Journal of Organometallic Chemistry, 335 (1987) 71–83
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Estimation of standard enthalpies of formation of crystalline inorganic and organometallic complexes

Alberto R. Dias, José A. Martinho Simões*, Clementina Teixeira,
Centro de Química Estrutural, Complexo I, Instituto Superior Técnico, 1096 Lisboa Codex (Portugal)

Claudio Airoldi and Aécio P. Chagas
Instituto de Química, Universidade Estadual de Campinas, Caixa Postal 6154, 13100 Campinas, S. Paulo (Brazil)

(Received April 21st, 1987)

Abstract

Good linear correlations have been found between standard enthalpies of formation of crystalline inorganic and organometallic complexes MX_nL_m and enthalpies of formation of ligands L or LH in their standard reference state. These correlations may be used to estimate enthalpies of formation of new complexes.

Introduction

A major concern in thermochemistry has been the development of methods for estimating standard enthalpies of formation. Organic molecules are the only ones for which it is possible to make reliable predictions of those quantities. Schemes devised by Laidler, by Benson and Buss, by Allen, by Pedley et al., and others [1–4], yield good results for $\Delta H_f^0(g)$ of many organic molecules. In addition, theoretical calculations of enthalpies of formation have been made for a large number of organic species, and the agreement with experiment is often satisfactory [5]. It is usually simple to obtain $\Delta H_f^0(l)$ from $\Delta H_f^0(g)$, since many empirical methods for estimating enthalpies of vaporization are available [6*].

The situation for organic molecules contrasts with the scarcity of prediction methods for inorganic and organometallic substances. Attempts to develop suitable procedures for inorganic compounds have been made by Hisham and Benson [7], Bratsch and Lagowski [8], and Sanderson [9]. For non-transition organometallic compounds, methods similar to those used for organic molecules can in principle be

---

* This and other references marked with asterisks indicate notes occurring in the list of references.

0022-328X/87/$03.50

applied [10], but the relatively small number of reliable experimental values of enthalpies of formation limits the number of available "terms". Theoretical methods have been used for these organometallic compounds, but their accuracy also suffers from the scarcity of experimental data [11].

One possible approach for estimating enthalpies of formation of organo-transition metal complexes is basically an extension of the Laidler scheme [12]. This method relies, however, on assumptions that are often difficult to assess, such as the transferability of bond enthalpies. In addition, the number of metal–ligand bond enthalpy terms presently available is rather small. Therefore, although there is evidence that the method may be of general use, it is desirable to look for alternatives. One of them is considered in this paper, and involves a correlation between the standard enthalpies of formation of crystalline metal compounds MX_nL_m and the enthalpies of formation of ligands L or LH in their standard reference state (rs), i.e. their stable physical state at 298.15 K and 1 atm. This correlation has been tested for transition metal compounds of the type MCp_2L_n (M = Ti, Mo, W; Cp = η^5-C_5H_5; L = H, alkyl, aryl, alkoxy, azobenzene, etc.; $n = 1$ or 2), $Cr(CO)_3L$, CrL_2 (L = η^6-arene), $Mn(CO)_5L$ (L = H, CH_3, C_6H_5, etc.), and adducts $MX_2 \cdot nL$ (M = Hg, Zn; X = halogen; L = Lewis base; $n = 1$ or 2). Thermochemical data for L or LH were taken from the Sussex-N.P.L. Tables [13] unless otherwise indicated.

Bis-cyclopentadienyl complexes

The thermochemistry of complexes MCp_2L_2 has been studied for several years. Standard enthalpies of formation of the crystalline solids are now available for over fifty complexes of titanium, molybdenum, and tungsten. Most of these data are summarized in three recent papers [12b, 12d, 14].

A plot of $\Delta H_f^0(TiCp_2L_2,c)$ versus $\Delta H_f^0(LH,rs)$ is shown in Fig. 1 [15*]. Two straight lines are drawn: one through points 10–21 (involving complexes containing titanium–carbonyl, titanium–oxygen and titanium–sulfur bonds) and the other through points 3–9 (complexes with titanium–carbon σ bonds). The least squares analyses of those two lines led to equations 1 [16*] and 2, respectively, with correlation factors of 0.9990 and 0.9996 (the uncertainties shown are standard deviations).

$$\Delta H_f^0(TiCp_2L_2,c) = (2.034 \pm 0.029)\Delta H_f^0(LH,rs) - (55.4 \pm 10.9) \qquad (1)$$

$$\Delta H_f^0(TiCp_2L_2,c) = (2.046 \pm 0.027)\Delta H_f^0(LH,rs) + (149.9 \pm 6.8) \qquad (2)$$

One point that deserves discussion concerns the slope of the two lines. Let us suppose that the correlation indicated by eq. 1 and 2 is perfect, i.e. 3, where a and b are constants, is obeyed. When this expression is compared with eq. 5, which is the enthalpy balance for reaction 4, two conclusions can be drawn. First, the slope has a value of 2, as a result of the number of ligands L bonded to the metal center. Second, for a given X (e.g. X = Cl), $b = -\Delta H^0(4) + \Delta H_f^0(TiCp_2X_2,c) - 2\Delta H_f^0(HX,rs)$, i.e $\Delta H^0(4)$ is constant for a series of ligands L.

$$\Delta H_f^0(TiCp_2L_2,c) = a\Delta H_f^0(LH,rs) + b \qquad (3)$$

$$TiCp_2L_2(c) + 2HX(rs) = TiCp_2X_2(c) + 2LH(rs) \qquad (4)$$

$$\Delta H_f^0(TiCp_2L_2,c) = 2\Delta H_f^0(LH,rs) - \Delta H^0(4) + \Delta H_f^0(TiCp_2X_2,c) - 2\Delta H_f^0(HX,rs) \qquad (5)$$

