Enthalpies of Formation of $[M(\eta\text{-}C_5H_5)_2(OOCR)_2]$ Complexes; M = Mo, W, or Ti and R = C_6H_5 or CF_3

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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. The results gave $\Delta H_f^{\ominus}\{[Mo(\eta\text{-}C_5H_5)_2(OOCC_6H_5)_2], c\} = -486.2 \pm 3.4$, $\Delta H_f^{\ominus}\{[Mo(\eta\text{-}C_5H_5)_2(OOCCF_3)_2], c\} = -1\,952.0 \pm 3.9$, $\Delta H_f^{\ominus}\{[W(\eta\text{-}C_5H_5)_2(OOCC_6H_5)_2], c\} = -448.9 \pm 3.5$, $\Delta H_f^{\ominus}\{[W(\eta\text{-}C_5H_5)_2(OOCCF_3)_2], c\} = -1\,914.5 \pm 3.8$, $\Delta H_f^{\ominus}\{[Ti(\eta\text{-}C_5H_5)_2(OOCC_6H_5)_2], c\} = -775.2 \pm 8.1$, and $\Delta H_f^{\ominus}\{[Ti(\eta\text{-}C_5H_5)_2(OOCCF_3)_2], c\} = -2\,219.0 \pm 8.0$ kJ mol^{-1}. The metal–oxygen mean bond-enthalpy contributions have been derived as $\bar{D}(Mo\text{–}OOCC_6H_5) \approx 305$, $\bar{D}(W\text{–}OOCC_6H_5) \approx 342$, $\bar{D}(Ti\text{–}OOCC_6H_5) \approx 432$, $\bar{D}(Mo\text{–}OOCCF_3) \approx 300$, $\bar{D}(W\text{–}OOCCF_3) \approx 337$, and $\bar{D}(Ti\text{–}OOCCF_3) \approx 417$ kJ mol^{-1}.

DATA on metal–ligand bond-enthalpy contributions in bent metallocenes are still very scarce. More reliable data are needed to expose trends and correlations between bond energies and parameters such as electronegativities, stretching frequencies, and bond distances, which are often used to explain patterns of reactivity and stability of these complexes.

Reaction–solution calorimetry proved to be a suitable technique for thermochemical studies of complexes of the type $[M(\eta\text{-}C_5H_5)_2L_2]$, particularly in the case of M = Mo or W.[1] The metal–ligand bond-enthalpy contributions so far derived (metal–halogens, metal–hydrogen, metal–methyl) can be regarded as ' basic ' data for future studies. The present work is a first attempt to investigate the influence of the nature of chemical groups in the ligands on the bond strength M–L. In particular, this paper deals with the effect of two different groups R, C_6H_5 and CF_3, on the bond-enthalpy contributions $\bar{D}$(M–OOCR).

Thermochemical measurements on reactions (1) and (2) (M = Mo, W, or Ti) were used as the main source of data to derive such bond-enthalpy contributions.

$$[M(\eta\text{-}C_5H_5)_2(OOCC_6H_5)_2](c) + 2HCl(soln) \longrightarrow [M(\eta\text{-}C_5H_5)_2Cl_2](soln) + 2C_6H_5COOH(soln) \quad (1)$$

$$[M(\eta\text{-}C_5H_5)_2(OOCCF_3)_2](c) + 2HCl(soln) \longrightarrow [M(\eta\text{-}C_5H_5)_2Cl_2](soln) + 2CF_3COOH(soln) \quad (2)$$

EXPERIMENTAL

Calorimeters.—All the reaction and solution enthalpies were measured in the reaction–solution calorimeter previously described.[1c] As far as the experimental technique is concerned,[1b,c] a nitrogen atmosphere was not needed, as all the compounds involved are air-stable.

The enthalpy of sublimation of $[Ti(\eta\text{-}C_5H_5)_2(OOCCF_3)_2]$ was measured with a Calvet high-temperature microcalorimeter (Setaram) by using the microcalorimetric vacuum-sublimation method.[2]

Compounds.—Complexes $[M(\eta\text{-}C_5H_5)_2L_2]$ (M = Mo, W, or Ti; L = $OOCC_6H_5$ or $OOCCF_3$) were prepared and purified as described in the literature.[3-5] The reaction solutions were prepared with B.D.H. AnalaR hydrochloric acid and Merck *p.a.* acetone, which were used without any further treatment. B.D.H. AnalaR benzoic acid was resublimed and Merck trifluoroacetic acid was distilled over phosphorus pentaoxide before use.

