

## Enthalpies of formation of $M(\eta\text{-C}_5\text{H}_5)_2\text{L}$ complexes ( $M = \text{Mo, W, Ti}$ ; $L = \text{C}_6\text{H}_4\text{O}_2, \text{C}_{10}\text{H}_6\text{O}_2, \text{C}_{14}\text{H}_8\text{O}_2$ )

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### Abstract

The standard molar enthalpies of formation, at 298.15 K, of five crystalline bent metallocenes,  $[M(\eta\text{-C}_5\text{H}_5)_2\text{L}]$  ( $M = \text{Mo, W, Ti}$ ) ( $\text{LH}_2 = 1,2\text{-benzenediol, C}_6\text{H}_4\text{-(OH)}_2$ ; 2,3-naphthalenediol,  $\text{C}_{10}\text{H}_6\text{(OH)}_2$ ; 9,10-phenanthrenediol,  $\text{C}_{14}\text{H}_8\text{(OH)}_2$ ), have been derived from enthalpies of hydrolyses in acid solution measured by precision solution-reaction calorimetry. The results were:  $\Delta H_f^\circ [\text{Mo}(\eta\text{-C}_5\text{H}_5)_2(\text{O}_2\text{C}_6\text{H}_4),\text{c}] = -130.6 \pm 2.9$ ,  $\Delta H_f^\circ [\text{Mo}(\eta\text{-C}_5\text{H}_5)_2(\text{O}_2\text{C}_{10}\text{H}_6),\text{c}] = -80.3 \pm 2.2$ ,  $\Delta H_f^\circ [\text{Mo}(\eta\text{-C}_5\text{H}_5)_2(\text{O}_2\text{C}_{14}\text{H}_8),\text{c}] = -53.25 \pm 10.4$ ,  $\Delta H_f^\circ [\text{W}(\eta\text{-C}_5\text{H}_5)_2(\text{O}_2\text{C}_6\text{H}_4),\text{c}] = -112.8 \pm 2.9$ ,  $\Delta H_f^\circ [\text{Ti}(\eta\text{-C}_5\text{H}_5)_2(\text{O}_2\text{C}_{14}\text{H}_8),\text{c}] = -322.6 \pm 12.7 \text{ kJ mol}^{-1}$ . The metal–oxygen bond strengths were evaluated as mean bond enthalpy terms ( $E$ ). Comparison with corresponding values in similar complexes reveals that small steric strain energy arises from the binding of a catechol type ligand to a metal atom.

### Introduction

Data on metal–ligand bond enthalpy contributions in bent metallocenes are still scarce. Reliable data are needed to establish trends in, or correlations between, bond energies and other physical parameters, such as bond distances, stretching frequencies, electronegativities, etc., which are often used to account for reactivities and stabilities of these complexes.

The difficulties of thermochemical measurements on organometallic compounds has often meant that metal–ligand bond enthalpies have been derived from data for which the accuracy must be suspect. Acquisition of new accurate values will permit some comparisons and may reveal trends so that the reliability of data previously available can be ascertained. The present study was directed towards evaluation of

the metal (Mo, W, Ti)-oxygen bond-enthalpy contributions in bent metallocenes of the type  $M(\eta\text{-C}_5\text{H}_5)_2\text{L}$ , where L is a bidentate ligand of a catechol type which forms a chelate ring with the metal.

The experimental technique used was solution-reaction calorimetry, which proved to be a suitable tool for these thermochemical studies on complexes of the type  $M(\eta\text{-C}_5\text{H}_5)_2\text{L}$ , particularly for  $M = \text{Mo, W, Ti}$ . The metal-ligand bond-enthalpy contributions derived in this work can be regarded as basic data for future studies.

## Experimental

### Calorimeter

The reaction and solution enthalpies were measured in a reaction-solution calorimeter with an all glass reaction vessel, similar in design to other calorimeters described in the literature [1-3]. Some other important details of the technique have been reported elsewhere [3,4]; for the solution calorimetry of the complexes studied in this work a nitrogen atmosphere was not needed, as all the compounds are air-stable. Although complexes of the type  $[M(\eta\text{-C}_5\text{H}_5)_2\text{L}]$  are not stable towards oxygen in solution, because their reactions with HCl are rapid it was unnecessary to take precautions to exclude oxygen from the system.

### Compounds

The compounds  $M(\eta\text{-C}_5\text{H}_5)_2(\text{O}_2\text{C}_6\text{H}_4)$  ( $M = \text{Mo, W}$ ) were prepared as described by Green et al. [5]. The previously unreported  $\text{Mo}(\eta\text{-C}_5\text{H}_5)_2(\text{O}_2\text{C}_{10}\text{H}_6)$  was prepared in a manner similar to that for the corresponding catecholate [5]. The previously unknown  $\text{Mo}(\eta\text{-C}_5\text{H}_5)_2(\text{O}_2\text{C}_{14}\text{H}_8)$  was prepared by the method used by Green [6] for the preparation of the tungsten complex;  $\text{Ti}(\eta\text{-C}_5\text{H}_5)_2(\text{O}_2\text{C}_{14}\text{H}_8)$  was prepared by the literature method [7], from  $\text{Ti}(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_2$ . All the compounds were purified and characterized by elemental analysis and by IR and NMR spectroscopy. Catechol,  $\text{C}_6\text{H}_4(\text{OH})_2$ , and 2,3-naphthalenediol,  $\text{C}_{10}\text{H}_6(\text{OH})_2$ , (Janssen Chimica) were purified by several sublimations in vacuum. 9,10-Phenanthrenediol,  $\text{C}_{14}\text{H}_8(\text{OH})_2$ , was prepared from 9,10-phenanthrenoquinone as described in the literature [8].