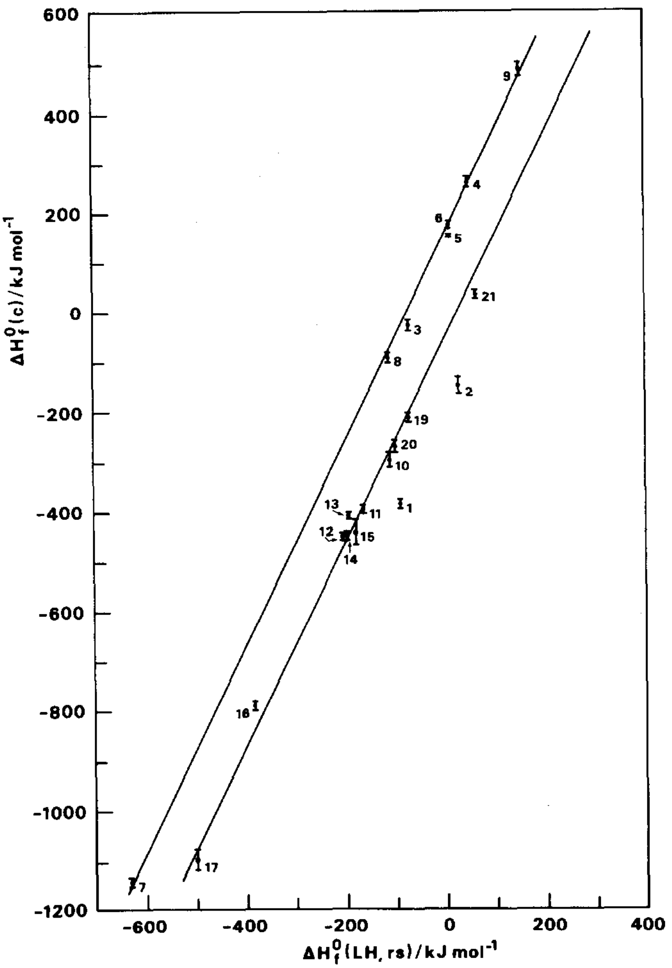

Fig. 1. $\Delta H_f^0(TiCp_2L_2,c)$ vs. ΔH_f^0(LH,rs) or ΔH_f^0(L,rs). Point numbers correspond to the following ligands: 1 = Cl, 2 = I, 3 = CH_3, 4 = C_6H_5, 5 = 3-$CH_3C_6H_4$, 6 = 4-$CH_3C_6H_4$, 7 = 4-$CF_3C_6H_4$, 8 = 4-$CH_3OC_6H_4$, 9 = $(C_5H_5)Fe(C_5H_4)$, 10 = CO, 11 = C_6H_5O, 12 = 2-$CH_3C_6H_4O$ 13 = 3-$CH_3C_6H_4O$, 14 = 4-$CH_3C_6H_4O$, 15 = 2-ClC_6H_4O, 16 = C_6H_5COO, 17 = CCl_3COO, 18 = CF_3COO (not represented in the figure), 19 = C_2H_5S, 20 = n-C_3H_7S, 21 = C_6H_5S.

Scheme 1 relates $\Delta H^0(4)$ to $\Delta H_g^0(4)$, the enthalpy change of reaction 4 in the gase phase for X = Cl (ΔH^0_{S1}, ΔH^0_{S2} and ΔH^0_V are sublimation or vaporization enthalpies). When $\Delta H_g^0(4)$ is expressed in terms of bond dissociation enthalpies and this is introduced in Scheme 1, eq. 6 is obtained. As discussed above, a linear

$$\begin{tikzcd}
TiCp_2L_2(c) + 2HCl(g) \arrow[r, phantom, "\overset{\Delta H^0(4)}{=}"] \arrow[d, "\Delta H^0_{S1}" left] & TiCp_2Cl_2(c) + 2LH(rs) \arrow[d, "\Delta H^0_{S2}" left] \\
TiCp_2L_2(g) + 2HCl(g) \arrow[r, phantom, "\overset{\Delta H^0_g(4)}{=}"] & TiCp_2Cl_2(g) + 2LH(g)
\end{tikzcd}$$

$\downarrow 0$ (for 2HCl) $\qquad \downarrow 2\Delta H^0_V$ (for 2LH)

Scheme 1

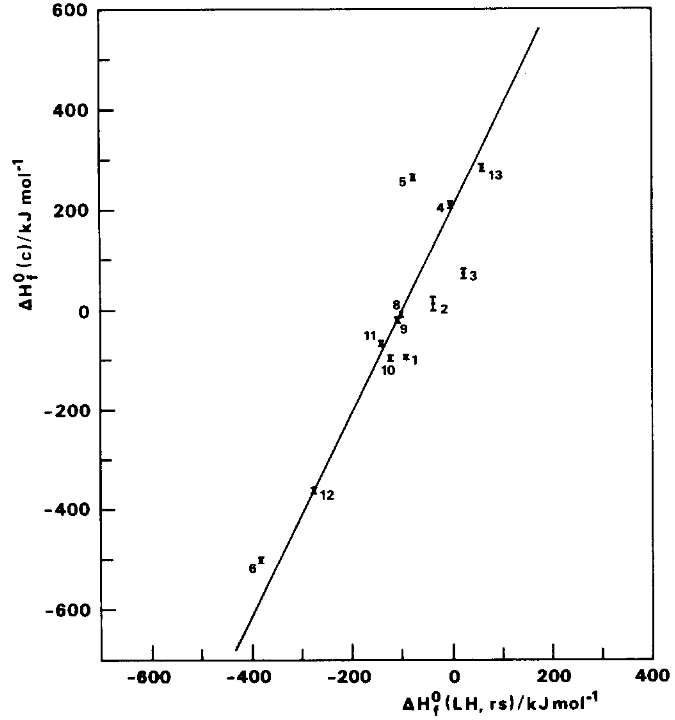

Fig. 2. $\Delta H_f^0(\text{MoCp}_2\text{L}_2,\text{c})$ vs. $\Delta H_f^0(\text{LH,rs})$. Point numbers correspond to the following ligands: 1 = Cl, 2 = Br, 3 = I, 4 = H, 5 = CH_3 6 = C_6H_5COO, 7 = CF_3COO (not represented in the figure), 8 = n-C_3H_7S, 9 = i-C_3H_7S, 10 = n-C_4H_9S, 11 = t-C_4H_9S, 12 = n-$C_{10}H_{21}S$, 13 = C_6H_5S.

$$\Delta H^0(4) = \left[2\bar{D}(\text{Ti}-\text{L}) - 2\text{D}(\text{L}-\text{H})\right] + \left[\Delta H^0_{\text{S1}} - 2\Delta H^0_{\text{V}}\right] \\ + \left[2D(\text{H}-\text{Cl}) - 2\bar{D}(\text{Ti}-\text{Cl}) - \Delta H^0_{\text{S2}}\right] \quad (6)$$

correlation (eq. 3) implies a constant $\Delta H^0(4)$ for a series of ligands L. Since the third bracketed term in eq. 6 is also constant, there are two possibilities, namely either the bond dissociation enthalpy difference and the vaporization enthalpy difference are constant or both differences depend on the ligand L but their sum remains constant. Transition metal–ligand bond dissociation enthalpies and ligand–hydrogen bond dissociation enthalpies often follow similar trends. On the other hand, the enthalpy of sublimation of the complex $TiCp_2L_2$ may reflect the enthalpy of vaporization of LH, so that differences $\Delta H^0_{\text{S1}} - 2\Delta H^0_{\text{V}}$ are nearly constant.

