jacket connected either to a thermostat (for 25 °C operations) or to a cryostat (for 0 °C operations). Stirring was performed by a Teflon-coated bar driven externally by a magnetic stirrer.

In a typical experiment the catalyst was charged in the reactor and the system was evacuated and filled with N_2. Then dry, N_2-saturated solvent (CH_2Cl_2) was introduced followed by 1-octene (final volume 8 mL). Finally H_2O_2 was injected through the silicone septum. The reaction mixture was periodically sampled, and the proceeding of the reaction was monitored with GLC. In the case of propylene, after addition of the solvent (DCE), the olefin was slowly flowed into the system for about 2 min and then maintained at constant pressure with the aid of a gas reservoir.

At the end of the reaction the organic phase was separated from the water phase, which was further extracted three times with small portions of organic solvent (CH_2Cl_2 or DCE). In the case of 1,2-epoxyoctane the organic phase was slowly evaporated to yield the crude product. This was distilled in vacuo to yield pure 1,2-epoxyoctane [bp 58–59 °C at 10 torr (lit.[38] bp 61 °C at 15 torr)]. Conversely, 1,2-epoxypropane was directly distilled from the organic phase at ambient pressure (bp 34 °C).

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Studies on the Transferability of Transition-Metal–Carbon and –Hydrogen Bond Enthalpies in Bis(cyclopentadienyl) Complexes

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New thermochemical studies involving the complexes $Ti(\eta^5\text{-}C_5H_5)_2(CH_3)_2$, $Ti(\eta^5\text{-}C_5H_5)_2(CH_3)Cl$, $Ti(\eta^5\text{-}C_5H_5)_2(C_6H_5)Cl$, and $W(\eta^5\text{-}C_5H_5)_2(H)I$ together with early data for the same type of molecules containing metal–carbon and metal–hydrogen bonds enabled a detailed discussion on the validity of transferring bond enthalpies. For this purpose, a method based on the bond enthalpy term concept, previously developed for complexes $M(\eta^5\text{-}C_5H_5)_2LL'$ ($L = L'$), was extended to molecules with $L \neq L'$. This method also yields estimates of metal–ligand first bond dissociation enthalpies. The thermodynamics of the recently reported symmetrization reactions between $Ti(\eta^5\text{-}C_5H_5)_2Cl_2$ and $Ti(\eta^5\text{-}C_5H_5)_2R_2$ ($R = CH_3$, C_6H_5) is also described in the present study.

Introduction

The large number of recent papers and surveys on the energetics of transition-metal–carbon and –hydrogen σ-bonds reflects the importance of this subject in several areas of chemistry.[1-3] Gas-phase techniques are mainly responsible for the rapid growth of the metal–ligand bond energies data bank. These data shed light on the nature of those bonds and enabled us to establish correlations, which can be used to predict new values.[4] Most of the published gas-phase studies, however, deal with organometallic fragments and seldom with coordinatively saturated complexes, these being of greater importance for the preparative chemist. Equilibrium and kinetic studies in solution have been made by several groups to determine metal–carbon and –hydrogen bond enthalpy data in organometallic complexes,[2a-g,i] but the fact that it is not always simple to find a suitable reaction to apply those methods limits their use. This is one of the reasons why the calorimeter, in any of its several versions, is still widely applied to study the thermochemistry of transition-metal–organo complexes.[2h-l]

Calorimetric experiments usually yield an enthalpy of formation and rarely a metal–ligand bond dissociation enthalpy or even a difference between two of these quantities.[1a] If a complex has two or more types of ligands and one is interested in the energetics of a specific metal–ligand bond, then the knowledge of all the remaining bond enthalpies is necessary. These auxiliary data come, of course, from studies involving other molecules, which usually contain only one type of ligand.

The transferability of bond enthalpies is a central question in the area of organometallic thermochemistry. Recognizing when it is valid to identify bond enthalpies in different molecules will produce more reliable estimates of enthalpies of formation of molecules for which thermochemistry is either difficult or even impossible to study in the laboratory (e.g. transient species) and will therefore

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enable us to predict the energetics of reactions involving those molecules. Although transferring bond enthalpies on the basis of, for example, similar bond lengths, has been a common procedure in many thermochemical studies,[1a,5,6] the accuracy of the values obtained in this way is often difficult to assess. In order to tackle this problem, a simple method that couples experimental results (enthalpies of formation) with theoretical calculations at the extended Hückel level has been developed.[1a,7] Useful but still limited information on the transferability of bond enthalpies has been obtained through the application of that method to a variety of organometallic systems. In this paper we report thermochemical studies of a few selected molecules, containing titanium–methyl, titanium–phenyl, and tungsten–hydrogen bonds, which are particularly suited for a discussion of the transferability problem. Some early values of transition-metal–carbon and –hydrogen bond enthalpies are reevaluated and included in the discussion.

