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Organometallic thermochemistry at CQE-IST. An overview

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Dedicated to Professor A.R. Dias on the occasion of his 60th birthday

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Abstract

A brief overview of the organometallic thermochemistry research made at Lisbon, for over 25 years is given in this paper. The examples presented illustrate how those studies motivated the building of new instrumentation, and how the obtained results were used to discuss the 'strength' of the transition metal–ligand bonds, rationalise reactivity trends, and develop empirical methods to estimate thermochemical data. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Thermochemistry; Bond enthalpies; Entropy changes

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1. Introduction

The word *stability* is frequently used when we try to characterise chemical compounds. In general, a compound is said to be stable if its chemical composition and structure do not change with time. However, s*tability* is a fairly ambiguous concept. The solid yellow compound $MoCp_2H_2$ ($Cp = \eta^5\text{-}C_5H_5$), which may apparently survive forever inside a Schlenk tube, at room temperature and under argon atmosphere, becomes black in a matter of seconds in the presence of oxygen. Therefore, a given molecule can exist only under certain physical and chemical conditions, and when it is said to be *stable*, one should ask: 'stable, relative to what?'

Thermodynamics provides the tools to quantify a type of stability generally known as the *thermodynamic stability*. The thermodynamic driving force of a given reaction is measured by the corresponding Gibbs energy change, $\Delta_r G$, with spontaneous reactions having $\Delta_r G < 0$. Under equilibrium conditions $\Delta_r G = 0$ and the standard Gibbs energy of the reaction, $\Delta_r G°$, is related to the corresponding equilibrium constant, K, by the following equation [1]:

$$\Delta_r G° = -RT \ln K \tag{1}$$

where R is the gas constant and T the absolute temperature. As K reflects the maximum yield of the reaction at a given temperature and pressure, a large positive value of $\Delta_r G°$ indicates *stability*, i.e. the reaction yield will be negligible and for all practical purposes the compound will not react. Conversely, *instability* will be characterised by a large negative value of $\Delta_r G°$.

The standard Gibbs energy of a reaction is related to the corresponding enthalpy, $\Delta_r H°$, and entropy, $\Delta_r S°$, given as

$$\Delta_r G° = \Delta_r H° - T\,\Delta_r S° \tag{2}$$

In some cases, the values of $\Delta_r H°$and $\Delta_r S°$ are experimentally available; generally, they can be calculated using the known values of the standard enthalpies of formation, $\Delta_f H°$, and entropies, $S°$, of all the species involved in the reaction. However, there is still a large paucity of thermochemical data for organometallic compounds, and this is particularly true for $S°$ and $\Delta_r S°$ [2–4]. Fortunately, many interesting reactions occur at temperatures not far from ambient and the enthalpy term in Eq. (2) is often dominant. Therefore,

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the thermodynamic stability of a given compound can be frequently evaluated by considering only the $\Delta_r H°$ value for the reaction of interest.

A large number of thermochemical studies have been focused on the thermodynamic stability of chemical bonds rather than the thermodynamic stability of molecules as a whole. Thermochemical measurements of 'bond strengths' are generally given in terms of bond dissociation enthalpies, bond enthalpy terms, and intrinsic bond enthalpies. Consider again the molecule $MoCp_2H_2$. The Mo–H *bond dissociation enthalpy*, $DH°$(Mo–H), is defined as the standard enthalpy of the gas phase reaction:

$$MoCp_2H_2\ (g) \rightarrow MoCp_2H\ (g) + H\ (g) \qquad (3)$$

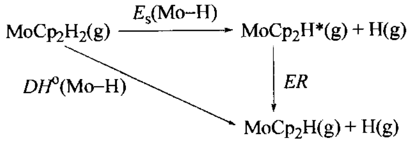
where the only event is the cleavage of a single Mo–H bond, at a given temperature (usually 298.15 K). The Mo–H *mean bond dissociation enthalpy*, $\langle DH° \rangle$(Mo–H), corresponds to the standard enthalpy of the gas phase reaction:

$$MoCp_2H_2\ (g) \rightarrow MoCp_2\ (g) + 2H\ (g) \qquad (4)$$

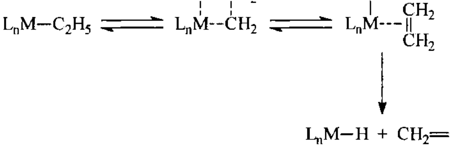
and is defined by $\langle DH° \rangle(\text{Mo–H}) = \Delta_r H°(4)/2$. On the other hand, the Mo–Cp and Mo–H bond enthalpy terms, E(Mo–Cp) and E(Mo–H), respectively, are related to the reaction:

$$MoCp_2H_2\ (g) \rightarrow Mo\ (g) + 2Cp\ (g) + 2H\ (g) \qquad (5)$$

and are given by: $\Delta_r H°(5) = 2E(\text{Mo–Cp}) + 2E(\text{Mo–H})$. Finally the definition of the Mo–H *intrinsic bond enthalpy* or *bond snap enthalpy*, E_s(Mo–H), is illustrated in Scheme 1. The asterisk in $MoCp_2H^*$ designates a fragment retaining the geometry of the precursor complex, and ER is the *reorganisation energy* associated with the relaxation of $MoCp_2H^*$ to originate $MoCp_2H$. It can be concluded from Scheme 1 that $E_s(\text{Mo–H}) = DH°(\text{Mo–H}) - ER$. The value of ER is not experimentally available, but can be estimated through quantum chemistry calculations.



Scheme 1.



Scheme 2.