The correlations found for the titanium complexes (Fig. 1) are not "perfect". They show, however, some similarity to eq. 3; in particular the slope is very close to that expected on the basis of the preceding discussion. Differences between experimental and calculated enthalpies of formation are usually less than ca. ±20 kJ mol^{-1}. Exceptions (see Fig. 1) are found for L = 3-$CH_3C_6H_4O$ (42 kJ mol^{-1}), C_6H_5COO (49 kJ mol^{-1}) and C_6H_5S (−40 kJ mol^{-1}).

For the analogous molybdenum and tungsten molecules the picture is rather similar, although fewer data are available. For example, only one point involving a complex with metal–carbon σ bonds is shown in Fig. 2 and 3 [17*]. The least

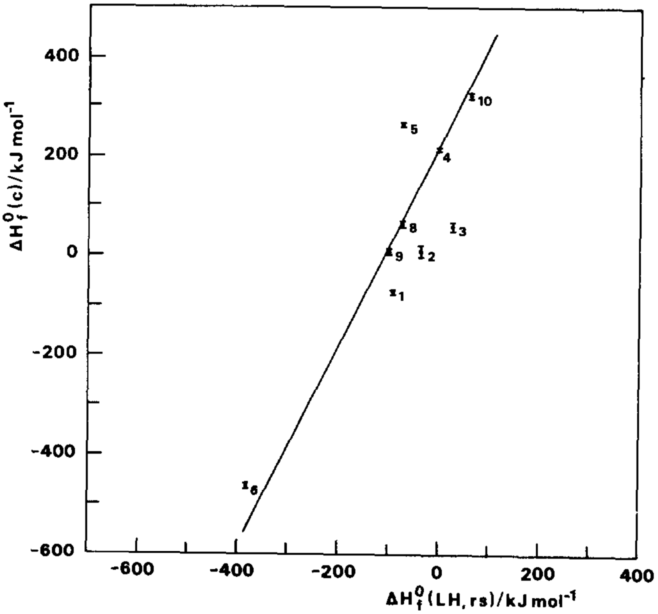

Fig. 3. $\Delta H_f^0(\mathrm{WCp_2L_2,c})$ vs. $\Delta H_f^0(\mathrm{LH,rs})$. Point numbers correspond to the following ligands: 1 = Cl, 2 = Br, 3 = I, 4 = H, 5 = CH_3 6 = C_6H_5COO, 7 = CF_3COO (not represented in the figure), 8 = C_2H_5S, 9 = n-C_3H_7S, 10 = C_6H_5S.

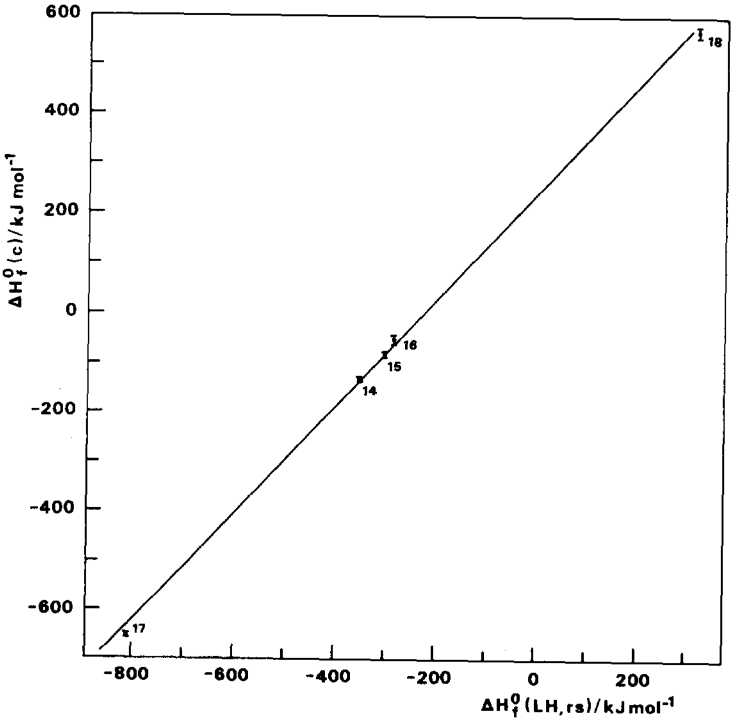

Fig. 4. $\Delta H_f^0(\mathrm{MoCp_2L,c})$ vs. $\Delta H_f^0(\mathrm{LH,rs})$ or $\Delta H_f^0(\mathrm{L,rs})$. Point numbers correspond to the following ligands: 14 = $C_6H_4O_2$, 15 = $C_{10}H_6O_2$, 16 = $C_{14}H_8O_2$, 17 = SO_4, 18 = $N_2(C_6H_5)_2$.

squares fitting led to eq. 7 and 8, respectively ($r = 0.9985$ and 0.9988). The point for $L = H$ falls in the line, for both molybdenum and tungsten complexes.

$$\Delta H_f^0(\mathrm{MoCp_2L_2,c}) = (2.011 \pm 0.041)\Delta H_f^0(\mathrm{LH,rs}) + (194.2 \pm 16.4) \qquad (7)$$

$$\Delta H_f^0(\mathrm{WCp_2L_2,c}) = (1.986 \pm 0.048)\Delta H_f^0(\mathrm{LH,rs}) + (219.3 \pm 22.6) \qquad (8)$$

As observed for the titanium complexes, the differences between experimental and calculated enthalpies of formation are usually less than ±20 kJ $\mathrm{mol^{-1}}$. Interestingly, the largest differences found are for the same ligands: C_6H_5COO (79 kJ $\mathrm{mol^{-1}}$ (Mo), 82 kJ $\mathrm{mol^{-1}}$ (W)) and C_6H_5S (−40 kJ $\mathrm{mol^{-1}}$ (Mo), −26 kJ $\mathrm{mol^{-1}}$ (W)). For $L = n\text{-}C_4H_9S$ ($M = Mo$), a larger discrepancy is also noticed (−39 kJ $\mathrm{mol^{-1}}$).