Experimental Section

Calorimetry. The reaction and solution enthalpies were measured in the reaction–solution calorimeter previously described.[8] To ensure an inert atmosphere in the calorimetric vessel, pure nitrogen was bubbled through the solvent for 45 min before each run involving the complex $W(Cp)_2(H)I$. This precaution was not needed for the titanium complexes, since they are unaffected by exposure to air or moisture for short periods. However, the glass ampules were filled under nitrogen or argon in every case.

Compounds. Complexes $Ti(Cp)_2(CH_3)_2$, $Ti(Cp)_2(CH_3)Cl$, $Ti(Cp)_2(C_6H_5)Cl$, and $W(Cp)_2(H)I$ ($Cp = \eta^5\text{-}C_5H_5$) were prepared, purified, and characterized as described in the literature.[9,10] The dimethyl complex was stored and handled at low temperatures whenever possible. The reaction solutions were prepared from Merck, P. A., hydrochloric acid, acetone, and toluene and BDH Analar iodine, which were used without further purification.

Reactions. Standard enthalpies of formation of the complexes studied were derived from thermochemical measurements of reactions 1–3 ($R = CH_3$, C_6H_5). The solutions used for reactions

$$Ti(Cp)_2(CH_3)_2(c) + 2HCl(soln) \rightarrow Ti(Cp)_2Cl_2(soln) + 2CH_4(g) \quad (1)$$

$$Ti(Cp)_2(R)Cl(c) + HCl(soln) \rightarrow Ti(Cp)_2Cl_2(soln) + RH(g/soln) \quad (2)$$

$$W(Cp)_2(H)I(c) + I_2(soln) \rightarrow W(Cp)_2I_2(c) + HI(soln) \quad (3)$$

1 and 2 were a 1:1 mixture of 8.3 mol dm^{-3} aqueous HCl and acetone (solution A) and a 1:4 mixture of 10.0 mol dm^{-3} aqueous HCl and acetone (solution B), respectively. The thermochemical disadvantages of these mixtures were discussed elsewhere.[11] For the tungsten complex a solution of toluene containing an excess (about twice the stoichiometric amount) of iodine was used.

The reactions involving the titanium complexes were found to be fast and quantitative, as reported in the literature.[9b,12] The reaction of $W(Cp)_2(H)I$ with iodine was assumed to be quantitative by analogy with the related reactions of $M(Cp)_2H_2$ (M = Mo, W).[8]

Table I. Auxiliary Thermochemical Data (kJ mol^{-1})

molecule	$\Delta H_f°$	$\Delta H_{s/v}°$ [a]
HCl(aq (8.3 mol dm^{-3})	−156.824 ± 0.004[b]	
HCl(soln A)	−162.47 ± 0.28[c]	
HCl(soln B)	−172.59 ± 0.51[c]	
$CH_4(g)$	−74.5 ± 0.4[d]	
$C_6H_6(l)$	49.0 ± 0.3[d]	33.85 ± 0.04[e]
HI(g)	26.36 ± 0.80[f]	
H(g)	217.997 ± 0.006[f]	
C(g)	716.67 ± 0.44[f]	
Cl(g)	121.302 ± 0.008[f]	
I(g)	106.762 ± 0.040[f]	

[a] Standard enthalpy of sublimation or vaporization. [b] Reference 14. [c] Reference 11. [d] Reference 16. [e] Reference 17. [f] Reference 18.

This is supported by the good agreement between the "cooling constant" (*K*) for each run and calibration in the calorimeter.[13] The products $Ti(Cp)_2Cl_2$ and $W(Cp)_2I_2$ were confirmed by IR spectroscopic analysis.

All the reaction and solution enthalpies presented are mean values from at least five independent experiments and refer to 298 K. The associated uncertainties are twice the standard deviations of those mean values.

Auxiliary Data. Standard enthalpies of formation, vaporization, and sublimation at 298 K, which were used in evaluating the thermochemical results, were quoted from data compilations or from previous papers[8,11,14–18] and are collected in Table I. Auxiliary data for recalculating early thermochemical values for $M(Cp)_2L_2$ complexes (M = Ti, Mo, W) containing metal–carbon bonds are listed elsewhere.[19,20]

Results and Discussion

The thermochemical results are summarized in Table II. ΔH_r stands for the enthalpy of reactions 1, 2, or 3; ΔH_{d1} refers to the enthalpy of solution of $Ti(Cp)_2Cl_2(c)$ in solutions A or B; for the titanium complexes ΔH_{d2} represents the enthalpy of solution of $CH_4(g)$ or $C_6H_6(l)$ in solutions A or B containing stoichiometric amounts of $Ti(Cp)_2Cl_2$, and for the tungsten complex it refers to the enthalpy of solution of HI(g) in toluene; ΔH_{d3} was determined by breaking ampules containing stoichiometric amounts of aqueous hydrochloric acid in the reaction medium (solutions A and B) in the case of the titanium systems; for the tungsten complex it represents the enthalpy of solution of $I_2(c)$ in toluene. ΔH_{d4}, which corresponds to the acid dilution effect, was obtained by breaking ampules containing stoichiometric amounts of distilled water in solutions A and B.