Bond dissociation enthalpies can also be used to calculate reaction enthalpies. For example, the enthalpy of the reaction:

$$MoCp_2H_2\ (g) + Cl_2\ (g) \rightarrow MoCp_2Cl_2\ (g) + H_2\ (g) \qquad (6)$$

is given by:

$$\Delta_r H°(6) = 2\langle DH° \rangle(\text{Mo–H}) + DH°(\text{Cl–Cl}) - 2\langle DH° \rangle(\text{Mo–Cl}) - DH°(\text{H–H}) \qquad (7)$$

Thermodynamically unstable compounds do not necessarily undergo spontaneous reactions. A very slow reaction may indicate *kinetic* rather than thermodynamic stability. The relationship between these two types of stability is not always simple as the former depends on the reaction mechanism and the latter is simply determined by the thermodynamics of the reactants and products. Nevertheless, a considerable number of empirical equations relating the rate constant, k, and the activation energy, E_a, with enthalpies of the reaction and bond dissociation enthalpies have been proposed [5]. These correlations may be expected if the rate-determining step of a reaction involves the homolytic cleavage of a bond and the fragments recombination barrier is small. A detailed discussion of the relationships between thermochemistry and kinetics is included in Ref. [6].

The distinction between the thermodynamic and kinetic stability of a compound or a chemical bond was the driving force to start the organometallic thermochemistry studies in Lisbon, some 25 years ago. At that time there was considerable debate in the literature regarding the 'strength' of transition metal–carbon bonds. Homoleptic species $(MR_n)_x$ containing transition metals (M) bonded to σ-hydrocarbyl ligands (R) were very difficult to prepare and the known compounds showed a high thermal instability (e.g. $TiMe_4$, $Me = CH_3$, decomposes a few degrees above −78°C and WMe_6 decomposes explosively at room temperature [7]). In contrast, numerous $(MR_n)_x$ derivatives of the main group elements were stable at room temperature [8]. These observations had led to the general belief that transition metal–carbon bonds were weak and therefore the instability of the transition metal σ-hydrocarbyls had a thermodynamic origin. However, this view was challenged by Wilkinson and Lappert and their co-workers, who, in the early 1970s, independently suggested that the instability of the transition metal σ-hydrocarbyls had a kinetic origin [8,9]. These authors pointed out that β-elimination (Scheme 2) was an important pathway for the thermal decomposition of the transition metal σ-hydrocarbyls and that stable complexes could often be prepared by using ligands without β-hydrogen atoms (e.g. Me_3CCH_2, Me_3SiCH_2, and $PhCH_2$). As shown in Scheme 2, the destabilisation of the four-centre transition state, owing to the stretching

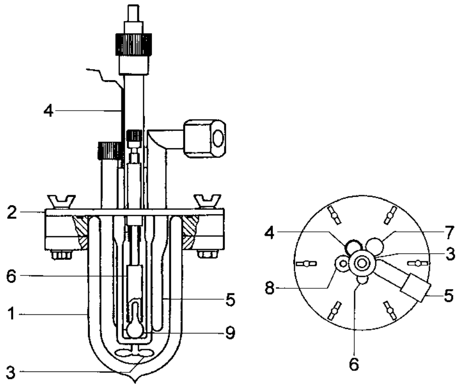


Fig. 1. Reaction-solution calorimeter: (1) Dewar vessel; (2) brass lid; (3) stirrer; (4) quartz crystal thermometer probe; (5) electrical resistance used for calibration; (6) ampoule breaking system; (7) and (8) inlets; and (9) glass ampoule [12,13].

of the metal–carbon bond, is compensated by the formation of an incipient metal–hydrogen bond. The pathway does not require the simple cleavage of the M–C σ bond. Hence, the thermodynamic stability of this bond could not be inferred from the decomposition temperature of the compound.

This controversy motivated Romão Dias, head of the Organometallic Chemistry group at the Centro de Química Estrutural-Instituto Superior Técnico (CQE-IST), and Calado, head of the Experimental Thermodynamics group at the same institution, to investigate the magnitude and trends of transition metal–ligand bond dissociation enthalpies. One of the conclusions of the joint discussions was the decision to hire a graduate student to work on the project (J.A.M.S.). The studies were to be centred on bis(η^5-cyclopentadienyl) complexes, MCp_2L_n ($M = Ti$, Zr, Hf, V, Nb, Ta, Mo, W; $L = H$, halogen, CO, alkyl, alkene, aryl, alkoxide, thiolate, phosphine, etc.; $n = 1-3$) for two main reasons: (i) the know-how for their preparation was available at CQE-IST, as all the synthetic work of the organometallic chemistry group was based on these systems; and (ii) bis(η^5-cyclopentadienyl) complexes seemed ideal for investigating the trends in bond dissociation enthalpies as it was possible to prepare a series of compounds of a given metal with various ligands and vice versa. After a number of exploratory experiments, involving several techniques, it was established that reaction-solution calorimetry was the method of choice to study the energetics of the M–L bonds in MCp_2L_n complexes. As most bis(η^5-cyclopentadienyl) compounds were oxygen-sensitive, it was necessary to develop an anaerobic calorimeter. Two groups from outside CQE-IST contributed significantly for the first steps of the experimental studies. A group from the University of Manchester (UK), headed by Skinner, Pilcher, and Connor [10], which was the leading authority on the thermochemistry of organometallic compounds; and the group of Ribeiro da Silva, at the University of Porto (Portugal) whose main interests were in the thermochemistry of coordination complexes.

