

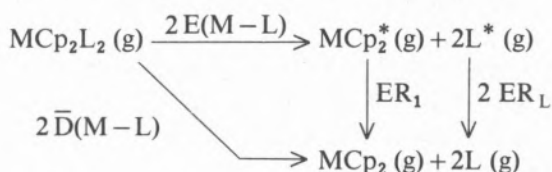


ON THE EVALUATION OF METAL-LIGAND "BOND STRENGTHS" IN $M(\eta-C_5H_5)_2L_2$ COMPLEXES

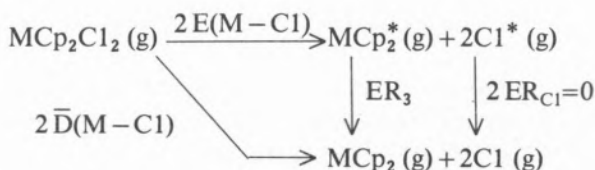
The methods of evaluating metal-ligand "bond strengths" in complexes $M(\eta-C_5H_5)_2L_2$ are discussed. Equations for the calculation of bond-enthalpy terms (E) and mean bond-disruption enthalpies (\bar{D}) are suggested. These equations contain parameters which might minimize the errors associated with some assumptions that have been used in previous articles.

1 — INTRODUCTION

We have been involved in a project concerned with the thermochemistry of MCp_2L_2 complexes (M = transition metal atom; $Cp = \eta-C_5H_5$; L = mono or polyatomic ligand) by using reaction-solution calorimetry (see, for example [1]). The main purpose of these studies has been the evaluation of metal-ligand bond strengths and the correlation of the obtained values with other molecular parameters such as metal-ligand bond lengths [2], ligand electronegativities [3], and ligand cone angles [4]. As discussed in an earlier paper [1] this task proved to be difficult. One of the problems we had to face was the meaning of the bond enthalpy values we were obtaining, i.e. how valid it was to regard them as measurements of metal-ligand bond strengths. Although this point was discussed in our paper [1] a full description of the calculation method was not given. It is therefore the objective of the present paper to analyze the equations we have been using in our thermochemical studies. Consider the thermochemical cycles A and B where the stars indicate that the fragments have the same structures they had in the respective complex, i.e. they are non-reorganized fragments. The energy changes associated with the reorganization reactions of these species are usually called *enthalpies of reorganization* (ER_1 , ER_3 , ER_L).



Cycle A



Cycle B

E and \bar{D} are known as *bond-enthalpy terms* and *mean bond-disruption enthalpies* respectively. From both cycles it can be noticed that only E values represent what is called "bond strengths". \bar{D} values are influenced by the reorganization enthal-

pies of the fragments and so attempts to correlate them to other molecular data may be meaningless. Equations (1) and (2) can be derived from cycles A and B⁽¹⁾:

$$2\bar{D}(M-L) = 2E(M-L) + ER_1 + 2ER_L = \\ = \Delta H_f^\circ(\text{MCp}_2, g) + 2\Delta H_f^\circ(L, g) - \\ - \Delta H_f^\circ(\text{MCp}_2L_2, g) \quad (1)$$

$$2\bar{D}(M-Cl) = 2E(M-Cl) + ER_3 = \\ = \Delta H_f^\circ(\text{MCp}_2, g) + 2\Delta H_f^\circ(Cl, g) - \\ - \Delta H_f^\circ(\text{MCp}_2Cl_2, g) \quad (2)$$

Subtracting (2) from (1) we obtain

$$\bar{D}(M-L) - \bar{D}(M-Cl) = \Delta H_f^\circ(L, g) - \\ - \Delta H_f^\circ(Cl, g) - \\ - [\Delta H_f^\circ(\text{MCp}_2L_2, g) - \\ - \Delta H_f^\circ(\text{MCp}_2Cl_2, g)]/2 \quad (3)$$

As, by definition

$$ER_L = \Delta H_f^\circ(L, g) - \Delta H_f^\circ(L^*, g) \quad (4)$$

we arrive at

$$E(M-L) - E(M-Cl) = \Delta H_f^\circ(L^*, g) - \\ - \Delta H_f^\circ(Cl, g) - [\Delta H_f^\circ(\text{MCp}_2L_2, g) - \\ - \Delta H_f^\circ(\text{MCp}_2Cl_2, g)]/2 + (ER_3 - ER_1)/2 \quad (5)$$

