2} \approx \Delta H_{d2}'$. It should also be mentioned that in the experiments involving the dissolution of $[Ti(\eta\text{-}C_5H_5)_2Cl_2]$ a small solid residue of the complex was always observed. However, the resulting error must lie within the uncertainty interval for $\Delta H_{d2}$ (Table 2).

The standard enthalpy of formation of HCl in solution 1, $\Delta H_{d3}$, was obtained as described in a previous paper,[20] giving $\Delta H_f^\circ$(HCl, soln 1) = −186.24 ± 0.52 kJ $mol^{-1}$.

The standard enthalpy of formation of $[Ti(\eta\text{-}C_5H_5)_2(N_3)_2]$ (c) was finally derived by using the above results and the appropriate auxiliary data.

$[Ti(\eta\text{-}C_5H_5)_2(NC_8H_6)_2]$.—The thermochemical results and the standard enthalpy of formation of the crystalline complex are also collected in Table 2. $\Delta H_r$ represents the enthalpy of reaction (2), $\Delta H_{d2}$ refers to the enthalpy of solution of indole in solution 1, and $\Delta H_{d1}$ stands for the enthalpy of solution of $[Ti(\eta\text{-}C_5H_5)_2Cl_2]$ in solution 1 containing stoicheiometric amounts of indole. As in the case of the previous system, a small solid residue of $[Ti(\eta\text{-}C_5H_5)_2Cl_2]$ was observed in all the experiments involving the dissolution of the complex.

## Discussion

Equations (8) and (9) are based on several assumptions discussed in earlier papers[3,4] and can be used to evaluate Ti–N mean bond-enthalpy terms ($\bar{E}$) and mean bond-disruption enthalpies ($\bar{D}$) for both complexes. $E_{R1}$ and $E_{R3}$

$$\begin{aligned}\bar{E}(\text{Ti–N}) = {} & \bar{E}(\text{Ti–Cl}) + (\Delta H_r - \Delta H_{d1} - 2\Delta H_{d2})/2 + (\Delta H_s^\circ\{[Ti(\eta\text{-}C_5H_5)_2Cl_2]\} - \\ & \Delta H_s^\circ\{[Ti(\eta\text{-}C_5H_5)_2L_2]\})/2 + \Delta H_f^\circ(\text{HCl, soln}) + E(\text{L–H}) - \Delta H_f^\circ(\text{H,g}) + \Delta H_v^\circ(\text{HL}) - \\ & \Delta H_f^\circ(\text{Cl,g}) + (E_{r3} - E_{r1})/2 \end{aligned} \quad (8)$$

$$\begin{aligned}\bar{D}(\text{Ti–N}) = {} & \bar{E}(\text{Ti–Cl}) + (\Delta H_r - \Delta H_{d1} - 2\Delta H_{d2})/2 + (\Delta H_s^\circ\{[Ti(\eta\text{-}C_5H_5)_2Cl_2]\} - \\ & \Delta H_s^\circ\{[Ti(\eta\text{-}C_5H_5)_2L_2]\})/2 + \Delta H_f^\circ(\text{HCl, soln}) + D(\text{L–H}) - \Delta H_f^\circ(\text{H,g}) + \\ & \Delta H_v^\circ(\text{HL}) - \Delta H_f^\circ(\text{Cl,g}) + E_{R3}/2 \end{aligned} \quad (9)$$

represent the reorganization enthalpies of $Ti(\eta\text{-}C_5H_5)_2$ fragments from the complexes $[Ti(\eta\text{-}C_5H_5)_2L_2]$ (L = $N_3$ or $NC_8H_6$) and from $[Ti(\eta\text{-}C_5H_5)_2Cl_2]$, respectively. Extended-Hückel molecular-orbital calculations show that those reorganization enthalpies depend mainly upon the $(\eta\text{-}C_5H_5)$–Ti–$(\eta\text{-}C_5H_5)$ angle and less upon the Ti–$(\eta\text{-}C_5H_5)$ bond length. Furthermore, although the molecular structures of many $[Ti(\eta\text{-}C_5H_5)_2L_2]$ complexes reveal that Ti-$(\eta\text{-}C_5H_5)$ distances are generally constant and close to 206—207 pm, the $(\eta\text{-}C_5H_5)$-Ti-$(\eta\text{-}C_5H_5)$ angles are not constant. For example, for the complexes $[Ti(\eta\text{-}C_5H_5)_2Cl_2]$, $[Ti(\eta\text{-}C_5H_5)_2(N_3)_2]$, and $[Ti(\eta\text{-}C_5H_5)_2(NC_4H_4)_2]$ ($NC_4H_4$ = pyrrolate) the ring centroid angles are 130.97,[21] 132.2,[19] and 128.5°,[22] respectively. (As the molecular structure of $[Ti(\eta\text{-}C_5H_5)_2(NC_8H_6)_2]$ is not available, we assume that its centroid angle is similar to the one observed in the pyrrolate complex.)