The outcome of this project, and how it was further extended over the years to cover a variety of studies on organic, inorganic, and organometallic systems, was briefly reviewed four years ago in the last issue of *Revista Portuguesa de Química* [11]. The present paper is partly based on that account.

2. Bond dissociation enthalpies from reaction-solution calorimetric experiments

The basic design of the isoperibol reaction-solution calorimeter used in Lisbon is shown in Fig. 1 [12,13]. It consists of a transparent Dewar vessel (1), closed by a brass lid (2), which supports a stirrer (3), a Hewlett–Packard 28044A quartz crystal thermometer probe (4), a 48 Ω resistor for electrical calibration (5), and an ampoule breaking system (6). When necessary, the inlet (7) can be used to admit an inert gas inside the vessel. Inlet (8) may be closed by a septum, which enables samples of the liquid and the gaseous phases to be taken from the vessel, with a syringe, at the end of the calorimetric experiment, and analysed by gas–liquid chromatography [12,13]. The assembled vessel is immersed in a thermostatic water bath whose temperature is controlled at 298 ± 10^{-3} K by a Tronac PTC-40 unit. In a typical experiment, the energy equivalent of the calorimetric system, ε, is first obtained by an electrical calibration, in which current I is passed through the resistance (5) for a known period of time t, and the potential change V across 5 is measured. From the recorded temperature versus time curve, it is possible to derive the *adiabatic temperature change*, ΔT_{ad}, using, e.g. the Reganult–Pfaundler method [14–17]. Then:

$$\varepsilon = \frac{VIt}{\Delta T_{ad}} \tag{8}$$

where VIt represents the energy dissipated as heat in the resistance 5 during the calibration. The reaction or solution process under study immediately follows calibration and is started by breaking a thin-walled glass ampoule (9) containing the sample, in 125 ml of the calorimetric solution. The corresponding molar enthalpy change under isothermal conditions, ΔH_{ICP}, at the reference temperature of 298.15 K, is given by:

$$\Delta H_{ICP} = \frac{\varepsilon \, \Delta T_{ad}}{n} \tag{9}$$

where n is the amount of substance of sample and ΔT_{ad} the corresponding adiabatic temperature change.

The general method used to derive the metal–ligand (M–L) bond dissociation enthalpies from reaction-solution calorimetric experiments, can be illustrated by the study of $MoCp_2Et_2$ ($Et = C_2H_5$) [13]. In this case the enthalpy of the reaction:

$$\begin{aligned} &MoCp_2Et_2\ (cr) + 2(HCl{:}5.11C_6H_{14}O)(sln)\\ &\quad = MoCp_2Cl_2\ (cr) + 1.6C_2H_6\ (sln) + 0.4C_2H_6\ (g)\\ &\qquad + 10.22C_6H_{14}O\ (sln) \end{aligned} \qquad (10)$$

where $HCl{:}5.11C_6H_{14}O$ corresponds to a 1.34 M solution of HCl in isopropyl ether, was first determined using the apparatus in Fig. 1. This led to the enthalpy of formation of the complex from:

$$\begin{aligned} &\Delta_f H°(MoCp_2Et_2,\ cr)\\ &\quad = -\Delta_r H°(10) + 1.6\Delta_{sln}H° + 10.22\Delta_{diln}H°\\ &\qquad + 2\Delta_f H°(C_2H_6,\ g) + \Delta_f H°(MoCp_2Cl_2,\ cr)\\ &\qquad - 2\Delta_f H°(HCl{:}5.11C_6H_{14}O,\ sln) \end{aligned} \qquad (11)$$

where $\Delta_r H°(10)$ represents ΔH_{ICP} for reaction (10), $\Delta_{sln}H°$ is the enthalpy of solution of ethane in the calorimetric solvent, and $\Delta_{diln}H°$ the enthalpy associated with the dilution of the HCl solution inside the calorimeter, as a result of the reaction. From $\Delta_r H°(10) = -(194.8 \pm 1.4)$ kJ mol^{-1} [13], $\Delta_{sln}H° = -(11 \pm 2)$ kJ mol^{-1} [18], $\Delta_{diln}H° = -(0.13 \pm 0.04)$ kJ mol^{-1} [13], $\Delta_f H°(C_2H_6,\ g) = -(84.0 \pm 0.2)$ kJ mol^{-1} [19], $\Delta_f H°(MoCp_2Cl_2,\ cr) = -(95.8 \pm 2.5)$ kJ mol^{-1} [20], and $\Delta_f H°(HCl{:}5.11C_6H_{14}O,\ sln) = -(144.1 \pm 0.7)$ kJ mol^{-1} [13], it was possible to obtain $\Delta_f H°(MoCp_2Et_2,\ cr) = 200.3 \pm 4.6$ kJ mol^{-1} [13]. The enthalpy of sublimation of the complex was then derived as $\Delta_{sub}H°(MoCp_2Et_2) = 93.6 \pm 1.8$ kJ mol^{-1}, from vapour pressure versus temperature measurements by the Knudsen effusion method [13] and $\Delta_f H°(MoCp_2Et_2,\ g) = \Delta_f H°(MoCp_2Et_2,\ cr) + \Delta_{sub}H°(MoCp_2Et_2) = 293.9 \pm 4.9$ kJ mol^{-1} was finally calculated.