What happens for bidentate ligands, i.e. for complexes MCp_2L_n with $n = 1$? If the slope reflects the number of ligands, the it should have a value of one. This is in fact what is observed in eq. 9, which fits data for five molybdenum complexes (Fig. 4) containing metal–oxygen [18], and metal–nitrogen bonds ($r = 0.9994$) [19*].

$$\Delta H_f^0(\mathrm{MoCp_2L,c}) = (1.067 \pm 0.022)\Delta H_f^0(\mathrm{LH,rs}) + (236.0 \pm 9.9) \qquad (9)$$

Only three points are available for the analogous titanium molecules ($CH_3C_6H_3S_2$, *trans*-$N_2(C_6H_5)_2$ and 9,10-phenantrenediol [18*]). The correlation is given by eq. 10 ($r = 0.996$) [19*].

$$\Delta H_f^0(\mathrm{TiCp_2L,c}) = (1.091 \pm 0.095)\Delta H_f^0(\mathrm{LH,rs}) - (27.8 \pm 23.5) \qquad (10)$$

Arene-chromium complexes

The standard enthalpies of formation of complexes $Cr(\eta^6\text{-arene})_2$ and $Cr(CO)_3(\eta^6\text{-arene})$ have been determined by using Calvet microcalorimetry, and the data are collected in two recent publications [10a,20]. Figures 5 and 6 and the corresponding linear equations 11 ($r = 0.981$) and 12 ($r = 0.980$), respectively, indicate that the correlation can also be applied to those complexes. However, differences between experimental and calculated $\Delta H_f^0(c)$ are now usually in the

$$\Delta H_f^0(\mathrm{CrL_2,c}) = (1.988 \pm 0.177)\Delta H_f^0(\mathrm{L,rs}) + (91.8 \pm 14.5) \qquad (11)$$

$$\Delta H_f^0[\mathrm{Cr(CO)_3L,c}] = (0.968 \pm 0.070)\Delta H_f^0(\mathrm{L,rs}) - (473.3 \pm 10.2) \qquad (12)$$

range of ±30 kJ $\mathrm{mol^{-1}}$ for $Cr(CO)_3L$ and less than ca. ±20 kJ $\mathrm{mol^{-1}}$ for CrL_2. In the latter complexes the largest differences are for C_6H_6 (−48 kJ $\mathrm{mol^{-1}}$) and naphthalene (56 kJ $\mathrm{mol^{-1}}$). The point for $C_6H_5N(CH_3)_2$ was not included in the correlation.

As shown by eq. 13 and 14, "perfect" correlations between $\Delta H_f^0[\mathrm{Cr(CO)_3L,c}]$ and $\Delta H_f^0(\mathrm{L,rs})$ would imply a slope of one and a constant value of $\Delta H^0(13)$. If the enthalpy change of reaction 13 is expressed in terms of $Cr(CO)_3$–L bond dissociation enthalpy, eq. 15 is obtained (ΔH_S^0 and ΔH_V^0 are the sublimation enthalpy of the complex and the vaporization enthalpy of L). $\Delta H^0(13)$ will be constant if $D[\mathrm{Cr(CO)_3 - L}]$ and $\Delta H_S^0 - \Delta H_V^0$ are also constant or if they both change but their sum remains constant. Although experimental values for those bond dissociation enthalpies are not available, for the differences $D[\mathrm{Cr(CO)_3 - L}] - D[\mathrm{Cr(CO)_3 - L'}]$, which have been reported by Al-Takhin et al. [20], the highest value, $D[\mathrm{Cr(CO)_3}$ −

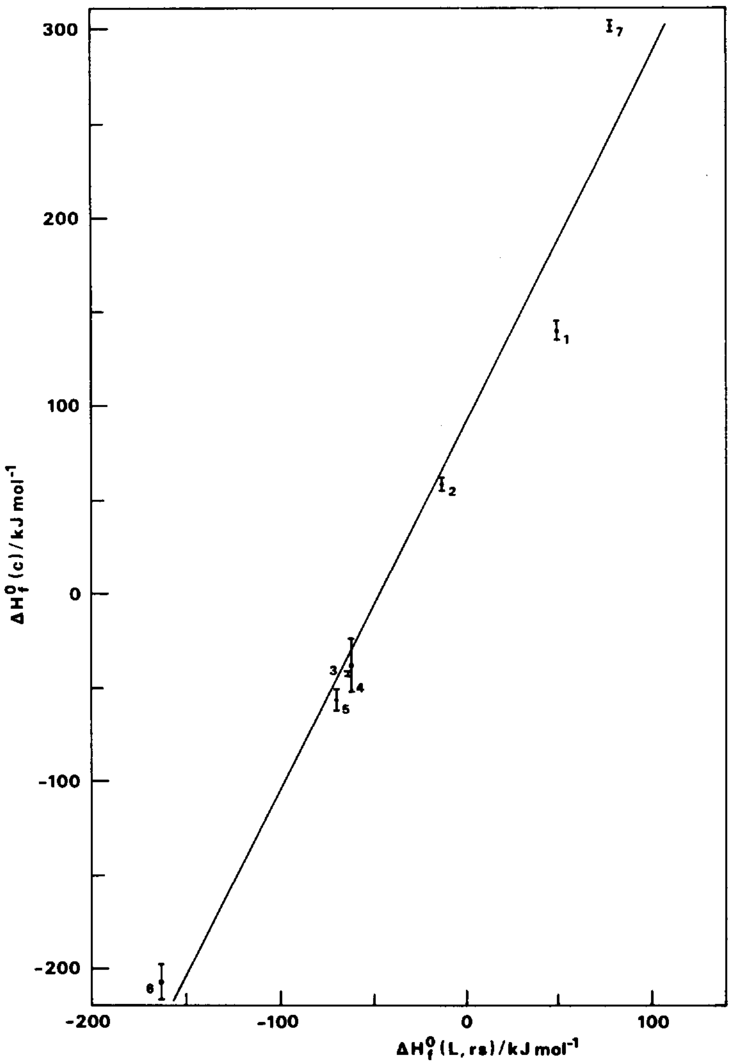

Fig. 5. $\Delta H_f^0(CrL_2,c)$ vs. $\Delta H_f^0(L,rs)$. Point numbers correspond to the following ligands: 1 = C_6H_6, 2 = $C_6H_5C_2H_5$, 3 = 1,3,5-$(CH_3)_3C_6H_3$, 4 = 1,2,4-$(CH_3)_3C_6H_3$, 5 = 1,2-$(C_2H_5)_2C_6H_4$, 6 = $C_6(CH_3)_6$ 7 = $C_{10}H_8$.