The dichloride  $M(\eta\text{-C}_5\text{H}_5)_2\text{Cl}_2$  ( $M = \text{Mo, W}$ ) were prepared [9] by addition of  $\text{CCl}_4$  to a solution of  $M(\eta\text{-C}_5\text{H}_5)_2\text{H}_2$  in acetone or toluene; the dihydrides  $M(\eta\text{-C}_5\text{H}_5)_2\text{H}_2$  were prepared as described by Green et al. [10].  $\text{Ti}(\eta\text{-C}_5\text{H}_5)_2\text{Cl}_2$  was prepared from  $\text{TiCl}_4$  by a published method [11],  $\text{Ti}(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_2$  was prepared as described in ref. 12.

The solvents for the calorimetric reactions were prepared from p.a. hydrochloric acid (Merck) and AnalaR acetone (B.D.H), used as supplied.

### Reactions

Thermochemical measurements on reaction (1) ( $M = \text{Mo, L} = \text{C}_6\text{H}_4\text{O}_2, \text{C}_{10}\text{H}_6\text{O}_2$  or  $\text{C}_{14}\text{H}_8\text{O}_2$ ;  $M = \text{W, L} = \text{C}_6\text{H}_4\text{O}_2$ ;  $M = \text{Ti, L} = \text{C}_{14}\text{H}_8\text{O}_2$ ) were used to derive the standard enthalpies of formation of the complexes studied. The compositions of the calorimetric solvents (Table 1) were chosen to ensure rapid and complete reaction for each complex (Table 1).

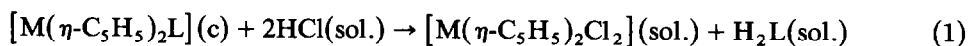


Table 1  
Composition of the reaction mixtures

System	M	Ligand	HCl (aq) (mol dm <sup>-3</sup> )	HCl (aq)/acetone (v/v)	Designation
I	Mo	C <sub>6</sub> H <sub>4</sub> (OH) <sub>2</sub>	8.3	1/1	A
II	Mo	C <sub>10</sub> H <sub>6</sub> (OH) <sub>2</sub>	8.3	1/1	A
III	Mo	C <sub>14</sub> H <sub>8</sub> (OH) <sub>2</sub>	8.3	1/1	A
IV	W	C <sub>6</sub> H <sub>4</sub> (OH) <sub>2</sub>	8.3	1/1	A
V	Ti	C <sub>14</sub> H <sub>8</sub> (OH) <sub>2</sub>	10.0	1/2	B

There are three possible disadvantages in using solvents A and B: (i) Acetone undergoes aldol condensation in acid, (ii) because of high vapour pressure of acetone, evaporation could result in a change of solvent composition, and (iii) oxidation could take place with solution of M( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Cl<sub>2</sub>. The aldol condensation and the oxidation of M( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Cl<sub>2</sub> are very slow, and would not introduce significant error in the short time scale of the hydrolyses. As calibration constants measured before and after hydrolyses were equal to within the expected experimental error, it was concluded that the effect of vaporisation of acetone was negligible. The thermal effect of breaking empty glass ampoules into the solvents was also checked.

The final states of the reactions (1) were checked by IR spectroscopy.

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

### Auxiliary data

The following standard enthalpies of formation at 298.15 K were used in calculating the thermochemical results (values in kJ mol<sup>-1</sup>).

$$\Delta H_f^\circ (\text{H}_2\text{O}, \text{l}) = -285.830 \pm 0.042 \text{ [13,14]}$$

$$\Delta H_f^\circ (\text{HCl in } 4.38\text{H}_2\text{O}, \text{aq}) = -154.042 \pm 0.006 \text{ [15]}$$

$$\Delta H_f^\circ (\text{HCl in } 5.55\text{H}_2\text{O}, \text{aq}) = -156.824 \pm 0.006 \text{ [15]}$$

$$\Delta H_f^\circ \{ [\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{Cl}_2], \text{c} \} = -95.8 \pm 2.5 \text{ [16]}$$

$$\Delta H_f^\circ \{ [\text{W}(\eta\text{-C}_5\text{H}_5)_2\text{Cl}_2], \text{c} \} = -71.1 \pm 2.5 \text{ [16]}$$

$$\Delta H_f^\circ \{ [\text{Ti}(\eta\text{-C}_5\text{H}_5)_2\text{Cl}_2], \text{c} \} = -383.2 \pm 7.5 \text{ [17]}$$

$$\Delta H_f^\circ \{ \text{C}_6\text{H}_4(\text{OH})_2, \text{c} \} = -354.1 \pm 1.1 \text{ [18]}$$

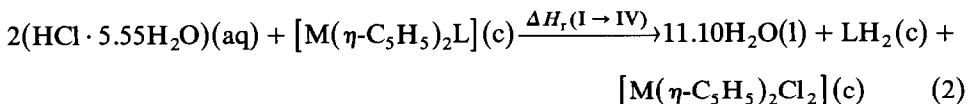
$$\Delta H_f^\circ \{ \text{C}_{10}\text{H}_6(\text{OH})_2, \text{c} \} = -302.4 \pm 1.7 \text{ [19]}$$

$$\Delta H_f^\circ \{ \text{C}_{14}\text{H}_8(\text{OH})_2, \text{c} \} = (-285 \pm 10) *$$

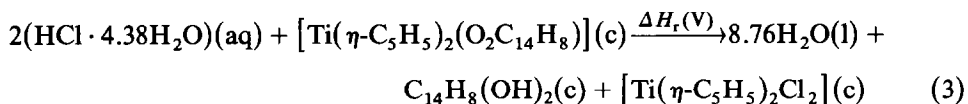
\* Estimated (Ref. 20).