The standard enthalpies of formation of the crystalline and gaseous complexes (Table III) were evaluated from the results collected in Table II, from $\Delta H_f°[Ti(Cp)_2Cl_2(c)]$, $\Delta H_f°[W(Cp)_2I_2(c)]$ (Table III), and from auxiliary data (Table I). For example $\Delta H_f°[Ti(Cp)_2(CH_3)Cl(c)] = -\Delta H_r + \Delta H_{d1} + \Delta H_{d2} - \Delta H_{d3} + 4.40\Delta H_{d4} + \Delta H_f°[Ti(Cp)_2Cl_2(c)] + \Delta H_f°[CH_4(g)] - \Delta H_f°[HCl\cdot 4.40H_2O(aq)]$. Table III also includes values corrected for acid dilution (ΔH_{d4}) for

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Table II. Thermochemical Results (kJ mol^{-1})

complex	ΔH_r	ΔH_{d1}	ΔH_{d2}	ΔH_{d3}	ΔH_{d4}
$Ti(Cp)_2(CH_3)_2$	−190.0 ± 5.6	5.2 ± 1.8[a]	0[b]	−5.65 ± 0.28[a]	−1.31 ± 0.03[c]
$Ti(Cp)_2(CH_3)Cl$	−49.3 ± 2.7	17.2 ± 1.3[d]	0[b]	−18.48 ± 0.51[a]	−3.66 ± 0.15[c]
$Ti(Cp)_2(C_6H_5)Cl$	−78.0 ± 1.2	17.2 ± 1.3[d]	3.27 ± 0.17[e]	−18.48 ± 0.51[a]	−3.66 ± 0.15[c]
$W(Cp)_2(H)I$	−130.1 ± 3.4		−29.6 ± 2.3[f]	15.92 ± 0.16[g]	

[a] Reference 11. [b] The solubility of methane in the reaction solutions was considered negligible. Values for the CH_4 molar fractions in water and in acetone under 1 atm of the gas can be found in: Wilhelm, E.; Battino, R.; Wilcock, R. J. *Chem. Rev.* **1977**, *77*, 219. Wilhelm, E.; Battino, R. *Chem. Rev.* **1973**, *73*, 1. [c] Reference 7. [d] Reference 24b. [e] Reference 19. [f] Calculated from solubility data. See reference 8. [g] Reference 8.

Table III. Enthalpies of Formation, $\Delta H_f°(c)$ and $\Delta H_f°(g)$ (kJ mol^{-1})

complex	$\Delta H_f°(c)$[a]	$\Delta H_s°$ [b]	$\Delta H_f°(g)$
$Ti(Cp)_2Cl_2$	−383.2 ± 7.5	118.8 ± 2.1	−264.4 ± 7.8
$Ti(Cp)_2(CH_3)_2$	−26.6 ± 9.6	(79.5 ± 8.4)[c]	52.9 ± 12.7
$Ti(Cp)_2(CH_3)Cl$	−234.7 ± 8.1	(110 ± 10)	−124.7 ± 12.9
$Ti(Cp)_2(C_6H_5)_2$	262.2 ± 8.9	(88 ± 8)	350.2 ± 12.0
$Ti(Cp)_2(C_6H_5)Cl$	−79.2 ± 7.8	(120 ± 10)	40.8 ± 12.7
$Ti(Cp)_2(3\text{-}CH_3C_6H_4)_2$	166.8 ± 9.4	(95 ± 8)	261.8 ± 12.3
$Ti(Cp)_2(4\text{-}CH_3C_6H_4)_2$	169.6 ± 9.6	(95 ± 8)	264.6 ± 12.5
$Ti(Cp)_2(4\text{-}CF_3C_6H_4)_2$	−1142.6 ± 8.3	(110 ± 8)	−1032.6 ± 11.5
$Ti(Cp)_2(4\text{-}CH_3OC_6H_4)_2$	−91.8 ± 8.5	(104 ± 8)	12.2 ± 11.7
$Ti(Cp)_2Fc_2$[d]	488.2 ± 12.1	(150 ± 15)	638.2 ± 19.3
$Mo(Cp)_2Cl_2$	−95.8 ± 2.5	(100.4 ± 4.2)	4.6 ± 4.9
$Mo(Cp)_2H_2$	210.3 ± 5.7	92.5 ± 2.1	302.8 ± 6.1
$Mo(Cp)_2(CH_3)_2$	262.4 ± 4.0	70.4 ± 4.2	332.8 ± 5.8
$W(Cp)_2Cl_2$	−71.1 ± 2.5	(104.6 ± 4.2)	33.5 ± 4.9
$W(Cp)_2I_2$	57.8 ± 7.6	(104.6 ± 4.2)	162.4 ± 8.7
$W(Cp)_2H_2$	214.8 ± 5.0	96.2 ± 2.1	311.0 ± 5.4
$W(Cp)_2(H)I$	168.7 ± 8.7	(100 ± 5)	268.7 ± 10.0
$W(Cp)_2(CH_3)_2$	263.4 ± 3.5	(74.6 ± 4.2)	338.0 ± 5.5

[a] Values for the dichloride complexes were obtained by static bomb combustion calorimetry (see text). [b] Values in parentheses are estimates. [c] Reference 15. [d] $Fc = (\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)$.