Figure 1 was obtained from extended-Hückel molecular-

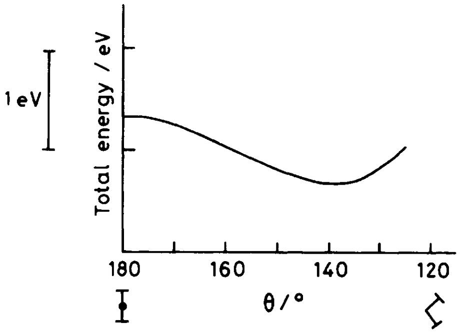

**Figure 1.** Total energy of $Ti(\eta-C_5H_5)_2$ fragment as a function of the angle θ between the ring normals

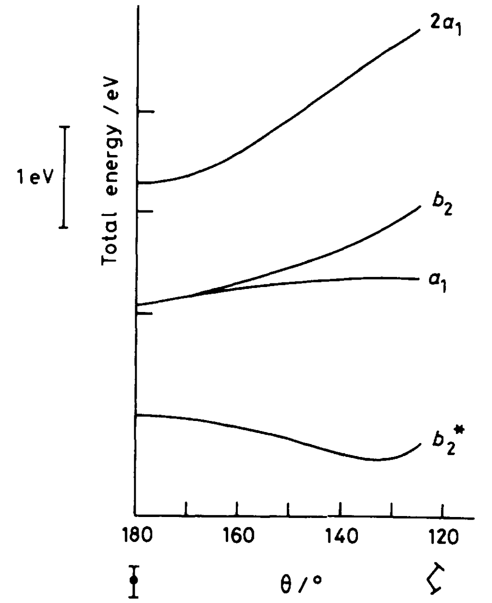

**Figure 2.** The $M(\eta-C_5H_5)_2$ orbitals as a function of θ (see also ref. 24)

**Table 3.** Reorganization enthalpies of $Ti(\eta-C_5H_5)_2$ fragments

| Parent compound | θ/° | $-E_R$/eV | $(E_{R3} - E_{R1})$/eV |
|---|---|---|---|
| $[Ti(\eta-C_5H_5)_2Cl_2]$ | 130.97 | 0.112 [a] | 0 |
| $[Ti(\eta-C_5H_5)_2(N_3)_2]$ | 132.2 | 0.083 [b] | −0.029 |
| $[Ti(\eta-C_5H_5)_2(NC_4H_4)_2]$ | 128.5 | 0.221 [b] | 0.109 |

[a] $E_{R3}$ value. [b] $E_{R1}$ value.

orbital calculations. It shows the change in total energy of a $Ti(\eta-C_5H_5)_2$ fragment as the angle θ between the ring normals decreases from 180 to 125°. As shown previously,[23] the most stable geometry is achieved with $\theta \approx 140°$ for a metal having two *d* electrons. A closer look at the frontier orbitals of the $Ti(\eta-C_5H_5)_2$ fragment (Figure 2), studied in detail by Lauher and Hoffmann,[24] makes this result understandable. The total energy potential surface closely follows the low energy $b_2$ * level, the highest occupied molecular orbital ($a_1$) remaining mostly non-bonding as the distortion proceeds. The presence of further *d* electrons would favour the configuration corresponding to $\theta = 180°$ because they would occupy the $b_2$ level which is destabilized with bending due to the steric repulsion between the cyclopentadienyl rings. This effect contributes more to the total energy than the stabilization of $b_2$ * and so the more stable configuration for $M(\eta-C_5H_5)_2$ fragments, where M has four *d* electrons (*e.g.* M = Mo or W), corresponds to $\theta = 180°$.

Bearing in mind the limitations imposed by the method used, differences in energy were calculated for $Ti(\eta-C_5H_5)_2$ fragments of the complexes $[Ti(\eta-C_5H_5)_2Cl_2]$, $[Ti(\eta-C_5H_5)_2(N_3)_2]$, and $[Ti(\eta-C_5H_5)_2(NC_4H_4)_2]$. From the results in Table 3 it can be seen that both differences are small, this being a consequence of the relative constancy of θ values. In kJ mol$^{-1}$ we have, for $[Ti(\eta-C_5H_5)_2(N_3)_2]$, $E_{R3} - E_{R1} \approx -2.8$ and, for $[Ti(\eta-C_5H_5)_2(NC_4H_4)_2]$, $E_{R3} - E_{R1} \approx 10.5$.