$\bar{D}(M-L)$ and $E(M-L)$ can be calculated through equations (3) and (5) once $\bar{D}(M-Cl)$ and $E(M-Cl)$ are known. As this is not the case is usual to assume that

$$E(M-Cl) = \bar{D}(M-Cl) \text{ in } \text{MC}l_n \\ = \bar{D}(M-Cl) \text{ in } \text{MCp}_2Cl_2 \quad (6)$$

This hypothesis is based on similar $M-Cl$ bond lengths in both molecules [1]. However, as stated above, only E values can correlate safely with bond lengths and so equations (6) should be replaced by

$$E(M-Cl) = \bar{D}(M-Cl) \text{ in } \text{MC}l_n \\ = E(M-Cl) \text{ in } \text{MCp}_2Cl_2 \quad (7)$$

(1) Using cycle B avoids the problem of estimating $\Delta H_f^\circ(\text{MCp}_2, g)$ (see equation (3)).

Accepting equations (6) is equivalent to say that $ER_3 = 0$ which is known to be wrong: $ER_3 < 0$ [5]. We shall therefore take hypothesis (7) as a starting point. In order to calculate $E(M-L)$ through equation (5) it is still necessary to obtain $\Delta H_f^\circ(L^*, g)$ and $(ER_3 - ER_1)$. All the other data are directly available in the literature or can be derived from experimental results.

2 — EVALUATION OF $\Delta H_f^\circ(L^*, g)$

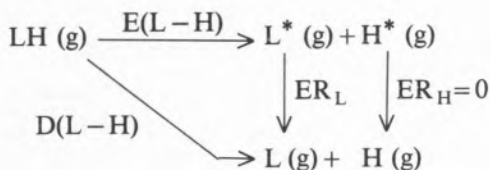
It is not possible to evaluate the enthalpy of formation of the fragment L^* from the complex MCp_2L_2 , but it is simple to obtain the enthalpy of formation of an equivalent fragment from a molecule LH . Therefore, if identical structures for L in MCp_2L_2 and LH are assumed the problem may be solved. Although the paucity of X-ray and neutron diffraction data prevents a suitable analysis of this assumption, it may be noticed that the average molecular parameters for most examples given in Table 1 are fairly similar. However this cannot be regarded as a general rule (see the case of $L = N_3$).

Table 1
Average molecular structural data for L in TiCp_2L_2 and LH .
Bond lengths in pm and bond angles in degrees

L	LH	TiCp_2L_2
C_6H_5	$r(C-C) = 139.7$ [6]	$r(C-C) = 139.0$ [7]
$\text{FeCp}(C_5H_4)$	$r(Fe-C) = 206.4$ $r(C-C) = 144.0$ [8]	$r(Fe-C) = 204$ $r(C-C) = 141$ [9]
N_3	$r(N-N) = 124.0$ 113.4 $N-N-N = 180$ [6]	$r(N-N) = 118$ 110 $N-N-N = 177$ [10]
NC_4H_4	$r(N-C) = 138.3$ $r(C-C) = 137.1$ 142.9 $C-N-C = 108.9$ $N-C-C = 108.1$ $C-C-C = 107.6$ [6]	$r(N-C) = 138$ $r(C-C) = 136$ 140 $C-N-C = 104.9$ $N-C-C = 110.8$ $C-C-C = 106.7$ [11]

From the thermochemical cycle C, where $E(L-H)$ is a *bond enthalpy term* and $D(L-H)$ is a *bond disruption enthalpy*⁽²⁾, it is possible to derive equation (8).

(2) $D(L-H)$ is usually known as *bond dissociation energy*.



Cycle C

$$\begin{aligned}
 \Delta H_f^\circ(\text{L}^*, \text{g}) &= E(L-H) - \Delta H_f^\circ(\text{H}, \text{g}) + \\
 &+ \Delta H_f^\circ(\text{LH}, \text{g})
 \end{aligned} \quad (8)$$

The enthalpy of formation of L^* can therefore be calculated once $E(L-H)$ is obtained. For this purpose it is possible to use at least three different methods: (1) The Laidler scheme; (2) the Sanderson model; (3) curves of bond enthalpy terms *versus* bond lengths.

2.1 — THE LAIDLER SCHEME

The Laidler scheme [12] is a widely used method to estimate enthalpies of formation of organic compounds in the gaseous state. Though generally less accurate [13] than the Benson group method [14-17], the Laidler scheme is more suitable for us because it deals with parameters called *bond energy terms* having an identical meaning to the E values, defined above.

COX and PILCHER [18] published a list of Laidler parameters for the estimation of enthalpies of atomization and formation. The values were selected so that they give the best agreement with results obtained by the Benson method. To our knowledge this is the most up to date recalculation of Laidler terms and it will therefore be used in the present paper.