Table IV. Energetics of Metal–Carbon and –Hydrogen Bonds (kJ mol^{-1})

complex	E(M–L)[a]	$\bar{D}$(M–L)[b]
$Ti(Cp)_2(CH_3)_2$	274 ± 5	298 ± 6
$Ti(Cp)_2(CH_3)Cl$	293 ± 11	
$Ti(Cp)_2(C_6H_5)_2$	287 ± 9	331 ± 10
$Ti(Cp)_2(C_6H_5)Cl$	290 ± 13	
$Ti(Cp)_2(3\text{-}CH_3C_6H_4)_2$	299 ± 10	342 ± 10
$Ti(Cp)_2(4\text{-}CH_3C_6H_4)_2$	297 ± 10	341 ± 10
$Ti(Cp)_2(4\text{-}CF_3C_6H_4)_2$	297 ± 10	340 ± 10
$Ti(Cp)_2(4\text{-}CH_3OC_6H_4)_2$	305 ± 9	349 ± 10
$Ti(Cp)_2Fc_2$[c]	278 ± 11	(331 ± 12)[d]
$Mo(Cp)_2H_2$	251 ± 8	251 ± 8
$Mo(Cp)_2(CH_3)_2$	142 ± 8	166 ± 8
$W(Cp)_2H_2$	305 ± 4	305 ± 4
$W(Cp)_2(H)I$	273 ± 14	
$W(Cp)_2(CH_3)_2$	197 ± 3	221 ± 3

[a] Values not corrected by $(ER_3 - ER_1)/2$ or $(ER_3' - ER_{13}')$. See text. [b] Values not corrected by $ER_3/2$. See text. [c] See note d for Table III. [d] Estimate based on $D(Fc\text{–}H) \sim D(C_6H_5\text{–}H)$.

complexes containing metal–carbon σ-bonds which have been reported earlier [19-21] (for complexes $M(Cp)_2(CH_3)_2$ (M = Mo, W) $\Delta H_{d4} = -1.93 \pm 0.04$),[7] together with some selected values for $M(Cp)_2H_2$ and $M(Cp)_2X_2$ complexes (M = Ti, Mo, W; X = H, Cl, I) that are relevant for the discussion.[8,15,22]

The values of $\Delta H_f°[Ti(Cp)_2R_2(c)]$ (R = CH_3, C_6H_5) differ noticeably from the ones reported by Tel'noi and coworkers that were obtained with a static bomb combustion calorimeter.[15] This disagreement is not surprising, and it had been noted before for other complexes.[8,11,19,22] A static bomb is unsuited to study the thermochemistry of this type of substances. One may argue that since all the values in Table III rely on the enthalpies of formation of the respective dichlorides (see below) which were determined by the same method, they are bound to be wrong. Although it is desirable to remeasure these quantities in a rotating bomb combustion calorimeter,[23] the fact that we have to use the available values leads only to a constant error in the enthalpies of formation of the complexes for each metal and has no influence on the bond enthalpy terms, E(M–L), and on the mean bond dissociation enthalpies, $\bar{D}$(M–L), presented in Table IV.

The calculation method for obtaining E(M–L) and $\bar{D}$(M–L) data in complexes $M(Cp)_2LL'$ (L = L′) has been discussed in detail,[1a,24] and only a brief account is given here for sake of clarity. The method leads to eq 4 and 5,

$$E(\text{M–L}) = E(\text{M–Cl}) + \Delta H_f°[\text{L}^*(g)] - \Delta H_f°[\text{Cl}(g)] - \{\Delta H_f°[\text{M(Cp)}_2\text{L}_2(g)] - \Delta H_f°[\text{M(Cp)}_2\text{Cl}_2(g)]\}/2 + (\text{ER}_3 - \text{ER}_1)/2 \quad (4)$$

$$\bar{D}(\text{M–L}) = E(\text{M–Cl}) + \Delta H_f°[\text{L}(g)] - \Delta H_f°[\text{Cl}(g)] - \{\Delta H_f°[\text{M(Cp)}_2\text{L}_2(g)] - \Delta H_f°[\text{M(Cp)}_2\text{Cl}_2(g)]\}/2 + \text{ER}_3/2 \quad (5)$$