The Knudsen cell mass-loss effusion set-up available at CQE-IST to measure the enthalpies of sublimation requires samples of 200–500 mg [21–23]. This hinders its application to many compounds, which are available only in much smaller amounts. To overcome this problem, a microcalorimetric apparatus for the measurement of $\Delta_{sub}H°$ by the vacuum-drop method [24] was developed recently [25]. This apparatus, which requires samples of less then 5 mg per experiment, is currently being applied, in conjunction with the Knudsen effusion method, to study a series of metalocenes [25,26]. These determinations are part of a project aiming to assess the reliability of atom–atom potential calculations [27,28] to predict the enthalpies of sublimation of organometallic species from structural data [26]. The measurement of $\Delta_{sub}H°$ for organometallic substances is frequently difficult, as many of these compounds are oxygen- and moisture-sensitive and decompose on heating in vacuum before yielding a detectable amount of vapour. Owing to the variety of metals and ligands in organometallic complexes it is virtually impossible to develop empirical correlations to estimate $\Delta_{sub}H°$, analogous to those available for organic compounds [29]. Therefore, the atom–atom potential calculations appears to be an attractive approach.

In principle the value of $\Delta_f H°(MoCp_2Et_2,\ g)$ indicated above could be used to obtain $\langle DH°\rangle$(Mo–Et) from the following reaction

$$MoCp_2Et_2\ (g) \rightarrow MoCp_2\ (g) + 2Et\ (g) \qquad (12)$$

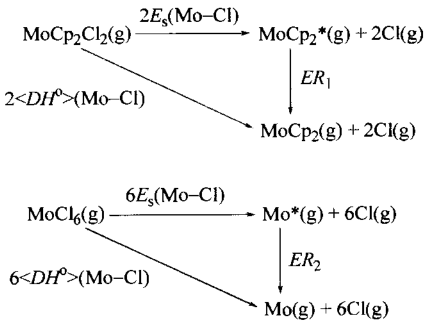
if the enthalpy of formation of $MoCp_2$ was known. Unfortunately, no experimental determination of the enthalpy of formation of a transient species MCp_2 has been carried out yet (this is still one of the 'holy grails' of organometallic thermochemistry). To overcome this problem, $\langle DH°\rangle$(Mo–Et) and all other bond dissociation enthalpy values reported until now for MCp_2L_n compounds have been anchored on to the M–Cl mean bond dissociation enthalpies of the corresponding dichlorides. This was carried out by considering reaction (13) and Eq. (14):

$$MCp_2L_n\ (g) + 2Cl\ (g) \rightarrow MCp_2Cl_2\ (g) + nL\ (g) \qquad (13)$$

$$\begin{aligned} &\langle DH°\rangle(M\text{–}L)\\ &= \frac{2\langle DH°\rangle(M\text{–}Cl)}{n} + \frac{\Delta_f H°(MCp_2Cl_2,\ g)}{n} + \Delta_f H°(L,\ g)\\ &\quad \frac{-\Delta_f H°(MCp_2L_n,\ g)}{n} - \frac{2\Delta_f H°(Cl,\ g)}{n} \end{aligned} \qquad (14)$$

The calculation of $\langle DH°\rangle$(Mo–Et) from Eq. (14) requires the knowledge of $\langle DH°\rangle$(Mo–Cl). As this value is also not available, it was assumed that $\langle DH°\rangle$(Mo–Cl) in $MoCp_2Cl_2$ was identical to $\langle DH°\rangle(Mo\text{–}Cl) = 303.8 \pm 7.1$ kJ mol^{-1} in the homoleptic molecule $MoCl_6$, as proposed by Tel'noi and Rabinovich [30]. This result, in conjunction with $\Delta_f H°(MCp_2Et_2,\ g)$ quoted above, $\Delta_f H°(MCp_2Cl_2,\ g) = 4.6 \pm 4.9$ kJ mol^{-1} [20], $\Delta_f H°(Et,\ g) = 119 \pm 4$ kJ mol^{-1} [31], and $\Delta_f H°(Cl,\ g) = 121.679$ kJ mol^{-1} [32], lead to $\langle DH°\rangle(Mo\text{–}Et) = 156 \pm 9$ kJ mol^{-1}. The rational for the 'educated guess' of $\langle DH°\rangle$(Mo–Cl) made by Tel'noi and Rabinovich is worth mentioning. The starting assumption was that the bond dissociation enthalpies are approximately transferable between bonds of the same type and with similar bond lengths. Hence, the Mo–Cl bond distance in $MoCl_6$ should be close to $r_{Mo\text{–}Cl} = 247$ pm in $MoCp_2Cl_2$ [33]. Unfortunately the structural data necessary for comparison were lacking as the structure of $MoCl_6$ was not (and still is not) experimentally determined. However, it was known that $r_{Mo\text{–}Cl} = 227 \pm 2$ pm in $MoCl_5$ [34]. As it was expected that the bond dissociation enthalpies decrease with the increasing bond lengths, and $\langle DH°\rangle$(Mo–Cl) was 38 kJ mol^{-1} smaller in the molybdenum hexachloride than in the pentachloride [30], Tel'noi and Rabinovich postulated that $\langle DH^\circ \rangle$(Mo–Cl) in $MoCp_2Cl_2$ and $MoCl_6$ are similar.