2.2 — THE SANDERSON MODEL

Sanderson also proposed a method to calculate bond enthalpy terms⁽³⁾, based on his electronegativity scale [19, 20]. As stated previously [1] this model leads to wide disagreements with results obtained experimentally (e.g. enthalpies of atomization) in some cases, though it provides fairly accurate values in many others.

(3) In his own words: contributing bond energies [19].

2.3 — BOND ENTHALPY/BOND LENGTH CURVES

A third method to obtain bond enthalpy terms is the correlation of these parameters with bond lengths. HOUSECROFT *et al.* [21] quoted a few empirical relationships between the two quantities and decided to use the simple equation (where k and A are constants)

$$E = A r^{-k} \quad (9)$$

for metal-metal bonds in carbonyl clusters. Equations of identical form had already been applied by several authors. For example, SKINNER [22] reviewed this subject and suggested correlations for C-C, C-H, C-O, C-N, N-O, C-Cl, C-S, and S-O bonds.

Table 2 contains thermochemical and structural data of some molecules involving C-C and C-H bonds. The curve of fig. 1 was drawn by using the first five $E(\text{C-C})$ and $r(\text{C-C})$ values of Table 2, taken from a paper by CAVELL *et al.*⁽⁴⁾ [25]. From this curve we could derive other carbon-carbon bond enthalpy terms for new molecules (values

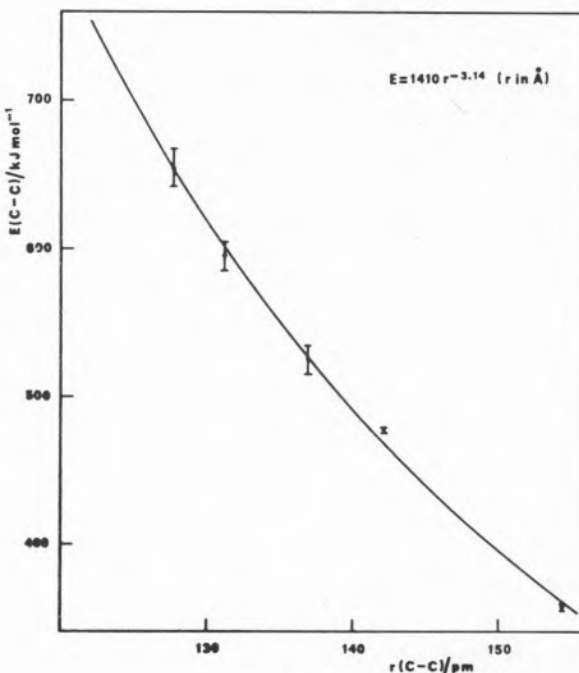


Fig. 1
Bond enthalpy/bond length curve for C-C bonds

(4) The curve of fig. 1 is also presented in Cavell's work.

Table 2
Thermochemical and structural data for C—C and C—H bonds (see text for explanations). Enthalpy values in kJ mol⁻¹ and bond lengths in pm

Substance	$\Delta H_f^\circ(\text{g})^{(a)}$	$\Delta H_a^{(b)}$	$E(\text{C—C})^{(d)}$	$r(\text{C—C})^{(d)}$	$E(\text{C—H})$	$r(\text{C—H})$
Diamond	—	714.81 ^(c)	357.4	154.4	—	—
Graphite	—	716.67	477.8	142.1	—	—
b $^3\Sigma_g^-, \text{C}_2$	—	—	525.5 ± 10	136.9	—	—
a $^3\Pi_u, \text{C}_2$	—	—	595 ± 10	131.2	—	—
$^1\Sigma_g^+, \text{C}_3$	—	—	655 ± 13	127.7	—	—
CH ₄	-74.5 ± 0.4	1663.2	—	—	415.8	109.40 ^(e)
C ₂ H ₂	228.0 ± 1.0	1641.3	(779)	120.8 ^(f)	431	105.8 ^(f)
C ₂ H ₄	52.2 ± 1.2	2253.1	(565)	$133.8 \pm 0.1^{(e)}$	422	$108.7 \pm 0.2^{(e)}$
C ₂ H ₆	-84.0 ± 0.2	2825.3	(368)	$153.4 \pm 0.2^{(e)}$	410	$109.5 \pm 0.2^{(e)}$
C ₆ H ₆	82.9 ± 0.3	5525.1	(494)	$139.7 \pm 0.1^{(g)}$	427	$108.4 \pm 0.5^{(g)}$