$C_6(CH_3)_6$], exceeds the lowest, $D[Cr(CO)_3 - C_6H_5CO_2CH_3]$, by 90 kJ mol^{-1}. This suggests that $\Delta H^0(13)$ is "constant" because the intramolecular enthalpy

$$Cr(CO)_3L(c) = Cr(CO)_3(g) + L(rs) \tag{13}$$

$$\Delta H_f^0[Cr(CO)_3L,c] = \Delta H_f^0(L,rs) - \Delta H^0(13) + \Delta H_f^0[Cr(CO)_3,g] \tag{14}$$

$$\Delta H^0(13) = D[Cr(CO)_3 - L) + \Delta H_S^0 - \Delta H_V^0 \tag{15}$$

change is offset by the intermolecular enthalpy change ($\Delta H_S^0 - \Delta H_V^0$). A fact which apparently contradicts this conclusion is that for $Cr(CO)_3L$ complexes the correlation holds if $\Delta H_f^0[Cr(CO)_3L,g]$ is plotted against $\Delta H_f^0(L,g)$ [20]. This point will be further discussed below.

Manganese complexes

Another family that can be used to test the linear correlation is provided by $Mn(CO)_5L$ complexes. These have also been studied by Calvet microcalorimetry [21]. Figure 7 shows the usual plot, i.e. $\Delta H_f^0[Mn(CO)_5L,c]$ vs. $\Delta H_f^0(LH,rs)$. A line, not shown in the figure, was drawn through all points corresponding to molecules containing metal–carbon bonds, except for L = CF_3 and CF_3CO. Interestingly, the value for L = $Mn(CO)_5$ fits the correlation and was therefore included in the least squares analysis (eq. 16, $r = 0.9998$). It is noted, however, that the slope in eq. 16 is not as close to one as in previous cases, despite the fact that the correlation is rather good.

$$\Delta H_f^0[Mn(CO)_5L,c] = (1.212 \pm 0.013)\Delta H_f^0(LH,rs) - (736.6 \pm 4.3) \qquad (16)$$

When the correlations for the bis-cyclopentadienyl complexes are recalled, the decision to draw a straight line through all the points may be questioned. Data for the manganese complexes involve four molecules with "pure" metal–carbon σ bonds (points 5–8) and three others where oxygen is also donating electrons to the metal (points 9–11). The least squares fitting of points 5–8 (Fig. 7) and 9–11 (Fig. 7) led to eq. 17 ($r = 0.9999$) and 18 ($r = 0.9995$), respectively, where the slopes are now closer to the expected value [22*]. Differences between experimental and calculated $\Delta H_f^0(c)$ are very small in both cases: less than ca. ±10 kJ mol^{-1}.

$$\Delta H_f^0[Mn(CO)_5R,c] = (1.047 \pm 0.010)\Delta H_f^0(RH,rs) - (733.1 \pm 3.7) \qquad (17)$$

$$\Delta H_f^0[Mn(CO)_5COR,c] = (1.009 \pm 0.032)\Delta H_f^0(RCHO,rs) - (770.7 \pm 15.2) \qquad (18)$$

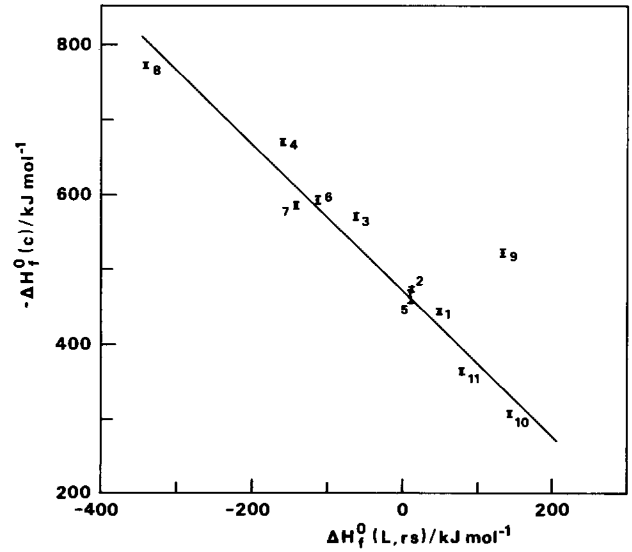

Fig. 6. $\Delta H_f^0(Cr(CO)_3L,c)$ vs. $\Delta H_f^0(L,rs)$. Point numbers correspond to the following ligands: 1 = C_6H_6, 2 = $C_6H_5CH_3$, 3 = 1,3,5-$(CH_3)_3C_6H_3$, 4 = $C_6(CH_3)_6$, 5 = C_6H_5Cl, 6 = $C_6H_5OCH_3$, 7 = $C_6H_5COCH_3$, 8 = $C_6H_5COOCH_3$, 9 = $C_6H_5N(CH_3)_2$, 10 = cy-C_7H_8, 11 = $C_{10}H_8$.

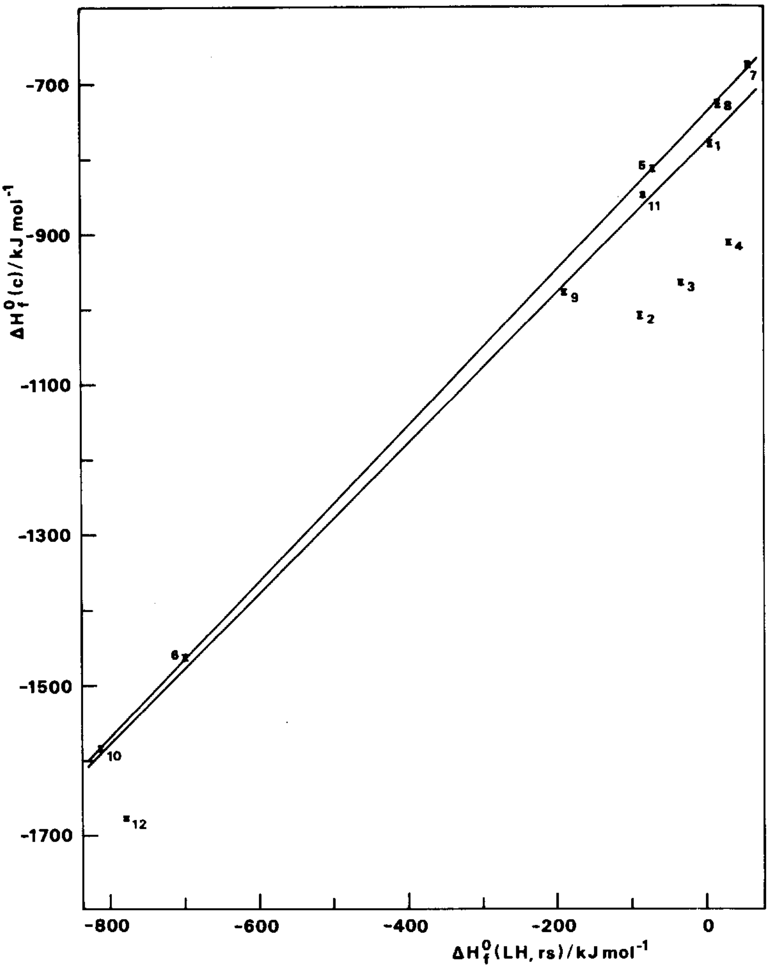

Fig. 7. ΔH_f^0(Mn(CO)$_5$L,c) vs. ΔH_f^0(LH,rs). Point numbers correspond to the following ligands: 1 = H, 2 = Cl, 3 = Br, 4 = I, 5 = CH_3, 6 = CF_3, 7 = C_6H_5, 8 = $C_6H_5CH_2$, 9 = CH_3CO, 10 = CF_3CO, 11 = C_6H_5CO, 12 = Mn(CO)$_5$.