Reactions.—All the solutions used in the thermochemical studies of reactions (1) and (2) were mixtures of aqueous hydrochloric acid and acetone (Table 1). Each mixture had to be chosen in order to ascertain a rapid and complete solubilization of the respective complex. Using the solutions presented in Table 1 reactions (1) and (2) were completed in less than 5 min.

TABLE 1

Solutions of aqueous HCl and acetone used in reactions (1) and (2)

Reaction	M	HCl (aq)/ mol dm^{-3}	v : v *	Designation
(1)	Mo, W, Ti	8.3	1 : 1	A
(2)	Mo, Ti	10.0	1 : 4	B
	W	10.0	1 : 1	C

* Volumetric ratio [HCl(aq) : acetone].

The use of solutions A, B, and C has the following disadvantages: a change in composition of the solutions through evaporation of the acetone, in consequence of its low boiling point; and that acetone undergoes aldolic condensation in acid media. Several calibration constants (ε) were determined, before and after some runs, to determine the effect of these two sources of errors. The effect of breaking empty glass ampoules in the solutions was also checked. These tests led to the conclusion that neither changes in ε nor the temperature drop caused by breaking empty bulbs were significant relative to the precision of the experimental reaction and solution enthalpies. A third potential source of error, due to oxidation of $[M(\eta\text{-}C_5H_5)_2Cl_2]$ (M = Mo or W) in solution, was considered, but is not significant since the oxidation of $[M(\eta\text{-}C_5H_5)_2Cl_2]$ (M = Mo or W) is a very slow process. In like manner aldolic condensation is too slow to influence the accuracy of the experimental results.

The final states of reactions (1) and (2) for M = Mo or W were demonstrated by Harriss *et al.*[3] The products of the same reactions for M = Ti were identified by i.r. spectroscopy.

All the thermochemical results presented are mean values from five independent experiments and are referred to 298.15 K. The associated uncertainties are twice the standard deviations of those means.

Auxiliary Data.—The following standard enthalpies of formation at 298 K were used in evaluating the thermochemical results (values in kJ mol^{-1}): $\Delta H_f^\ominus$[HCl, aq (8.3 mol dm^{-3})] $= -156.824 \pm 0.004$; [6] $\Delta H_f^\ominus$[HCl, aq (10.0 mol dm^{-3})] $= -154.106 \pm 0.004$; [6] $\Delta H_f^\ominus\{[\mathrm{Mo}(\eta\text{-}\mathrm{C}_5\mathrm{H}_5)_2\mathrm{Cl}_2], \mathrm{c}\} = -95.8 \pm 2.5$; [7] $\Delta H_f^\ominus\{[\mathrm{W}(\eta\text{-}\mathrm{C}_5\mathrm{H}_5)_2\mathrm{Cl}_2], \mathrm{c}\} = -71.1 \pm 2.5$; [7] $\Delta H_f^\ominus\{[\mathrm{Ti}(\eta\text{-}\mathrm{C}_5\mathrm{H}_5)_2\mathrm{Cl}_2], \mathrm{c}\} = -383.2 \pm 7.5$; [7] $\Delta H_f^\ominus(\mathrm{C}_6\mathrm{H}_5\mathrm{COOH}, \mathrm{c}) = -384.9 \pm 0.6$; [8] $\Delta H_f^\ominus(\mathrm{CF}_3\mathrm{COOH}, \mathrm{l}) = -1\,069.2 \pm 1.1$; [8] $\Delta H_f^\ominus(\mathrm{Cl}, \mathrm{g}) = 121.302 \pm 0.008$; [9] $\Delta H_f^\ominus(\mathrm{C}_6\mathrm{H}_5\mathrm{COO}^\bullet, \mathrm{g}) = -76.3 \pm 3.0$; $\Delta H_f^\ominus(\mathrm{CF}_3\mathrm{COO}^\bullet, \mathrm{g}) = -815.7 \pm 10$. The enthalpy of formation of the benzoate radical was calculated from $D(\mathrm{O{-}O}) = 125.5 \pm 4.2$ kJ mol^{-1} in $(\mathrm{C}_6\mathrm{H}_5\mathrm{COO})_2$ [10] and from $\Delta H_f^\ominus[(\mathrm{C}_6\mathrm{H}_5\mathrm{COO})_2, \mathrm{g}] = -278.2 \pm 4.2$ [8] kJ mol^{-1}. The value of the enthalpy of formation of the trifluoroacetate radical is based on $\bar{D}(\mathrm{CH}_3\mathrm{COO{-}H}) = 433 \pm 10$ [11] kJ mol^{-1}, assumed equal to $\bar{D}(\mathrm{CF}_3\mathrm{COO{-}H})$, on $\Delta H_f^\ominus(\mathrm{CF}_3\mathrm{COOH}, \mathrm{g}) = -1\,030.7 \pm 1.4$ [8] kJ mol^{-1}, and on $\Delta H_f^\ominus(\mathrm{H}, \mathrm{g}) = 217.997 \pm 0.006$ [9] kJ mol^{-1}.