(a) Enthalpies of formation taken from Sussex — N.P.L. Tables [23]

(b) Enthalpies of formation of the elements taken from CODATA [24]

(c) Values of $\Delta H_f^\circ(\text{C, di})$ taken from COX and PILCHER book [18]

(d) First five values quoted from CAVELL *et al.* [25]

(e) Values taken from [27]

(f) Values taken from [28]

(g) Values taken from [6]

in parentheses) after knowing their respective carbon-carbon lengths. These results, together with the enthalpies of atomization (ΔH_a) were used to evaluate $E(\text{C—H})$ in each case and to obtain fig. 2. The straight line defined in this figure was assumed by SKINNER almost forty years ago [22]. It may be noticed that the errors caused by this assumption are not large especially if we consider the uncertainties in $r(\text{C—H})$. On the other hand the $E(\text{C—H})$ for acetylene does not seem very reliable as it was derived from an $E(\text{C—C})$ value obtained by an extrapolation of the curve of fig. 2.

The usefulness of the bond enthalpy/ bond length method is apparent from the two examples chosen to illustrate it. However this is not always so. For example the method cannot be applied with the same confidence to N—H and N—N bonds. The $E(\text{N—H})/r(\text{N—H})$ curve can be drawn from data of NH₃, NH₂, and NH and then used to obtain e.g. $E(\text{N—H})$ in hydrazine. This value and $\Delta H_a(\text{N}_2\text{H}_4)$ give $E(\text{N—N})$, which, together with

data from N₂ and N₃, is, in turn, used to obtain $E(\text{N—N})/r(\text{N—N})$ curve. The first difficulty of this procedure is self-evident as both curves are defined with only three points. Secondly the quality of some of the data can also be argued, particularly in the case of N₃, whose enthalpy of formation is still the subject of controversy [26]. The uncertainties in some bond lengths should also be considered: even the relatively small error assigned to $r(\text{N—H})$ in NH₂, *ca.* ± 0.5 pm [6], becomes very important when defining the curve. Of course the situation is much less serious in N—H bonds than in N—N bonds because $E(\text{N—N})/r(\text{N—N})$ curve is rather steep and therefore small errors in $r(\text{N—N})$ can lead to large errors in $E(\text{N—N})$.

Fortunately in our experimental work we have only been dealing with ligands involving L—H bonds and for these the method is satisfactory, even in the case of N—H bonds. It also provides reliable terms for O—H and S—H bonds — a fact that should be expected as these bond lengths are fairly constant in different molecules.