Finally, it should be noted that the pattern observed for L = H and L = halogen in Fig. 7 is similar to that observed for the bis-cyclopentadienyl complexes.

Group II adducts

Reaction-solution calorimetric studies on group II adducts $MX_2 \cdot nL$, where X = halogen and L = Lewis base led to an extensive set of data for the standard enthalpies of formation of the complexes. Since it was considered desirable to test the correlation to non-organometallic molecules, some of those values were used for that purpose [23].

Figure 8 shows a plot of $\Delta H_f^0(ZnCl_2 \cdot 2L,c)$ for several oxygen and nitrogen donors, and eq. 19 represents the least squares fit for all points ($r = 0.998$).

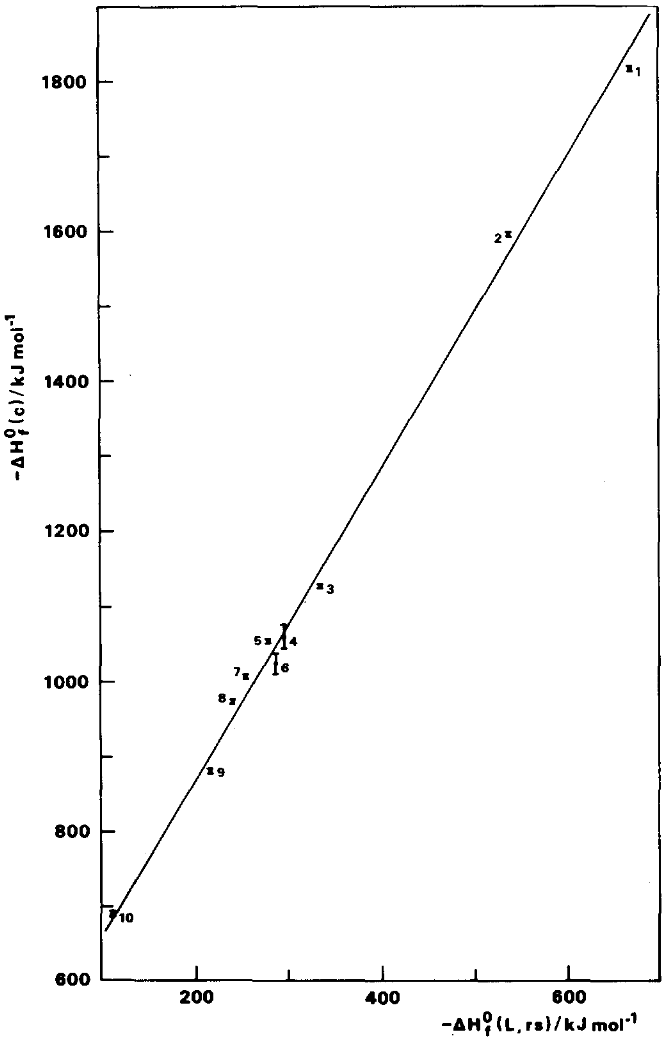

Fig. 8. $\Delta H_f^0(ZnCl_2 \cdot 2L,c)$ vs. $\Delta H_f^0(L,rs)$. Point numbers correspond to the following ligands: 1 = $(C_2H_5)_3PO$, 2 = $[(CH_3)_2N]_3PO$, 3 = $(H_2N)_2CO$, 4 = $(CH_3NH)_2CO$, 5 = $(CH_3)[N(CH_3)_2]CO$, 6 = $(CH_3NH)(H_2N)CO$, 7 = $[(CH_3)_2N]_2CO$, 8 = $[(CH_3)_2N](H)CO$, 9 = $(C_6H_5CH_2)_3PO$, 10 = $(C_6H_5)_3PO$.

Estimates of $\Delta H_f^0(c)$ made through this equation agree with experimental values within ca. ± 20 kJ mol^{-1}.

$$\Delta H_f^0(ZnCl_2 \cdot 2L,c) = (2.076 \pm 0.048)\Delta H_f^0(L,rs) - (456.8 \pm 17.0) \tag{19}$$

Tests were also made by using data for $ZnBr_2 \cdot 2L$ (the ligands considered are those corresponding to points 2–8 and 10 of Fig. 8), $ZnI_2 \cdot 2L$ (points 2,3,5,7,8,10), and $HgCl_2 \cdot L$ (points 1 and 3–8). The correlation is satisfactory for the iodides and for the mercury complexes, but less so for the bromides, as shown by equations 20 ($r = 0.997$), 21 ($r = 0.998$), and 22 ($r = 0.946$), respectively.

$$\Delta H_f^0(ZnI_2 \cdot 2L,c) = (2.132 \pm 0.081)\Delta H_f^0(L,rs) - (265.1 \pm 25.9) \tag{20}$$

$$\Delta H_f^0(\mathrm{HgCl_2 \cdot L,c}) = (0.993 \pm 0.027)\Delta H_f^0(\mathrm{L,rs}) - (247.3 \pm 9.7) \quad (21)$$

$$\Delta H_f^0(\mathrm{ZnBr_2 \cdot 2L,c}) = (2.280 \pm 0.319)\Delta H_f^0(\mathrm{L,rs}) - (289.8 \pm 99.5) \quad (22)$$

General discussion

The enthalpy content of a molecule reflects the enthalpy content of its fragments. A correlation between standard enthalpies of formation of a series of molecules containing a common moiety and standard enthalpies of formation of the different fragments bonded to that moiety is thus not unexpected. It is, however, surprising to find good linear relationships between enthalpies of formation of the molecules and fragments in their standard reference states. Attempts to explain this behaviour led to the conclusion that a compensation of intra- and inter-molecular enthalpy changes may account for the observed linearity. This is supported by the fact that the least squares fittings involving ΔH_f^0(complex,c) vs. ΔH_f^0(ligand,rs) are usually of better quality than those of ΔH_f^0(complex,c) vs. ΔH_f^0(ligand,g). For example, when eq. 6 is considered, the crystal-gas correlation implies $\Delta H_V^0 = 0$, thus perturbing the "intermolecular compensation". Unfortunately, very few accurate standard enthalpies of formation of the complexes in the gas phase are available, and so those ideas cannot be thoroughly tested by plotting ΔH_f^0(complex,g) vs. ΔH_f^0(ligand,g).