which include the reorganization energies ER_1 and ER_3 of moieties $M(Cp)_2$ from the complex $M(Cp)_2L_2$ and from the "reference" molecule $M(Cp)_2Cl_2$, respectively. E(M–Cl) are the bond enthalpy terms for the metal chlorides $TiCl_4$ (430.5 ± 1.3 kJ mol^{-1}), $MoCl_6$ (303.8 ± 7.1 kJ mol^{-1}), and WCl_6 (347.3 ± 0.8 kJ mol^{-1}), which were therefore transferred to the molecules $M(Cp)_2Cl_2$. The enthalpies of formation of polyatomic nonreorganized fragments (L*) were evaluated by considering identical geometries of L in the molecules LH and $M(Cp)_2L_2$ and by taking the Laidler terms E(L–H). As discussed elsewhere, this procedure provides a set of internally consistent data.[1a] The metal–carbon bond enthalpy terms in Table IV rely on E(L–H) = 415.8 ± 0.1, 420.6 ± 8.4, and 411 ± 8 kJ mol^{-1} for L = CH_3, RC_6H_4, and ferrocenyl, respectively.[17,19] The values presented here differ slightly from those originally reported due to the correction for the acid dilution (ΔH_{d4}). The same happens for the mean bond dissociation enthalpies shown in Table IV, which are based on D(L–H) = 439.7 ± 0.8 and 464.0 ± 8.4 kJ mol^{-1} for L = CH_3 and RC_6H_4, respectively (see also footnote *d* of Table IV).[25]

Estimates of ER_1 and ER_3 have been made by using extended Hückel calculations.[26] Since the energy of

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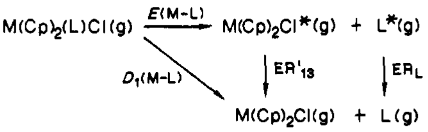
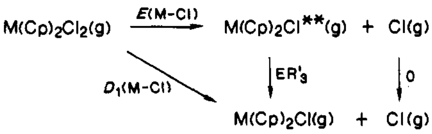
(26) See, for example, ref 1a and references cited therein.

Scheme I



Scheme II



fragments $M(Cp)_2$ is mainly a function of the centroid angles Cp-M-Cp and for most $M(Cp)_2L_2$ complexes these angles are close to the ones observed in $M(Cp)_2Cl_2$ (~ 131°), differences $(ER_3 - ER_1)/2$ are negligible. For example, Cp-Ti-Cp in the diphenyl complex (135.9°)[27] leads to $(ER_3 - ER_1)/2 \sim -1$ kJ mol^{-1}.[1a] However, this is not always so. Strong σ donors such as hydrides lead to wide centroid angles in Mo and W complexes, implying large values for that correction term. A typical example is provided by the molecule $Mo(Cp)_2H_2$, where the Cp-Mo-Cp angle is 145.8°,[28] yielding $(ER_3 - ER_1)/2 \sim -33$ kJ mol^{-1}.[1a]

E(M-L) data in Table IV for $M(Cp)_2L_2$ complexes are *not* affected by the corrections due to $(ER_3 - ER_1)/2$. Two reasons account for this, the first being a consequence of the above discussion: although the molecular structures of most compounds are not available, it is reasonable to expect that those corrections are always small, except for $M(Cp)_2$ fragments from the molybdenum and tungsten dihydrides. These two E(M-H) values may be lowered by ca. 30-40 kJ mol^{-1}.[1a] Secondly, we prefer to use the results obtained from the extended Hückel calculations in a semiquantitative way.

Data for the mean bond dissociation enthalpies shown in Table IV are also not corrected. The reorganization enthalpy ER_3 is negligible for the fragment $M(Cp)_2$ from $Ti(Cp)_2Cl_2$ (-10 kJ mol^{-1}) but not so for the molybdenum and tungsten analogues: $\bar{D}$(Mo-L) and $\bar{D}$(W-L) may be lowered by ca. 40-50 kJ mol^{-1}.[1a]

The evaluation of bond enthalpy data for complexes $M(Cp)_2LL'$ ($L \neq L'$) is a simple extension of the method used for L = L′. Schemes I and II lead to eq 6 and 7, which

$$E(\text{M-L}) = E(\text{M-Cl}) + \Delta H_f^\circ[\text{L*(g)}] - \Delta H_f^\circ[\text{Cl(g)}] - \{\Delta H_f^\circ[\text{M(Cp)}_2\text{(L)Cl(g)}] - \Delta H_f^\circ[\text{M(Cp)}_2\text{Cl}_2\text{(g)}]\} + (ER_3' - ER_{13}') \quad (6)$$

$$D_1(\text{M-L}) = E(\text{M-Cl}) + \Delta H_f^\circ[\text{L(g)}] - \Delta H_f^\circ[\text{Cl(g)}] - \{\Delta H_f^\circ[\text{M(Cp)}_2\text{(L)Cl(g)}] - \Delta H_f^\circ[\text{M(Cp)}_2\text{Cl}_2\text{(g)}]\} + ER_3' \quad (7)$$

resemble (4) and (5). However, the reorganization energies ER_{13}' and ER_3' now refer to fragments $M(Cp)_2Cl$ from $M(Cp)_2(L)Cl$ and from $M(Cp)_2Cl_2$, respectively. Another important difference is that eq 7 contains the *first* bond dissociation enthalpy, D_1(M-L), and not $\bar{D}$(M-L) as in eq 5.