RESULTS

$[\mathrm{M}(\eta\text{-}\mathrm{C}_5\mathrm{H}_5)_2(\mathrm{OOCC}_6\mathrm{H}_5)_2]$ *Complexes.*—The thermochemical results obtained for the three complexes are summarised in Table 2, where ΔH_r represents the enthalpy of reaction (1).

TABLE 2

Thermochemical results (kJ mol^{-1}) for reaction (1)

$[\mathrm{M}(\eta\text{-}\mathrm{C}_5\mathrm{H}_5)_2\text{-}(\mathrm{OOCC}_6\mathrm{H}_5)_2]$	M = Mo	M = W	M = Ti
ΔH_r	-10.0 ± 1.2	-10.73 ± 0.63	-5.4 ± 2.0
ΔH_{d1}	2.2 ± 1.1	12.6 ± 1.9	5.2 ± 1.8
ΔH_{d2}	21.14 ± 0.45	21.89 ± 0.61	21.14 ± 0.45
ΔH_{d3}	-5.65 ± 0.28	-5.65 ± 0.28	-5.65 ± 0.28
$\Delta H_f^\ominus$ (c)	-486.2 ± 3.4	-448.9 ± 3.7	-775.2 ± 8.1

In order to determine the standard enthalpies of formation of $[\mathrm{M}(\eta\text{-}\mathrm{C}_5\mathrm{H}_5)_2(\mathrm{OOCC}_6\mathrm{H}_5)_2]$ (c) complexes and the differences between the bond-enthalpy contributions $[\bar{D}(\mathrm{M{-}OOCC}_6\mathrm{H}_5) - \bar{D}(\mathrm{M{-}Cl})]$ it was necessary to obtain $\Delta H_f^\ominus$(HCl, soln A). In each run the number of moles of HCl in solution was *ca.* 519×10^{-3}. On the other hand the number of moles of each complex was always less than 0.5×10^{-3}. Thus it can be assumed that the composition of the calorimetric solution remained constant in each experiment. Consider reaction (3) where n represents the number of

$$n\,\mathrm{HCl}(\mathrm{aq}, 8.3\ \mathrm{mol\ dm^{-3}}) + m\,\mathrm{HCl}(\mathrm{soln\ A}) \longrightarrow (n+m)\,\mathrm{HCl}(\mathrm{soln\ A'}) \quad (3)$$

moles of HCl which takes part in reaction (1) and m stands for the average number of moles of HCl in the calorimetric solution. Since $m \gg n$, A $\simeq$ A$'$ and the enthalpy change associated with (3), ΔH_{d3}, can be written [in kJ per mol of HCl (aq, 8.3 mol dm^{-3})] as equation (4).

$$\Delta H_{d3} = \Delta H_f^\ominus(\mathrm{HCl, soln\ A}) - \Delta H_f^\ominus[\mathrm{HCl, aq}\ (8.3\ \mathrm{mol\ dm^{-3}})] \quad (4)$$

The value of ΔH_{d3} was obtained by breaking ampoules containing stoicheiometric amounts of HCl (aq, 8.3 mol dm^{-3}) in solution A. The final value, presented in Table 2, together with $\Delta H_f^\ominus$[HCl, aq (8.3 mol dm^{-3})] led to $\Delta H_f^\ominus$(HCl, soln A) $= -162.47 \pm 0.28$ kJ mol^{-1}.