The transferability of bond dissociation enthalpies amongst different molecules has been a topic of immense debate in organometallic thermochemistry [35]. It is generally believed that the bond snap energies (E_s, see Scheme 1), which do not contain the reorganisation enthalpies of the fragments formed by the cleavage of bonds, should afford more meaningful correlations with bond lengths than bond dissociation enthalpies. On the basis of this hypothesis, the transferability of $\langle DH^\circ \rangle$(Mo–Cl) from molybdenum hexachloride to bis(η^5-cyclopentadienyl)molybdenum dichloride, assumed by Tel'noi and Rabinovich, implies that $ER_1/2 = ER_2/6$ in Scheme 3, where ER_2 is the enthalpy of relaxation of Mo from the state of hybridisation necessary to form the six Mo–Cl bonds in $MoCl_6$ to the ground state. Although this may not be the case, it should be noted that the estimated differences in the $\langle DH^\circ \rangle$(M–Cl) values for the anchors of different metals are frequently large enough (e.g. $\langle DH^\circ \rangle$(Ti–Cl) $= 430.5 \pm 1.3$ kJ mol^{-1}; $\langle DH^\circ \rangle$(Mo–Cl) $= 303.8 \pm 7.1$ kJ mol^{-1}; $\langle DH^\circ \rangle$(W–Cl) $= 347.3 \pm 0.8$ kJ mol^{-1}) to allow at least a qualitative discussion of how $\langle DH^\circ \rangle$(M–L) vary with M. The contribution of the reorganisation energies may also cancel when comparing similar complexes. For example, $\langle DH^\circ \rangle$(W–Br) $= 296 \pm 7$ kJ mol^{-1} in WBr_6 and $\langle DH^\circ \rangle$(Ti–I) $= 294 \pm 2$ kJ mol^{-1} in TiI_4 are in excellent agreement with the corresponding values of $\langle DH^\circ \rangle$(W–Br) $= 298 \pm 7$ kJ mol^{-1} in WCp_2Br_2 and $\langle DH^\circ \rangle$(Ti–I) $= 298 \pm 9$ kJ mol^{-1} in $TiCp_2I_2$, which are anchored on $\langle DH^\circ \rangle$(M–Cl) in WCl_6 and $TiCl_4$, respectively [20]. Finally, the errors associated with the selection of the anchor do not affect the discussion of the energetics of reactions such as:



Scheme 3.

$$MoCp_2H_2(g) + I_2(g) \rightarrow MoCp_2I_2(g) + H_2(g) \qquad (15)$$

The enthalpy of this reaction is given by $\Delta_r H^\circ(15) = 2\langle DH^\circ \rangle(\text{Mo–H}) - 2\langle DH^\circ \rangle(\text{Mo–I}) + DH^\circ(\text{I–I}) - DH^\circ$(H–H) and the contribution of the anchor is eliminated when the difference $\langle DH^\circ \rangle$(Mo–H) $-$ $\langle DH^\circ \rangle$(Mo–I) is computed.

Table 1
Enthalpies of β-hydride elimination reactions (16) and (17) for various transition metal and actinide systems [11]

Complex [a]	$\Delta_r H^\circ$ (kJ mol^{-1})	
	L = Et	L = Bu
Th(Cp*)$_2$L$_2$	82 ± 11	63 ± 14
Th(Cp*)$_2$(O-*t*-Bu)L	94 ± 11	72 ± 18
Th(Cp*)$_2$(Cl)L	77 ± 11	66 ± 16
Th(Cp*)$_2$[OCH(*t*-Bu)$_2$]L	113 ± 18	102 ± 18
U(Cp*)$_2$[OSi(*t*-Bu)(Me)$_2$]L	109 ± 10	98 ± 14
Zr(Cp*)$_2$L$_2$	79 ± 7	68 ± 12
Hf(Cp*)$_2$L$_2$	94 ± 11	72 ± 15
Mo(Cp)$_2$L$_2$	51 ± 13	41 ± 17
Mo(Cp)(CO)$_3$L	55 ± 13	44 ± 15
W(Cp)$_2$L$_2$	44 ± 8	33 ± 13
Mn(CO)$_5$L	76 ± 12	65 ± 16
Rh(tmp)L	104	93
Ir(Cl)(CO)(PMe$_3$)$_2$(I)L	39 ± 9	20 ± 22
Pt(PR$_3$)$_2$(Cl)L	51 ± 37	40 ± 38

[a] Cp = η^5-C_5H_5; Cp* = η^5-C_5Me_5; tmp = 5,10,15,20-tetrakis(2,4,6-trimethylphenyl)porphyrinato dianion.

3. Energetics of β-hydride elimination

As stated above, the bond dissociation enthalpy data obtained from reaction-solution calorimetric experiments have been used, by others and us, to investigate the trends in the chemical reactivity of organometallic complexes. The scope of these studies can be illustrated by the discussion of the β-hydride elimination reaction (Scheme 2) which is the most important decomposition pathway for transition metal, lanthanide, and actinide alkyl complexes containing β-hydrogen substituents, and a key elementary step in many catalytic cycles [36]. For ethyl and butyl (Bu) derivatives, the reaction can be represented by Eqs. (16) and (17), respectively.

$$L_nM\text{–Et} \rightarrow L_nM\text{–H} + H_2C{=}CH_2 \qquad (16)$$

$$L_nM\text{–Bu} \rightarrow L_nM\text{–H} + H_2C{=}CHEt \qquad (17)$$

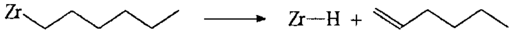
where L_nM is a coordinatively unsaturated metal complex with n ancillary ligands, L. The enthalpies of reactions (16) and (17), $\Delta_r H^\circ(16)$ and $\Delta_r H^\circ(17)$, can be expressed in terms of bond dissociation enthalpies by Eqs. (18) and (19), respectively.

$$\Delta_r H^\circ(16) = DH^\circ(\text{M–Et}) + DH^\circ(C_2H_4\text{–H}) - DH^\circ(\text{M–H}) \qquad (18)$$

$$\Delta_r H^\circ(17) = DH^\circ(\text{M–Bu}) + DH^\circ(C_4H_8\text{–H}) - DH^\circ(\text{M–H}) \qquad (19)$$