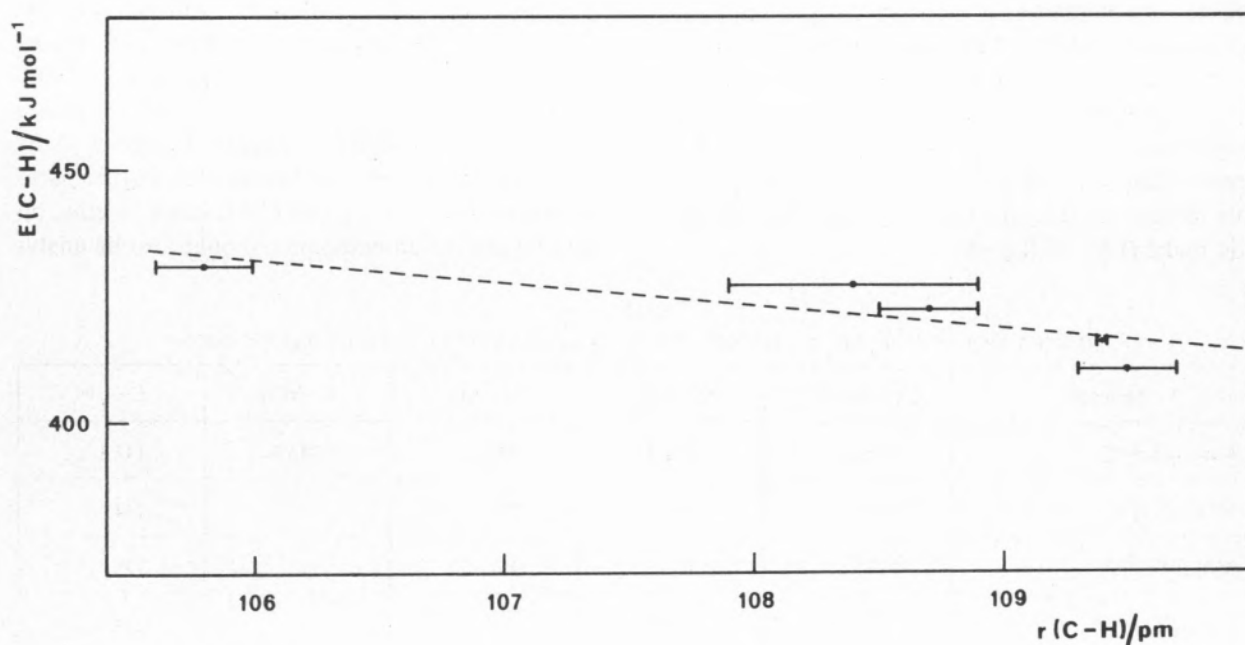


Fig. 2
Bond enthalpy/bond length curve for C-H bonds

2.4 — COMPARISON OF THE METHODS

The enthalpy of atomization of a molecule can be calculated by summing up all the bond enthalpy terms for that molecule. These terms can in principle be obtained from any of the three methods described. The question to be answered is therefore whether they yield identical values for the same bond. Although a throughout analysis of this point is beyond the aim of the present paper⁽⁵⁾ it is possible to make an idea of the agreement between the methods from the few examples given in Table 3, all involving C-H bonds. It is noticed that the Laidler and graphical methods give fairly identical values for C-H bonds and therefore we may consider any of them for evaluating $\Delta H_f^\circ(L^*, g)$ through equation (8). As a rule we still prefer to use the Laidler method because it is the most reliable. Only in cases where it is doubtful which parameter to select, such as $E(CpFeC_5H_4-H)$ [2] do we apply bond enthalpy/ bond length curves.

Table 3

Bond enthalpy terms obtained from the three methods.
Values in $kJ\ mol^{-1}$

Bond	E(Laidler) ^(a)	E(graphical) ^(b)	E(Sanderson) ^(c)
CH ₃ -H	(410.8)	415.8	413
CHC-H	435.9	431	422
CH ₂ CH-H	423.4	422	414
CH ₃ CH ₂ -H	410.8	410	412
C ₆ H ₅ -H	420.6	427	413

(a) There is no Laidler parameter for CH₃-H. The closest value is $E(C-H)_p = 410.8\ kJ\ mol^{-1}$. All Laidler terms were quoted from [18].

(b) Values from Table 2.

(c) Values recalculated by SANDERSON method. This author recommends $E(C_6H_5-H) = 407\ kJ\ mol^{-1}$ [20].

3 — EVALUATION OF (ER_3-ER_1)

When fragments MCp_2^* from complexes MCp_2Cl_2 and MCp_2L_2 have identical structures we can consider $(ER_3-ER_1)=0$ (see cycles A and B). This is

(5) It is desirable a revision and an extension of SKINNER'S work [22] to allow a meaningful comparison between the methods. This is presently being done.

indeed what happens for some MCp_2L_2 compounds presented in Table 4. In other examples, however, we notice large variations of $\text{Cp}-\text{M}-\text{Cp}$ angles. When the ligand L is a strong σ -donor or a weak π -acceptor the $\text{Cp}-\text{M}-\text{Cp}$ angles are considerably greater than $\text{Cp}-\text{M}-\text{Cp}$ angles in MCp_2Cl_2 [29]. For these cases it seems unwise to use equation (5) and make $(\text{ER}_3 - \text{ER}_1) = 0$.

A correct use of equation (5) will be possible when a plot of reorganization enthalpies *versus* $\text{Cp}-\text{M}-\text{Cp}$ angles is available for each metal⁽⁶⁾. It will then be easy to correct all $E(\text{M}-\text{L})$ values determined so far if the molecular structures of the complexes are known. The influence of other parameters, such as $\text{M}-\text{Cp}$ and $\text{C}-\text{C}$ bond lengths, on the reorganization enthalpies should also be analy-

Table 4
Structural data for MCp_2L_2 complexes ($\text{M} = \text{Mo}, \text{Ti}$). Bond lengths in pm and bond angles in degrees