In the case of M = Mo or Ti, the enthalpies of solution of $[\mathrm{M}(\eta\text{-}\mathrm{C}_5\mathrm{H}_5)_2\mathrm{Cl}_2]$ (c) in solvent A and of $\mathrm{C}_6\mathrm{H}_5\mathrm{COOH}$ (c) in the same solvent containing stoicheiometric amounts of $[\mathrm{M}(\eta\text{-}\mathrm{C}_5\mathrm{H}_5)_2\mathrm{Cl}_2]$ are represented in Table 2 by ΔH_{d1} and ΔH_{d2} respectively. It can be noticed that the same value for ΔH_{d2} was adopted for both systems. Two measurements of the enthalpy of solution of $\mathrm{C}_6\mathrm{H}_5\mathrm{COOH}$ (c) in solvent A containing $[\mathrm{Ti}(\eta\text{-}\mathrm{C}_5\mathrm{H}_5)_2\mathrm{Cl}_2]$ yielded results very close to ΔH_{d2} for the molybdenum system.

For M = W, ΔH_{d1} and ΔH_{d2} represent the enthalpy of solution of $[\mathrm{W}(\eta\text{-}\mathrm{C}_5\mathrm{H}_5)_2\mathrm{Cl}_2]$ (c) in solvent A containing stoicheiometric amounts of benzoic acid and the enthalpy of solution of $\mathrm{C}_6\mathrm{H}_5\mathrm{COOH}$ (c) in solvent A, respectively.

The standard enthalpies of formation of the $[\mathrm{M}(\eta\text{-}\mathrm{C}_5\mathrm{H}_5)_2(\mathrm{OOCC}_6\mathrm{H}_5)_2]$ (c) complexes were finally derived (Table 2) using the above mentioned results and the relevant auxiliary data.

Finally it can be noted that in the experiments involving dissolution of $[\mathrm{Ti}(\eta\text{-}\mathrm{C}_5\mathrm{H}_5)_2\mathrm{Cl}_2]$ (c) a small solid residue of the complex was always observed. However, as this amount never exceeded *ca.* 5% of the total mass of $[\mathrm{Ti}(\eta\text{-}\mathrm{C}_5\mathrm{H}_5)_2\mathrm{Cl}_2]$ the resulting error lies well within the uncertainty intervals.

$[\mathrm{M}(\eta\text{-}\mathrm{C}_5\mathrm{H}_5)_2(\mathrm{OOCCF}_3)_2]$ *Complexes.*—The enthalpies of reactions (2), ΔH_r, and other thermochemical results obtained for the three systems are presented in Table 3.

TABLE 3

Thermochemical results (kJ mol^{-1}) for reaction (2)

$[\mathrm{M}(\eta\text{-}\mathrm{C}_5\mathrm{H}_5)_2\text{-}(\mathrm{OOCCF}_3)_2]$	M = Mo	M = W	M = Ti
ΔH_r	17.06 ± 0.79	20.9 ± 1.4	21.38 ± 0.74
ΔH_{d1}	-12.9 ± 1.3	8.78 ± 0.55	11.81 ± 0.96
ΔH_{d2}	-16.50 ± 0.52	-5.59 ± 0.49	-16.50 ± 0.52
ΔH_{d3}	-18.48 ± 0.51	-5.06 ± 0.22	-18.48 ± 0.51
$\Delta H_f^\ominus$(c)	$-1\,952.0 \pm 3.9$	$-1\,914.5 \pm 3.8$	$-2\,219.0 \pm 8.0$

The enthalpies of formation of HCl (soln B) and HCl (soln C) were derived by using similar arguments to the one described for $[\mathrm{M}(\eta\text{-}\mathrm{C}_5\mathrm{H}_5)_2(\mathrm{OOCC}_6\mathrm{H}_5)_2]$ complexes. Quoting the value of $\Delta H_f^\ominus$[HCl, aq (10.0 mol dm^{-3})] and the ΔH_{d3} results (Table 3) we arrive at $\Delta H_f^\ominus$(HCl, soln B) $= -172.59 \pm 0.51$ kJ mol^{-1} and $\Delta H_f^\ominus$(HCl, soln C) $= -159.17 \pm 0.22$ kJ mol^{-1}.