The geometries of the complexes $Ti(Cp)_2(CH_3)Cl$ and $Ti(Cp)_2(C_6H_5)Cl$ are not available, and therefore estimates of ER_{13}' cannot be made. If, however, it is assumed that $ER_{13}' \sim ER_3'$ for both cases, the values of $E(Ti-CH_3)$ and $E(Ti-C_6H_5)$ shown in Table IV are obtained. The use of eq 7 for the same complexes leads to $D_1(Ti-CH_3) = (317 \pm 11) + ER_3'$ and $D_1(Ti-C_6H_5) = (333 \pm 13) + ER_3'$ kJ mol^{-1}. This reorganization energy was calculated as -41 kJ mol^{-1},[29] which therefore suggests a considerable decrease of the above values.

Table V. Enthalpies of the Symmetrization Reactions $Ti(Cp)_2R_2 + Ti(Cp)_2Cl_2 \rightarrow 2Ti(Cp)_2(R)Cl$

R	ΔH/kJ mol^{-1} crystal	gas phase
CH_3	-60 ± 20	-38 ± 30
C_6H_5	-37 ± 19	-4 ± 29

The usefulness of the bond enthalpy term and its calculation method have been evidenced before.[30] Data for titanium-carbon bonds in Table IV show that E values fall in a narrow range, enabling the prediction of enthalpies of formation of new complexes with an acceptable uncertainty. Several other conclusions can be drawn from the obtained E(Ti-C) results, in addition to those previously reported.[1a,19,20] It is noted that for the complexes $Ti(Cp)_2R_2$ and $Ti(Cp)_2(R)Cl$, E(Ti-C) is remarkably constant for R = C_6H_5 while for R = CH_3 it is not. Although the difference between the titanium-methyl bond enthalpies may be considerably reduced if the uncertainty intervals are considered, it suggests that either $Ti-CH_3$ or both $Ti-CH_3$ and Ti-Cl bonds are slightly strengthened in the mixed complex, as compared to those in $Ti(Cp)_2(CH_3)_2$ and $Ti(Cp)_2Cl_2$. In the last case, it should be noted that the value shown in Table IV is an upper limit since it relies on constant titanium-chlorine terms in $Ti(Cp)_2Cl_2$ and in $Ti(Cp)_2(CH_3)Cl$.

Differences $D(M-C_6H_5) - D(M - CH_3)$ for the complexes [Cp* = η^5-$C_5(CH_3)_5$] $Rh(Cp^*)[P(CH_3)_3](R)H$ (~53 kJ mol^{-1}),[2c] $Th(Cp^*)_2R_2$ (~55 kJ mol^{-1}),[31] $Zr(Cp)_2R_2$ (~17 kJ mol^{-1}),[1a,15] and $Mn(CO)_5R$ (16 kJ mol^{-1})[1a,32] are comparable with $D(Ti-C_6H_5) - D(Ti-CH_3)$ ~33 kJ mol^{-1} obtained in the present study.

Kinetic studies by Puddephatt and Stalteri[33] on the symmetrization reactions 8 and 9 led to the conclusion that

$$Ti(Cp)_2(CH_3)_2 + Ti(Cp)_2Cl_2 \rightarrow 2Ti(Cp)_2(CH_3)Cl \quad (8)$$

$$Ti(Cp)_2(C_6H_5)_2 + Ti(Cp)_2Cl_2 \rightarrow 2Ti(Cp)_2(C_6H_5)Cl \quad (9)$$

the complexes $Ti(Cp)_2R_2$, with R = CH_3 and C_6H_5, have similar reactivities. The enthalpies of reaction, ΔH (crystal) in Table V, which were obtained directly from the enthalpies of formation (Table III) seem to support that conclusion, particularly if the uncertainty intervals are considered. The mean values imply, however, that the thermodynamics are more favorable for the methyl complexes, which is in agreement with recent experiments involving the analogous zirconium compounds.[34] All our discussion relies on the reasonable assumption that the enthalpies of solution of the crystalline complexes will cancel.

The gas-phase ΔH values in Table V were also calculated from the enthalpies of formation of the complexes (Table III), and the (probably overestimated) uncertainties reflect our present ignorance about how to predict accurate enthalpies of sublimation. Those reaction enthalpies can also be evaluated by using first bond dissociation enthalpies

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[27] (a) Kocman, V.; Rucklidge, J. C.; O'Brien, R. J.; Santo, W. *J. Chem. Soc. D.* **1971**, 1340. (b) Rucklidge, J. C., private communication.