Molecule	$\text{Cp}-\text{M}-\text{Cp}$	$\text{M}-\text{Cp}^{(a)}$	$\text{M}-\text{C}^{(a)}$	$\text{C}-\text{H}^{(b)}$	$\text{C}-\text{C}^{(b)}$
MoCp_2H_2 [30]	145.8	194.4	229	107.7	142.1
MoCp_2D_2 [31]	148.2	196	232		144
MoCp_2Cl_2 [31]	130.5	198	231		138
TiCp_2Cl_2 [32]	130.97	205.9			138
$\text{TiCp}_2(\text{CO})_2$ [33]	138.6		235		
$\text{TiCp}_2(\text{NC}_4\text{H}_4)_2$ [11]	128.5		239		
$\text{TiCp}_2(\text{SC}_6\text{H}_5)_2$ [34]	132.4	207	239	109	140.5
$\text{TiCp}_2(\text{C}_5\text{H}_5)_2$ [35]	129.9	207.8	238.1	89	136.5
$\text{TiCp}_2(\text{C}_6\text{H}_5)_2$ [7, 36]	135.9		231		134
TiCp_2Fc_2 [9] ^(c)	131.2		241		141
$\text{TiCp}_2(\text{N}_3)_2$ [10]	132.2	204.5	235-239		134-145

(a) $\text{M}-\text{Cp}$ is metal-ring centroid distance and $\text{M}-\text{C}$ is metal-carbon distance. Both are average values.

(b) Average values (except for $\text{TiCp}_2(\text{N}_3)_2$) of $\text{C}-\text{H}$ and $\text{C}-\text{C}$ bond lengths in the $\eta-\text{Cp}$ rings bonded to Mo or Ti.

(c) Fc = ferrocenyl.

In fact, extended Hückel molecular orbital calculations made by HOFFMANN *et al.* [5] reveal that the energy change associated with the reorganization of MoCp_2 and WCp_2 fragments from an angle $\text{Cp}-\text{M}-\text{Cp} = 130^\circ$ to 145° is about -0.437 eV or -42 kJ mol⁻¹ (figs. 3 and 4). 145° and 130° are close to the $\text{Cp}-\text{Mo}-\text{Cp}$ angles for MoCp_2H_2 and MoCp_2Cl_2 respectively. Therefore, as predicted in a previous paper [1], the published result for $E(\text{Mo}-\text{H})$, calculated on the basis of $(\text{ER}_3 - \text{ER}_1) = 0$, must be about 21 kJ higher than the correct value. An identical excess may be assumed for $E(\text{W}-\text{H})$, though in this case we are not aware of reported molecular structures for the complexes.

sed, although it is reasonable to expect that bond angle variations account for the largest fraction of the energy changes.

4 — CONCLUSIONS

In our previous thermochemical studies on MCp_2L_2 complexes we have always taken hypothesis (6) as the starting point. The present method of evaluating bond-enthalpy terms and mean bond-disruption enthalpies by considering relations (7) and also the reorganization enthalpies of the fragments

(6) This work is presently being done in our laboratory.

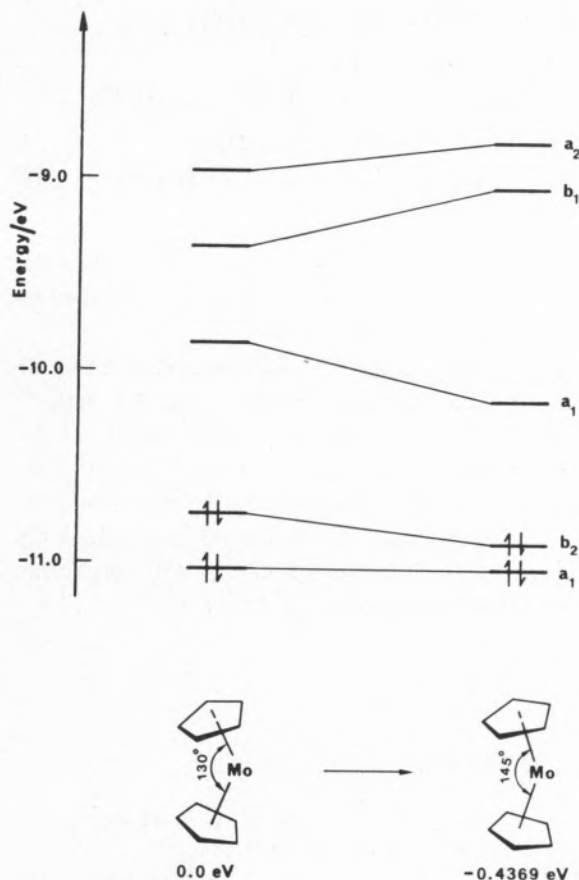


Fig. 3

Energy of $MoCp_2$ orbitals for two values of $Cp-Mo-Cp$ angle [5]. $Mo-Cp$ and $C-C$ bond lengths were taken as 215 and 142 pm respectively