While a more perfect understanding of the linear correlations presented is desirable, their value is apparent. From a practical point of view, for example, for predicting the energetics of reactions in solution, estimates of ΔH_f^0(complex) in the crystalline state are more useful than those for the gas state. Moreover, the input data [ΔH_f^0(L/LH)] are always referred to the standard reference state, and not necessarily to the gaseous state, thus avoiding the need to know or estimate enthalpies of sublimation or vaporization of the ligands.

The method that relies on transferring metal–ligand bond enthalpy terms [12] may yield more accurate ΔH_f^0(complex,c) than the linear equations. As a result of the uncertainties affecting the slopes, this applies particularly to those ligands whose enthalpy of formation is very large. However, it is obvious that an estimate of an enthalpy of formation involving, e.g., a tungsten–sulfur bond by use of the bond enthalpy term method requires the availability of thermochemical data for other molecules containing similar bonds. For example, it would not be a simple exercise to predict the standard enthalpies of formation of complexes such as $\mathrm{MoCp_2[N_2(C_6H_5)_2]}$ or $\mathrm{MoCp_2(C_2H_4)}$ through the bond enthalpy term method. The value for the first of these molecules is fitted by eq. 9, and the value for the second is estimated as 292 kJ mol^{-1} (from $\Delta H_f^0(\mathrm{C_2H_4,g})$ [13]), matching a preliminary experimental result [24]. The same equation can in principle be used to predict the energetics of other interesting species, such as metal carbenes or metallacycles. For example, $\Delta H_f^0[\mathrm{MoCp_2(CH_2),c}] = 157$ kJ mol^{-1} and $\Delta H_f^0[\mathrm{MoCp_2(CCl_2),c}] = 104$ kJ mol^{-1} were obtained from $\Delta H_f^0(\mathrm{CH_4,g})$ and $\Delta H_f^0(\mathrm{CH_2Cl_2,l})$ [13]. The reliability of these and other values estimated through the available correlations needs, of course, to be assessed by experimental thermochemical studies. Will those metal-carbenes and/or metallacycles fit the correlations for bidentate ligands (e.g., eq. 9 and 10) or will they give a different intercept? The example provided by the manganese complexes has shown that some caution has to be used when defining a "family", i.e. the intercept of the straight line.

The reliability of estimating enthalpies of formation of complexes such as MCp_2R_2 (M = Mo, W; R = alkyl, aryl) is, on the other hand, more easily accepted, since it is based on a large number of experimental data for the analogous titanium molecules. Those alkyl and aryl complexes must fit straight lines (slope ~ 2) drawn through the points corresponding to $MCp_2(CH_3)_2$ in Fig. 2 and 3. Experimental studies involving the complexes $MoCp_2(C_2H_5)_2$ and $MoCp_2(n\text{-}C_4H_9)_2$ are in progress, and will enable this be to be checked [24].

The temptation to assess experimental values by use of the correlations must be resisted. It should be noted, however, that some published values that have been substantially changed later, do not fit the correlation to which they relate. This is the case, for example, for results from early combustion studies on $TiCp_2(CH_3)_2$ and $TiCp_2(C_6H_5)_2$ [25]. Alternative experimental values exist for some other ΔH_f^0(complex,c) used to define the correlations presented here, and use of these sometimes lowers the standard deviations. The choice of a full set of values obtained in one laboratory has at least the advantage of avoiding meaningless attempts to obtain better fittings.

Can thermochemistry of coordination and organometallic complexes be "reduced" to thermochemistry of organic and inorganic ligands? The answer probably depends on how accurately one wishes to estimate enthalpies of formation of those complexes. The linear equations found in the present paper indicate that reliable data can be obtained for most molecules used to test those correlations. Future efforts should be aimed at improving the accuracy of experimental data, extending the tests to a larger number of different types of complexes, and to providing a better understanding of the factors which define a "family".

Acknowledgments

This project was financed by Instituto Nacional de Investigação Científica, Portugal. We also thank Junta Nacional de Investigação Científica e Tecnológica (Portugal) and Conselho Nacional de Pesquisa (Brazil) for providing the funds for the collaboration between our groups.

References

1 J.D. Cox and G. Pilcher, Thermochemistry of Organic and Organometallic Compounds, Academic Press, London and New York, 1970.

2 S.W. Benson, Thermochemical Kinetics, Wiley, New York, 1976.

3 J.B. Pedley, R.D. Naylor, and S.P. Kirby, Thermochemical Data of Organic Compounds, 2nd edit., Chapman and Hall, London and New York, 1986.

4 (a) R.T. Sanderson, Chemical Bonds and Bond Energy, 2nd edit., Academic Press, New York 1976; (b) R.T. Sanderson, Polar Covalence, Academic Press, New York, 1983; (c) R.T. Sanderson, J. Am. Chem. Soc., 97 (1975) 1367; (d) R.T. Sanderson, J. Org. Chem., 47(1982)3835.

5 See, for example: (a) M.J.S. Dewar and D.M. Storch, J. Am. Chem. Soc., 107 (1985) 3898; (b) M.J.S. Dewar, E.G. Zoebisch, E.F. Healy, and J.J.P. Stewart, J. Am. Chem. Soc., 107 (1985) 3902; (c) M.J.S. Dewar, J. Phys. Chem., 89(1985)2145.

6 See, for example, R.C. Reid, J.M. Prausnitz, and T.K. Sherwood, The Properties of Gases and Liquids, 3rd edit., McGraw-Hill, New York, 1977. No reliable methods for estimating accurate values of enthalpies of sublimation are presently available. See also ref. 1.

7 (a) M.W.M. Hisham and S.W. Benson, J. Phys. Chem., 89(1985)1905. (b) M.W.M. Hisham and S.W. Benson, J. Phys. Chem., 89(1985)3417. (c) M.W.M. Hisham and S.W. Benson, J. Phys. Chem., 90(1986)885.

8 S.G. Bratsch and J.J. Lagowski, J. Phys. Chem., 89(1985)3310 and refs. cited therein.

9 See refs. 4a, 4b and: (a) R.T. Sanderson, J. Am. Chem. Soc., 105(1983)2259; (b) R.T. Sanderson, Inorg. Chem., 25(1986)1856; (c) R.T. Sanderson, Inorg. Chem., 25(1986)3518.