[28] Schultz, A. J.; Stearley, K. L.; Williams, J. M.; Mink, R.; Stucky, G. D. *Inorg. Chem.* **1977**, *16*, 3303.

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[30] See, for example, refs 1a and 7.

[31] Bruno, J. W.; Marks, T. J.; Morss, L. R. *J. Am. Chem. Soc.* **1983**, *105*, 6824.

[32] Connor, J. A.; Zafarani-Moattar, M. T.; Bickerton, J.; El Saied, N. I.; Suradi, S.; Carson, R.; Al Takhin, G.; Skinner, H. A. *Organometallics* **1982**, *1*, 1166.

[33] Puddephatt, R. J.; Stalteri, M. A. *Organometallics* **1983**, *2*, 1400.

[34] Jordan, R. F. *J. Organomet. Chem.* **1985**, *294*, 321.

obtained from E(M–L) data coupled with extended Hückel calculations.[29]

The activation enthalpy for the thermal decomposition reaction of $Ti(Cp)_2(C_2H_5)Cl$ was measured by Fushman et al.,[35] and the result (150 kJ mol^{-1}) was identified with $D_1(Ti–C_2H_5)$ by assuming that the activation enthalpy for the recombination of the titanium fragment with ethyl radical is close to zero. Our estimate for $D_1(Ti–CH_3)$ in $Ti(Cp)_2(CH_3)Cl$, ca. 276 kJ mol^{-1} (see above), strongly suggests that Fushman's value is too low, the reason probably being that the chemistry of the thermal decomposition is certainly more complex than the simple fission of the titanium–ethyl bond.[36] Also, the activation barrier for recombination may not be negligible, as suggested by the extended Hückel calculations, which yield $ER_{13}' \sim -41$ kJ mol^{-1} (assuming that the fragment $Ti(Cp)_2Cl$ has similar geometries in $Ti(Cp)_2Cl_2$ and in the ethyl compound).[29]

As a final comment concerning the titanium complexes, it is noted that $D_1(Ti–CH_3)$ in $Ti(Cp)_2(CH_3)_2$[29] is very similar to $D_1(Ti–CH_3)$ in $Ti(Cp)_2(CH_3)Cl$, the difference being ca. 9 kJ mol^{-1}, matching the one observed for compounds $Th(Cp^*)_2(C_2H_5)_2$ and $Th(Cp^*)_2(C_2H_5)Cl$.[31]

Equation 6 can easily be modified to calculate E(W–H) in $W(Cp)_2(H)I$. For the sake of simplicity, the "reference" molecule is now $W(Cp)_2I_2$, where E(W–I) = 268 kJ mol^{-1}.[8] This value, together with the enthalpies of formation of the gaseous complexes (Table III) and the auxiliary data (Table I), leads to $E(W–H) = 273 + ER_3' - ER_{13}'$, where the reorganization energies refer to fragment $W(Cp)_2I$. In the absence of detailed structural data for the two complexes involved, we shall assume that $ER_3' \sim ER_{13}'$. The 273 kJ mol^{-1} are therefore to be compared with E(W–H) = 305 kJ mol^{-1} in $W(Cp)_2H_2$ (Table IV). However, this value is not corrected with the term $(ER_3 - ER_1)/2$ (see eq 4), ER_1 and ER_3 representing the reorganization energies of $M(Cp)_2$ moieties from the complexes $W(Cp)_2H_2$ and $W(Cp)_2Cl_2$, respectively. Although structural data are not available, the angles Cp–W–Cp can be predicted from the analogous molybdenum molecules and thus $(ER_3 - ER_1)/2$ can be estimated from the published curves.[1a] This has in fact already been done above, when discussing the correction for E(M–H) in $M(Cp)_2H_2$. For tungsten, a value of ca. −37 kJ mol^{-1} is estimated, giving $E(W–H) \sim 268$ kJ mol^{-1}, which is in good agreement with E(W–H) in $W(Cp)_2(H)I$. This strongly supports the validity of the transferability of W–H bond enthalpy terms, even if the corrections terms are considered as being crude approximations.

The evaluation of D_1(W–H) in $W(Cp)_2(H)I$ requires the estimation of ER_3' which, as mentioned above, is hindered by the absence of structural data. Nevertheless, extended Hückel calculations for other complexes lead us to expect that this quantify must be substantially lower (by ca. 50 kJ mol^{-1}) than D_1(W–H) in $W(Cp)_2H_2$, since the reorganization energy is predicted to be more negative for $W(Cp)_2I$ than for $W(Cp)_2H$.[29]