## Results

The thermochemical reactions from which the enthalpies of formation of  $[M(\eta\text{-C}_5\text{H}_5)_2L](c)$ , ( $M = \text{Mo}, \text{W}$ ) and ( $L = \text{C}_6\text{H}_4\text{O}_2, \text{C}_{10}\text{H}_6\text{O}_2, \text{C}_{14}\text{H}_8\text{O}_2$ ) were determined, were



For  $[\text{Ti}(\eta\text{-C}_5\text{H}_5)_2(\text{O}_2\text{C}_{14}\text{H}_8)](c)$ , the thermochemical reaction was



The enthalpies  $\Delta H_r(\text{I})$ ,  $\Delta H_r(\text{II})$ ,  $\Delta H_r(\text{III})$ ,  $\Delta H_r(\text{IV})$  and  $\Delta H_r(\text{V})$  of these reactions were determined indirectly from the enthalpies of stepwise solution of reactants and products, in stoichiometric ratio, in the calorimeter solvent. These individual enthalpies are listed in order ( $\Delta H_{d1}$  to  $\Delta H_{d18}$ ) in Table 2 for the Mo and W complexes and in Table 3 for the Ti complex.

The standard enthalpies of reactions for the systems studied, are related to the stepwise solution enthalpies, through the eqs. 4–8:

$$\Delta H_r(\text{I}) = 2\Delta H_{d1} + \Delta H_{d2} - 11.10\Delta H_{d6} + \Delta H_{d7} - \Delta H_{d8} = -5.63 \pm 0.80 \text{ kJ mol}^{-1} \quad (4)$$

$$\Delta H_r(\text{II}) = 2\Delta H_{d1} + \Delta H_{d3} - 11.10\Delta H_{d6} - \Delta H_{d9} - \Delta H_{d10} = -4.30 \pm 0.68 \text{ kJ mol}^{-1} \quad (5)$$

$$\Delta H_r(\text{III}) = 2\Delta H_{d1} + \Delta H_{d4} - 11.10\Delta H_{d6} - \Delta H_{d11} - \Delta H_{d12} = -13.9 \pm 1.0 \text{ kJ mol}^{-1} \quad (6)$$

Table 2

Enthalpies of solution and reaction at 298.15 K

Reaction	Number of experiments	$\Delta H_{di}$ (kJ mol <sup>-1</sup> )
$\text{HCl} \cdot 5.55\text{H}_2\text{O}(\text{aq}) + \text{Solvent A} \rightarrow \text{Solution A}_1$	5	$\Delta H_{d1} = -5.393 \pm 0.090$
$[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2(\text{O}_2\text{C}_6\text{H}_4)](c) + \text{Solution A}_1 \rightarrow \text{Solution F}_1$	6	$\Delta H_{d2} = -13.63 \pm 0.68$
$[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2(\text{O}_2\text{C}_{10}\text{H}_6)](c) + \text{Solution A}_1 \rightarrow \text{Solution F}_2$	5	$\Delta H_{d3} = -8.33 \pm 0.31$
$[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2(\text{O}_2\text{C}_{14}\text{H}_8)](c) + \text{Solution A}_1 \rightarrow \text{Solution F}_3$	5	$\Delta H_{d4} = -11.89 \pm 0.58$
$[\text{W}(\eta\text{-C}_5\text{H}_5)_2(\text{O}_2\text{C}_6\text{H}_4)](c) + \text{Solution A}_1 \rightarrow \text{Solution F}_4$	6	$\Delta H_{d5} = +19.94 \pm 0.61$
$\text{H}_2\text{O}(\text{l}) + \text{Solvent A} \rightarrow \text{Solution A}_2$	5	$\Delta H_{d6} = -1.102 \pm 0.010$
$\text{C}_6\text{H}_4(\text{OH})_2(c) + \text{Solution A}_2 \rightarrow \text{Solution A}_3$	6	$\Delta H_{d7} = +13.98 \pm 0.17$
$[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{Cl}_2](c) + \text{Solution A}_3 \rightarrow \text{Solution F}_1$	5	$\Delta H_{d8} = -20.53 \pm 0.34$
$\text{C}_{10}\text{H}_6(\text{OH})_2(c) + \text{Solution A}_2 \rightarrow \text{Solution A}_4$	5	$\Delta H_{d9} = +13.70 \pm 0.23$
$[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{Cl}_2](c) + \text{Solution A}_4 \rightarrow \text{Solution F}_2$	5	$\Delta H_{d10} = -16.28 \pm 0.54$
$\text{C}_{14}\text{H}_8(\text{OH})_2(c) + \text{Solution A}_2 \rightarrow \text{Solution A}_5$	6	$\Delta H_{d11} = +17.19 \pm 0.29$
$[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{Cl}_2](c) + \text{Solution A}_5 \rightarrow \text{Solution F}_3$	6	$\Delta H_{d12} = -13.75 \pm 0.78$
$[\text{W}(\eta\text{-C}_5\text{H}_5)_2\text{Cl}_2](c) + \text{Solution A}_3 \rightarrow \text{Solution F}_4$	5	$\Delta H_{d13} = +6.20 \pm 0.51$