Table 1 lists the enthalpies of β-hydride elimination for the various organometallic systems. These values were calculated from $DH°(C_2H_4\text{–}H) = 151.5 \pm 4.0$ kJ mol^{-1} [31,37] and $DH°(C_4H_8\text{–}H) = 144.1 \pm 8.0$ kJ mol^{-1} [31,37], and from the experimentally measured or estimated M–H, M–Et and M–Bu bond dissociation enthalpy data previously selected from the literature [11]. Analysis of Table 1 suggests that, with the notable exception of the rhodium system, the reaction is more endothermic, and therefore less favourable for actinides and early transition metal complexes than for the late transition metal complexes. In addition, β-hydride elimination from a butyl ligand to give 1-butene is more favourable than the corresponding reaction for an ethyl ligand.

In reactions (16) and (17) a terminal alkene is generated by β-hydride elimination. It is interesting to compare the thermochemistry of this type of reaction with that of a reaction in which a non-terminal alkene is formed, and also with the thermochemistry of a reaction that yields a cyclic alkene from a cyclic alkyl. Reaction-solution calorimetry studies of $Zr(Cp)_2(Cl)R$ (R = H, alkyl) complexes from our laboratory [38] allow us to make these comparisons. The enthalpies of the following reactions: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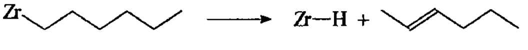
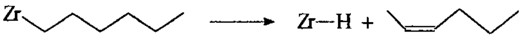
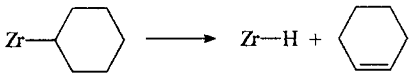

(21)


(22)


(23)

are given by the equations:

$$\Delta_r H°(20) = DH°(\text{Zr–Hx}) + DH°(\text{1-hexene–H}) - DH°(\text{Zr–H}) \quad (24)$$

$$\Delta_r H°(21) = DH°(\text{Zr–Hx}) + DH°(E - \text{2-hexene–H}) - DH°(\text{Zr–H}) \quad (25)$$

$$\Delta_r H°(22) = DH°(\text{Zr–Hx}) + DH°(Z\text{-2-hexene–H}) - DH°(\text{Zr–H}) \quad (26)$$

$$\Delta_r H°(23) = DH°(\text{Zr–Cy}) + DH°(\text{cyclohexene–H}) - DH°(\text{Zr–H}) \quad (27)$$

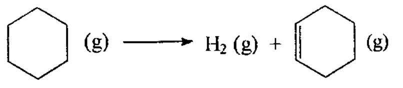
where Hx = hexyl and Cy = cyclohexyl. By using, $DH°(\text{Zr–H}) = 364 \pm 5$ kJ mol^{-1} [38], $DH°(\text{Zr–Hx}) = 317 \pm 10$ kJ mol^{-1} [38], $DH°(\text{Zr–Cy}) = 319 \pm 7$ kJ mol^{-1} [38], $DH°(\text{1-hexene–H}) = 141.4 \pm 8.2$ kJ mol^{-1} [31,37], $DH°(E\text{-2-hexene–H}) = 131.0 \pm 8.1$ kJ mol^{-1} [31,37], $DH°(Z\text{-2-hexene–H}) = 132.6 \pm 8.1$ kJ mol^{-1} [31,37], and $DH°(\text{cyclohexene–H}) = 155.1 \pm 4.0$ kJ mol^{-1} [31,37], it is concluded that $\Delta_r H°(20) = 94 \pm 14$ kJ mol^{-1}, $\Delta_r H°(21) = 84 \pm 14$ kJ mol^{-1}, $\Delta_r H°(22) = 86 \pm 14$ kJ mol^{-1}, and $\Delta_r H°(23) = 110 \pm 10$ kJ mol^{-1}. These results indicate that, at least for the Zr system under study, it is less favourable to obtain a terminal alkene by β-hydride elimination, than a non-terminal alkene. It can also be concluded that it is less favourable to generate a cyclic alkene than a linear (terminal or non-terminal) alkene. Note that, since $DH°(\text{Zr–Hx}) \approx DH°(\text{Zr–Cy})$, this last conclusion is mainly because of the fact that $DH°(\text{cyclohexene–H})$ considerably exceeds $DH°(\text{1-hexene–H})$, $DH°(E\text{-2-hexene–H})$, and $DH°(Z\text{-2-hexene–H})$.

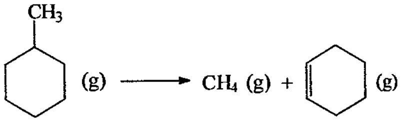
4. A simple method to estimate the entropy changes in organometallic reactions