Equation (8) was derived by assuming that the fragment L has identical structures in the complex $[M(\eta-C_5H_5)_2L_2]$ and in the molecule HL.[3,4] In this case $E$(L–H) is equal to the bond-enthalpy term in HL and can be obtained by choosing the appropriate Laidler term or by using a bond enthalpy–bond length curve.[3,4] Let us accept that the assumption holds for $N_3$ and for $NC_8H_6$. The Laidler term is taken as 377 ±8 kJ mol$^{-1}$ in both cases, comparing well with $E(N_3-H) \approx 376$ kJ mol$^{-1}$, obtained from a N–H bond enthalpy–bond length curve [$r(N_3-H) = 102.1$ pm, ref. 25] drawn from data for $NH_3$, $NH_2$, and NH.[26] Taking $\bar{E}(Ti-Cl) \approx 430.5$ kJ mol$^{-1}$ (ref. 3) and using auxiliary thermochemical data (including the estimated enthalpies of sublimation of the complexes, presented in Table 4) and the obtained values for $E_{R3} - E_{R1}$, it is now possible to derive $\bar{E}(Ti-N_3) \approx 376$ kJ mol$^{-1}$ and $\bar{E}(Ti-NC_8H_6) \approx 334$ kJ mol$^{-1}$.

These results are compatible with the titanium-nitrogen bond lengths $r(Ti-N_3) = 203$ pm[19] and $r(Ti-NC_8H_6) \approx 209$ pm.* Nevertheless they can be questioned because it is known that the structure of $N_3$ is different in the complex and in hydrogen azide:[19,25] in $[Ti(\eta-C_5H_5)_2(N_3)_2]$ the N–N bond lengths are shorter and the angle N–N–N is about 177°.

Molecular-orbital theory can be used to evaluate the energy change of the fragment $N_3$ as a function of the total length of the molecule. Thus we can calculate the reorganization enthalpy of $N_3$ when it goes from the complex to $HN_3$. The obtained value, *ca.* −48 kJ mol$^{-1}$, leads to $\bar{E}(Ti-N_3) \approx 328$ kJ mol$^{-1}$. (The change in N–N–N angle from 180° in $HN_3$ to 177° in the complex did not significantly contribute to the above value, as it corresponds only to about 0.3 kJ mol$^{-1}$.)

Unfortunately the molecular structure of the indolate complex is not available and so we cannot compute the equivalent reorganization enthalpy in this case. However, from the data for $[Ti(\eta-C_5H_5)_2(NC_4H_4)_2]$ and $C_4H_5N$[22,25] it seems reasonable to say that the fragment $NC_8H_6$ is also stabilized in the complex, relative to the indole molecule, but perhaps less than in the case of $N_3$ (all the distances are shorter in the complex but the angular strain increases). This would imply that the 'real' $\bar{E}(Ti-NC_8H_6)$ is smaller than 334 kJ mol$^{-1}$.

Values of $\bar{D}(Ti-N_3)$ and $\bar{D}(Ti-NC_8H_6)$ can be calculated through equation (9) if nitrogen–hydrogen bond-dissociation energies in hydrogen azide and indole are known. Only $D(N_3-H)$ is available in the literature, although there is a serious discrepancy between two recommended values.[27] Quoting the more recent one, *ca.* 385 ± 21 kJ mol$^{-1}$,[27] we obtain $\bar{D}(Ti-N_3) \approx 380$ kJ mol$^{-1}$ (from Table 3: $E_{R3}/2 \approx -5$ kJ mol$^{-1}$).

Table 4 summarizes all the calculated bond-enthalpy values. From this Table and as a final conclusion we wish to emphasize the importance of the reorganization enthalpy difference of the ligand L between the complex and the organic

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* It was assumed that $r(Ti-NC_8H_6) \approx r(Ti-NC_4H_4) = 209$ pm.[22]

**Table 4.** Thermochemical data and titanium-nitrogen mean bond-enthalpy contributions (values in kJ mol$^{-1}$)

| | Complex | |
|---|---|---|
| Parameter | $[Ti(\eta\text{-}C_5H_5)_2(N_3)_2]$ | $[Ti(\eta\text{-}C_5H_5)_2(NC_8H_6)_2]$ |
| $\Delta H_s^\ominus$ [a] | (70 ± 10) | (109 ± 10) |
| $\Delta H_f^\ominus$(g) | 506.4 ± 14.4 | 328.9 ± 15.6 |
| $\bar{E}$(Ti–N) [b] | 376 ± 10<br>328 [c] | 334 ± 10 |
| $\bar{D}$(Ti–N) [b] | 380 ± 22 [d]<br>385 [e] | — |

[a] Estimated values. [b] The uncertainty intervals do not allow for the errors associated with the molecular-orbital calculations. [c] Value affected by the reorganization enthalpy of $N_3$ (see text). [d] Value not including $E_{R3}/2$. [e] Value including $E_{R3}/2$.

molecule HL. This has to be considered for most cases if reliable mean bond-enthalpy terms are to be derived. The term $E_{R3}/2$ does not amount to a large correction of mean bond-disruption enthalpies in the case of titanium complexes. However, for metals such as molybdenum and tungsten, where the 'stable' configuration of the fragment $M(\eta\text{-}C_5H_5)_2$ corresponds to $\theta = 180°$, the value of $E_{R3}/2$ cannot be ignored.

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