Table 3  
Enthalpies of solution and reaction at 298.15 K

Reaction	Number of experiments	$\Delta H_{di}$ (kJ mol <sup>-1</sup> )
HCl · 4.38H <sub>2</sub> O (aq) + Solvent B → Solution B <sub>1</sub>	5	$\Delta H_{d14} = -11.01 \pm 0.22$
[Ti(η-C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> (O <sub>2</sub> C <sub>14</sub> H <sub>8</sub> )] (c) + Solution B <sub>1</sub> → Solution F <sub>5</sub>	5	$\Delta H_{d15} = -9.7 \pm 1.1$
H <sub>2</sub> O (l) + Solvent B → Solution B <sub>2</sub>	6	$\Delta H_{d16} = -2.386 \pm 0.085$
C <sub>14</sub> H <sub>8</sub> (OH) <sub>2</sub> (c) + Solution B <sub>2</sub> → Solution B <sub>3</sub>	5	$\Delta H_{d17} = +13.41 \pm 0.28$
[Ti(η-C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> (O <sub>2</sub> C <sub>14</sub> H <sub>8</sub> )] (c) + Solution B <sub>3</sub> → Solution F <sub>5</sub>	5	$\Delta H_{d18} = +13.32 \pm 0.40$

$$\Delta H_r(\text{IV}) = 2\Delta H_{d14} + \Delta H_{d15} - 11.10\Delta H_{d16} - \Delta H_{d17} - \Delta H_{d18} = +1.21 \pm 0.82 \text{ kJ mol}^{-1} \quad (7)$$

$$\Delta H_r(\text{V}) = 2\Delta H_{d14} + \Delta H_{d15} - 8.76\Delta H_{d16} - \Delta H_{d17} - \Delta H_{d18} = -37.5 \pm 1.6 \text{ kJ mol}^{-1} \quad (8)$$

The standard enthalpies of formation of the crystalline complexes (Table 4) were derived from the above enthalpies of reaction ( $\Delta H_r$ ) and the appropriate auxiliary data. Estimated values of the enthalpies of sublimation [20] and calculated values for  $\Delta H_f^\circ(\text{g})$  are also listed in Table 4.

### Discussion

To make an assessment of the metal–ligand bond strengths it is necessary to consider the thermochemical cycles **A** and **B**, where the stars indicate that the structure of the fragments remains unchanged from that in the respective complex, i.e., they are non-reorganized fragments.  $ER_1$ ,  $ER_3$ ,  $ER_L$  are the enthalpies of reorganization of these fragments.

The  $E$  terms are known as bond enthalpy terms and, as they represent the enthalpy of disruption of the bonds without any reorganization energy, they are a direct measurement of the bond strengths; the  $D$  values, the mean bond-dissociation enthalpies, are influenced by the reorganization energy of the fragments, hence it is more difficult to correlate these with other molecular parameters, and so they have less significance in structural terms.

For cycle **A**,

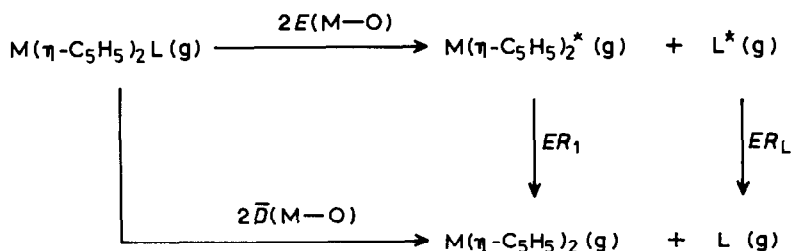
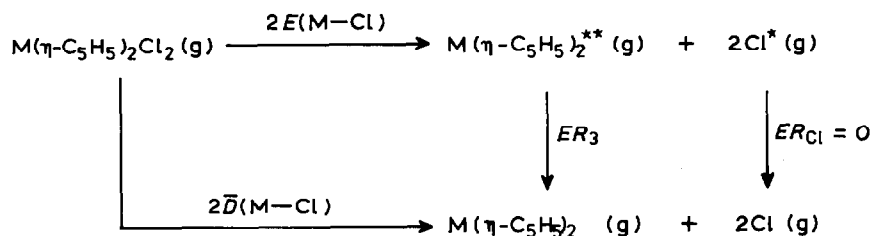
$$2\bar{D}(\text{M-O}) = 2E(\text{M-O}) + ER_1 + ER_L \quad (9)$$

$$= \Delta H_f^\circ [\text{M}(\eta\text{-C}_5\text{H}_5)_2, \text{g}] + \Delta H_f^\circ (\text{L}, \text{g}) - \Delta H_f^\circ \{ [\text{M}(\eta\text{-C}_5\text{H}_5)_2\text{L}], \text{g} \} \quad (9')$$

Table 4  
Standard enthalpies of formation,  $\Delta H_f^\circ(\text{c})$  and  $\Delta H_f^\circ(\text{g})$  in kJ mol<sup>-1</sup>