We have been discussing reactivity trends based on the exothermicity or endothermicity of a reaction, more exothermic meaning more favourable conversion of reactants into products. As stated above, this is frequently a reasonable approach as the enthalpic term in Eq. (2) is usually dominant at temperatures not too far from ambient. However, in some cases $T\Delta_r S°$ makes an important contribution or even determines the sign of $\Delta_r G°$. For example, studies of reaction:

$$Cr(CO)_3(PCy_3)_2 \text{ (sln)} + H_2 \text{ (sln)} \rightarrow Cr(CO)_3(PCy_3)_2(\eta^2\text{-}H_2) \text{ (sln)} \quad (28)$$

in tetrahydrofuran, led to $\Delta_r H°(28) = -30.5$ kJ mol^{-1} and $T\Delta_r S°(28) = -31.9$ kJ mol^{-1}, at 298.15 K [39], corresponding to $\Delta_r G°(28) = 1.4$ kJ mol^{-1}. In this case, ignoring the entropic contribution (i.e. making $\Delta_r G° \approx \Delta_r H°$) results in a very large error in the value of the equilibrium constant ($K = 1.8 \times 10^5$ instead of $K = 0.57$). Fortunately, the entropy of a reaction essentially depends on the net change of the internal and external degrees of freedom when reactants are converted into products and not on the types of bonds broken and formed. Therefore, $\Delta_r S°$ for the organometallic reactions can be identified frequently with the known $\Delta_r S°$ values for model organic or inorganic reactions that mimic the changes in the degrees of freedom of those organometallic reactions [40]. For example, an estimate of the entropy of reaction (23) can be made by using the following reactions:


(29)


(30)

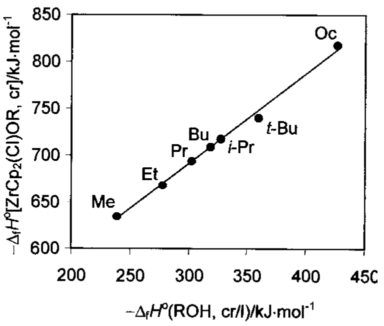
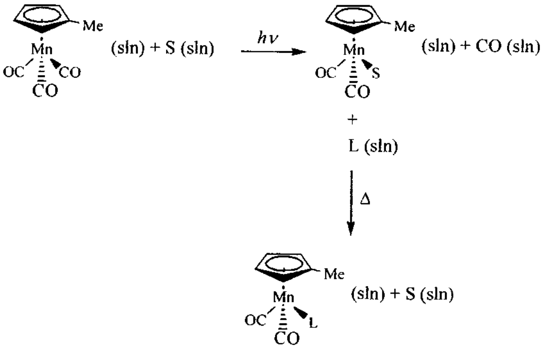
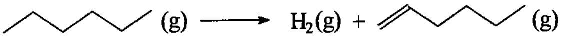


Fig. 2. Enthalpies of formation of $ZrCp_2(Cl)OR$ (cr) versus the enthalpies of formation of the corresponding alcohols, ROH (cr/l), for R = CH_3 (Me), C_2H_5 (Et), *n*-C_3H_7 (Pr), *i*-C_3H_7 (*i*-Pr), *n*-C_4H_9 (Bu), *t*-C_4H_9 (*t*-Bu), *n*-C_8H_{17} (Oc).

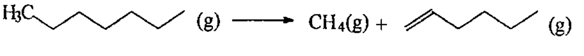


Scheme 4.

as models. The values of $T\Delta_rS°$ at 298.15 K for reactions (29) and (30) are 42.7 and 45.8 kJ mol^{-1}, respectively [32,41]. Note that, although different reactants and products are involved in reactions (29) and (30), the corresponding entropy changes are similar. It is therefore expected that, to a good approximation, the $T\Delta_rS°$ value for reaction (23) can be identified with the average of the above two values, ca. 44 kJ mol^{-1}, with a small error (less than 5 kJ mol^{-1} [40]). The exercise can be repeated for reaction (20) by using reactions (31) and (32):



(31)



(32)

as models. In these cases, $T\Delta_rS° = 37.9$ kJ mol^{-1} and $T\Delta_rS° = 42.6$ kJ mol^{-1}, respectively. The values are very similar to those obtained for reactions (29) and (30), showing that, in general, for β-hydride eliminations an entropic contribution of ca. 35–45 kJ mol^{-1} should be considered. This reaction is thus favoured by a $T\Delta_rS°$ term, which may offset $\Delta_rH°$ for late transition metal systems (Table 1).

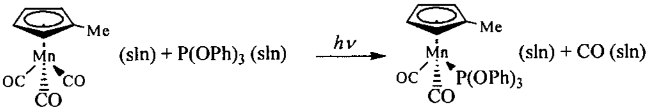
5. Estimation of enthalpies of formation of organometallic compounds: Tina's method

The growth rate of the organometallic thermochemistry database [2] is several orders of magnitude smaller than the rate at which new organometallic substances are being synthesised. This fostered the development of methods for estimating the enthalpies of formation and bond dissociation enthalpies of organometallic compounds [42]. Bond or group additivity schemes, which have been so successful in the case of organic molecules, are virtually impossible to transpose for organometallic systems, owing to the many possible combinations of metals and ligands. One of us (C.T.) first noted that good linear correlations could be obtained by plotting the enthalpies of formation of series of MX_nL_m compounds versus the enthalpies of formation of the ligands L or LH, both in their standard reference states and in the gas phase, at 298.15 K. These correlations, which hold for a large variety of inorganic and organometallic compounds [43–45], can be used to assess and estimate experimental data, and are illustrated in Fig. 2 for the $ZrCp_2(Cl)OR$ system [38].