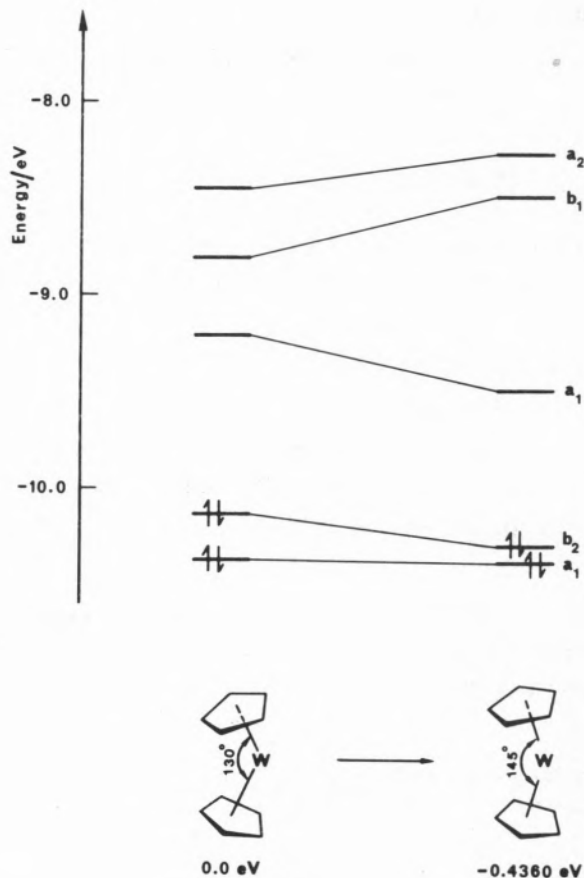


Fig. 4

Energy of WCp_2 orbitals for two values of $Cp-W-Cp$ angle [5]. $W-Cp$ and $C-C$ bond lengths were taken as 220 and 142 pm respectively

MCp_2 and L prevents some drastic approximations made in the past, such as the constancy of $\bar{D}(M-Cp)$ values for all MCp_2L_2 complexes of a given metal.

By using equations (2) and (3) it is now possible to evaluate the error associated with assumption (6). We obtain

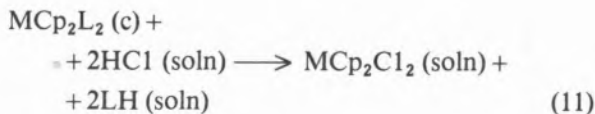
$$\begin{aligned} \bar{D}(M-L) = & E(M-C1) + ER_3/2 + \Delta H_f^\circ(L, g) - \\ & - \Delta H_f^\circ(C1, g) - [\Delta H_f^\circ(MCp_2L_2, g) - \\ & - \Delta H_f^\circ(MCp_2C1_2, g)]/2 \end{aligned} \quad (10)$$

If we make $ER_3=0$ the values of $\bar{D}(M-L)$ are higher (by $ER_3/2$) than they should be, since $ER_3 < 0$. (According to LAUHER and HOFFMANN

[29] the most stable configuration of a fragment MCp_2 ($M=Mo, W$) corresponds to an angle $Cp-M-Cp$ of 180°). They can be corrected once the curves reorganization enthalpies/ $Cp-M-Cp$ bond angles are established.

As we have shown equations (5) and (10) can be used to recalculate $E(M-L)$ and $\bar{D}(M-L)$ values. However, as stated in an early paper [1], the equations overestimate the uncertainty intervals of E and \bar{D} because they contain twice the error associated with $\Delta H_f^\circ(LH, c/\ell)$: one included in $\Delta H_f^\circ(L^*, g)$ or $\Delta H_f^\circ(L, g)$ and other in $\Delta H_f^\circ(MCp_2L_2, g)$. That is why we prefer to use new equations directly derived from the experimental values of enthalpies of reaction and solution.

In most of the complexes studied so far [1] the reactions whose enthalpies (ΔH_r) were determined with the calorimeter can be described by



To obtain $\Delta H_f^\circ(\text{MCp}_2\text{L}_2, \text{c})$ was also necessary to measure the enthalpies of solution of the complex $\text{MCp}_2\text{Cl}_2(\Delta H_{d1})$ and the compound $\text{LH}(\Delta H_{d2})$. Using all these values it is simple to arrive at

$$\begin{aligned} \bar{D}(\text{M}-\text{L}) = & E(\text{M}-\text{Cl}) + E\text{R}_3/2 + \\ & + (\Delta H_r - \Delta H_{d1} - 2\Delta H_{d2})/2 + \\ & + [\Delta H_s^\circ(\text{MCp}_2\text{Cl}_2) - \Delta H_s^\circ(\text{MCp}_2\text{L}_2)]/2 - \\ & - \Delta H_f^\circ(\text{LH c}/\ell) + \Delta H_f^\circ(\text{HCl, soln}) + \\ & + \Delta H_f^\circ(\text{L, g}) - \Delta H_f^\circ(\text{Cl, g}) \end{aligned} \quad (12)$$