	$\Delta H_f^\circ(\text{c})$	$\Delta H_{\text{subl}}^\circ$	$\Delta H_f^\circ(\text{g})$
[Mo(η-C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> (O <sub>2</sub> C <sub>6</sub> H <sub>4</sub> )]	-130.6 ± 2.9	(100 ± 8) <sup>a</sup>	-30.6 ± 8.5
[Mo(η-C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> (O <sub>2</sub> C <sub>10</sub> H <sub>6</sub> )]	-80.3 ± 3.2	(135 ± 8) <sup>a</sup>	+54.7 ± 8.6
[Mo(η-C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> (O <sub>2</sub> C <sub>14</sub> H <sub>8</sub> )]	-53.3 ± 10.4	(145 ± 8) <sup>a</sup>	+91.7 ± 13.1
[W(η-C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> (O <sub>2</sub> C <sub>6</sub> H <sub>4</sub> )]	-112.8 ± 2.9	(104 ± 8) <sup>a</sup>	-8.8 ± 8.5
[Ti(η-C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> (O <sub>2</sub> C <sub>14</sub> H <sub>8</sub> )]	-322.6 ± 12.7	(165 ± 8) <sup>a</sup>	-157.6 ± 15.0

<sup>a</sup> Estimated values [20].

**Cycle A****Cycle B**

and, for cycle B,

$$\begin{aligned}
 2\bar{D}(\text{M-Cl}) &= 2E(\text{M-Cl}) + ER_3 + ER_{\text{Cl}}' & (10) \\
 &= \Delta H_f^\circ [M(\eta\text{-C}_5\text{H}_5)_2, \text{g}] + 2\Delta H_f^\circ (\text{Cl}, \text{g}) - \Delta H_f^\circ \{ [M(\eta\text{-C}_5\text{H}_5)_2\text{Cl}_2], \text{g} \} & (10')
 \end{aligned}$$

subtracting (10) from (9),

$$\begin{aligned}
 2\bar{D}(\text{M-O}) - 2\bar{D}(\text{M-Cl}) &= 2E(\text{M-O}) - 2E(\text{M-Cl}) + ER_1 + ER_L - ER_3 & (11) \\
 &= \Delta H_f^\circ (\text{L}, \text{g}) - 2\Delta H_f^\circ (\text{Cl}, \text{g}) - \{ \Delta H_f^\circ [M(\eta\text{-C}_5\text{H}_5)_2\text{L}](\text{g}) - & (11') \\
 & \qquad \qquad \qquad \Delta H_f^\circ [M(\eta\text{-C}_5\text{H}_5)_2\text{Cl}_2](\text{g}) \}
 \end{aligned}$$

Rearrangement of eqs. 11, taking in consideration that, by definition

$$ER_L = \Delta H_f^\circ (\text{L}, \text{g}) - \Delta H_f^\circ (\text{L}^*, \text{g}), \quad (12)$$

gives eq. 13:

$$\begin{aligned}
 2E(\text{M-O}) - 2E(\text{M-Cl}) &= 2\bar{D}(\text{M-O}) - 2\bar{D}(\text{M-Cl}) + (ER_3 - ER_1) - ER_L = & (13) \\
 & - 2\Delta H_f^\circ (\text{Cl}, \text{g}) - [ \Delta H_f^\circ [M(\eta\text{-C}_5\text{H}_5)_2\text{L}](\text{g}) - \Delta H_f^\circ [M(\eta\text{-C}_5\text{H}_5)_2\text{Cl}_2](\text{g}) ] \\
 & \qquad \qquad \qquad + (ER_3 - ER_1) + \Delta H_f^\circ (\text{L}^*, \text{g}) & (13')
 \end{aligned}$$

$\bar{D}(\text{M-O})$  and  $E(\text{M-O})$  can then be calculated from eqs. 11 and 13, respectively, provided that  $\bar{D}(\text{M-Cl})$ ,  $E(\text{M-Cl})$  and the standard enthalpies of formation and the reorganization energies there indicated, are known.

Table 5

Thermochemical values (in  $\text{kJ mol}^{-1}$ ) in complexes of the type  $[\text{M}(\eta\text{-C}_5\text{H}_5)_2\text{Cl}_2]$ 

M	$E(\text{M}-\text{Cl})^a$	$ER_3$	$\bar{D}(\text{M}-\text{Cl})$
Mo	$303.8 \pm 7.1$	$-82^b$	$262.8 \pm 7.1$
W	$347.3 \pm 0.8$	$-107^b$	$293.8 \pm 0.8$
Ti	$430.5 \pm 1.3$	$-10^c$	$425.5 \pm 1.3$

<sup>a</sup> Ref. 17. <sup>b</sup> Ref. 26. <sup>c</sup> Ref. 25.