10 (a) G. Pilcher and H.A. Skinner, The Chemistry of the Metal–Carbon Bond; F.R. Hartley and S. Patai (Eds.), John Wiley, New York, 1982; chapter 2; (b) M.B. Smith, J. Organomet. Chem., 76(1974)171.

11 (a) M.J.S. Dewar, G.L. Grady, and J.J.P. Stewart, J. Am. Chem. Soc., 106(1984)6771; (b) M.J.S. Dewar, J.E. Friedheim, and G.L. Grady, Organometallics, 4(1985)1784; (c) M.J.S. Dewar, G.L. Grady, K.M. Merz, Jr., and J.J.P. Stewart, Organometallics, 4(1985)1964; (d) M.J.S. Dewar, M.K. Holloway, G.L. Grady, and J.J.P. Stewart, Organometallics, 4(1985)1973; (e) M.J.S. Dewar, J. Friedheim, G. Grady, E.F. Healy, and J.J.P. Stewart, Organometallics, 5(1986)375; (f) M.J.S. Dewar and K.M. Merz, Jr., Organometallics, 5(1986) 1494.

12 (a) J.A. Martinho Simões and J.L. Beauchamp, Chem. Rev., to be published; (b) M.J. Calhorda, M.A.A.F. de C.T. Carrondo, A.R. Dias, A.M.T.S. Domingos, J.A. Martinho Simões, and C. Teicxeira, Organometallics, 5(1986)660; (c) M.J. Calhorda, A.R. Dias, A.M. Galvão, and J.A. Martinho Simões, J. Organometal. Chem., 307(1986)167; (d) M.J. Calhorda, A.R. Dias, M.E. Minas da Piedade, M.S. Salema, and J.A. Martinho Simões, Organometallics, 6 (1987) 734.

13 J.B. Pedley and J. Rylance, Sussex-N.P.L. Computer Analysed Thermochemical Data: Organic and Organometallic Compounds, University of Sussex, Brighton, 1977.

14 A.R. Dias, P.B. Dias, H.P. Diogo, A.M. Galvão, E.M. Minas da Piedade, and J.A. Martinho Simões., Organometallics, 6 (1987) 1427.

15 The only value not reported in refs. 12b, 12d and 14 is: $\Delta H_f^0[\mathrm{TiCp_2(SC_2H_5)_2,c}] = -211.3 \pm 8.2$ kJ mol^{-1}. (A.R. Dias, J.A. Martinho Simões, and C. Teixeira, to be published).

16 For L = CO ΔH_f^0(LH,rs) is replaced by ΔH_f^0(L,rs).

17 The only values not reported in refs. 12b, 12d and 14 are: $\Delta H_f^0[\mathrm{WCp_2(SC_2H_5)_2,c}] = 62.7 \pm 5.3$ kJ mol^{-1} and $\Delta H_f^0[\mathrm{WCp_2(SC_6H_5)_2,c}] = 319.9 \pm 5.5$ kJ mol^{-1}. (A.R. Dias, J.A. Martinho Simões, and C. Teixeira, to be published).

18 Data for the standard enthalpies of formation of $\mathrm{MCp_2L}$ and LH (LH = catechol, 2,3-dihydroxynaphthalene and 9,10-phenanthrenediol) were quoted from M.D.M.C. Ribeiro da Silva, Tese de Doutoramento, University of Porto, 1985.

19 For L = *trans*-azobenzene ΔH_f^0(LH,rs) is replaced by ΔH_f^0(L,rs).

20 G. Al-Takhin, J.A. Connor, H.A. Skinner, and M.T. Zafarani-Moattar, J. Organomet. Chem. 260(1984)189.

21 J.A. Connor, M.T. Zafarani-Moattar, J. Bickerton, N.I. El Saied, S. Suradi, R. Carson, G. Al Takhin, and H.A. Skinner, Organometallics, 1(1982)1166.

22 $\Delta H_f^0(\mathrm{CF_3CHO,l})$ is estimated as -810 ± 15 kJ mol^{-1}.

23 Data taken from refs. 1, 3, and: (a) M.R. de M.C. Santos, Tese de Mestrado, University of Campinas, 1985; (b) R.A. Jorge, C. Airoldi, and A.P. Chagas, J. Chem. Soc., Dalton Trans. (1978)1102. (c) J. de A. Simoni, A.P. Chagas, and C. Airoldi, J. Chem. Soc., Dalton Trans. (1980)156; (d) J.C. Queiroz, C. Airoldi, and A.P. Chagas, J. Inorg. Nucl. Chem., 43(1981)1207; (e) C. Airoldi, A.P. Chagas, and F.P. Assunção, J. Chem. Soc., Dalton Trans., (1980)1823; (f) F.P. Assunção, A.P. Chagas, and C. Airoldi, J. Chim. Phys., 79(1982)253; (g) F.P. Assunção, A.P. Chagas, and C. Airoldi, Can. J. Chem., 60(1982)2132; (h) O.A. de Oliveira, A.P. Chagas, and C. Airoldi, Inorg. Chem., 22(1983)136; (i) J. de A. Simoni, C. Airoldi, and A.P. Chagas, An. Acad. Brasil. Ciênc., 55(1983)254; (j) J.C. Queiroz, C. Airoldi, and A.P. Chagas, J. Chem. Soc., Dalton Trans., (1985)1103; (k) J.C. de Queiroz, C. Airoldi, and A.P. Chagas, J. Chem. Thermodyn., 18(1986)709. (l) D.D. Wagman, W.H. Evans, V.B. Parker, I. Halow, S.M. Bailey, and R.H. Schumm, Selected Values of Thermodynamic Properties, Technical Note 270-3, National Bureau of Standards, Washington, D.C., 1968; (m) S.B. Hartley, W.S. Holmes, J.K. Jacques, M.F. Mole, and J.C. McCoubrey, Quart. Rev. 17(1963)204; (n) M.F. Mole, W.S. Holmes, and J.C. McCoubrey, J. Chem. Soc., (1964)5144; (o) T.F. Vasileva, E.N. Zhiltsova, and A.A. Vvedenskii, Russ. J. Phys. Chem., 46(1972)315; (p) A. Luttringhaus, and H.W. Dirksen, Angew. Chem. Int. Ed. Engl. 31(1964)260; (q) R. Gopal, and S.A. Rizvi, J. Indian Chem. Soc., 45(1968)13; (r) K. Suzuki, S. Onishi, T. Koide, and S. Seki, Bull. Chem. Soc. Japan, 29(1956)127.

24 A.R. Dias, M.E. Minas de Piedade, and J.A. Martinho Simões, unpublished data.

25 V.I. Tel'noi and I.B. Rabinovich, Russ. Chemical Rev., 46(1977)689.