From cycle C and equation (13) we obtain $\Delta H_f^\circ(\text{L, g})$ given in terms of the enthalpy of sublimation or vaporization of $\text{LH}(\Delta H_v^\circ)$:

$$\Delta H_f^\circ(\text{LH, g}) = \Delta H_v^\circ(\text{LH}) + \Delta H_f^\circ(\text{LH, c}/\ell) \quad (13)$$

$$\begin{aligned} \Delta H_f^\circ(\text{L, g}) = & D(\text{L}-\text{H}) - \Delta H_f^\circ(\text{H, g}) + \\ & + \Delta H_v^\circ(\text{LH}) + \Delta H_f^\circ(\text{LH, c}/\ell) \end{aligned} \quad (14)$$

Introducing this equation in (12) we finally obtain:

$$\begin{aligned} \bar{D}(\text{M}-\text{L}) = & E(\text{M}-\text{Cl}) + E\text{R}_3/2 + \\ & + (\Delta H_r - \Delta H_{d1} - 2\Delta H_{d2})/2 + \\ & + [\Delta H_s^\circ(\text{MCp}_2\text{Cl}_2) - \Delta H_s^\circ(\text{MCp}_2\text{L}_2)]/2 + \\ & + \Delta H_f^\circ(\text{HCl, soln}) + D(\text{L}-\text{H}) - \\ & - \Delta H_f^\circ(\text{H, g}) + \Delta H_v^\circ(\text{LH}) - \Delta H_f^\circ(\text{Cl, g}) \end{aligned} \quad (15)$$

Although this equation is equivalent to (10) it does not contain the enthalpy of formation of LH but its enthalpy of sublimation or vaporization. Therefore the use of equation (15) allows the evaluation of $\bar{D}(\text{M}-\text{L})$ even when $\Delta H_f^\circ(\text{LH, c}/\ell)$ is unknown. This can be an important advantage because ΔH_v° or ΔH_s° are quantities usually easier to measure or to estimate than ΔH_f° .

It is possible to derive an equation identical to (15) for $E(\text{M}-\text{L})$ by eliminating $\Delta H_f^\circ(\text{L}^*, \text{g})$:

$$\begin{aligned} E(\text{M}-\text{L}) = & E(\text{M}-\text{Cl}) + (E\text{R}_3 - E\text{R}_1)/2 + \\ & + (\Delta H_r - \Delta H_{d1} - 2\Delta H_{d2})/2 + \\ & + [\Delta H_s^\circ(\text{MCp}_2\text{Cl}_2) - \Delta H_s^\circ(\text{MCp}_2\text{L}_2)]/2 + \\ & + \Delta H_f^\circ(\text{HCl, soln}) + E(\text{L}-\text{H}) - \\ & - \Delta H_f^\circ(\text{H, g}) + \Delta H_v^\circ(\text{LH}) - \Delta H_f^\circ(\text{Cl, g}) \end{aligned} \quad (16)$$

the conclusions being the same as for equation (15). When LH is a gas the term ΔH_v° is cancelled in equations (15) and (16).

Finally, in conclusion, we wish to emphasize that in order to make the best possible use of the thermochemical data for MCp_2L_2 complexes, i.e. to evaluate metal ligand "bond-strengths" using equations (15) and (16), it is essential to have available the following data: (1) molecular structures, (2) bond enthalpy/ bond length curves, (3) reorganization enthalpies for the MCp_2^* fragments⁽⁷⁾.

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(7) The structural studies of MCp_2^* fragments are even more important in the case of $\text{MCp}_2\text{L}^1\text{L}^2$ complexes ($\text{L}^1 \neq \text{L}^2$) as will be discussed in a future communication.

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RESUMO

Analisa-se os métodos de cálculo de "energias de ligação" metal-ligando em complexos do tipo $M(\eta-C_5H_5)_2L_2$. Sugerem-se equações para a determinação de termos de entalpia de ligação (E) e de entalpia de dissociação média (\bar{D}). Essas equações contêm parâmetros que poderão minimizar os erros inerentes a algumas aproximações, até agora adoptadas, nos métodos de cálculo referidos.