It has sometimes been assumed [3,4,21–24] that values of  $\bar{D}(\text{M}-\text{Cl})$  in  $\text{M}(\eta\text{-C}_5\text{H}_5)_2\text{Cl}_2$  are equal to the mean bond dissociation enthalpies in  $\text{MCl}_n$  ( $n = 4$  for  $\text{M} = \text{Ti}$  and  $n = 6$  for  $\text{M} = \text{Mo}, \text{W}$ ). This assumption, which is supported by similarities between internuclear distances  $\text{M}-\text{Cl}$  bonds in the complexes and in  $\text{MCl}_n$  compounds [17], implies that  $ER_3 = 0$ , which has been shown to be implausible [20,25,26]. However, only  $E$  values should be correlated with bond lengths, particularly when large reorganization enthalpies are involved, and so a more sensible assumption must be that in eq. 14:

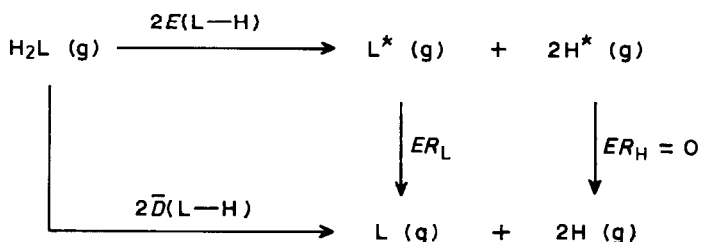
$$\{E(\text{M}-\text{Cl}) \text{ in } [\text{M}(\eta\text{-C}_5\text{H}_5)_2\text{Cl}_2]\} = \{\bar{D}(\text{M}-\text{Cl}) \text{ in } \text{MCl}_n\} \quad (14)$$

and this equation has been used in this paper. Use of this assumption gave the values in Table 5 [17]. The reorganization enthalpies of  $\text{M}(\eta\text{-C}_5\text{H}_5)_2$  fragments in  $[\text{M}(\eta\text{-C}_5\text{H}_5)_2\text{Cl}_2]$  complexes,  $ER_3$ , were obtained from extended Hückel molecular orbital calculations by Calhorda et al., for  $\text{M} = \text{Mo}, \text{W}$  [26] and  $\text{Ti}$  [25], and are reported in Table 5 together with the derived values for  $D(\text{M}-\text{Cl})$  in  $[\text{M}(\eta\text{-C}_5\text{H}_5)_2\text{Cl}_2]$  type complexes.

In order to use eq. 13' to calculate  $E(\text{M}-\text{O})$  values for the complexes studied in this work, it is necessary to know the values of  $ER_1$  for the various complexes and of  $\Delta H_f^\circ(\text{L}^*, \text{g})$ . The reorganization energy of the fragments  $\text{M}(\eta\text{-C}_5\text{H}_5)_2^{**}$  and  $\text{M}(\eta\text{-C}_5\text{H}_5)_2^*$  from the parent compounds  $[\text{M}(\eta\text{-C}_5\text{H}_5)_2\text{Cl}_2]$  and  $[\text{M}(\eta\text{-C}_5\text{H}_5)_2\text{L}]$ , respectively,  $ER_3$  and  $ER_1$ , will only have the same value if their structures are the same. Extended Hückel molecular orbital calculations by Calhorda et al. [25,26] show that the reorganization enthalpies are mainly dependent on the  $\eta(\text{C}_5\text{H}_5)\text{-M-}\eta(\text{C}_5\text{H}_5)$  angles ( $\theta$ ) and to a lesser extent on the metal–ring and C–C bond distances. Hoffman [27] showed that the most stable geometry for the  $\text{M}(\eta\text{-C}_5\text{H}_5)_2$  fragment of a metal with two  $d$  electrons (Ti) has an angle between the two  $\eta\text{-C}_5\text{H}_5$  rings close to  $140^\circ$ , and that for a metal with four  $d$  electrons (Mo, W) the corresponding angle is close to  $180^\circ$ . It was pointed out that in the cases where structures are known, the structures of the  $(\eta\text{-C}_5\text{H}_5)$  rings and the metal–ring bond distances are almost constant in  $[\text{M}(\eta\text{-C}_5\text{H}_5)_2\text{L}_2]$  complexes, but this is not the case for the  $\theta$  angles, and accounts for the importance of the reorganization enthalpies of the  $\text{M}(\eta\text{-C}_5\text{H}_5)_2$  fragments and their dependence on the respective  $\theta$  angles in the parent complexes. There are no published structures for the complexes studied in this work, but it is clear from the literature that the corrections  $(ER_3 - ER_1)/2$  for the calculation of the bond energy terms (eq. 13') in previously studied cases are less than  $-5 \text{ kJ mol}^{-1}$ , which is smaller than the uncertainty in the  $E(\text{M}-\text{L})$  values. In view of the impossibility of the calculation of the  $ER_1$  values for the complexes studied in this paper, owing to the absence of the necessary data, we have not made any estimates, and the calculated  $E(\text{M}-\text{O})$  values do not include

$(ER_3 - ER_1)/2$  corrections. In all cases in which this term has been properly calculated, it was small.

The calculation of  $\Delta H_f^\circ(L^*,g)$  can be made from eq. 15, where  $E(L-H)$  is a bond enthalpy term, as shown in cycle C.