In the cases of M = Mo or Ti, ΔH_{d1} and ΔH_{d2} (Table 3) stand respectively for the enthalpy of solution of $[\mathrm{M}(\eta\text{-}\mathrm{C}_5\mathrm{H}_5)_2\mathrm{Cl}_2]$ (c) in solvent B containing stoicheiometric amounts of trifluoroacetic acid and for the enthalpy of solution of $\mathrm{CF}_3\mathrm{COOH}$ (l) in solvent B. In the case of M = W, ΔH_{d1} and ΔH_{d2} represent the equivalent enthalpies for the tungsten system and solvent C.

It was observed that a small fraction (less than 10%) of the complex $[\mathrm{W}(\eta\text{-}\mathrm{C}_5\mathrm{H}_5)_2(\mathrm{OOCCF}_3)_2]$ remained unreacted in the crystalline state. Changes of the stirring speed and direction or trials made with solvents with different compositions did not improve the solubility and the extent of reaction of the complex. Therefore the value of ΔH_r presented in Table 3 could be *ca.* 2 kJ mol^{-1} below the correct result.

The values of $\Delta H_f^\ominus\{[\mathrm{M}(\eta\text{-}\mathrm{C}_5\mathrm{H}_5)_2(\mathrm{OOCCF}_3)_2], \mathrm{c}\}$ shown in Table 3 were derived by using the above results together with the auxiliary data already given.

From vacuum-sublimation measurements at 416 K a value of $\Delta H_s^\ominus\{[\mathrm{Ti}(\eta\text{-}\mathrm{C}_5\mathrm{H}_5)_2(\mathrm{OOCCF}_3)_2]\} = 108 \pm 8$ kJ mol^{-1} was obtained.

DISCUSSION

The standard enthalpies of formation of crystalline and gaseous complexes $[\mathrm{M}(\eta\text{-}\mathrm{C}_5\mathrm{H}_5)_2(\mathrm{OOCR})_2]$ are collected in Table 4. The heats of sublimation at 298 K are also included.

TABLE 4

Enthalpies of formation, $\Delta H_f^\ominus$ (c) and $\Delta H_f^\ominus$ (g) in kJ mol^{-1}

Compound	$\Delta H_f^\ominus$(c)	$\Delta H_s^\ominus$	$\Delta H_f^\ominus$(g)
$[Mo(\eta\text{-}C_5H_5)_2(OOCC_6H_5)_2]$	−486.2 ±3.4	94 ± 10 *	−392.2 ±11
$[W(\eta\text{-}C_5H_5)_2(OOCC_6H_5)_2]$	−448.9 ±3.7	98 ± 10 *	−350.9 ±11
$[Ti(\eta\text{-}C_5H_5)_2(OOCC_6H_5)_2]$	−775.2 ±8.1	112 ± 8 *	−663.2 ±11
$[Mo(\eta\text{-}C_5H_5)_2(OOCCF_3)_2]$	−1 952.0 ±3.9	90 ± 10 *	−1 862.0 ±11
$[W(\eta\text{-}C_5H_5)_2(OOCCF_3)_2]$	−1 914.5 ±3.8	94 ± 10 *	−1 820.5 ±11
$[Ti(\eta\text{-}C_5H_5)_2(OOCCF_3)_2]$	−2 219.0 ±8.0	108 ± 8	−2 111.0 ±11

* Estimated value.