Recent spectroscopic studies by Girling et al.[37] show that M–H bond strength increases substantially from 4d to 5d elements, which is consistent with our results for molybdenum and tungsten: the difference E(W–H) − E(Mo–H) determined from Table IV (ca. 50 kJ mol^{-1}) holds when the corrections $(ER_3 - ER_1)/2$ are considered. Hoff reports that $D_1(Mo–H) = 276 \pm 33$ kJ mol^{-1} in $Mo(Cp)(CO)_3H$, but this value relies on $\bar{D}(Mo–Cp) - \bar{D}(Mo–C_6H_6) \sim 125$ kJ mol^{-1}.[2i] Although the result for $\bar{D}$(Mo–Cp) may change, as suggested by ongoing combustion experiments,[23] recent data indicate that the above difference is considerably higher, ca. 160 kJ mol^{-1},[5] implying $D_1(Mo–H) \sim 240$ kJ mol^{-1}. The calculation of the reorganization energy of $Mo(Cp)(CO)_3$ fragment would be needed to compare E(Mo–H) in that complex with the one reported here [251 + $(ER_3 - ER_1)/2 \sim 218$ kJ mol^{-1}], but the assumption of a constant Mo – H bond enthalpy term seems reasonable.

A thorough analysis of the energetics of M–H and M–CH_3 bonds (M = Mo, W) has been made elsewhere[1a,29] and will not be repeated here. However, we wish to emphasize again the importance of reorganization energies when discussing (and applying) the transferability of metal–ligand bond enthalpies. This has been sufficiently stressed here through the evaluation of "corrected" bond enthalpy terms, but it can be more briefly explained by using a different approach. Consider the molecules $M(Cp)_2L_2$, $M(Cp)_2LL'$, and $M(Cp)_2L_2'$ in the gas phase, for which the enthalpies of formation are available. Two equations similar to (4) can be obtained by considering for example $M(Cp)_2L_2'$ as the reference molecule. These equations contain the reorganization energies of $M(Cp)_2$ fragments from $M(Cp)_2L_2$ (ER_1), $M(Cp)_2LL'$ (ER_{13}), and $M(Cp)_2L_2'$ (ER_3), and also the bond enthalpy terms E(M–L) and E(M–L′), each assumed to be a constant. In eq 10, which

$$ER_{13} - ER_1/2 - ER_3/2 = \Delta = -\Delta H_f^\circ[M(Cp)_2LL'(g)] + \{\Delta H_f^\circ[M(Cp)_2L_2(g)] + \Delta H_f^\circ[M(Cp)_2L_2'(g)]\}/2 \quad (10)$$

was derived on this basis, the theoretical quantities are collected in the left-hand side and the experimental data in the right-hand side.

For the titanium complexes (L′ = Cl) experimental Δ values are 19 ± 15 (L = CH_3) and 2 ± 15 kJ mol^{-1} (L = C_6H_5). The theoretical values for Δ are close to zero in both cases. There is a more ambiguous situation for the tungsten complex (L′ = I; L = H) since the reorganization energies of $M(Cp)_2$ fragments are strongly dependent on the angle Cp–W–Cp and this is difficult to guess for $W(Cp)_2(H)I$. The experimental value for Δ (−32 ± 11 kJ mol^{-1}) suggests an intermediate value with respect to the same angles in $W(Cp)_2H_2$ and $W(Cp)_2I_2$, probably closer to the last one. Attempts to produce a crystal of $W(Cp)_2(H)I$ suitable for X-ray studies have not yet been successful.

Conclusions

Transferring bond enthalpies is a common procedure for estimating the energetics of many organometallic reactions. It is therefore desirable to improve our ability to use it reliably. This paper is mainly a contribution toward that goal. By using bond enthalpy terms together with simple calculations of reorganization energies, it is possible to predict enthalpies of formation of new complexes or even to estimate partial bond dissociation enthalpies.

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Registry No. $Ti(Cp)_2Cl_2$, 1271-19-8; $W(Cp)_2I_2$, 12184-31-5; $Ti(Cp)_2(CH_3)_2$, 1271-66-5; $Ti(Cp)_2(CH_3)Cl$, 1278-83-7; $Ti(Cp)_2(C_6H_5)Cl$, 12663-63-7; $W(Cp)_2(H)I$, 83526-23-2; $Ti(Cp)_2(C_6H_5)_2$, 1273-09-2; $Ti(Cp)_2(3–CH_3C_6H_4)_2$, 12156-57-9; $Ti(Cp)_2(4–CH_3C_6H_4)_2$, 12156-58-0; $Ti(Cp)_2(4–CF_3C_6H_4)_2$, 12156-39-7; $Ti(Cp)_2(4–CH_3OC_6H_4)_2$, 12156-55-7; $Ti(Cp)_2Fc$, 65274-19-3; $Mo(Cp)_2Cl_2$, 12184-22-4; $Mo(Cp)_2H_2$, 1291-40-3; $Mo(Cp)_2(CH_3)_2$, 39333-52-3; $W(Cp)_2Cl_2$, 12184-26-8; $W(Cp)_2H_2$, 1271-33-6; $W(Cp)_2(CH_3)_2$, 39333-53-4.

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