### Cycle C

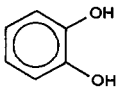
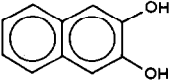
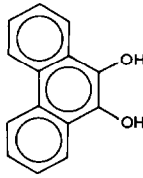
$$\Delta H_f^\circ(L^*,g) = 2E(L-H) - 2\Delta H_f^\circ(H,g) + \Delta H_f^\circ(H_2L,g) \quad (15)$$

$$\Delta H_f^\circ(L,g) = 2\bar{D}(L-H) - 2\Delta H_f^\circ(H,g) + \Delta H_f^\circ(H_2L,g) \quad (16)$$

$E(L-H)$  can be estimated by several well established methods: from the Laidler scheme [28,29], by the Sanderson method [30-32], or from a correlation between bond enthalpies and bond lengths. The calculated  $\Delta H_f^\circ(L^*,g)$  derived by this last approach is for the  $L^*$  fragment in the ligand, which is usually taken to be the same as in the  $ML_n$  molecule, since one assumes that the structure of  $L$  is identical in  $H_2L$  and in  $ML_n$ . In the present work the Laidler parameter  $E(O-H) = 451.2 \text{ kJ mol}^{-1}$  [33] was used, from which, with  $\Delta H_f^\circ(H,g) = 217.997 \pm 0.006 \text{ kJ mol}^{-1}$  [14]

Table 6

Standard enthalpies of formation, in the gaseous state, of the ligands and radicals

H <sub>2</sub> L	$\Delta H_f^\circ(g)$ (kJ mol <sup>-1</sup> )	
	H <sub>2</sub> L	L*
	$-267.8 \pm 1.7^a$	$198.6 \pm 1.7$
	$-181.3 \pm 2.7^b$	$285.1 \pm 2.7$
	$(-144 \pm 6)^c$	$322 \pm 6$

<sup>a</sup> Ref. 18. <sup>b</sup> Ref. 19. <sup>c</sup> Estimated [20].



Table 7

Bond enthalpy terms and difference on mean bond dissociation enthalpies

Complex	$E(\text{M-O})$ ( $\text{kJ mol}^{-1}$ )	$[\bar{D}(\text{M-O}) - \bar{D}(\text{O-H})]$ ( $\text{kJ mol}^{-1}$ )
$[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2(\text{O}_2\text{C}_6\text{H}_4)]$	$299 \pm 9$	$-193 \pm 9$
$[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2(\text{O}_2\text{C}_{10}\text{H}_6)]$	$300 \pm 9$	$-192 \pm 9$
$[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2(\text{O}_2\text{C}_{14}\text{H}_8)]$	$300 \pm 10$	$-192 \pm 10$
$[\text{W}(\eta\text{-C}_5\text{H}_5)_2(\text{O}_2\text{C}_6\text{H}_4)]$	$346 \pm 5$	$-158 \pm 5$
$[\text{Ti}(\eta\text{-C}_5\text{H}_5)_2(\text{O}_2\text{C}_{14}\text{H}_8)]$	$416 \pm 9$	$-40 \pm 9$

and the values of  $\Delta H_f^\circ(\text{H}_2\text{L},\text{g})$  (Table 6), the values for the  $\Delta H_f^\circ(\text{L}^*,\text{g})$  of the various ligands were calculated (Table 6).

To calculate the standard enthalpy of formation of the reorganized fragment L,  $\Delta H_f^\circ(\text{L},\text{g})$ , the mean dissociation energy,  $\bar{D}(\text{O-H})$ , is needed. In the literature, values are available for  $\bar{D}(\text{O-H})$  for eight aliphatic alcohols,  $\text{CH}_3\text{OH}$  to  $t\text{-C}_4\text{H}_9\text{OH}$ , in ethanoic, n-propanoic and n-butanoic acids, and for phenol and benzoic acid. There are no published values for compounds of the catechol type and so, in this work, we made no estimates because of the lack of a basis for them. Although it is not possible to calculate  $\bar{D}(\text{M-O})$  for the bent metallocenes presented on this work, it is possible to calculate a value of  $\{\bar{D}(\text{M-O})_{\text{complex}} - \bar{D}(\text{O-H})_{\text{ligand}}\}$ , by combining eqs. 11' and 16 to give eq. 17.

$$2\bar{D}(\text{M-O}) - 2\bar{D}(\text{O-H}) = 2\bar{D}(\text{M-Cl}) - \Delta H_f^\circ\{[\text{M}(\eta\text{-C}_5\text{H}_5)_2\text{L}],\text{g}\} + \Delta H_f^\circ\{[\text{M}(\eta\text{-C}_5\text{H}_5)_2\text{Cl}_2],\text{g}\} - 2\Delta H_f^\circ(\text{Cl},\text{g}) - 2\Delta H_f^\circ(\text{H},\text{g}) + \Delta H_f^\circ(\text{H}_2\text{L},\text{g}) \quad (17)$$

Taking the literature values (in  $\text{kJ mol}^{-1}$ ):  $\Delta H_f^\circ(\text{Cl},\text{g}) = 121.30 \pm 0.01$  [14],  $\Delta H_f^\circ\{[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{Cl}_2],\text{g}\} = 4.6 \pm 4.9$  [16],  $\Delta H_f^\circ\{[\text{W}(\eta\text{-C}_5\text{H}_5)_2\text{Cl}_2],\text{g}\} = 33.5 \pm 4.9$  [16] and  $\Delta H_f^\circ\{[\text{Ti}(\eta\text{-C}_5\text{H}_5)_2\text{Cl}_2],\text{g}\} = -266.0 \pm 8.9$  [17], and the other thermochemical quantities derived above, eq. 13' and 17 allow calculation of  $E(\text{M-O})$  and  $[\bar{D}(\text{M-O}) - \bar{D}(\text{O-H})]$ , respectively, and the results are listed in Table 7.