TABLE 5

Bond enthalpy contributions (kJ mol^{-1})

Compound	$\bar{D}$(M–OOCR) − $\bar{D}$(M–Cl)	$\bar{D}$(M–OOCR)
$[Mo(\eta\text{-}C_5H_5)_2(OOCC_6H_5)_2]$	0.8 ± 6	304.6
$[W(\eta\text{-}C_5H_5)_2(OOCC_6H_5)_2]$	−5.4 ± 6	341.9
$[Ti(\eta\text{-}C_5H_5)_2(OOCC_6H_5)_2]$	1.8 ± 5	432.3
$[Mo(\eta\text{-}C_5H_5)_2(OOCCF_3)_2]$	−3.7 ± 12	300.3
$[W(\eta\text{-}C_5H_5)_2(OOCCF_3)_2]$	−10.0 [illegible] 12	337.3
$[Ti(\eta\text{-}C_5H_5)_2(OOCCF_3)_2]$	−13.7 ± 11	416.8

The mean bond-enthalpy contribution differences [$\bar{D}$(M–OOCR) − $\bar{D}$(M–Cl)] (Table 5) were obtained from equation (5) *,† where the enthalpies of sublimation of

$$\bar{D}(\text{M–OOCR}) - \bar{D}(\text{M–Cl}) = (\Delta H_r - \Delta H_{d1} - 2\Delta H_{d2})/2 + (\Delta H_s^\ominus\{[M(\eta\text{-}C_5H_5)_2Cl_2]\} - \Delta H_s^\ominus\{[M(\eta\text{-}C_5H_5)_2(OOCR)_2]\})/2 - \Delta H_f^\ominus(\text{RCOOH, c,l}) + \Delta H_f^\ominus(\text{HCl, soln A,B,C}) + \Delta H_f^\ominus(\text{RCOO}^\bullet\text{, g}) - \Delta H_f^\ominus(\text{Cl, g}) \quad (5)$$

the complexes $[M(\eta\text{-}C_5H_5)_2Cl_2]$ were taken as 100.4 ± 4.2,[7] 104.6 ± 4.2,[7] and 118.8 ± 2.1 [7] kJ mol^{-1} respectively for M = Mo, W, and Ti.

Values of $\bar{D}$(M–OOCR) were calculated by assuming that $\bar{D}$(M–Cl) in $[M(\eta\text{-}C_5H_5)_2Cl_2]$ complexes are equal to the mean bond dissociation energies [7] in MCl_6 for M = Mo or W (303.8 and 347.3 kJ mol^{-1} respectively) and in MCl_4 for M = Ti (430.5 kJ mol^{-1}). Both these hypotheses are due to Tel'noi and Rabinovich [7] and the former has recently been tested.[1d]

In ML_n compounds (L = Cl or OR) the difference [$\bar{D}$(M–OR) − $\bar{D}$(M–Cl)] is usually positive.[7,12,13] However when M = Ti many examples can be found where $\bar{D}$(Ti–OR) ≈ $\bar{D}$(Ti–Cl).[7] The resemblance between $\bar{D}$(M–OOCR) and $\bar{D}$(M–Cl) for a given metal and for R = C_6H_5 or CF_3 seems to be the main conclusion drawn from values of Table 5. It is difficult to ascribe the influence of group R to the changes observed in $\bar{D}$(M–OOCR) for each metal, considering the uncertainties that affect the bond-energy differences. If the mean values are accepted $\bar{D}$(M–OOCC$_6$H$_5$) > $\bar{D}$(M–OOCCF$_3$). Nevertheless this result conflicts with a correlation found between mean bond-enthalpy contributions, $\bar{D}$(M–L), in $[M(\eta\text{-}C_5H_5)_2L_2]$ complexes and ligand electronegativities, χ_L.[1e] The correlation suggests that the increase in χ_L is followed by an increase in $\bar{D}$(M–L). Using a method proposed by Huheey,[14] the group electronegativities (in Mulliken's scale) of $C_6H_5COO^\bullet$ and $CF_3COO^\bullet$ were calculated as 8.9 and 11.7 respectively.