6. Photocalorimetry: photosubstitution of carbonyl by phosphites in the complex $Mn(\eta^5\text{-}C_5H_4Me)(CO)_3$

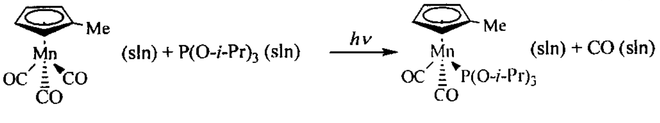
The reaction-solution calorimeter indicated in Fig. 1 is suitable for investigating thermally activated reactions. However, not all reactions occur by thermal activation. For example, the replacement of the carbonyl ligands in $Mn(Cp')(CO)_3$ ($Cp' = \eta^5\text{-}C_5H_4Me$) by nucleophiles can only be achieved photochemically. This method is used in the synthesis of $Mn(Cp')(CO)_2L$ complexes, according to Scheme 4, where S represents the solvent (S = diethyl ether, tetrahydrofuran, alkanes, etc.) and L a donor ligand (L = thiol, phosphine, phosphite, amine, pyridine, etc.). Very often these photochemical reactions are clean under carefully selected conditions and can be thermochemically studied using a *photocalorimeter*. The basic principles, applications, and types of instruments used in photocalorimetry have been reviewed [46,47].

The enthalpies of the reactions:



$\Delta_rH° = -(15.7 \pm 0.5)$ kJ.mol^{-1}

(33)



$\Delta_rH° = -(18.6 \pm 0.9)$ kJ.mol^{-1}

(34)

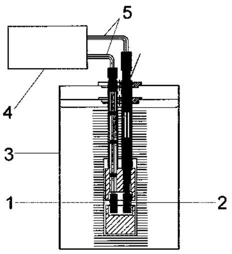


Fig. 3. Photomicrocalorimeter: (1) photoinert reference cell; (2) sample cell; (3) thermostatic jacket; (4) light source; and (5) fibre optics system [47].

in heptane solution, under argon atmosphere, were measured by using the photomicrocalorimeter indicated in Fig. 3 [48]. The instrument is based on the Thermal Activity Monitor (TAM) from ThermoMetric and was developed by Teixeira and co-workers [47]. An inert reference (1) and the sample (2) cells, placed inside a thermostatic jacket (3), were irradiated simultaneously with light of 400 nm wavelength and a bandpath of 45 nm. The source (4) was a 100 W tungsten lamp and the irradiation wavelength was selected by using a series of filters. A fibre optics system (5) guided the light into the cells.

The enthalpies of reactions (33) and (34) can be identified with the differences in bond dissociation enthalpies in solution, $DH_{\mathrm{soln}}(\mathrm{Mn{-}CO}) - DH_{\mathrm{soln}}[\mathrm{Mn{-}P(OPh)_3}]$ and $DH_{\mathrm{soln}}(\mathrm{Mn{-}CO}) - DH_{\mathrm{soln}}[\mathrm{Mn{-}P(O\text{-}}i\mathrm{\text{-}Pr)_3}]$, respectively. The results obtained thus indicate that $DH_{\mathrm{soln}}(\mathrm{Mn{-}CO}) < DH_{\mathrm{soln}}[\mathrm{Mn{-}P(OPh)_3}] < DH_{\mathrm{soln}}[\mathrm{Mn{-}P(O\text{-}}i\mathrm{\text{-}Pr)_3}]$. It seems reasonable to assume that the solvation enthalpies of reactants and products in reactions (33) and (34) nearly cancel each other. It is therefore expected that this trend should also be observed in the gas phase. These conclusions are supported by other experimental data: $\mathrm{P(O\text{-}}i\mathrm{\text{-}Pr)_3}$ is more basic than $\mathrm{P(OPh)_3}$, judging from the pK_a of the corresponding protonated species in aqueous solution, 4.08 and −2.0, respectively [49]. In addition, $\nu_{\mathrm{CO}} = 2086.3$ cm^{-1} in $[\mathrm{Mn(Cp')(CO)_2P(OPh)_3}]$ and $\nu_{\mathrm{CO}} = 2075.2$ cm^{-1} in $[\mathrm{Mn(Cp')(CO)_2P(O\text{-}}i\mathrm{\text{-}Pr)_3}]$ can be estimated by using the $^{\mathrm{FT}}\chi$ parameters in Ref. [49], suggesting that $\mathrm{P(O\text{-}}i\mathrm{\text{-}Pr)_3}$ is the strongest σ-donor. Finally, bond dissociation enthalpies derived from reaction-solution calorimetric results of the same type of ligand substitution reactions in molybdenum complexes also support the above trend [48,50].

7. Concluding remarks

The examples described in the previous paragraphs illustrate how we have been using the thermochemical methodologies to examine several issues in organometallic chemistry. Some of those problems are still being addressed by more laboratory work. The thermodynamic stability of organometallic substances and metal–ligand bonds, for instance, which has been at the centre of our research interests for many years, still plays a significant role in our group's activity. Besides new experiments and the development of estimation methods, the work in this area now includes a comprehensive analysis of literature data [2].

The above studies illustrated only three techniques used in our research — reaction-solution calorimetry, photocalorimetry, and vapour pressure versus temperature measurements by the Knudsen effusion method. Other experimental methods (micro and macrocombustion calorimetry, photoacoustic calorimetry, and ion-cyclotron resonance mass spectrometry) have been added to our thermochemical tools, extending the range of problems of our interest. Some of these techniques are in operation at other institutions (Faculdade de Ciências da Universidade de Lisboa and Instituto Tecnológico e Nuclear) but the scientific interaction among all members of the 'Lisbon thermochemistry group' remains very strong. Microcombustion calorimetry, e.g. has allowed the study of the energetics of fullerenes [51], polycyclic unsaturated hydrocarbons [52], and models of DNA photoliases [53]. Macrocombustion calorimetry in conjunction with computational chemistry results was used to discuss the energetics of the carbon–halogen bonds in halogeno acetic acids [54]. Photoacoustic calorimetry, and ion-cyclotron resonance mass spectrometry are being used to investigate the energetics of transient species, in solution and in the gas phase [55].

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