The values of  $[\bar{D}(\text{M-O}) - \bar{D}(\text{O-H})]$  are in close agreement for the molybdenum complexes, showing that either  $\bar{D}(\text{O-H})$  in the ligands and  $\bar{D}(\text{Mo-O})$  in these complexes are each constant or follow precisely the same trend in the free ligands and in the complexes. The  $\bar{D}(\text{M-O})$  values can only be derived when values of  $\bar{D}(\text{O-H})$  in the ligands become available. There is little profit in estimating  $\bar{D}(\text{O-H})$  values in these cases, not only because of the scarcity of good values on which to base the estimates, but also because a discussion of the derived  $\bar{D}(\text{M-O})$  values would necessarily involve discussion of the assumptions involved.

The  $E(\text{M-O})$  values can be considered in relation to the structures of the complexes, and for comparison, corresponding values for similar bonds in other complexes [23,24] are listed in Table 8; these data can appropriately be used for comparison because the derivation method was the same as that used in the present paper.

It is apparent that in the case of titanium complexes,  $E(\text{Ti-O})$  is approximately  $31 \text{ kJ mol}^{-1}$  less in phenanthrolyate complex than in phenolate and carboxylate complexes,  $E(\text{Mo-O})$  is approximately  $19 \text{ kJ mol}^{-1}$  less in the catecholate type complex than in the carboxylates, and  $E(\text{W-O})$  is approximately  $10 \text{ kJ mol}^{-1}$  less in the catecholate than in the carboxylates. In the catecholate type complexes, the

Table 8

Bond enthalpy terms in  $[M(\eta\text{-C}_5\text{H}_5)_2\text{L}_2]$ 

L	$E(\text{M-O})$ ( $\text{kJ mol}^{-1}$ )		
	M = Mo	M = W	M = Ti
$\text{C}_6\text{H}_5\text{OCO}$	$320 \pm 12$	$357 \pm 10$	$448 \pm 9$
$\text{CF}_3\text{OCO}$	$318 \pm 12$	$356 \pm 10$	$435 \pm 9$
$\text{CCl}_3\text{OCO}$			$448 \pm 9$
$\text{C}_6\text{H}_5\text{O}$			$455 \pm 9$
Average	319	356	447

ligand is bound to the metal through two oxygen atoms which are part of a 5-membered ring and some steric strain energy is expected, resulting in the differences given above. It is reasonable that the order of these strain energies are for  $\text{Ti} > \text{Mo} > \text{W}$ , because the bond lengths are in same the order  $r(\text{Ti-O}) < r(\text{Mo-O}) < r(\text{W-O})$ .

This work suggests that in  $[\text{Ti}(\eta\text{-C}_5\text{H}_5)_2(\text{phenanthroline})]$ , there is a steric strain-energy of ca.  $62 \text{ kJ mol}^{-1}$ , in  $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2(\text{catecholate})]$  this drops to ca.  $38 \text{ kJ mol}^{-1}$  and in  $[\text{W}(\eta\text{-C}_5\text{H}_5)_2(\text{catecholate})]$  falls further to ca.  $20 \text{ kJ mol}^{-1}$ . The trend in these values appears to be reasonable, but it would be unwise to place great significance upon the absolute values, since some of the auxiliary data used in the derivations are not of the highest quality and additional uncertainty arises because of the necessity of estimating enthalpies of sublimation, particular those of the complexes.

The available set of metal-oxygen, metal-sulfur, metal-halogen, metal-hydrogen and metal-alkyl bond-enthalpy values in bent metallocenes of molybdenum,

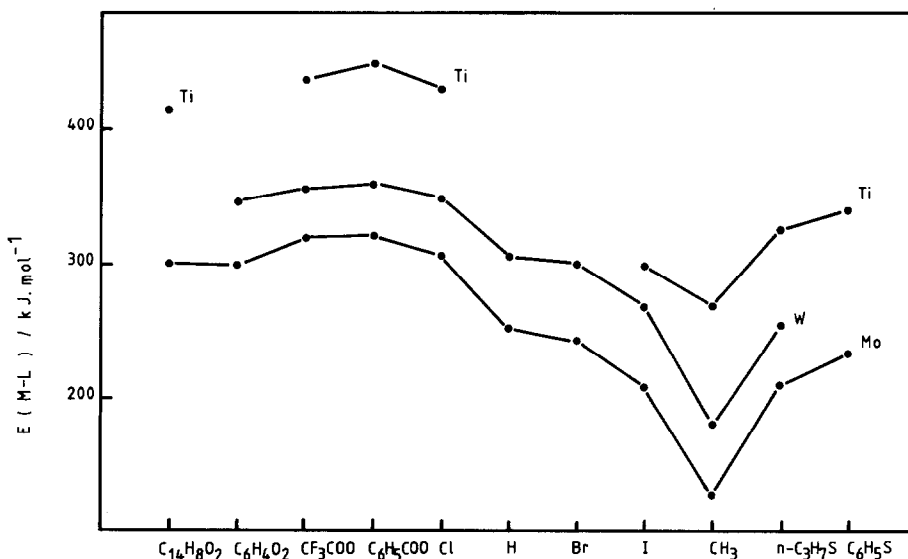


Fig. 1. Variation of  $E(\text{M-L})$  ( $\text{M} = \text{Mo}, \text{W}$  or  $\text{Ti}$ ) as a function of  $\text{L}$ .

tungsten and titanium are compared in Fig. 1, which includes the results of this work together with other bond-enthalpy terms from the literature [26,34].

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