The values shown in Table 5 are based on $\Delta H_f^\ominus(CF_3COO^\bullet$, g) = −815.7 ± 10 kJ mol^{-1} which, as stated before, was derived from $\bar{D}$(CH$_3$COO–H) = 433 ± 10 [11] kJ mol^{-1}. If this recent value was replaced by the previously accepted $\bar{D}$(RCOO–H) in carboxylic acids, *ca.* 460 ± 17 [15] kJ mol^{-1}, the trend in $\bar{D}$(M–OOCR) would be reversed *i.e.* $\bar{D}$(M–OOCCF$_3$) > $\bar{D}$(M–OOCC$_6$H$_5$) > $\bar{D}$(M–Cl). Therefore it may well be possible that $\Delta H_f^\ominus(CF_3COO^\bullet$, g) lies somewhere in between the two values considered.

Tel'noi and co-workers used combustion calorimetry in thermochemical studies of some $[Ti(\eta\text{-}C_5H_5)_2L_2]$ complexes (L = Cl, CH_3, $CH_2C_6H_5$, C_6H_5, or $OOCC_6H_5$). The results they have obtained are summarised in a review by Tel'noi and Rabinovich.[7] For $\Delta H_f^\ominus\{[Ti(\eta\text{-}C_5H_5)_2(OOCC_6H_5)_2]$, c} they recommend −966.5 ± 12.6 kJ mol^{-1}, a value that lies well below the one presented in Table 4. In the same review the authors do not give a value for $\bar{D}$(Ti–OOCC$_6$H$_5$). However, in the original paper where the experimental work is described, Tel'noi *et al.*[16] arrived at $\bar{D}$(Ti–OOCC$_6$H$_5$) ≈ 456 kJ mol^{-1} a result that was based on early values of $\bar{D}$(Ti–C$_5$H$_5$) in $[Ti(\eta\text{-}C_5H_5)_2]$ and in $[Ti(\eta\text{-}C_5H_5)_2Cl_2]$, and on the equality $\Delta H_s^\ominus[(C_6H_5COO)_2] + \Delta H_s^\ominus\{[Ti(\eta\text{-}C_5H_5)_2]\} = \Delta H_s^\ominus\{[Ti(\eta\text{-}C_5H_5)_2(OOCC_6H_5)_2]\}$. Quoting the more recent values for the enthalpies of sublimation ($\Delta H_s^\ominus$) of dibenzoyl peroxide (97.9 ± 6.6 kJ mol^{-1}) [8] and of titanocene (58.6) [7] we find that Tel'noi's assumption leads to $\Delta H_s^\ominus\{[Ti(\eta\text{-}C_5H_5)_2(OOCC_6H_5)_2]\}$ = 156.5 kJ mol^{-1}, an excessively high value compared with the enthalpies of sublimation for other $[Ti(\eta\text{-}C_5H_5)_2L_2]$ complexes.[7] Furthermore taking $\Delta H_s^\ominus\{[Ti(\eta\text{-}C_5H_5)_2Cl_2]\}$ = 118.8 [7] kJ mol^{-1} and the probably more reasonable guess for $\Delta H_s^\ominus\{[Ti(\eta\text{-}C_5H_5)_2(OOCC_6H_5)_2]\}$ (Table 4), together with $\bar{D}$(Ti–C$_5$H$_5$) = 269 kJ mol^{-1} (also derived by Tel'noi and Rabinovich [7] and consistent with the thermochemical data of Table 5) we arrive at $\bar{D}$(Ti–OOCC$_6$H$_5$) = 528 kJ mol^{-1}, a value that seems too high to be accepted.

The preceding example indicates that static bomb combustion calorimetry may be unsuited to organotitanium compounds as complex as $[Ti(\eta\text{-}C_5H_5)_2L_2]$. In the particular case of L = CH_3 or C_6H_5 a simple comparison between the thermochemical values given in the original papers by Tel'noi *et al.*[16,17] and the ones cited or overlooked later [7] further demonstrates those difficulties and demands a re-examination of the values obtained so far.

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* Whereas the enthalpies of formation depend on Tel'noi and Rabinovich's [7] values for the chloro-complexes, the differences $\bar{D}$(M–OOCR) − $\bar{D}$(M–Cl) do not.

† It is assumed that $\bar{D}$(M–C$_5$H$_5$) is the same in the complexes studied and in the chloro-complexes.

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