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ESTIMATION OF STEPWISE M–L BOND DISSOCIATION ENTHALPIES IN $M(\eta\text{-}C_5H_5)_2L_2$ COMPLEXES

MARIA J. CALHORDA, ALBERTO R. DIAS, ADELINO M. GALVÃO
and JOSÉ A. MARTINHO SIMÕES

Centro de Química Estrutural, Complexo I, Instituto Superior Técnico, 1096 Lisboa Codex (Portugal)

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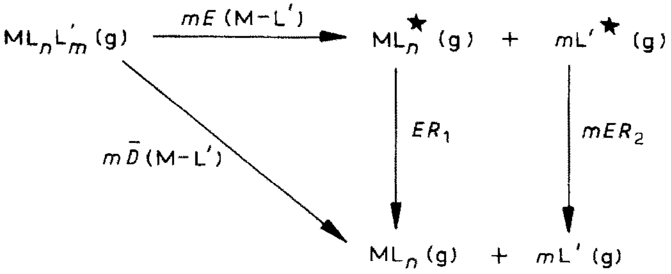
Summary

Stepwise bond dissociation enthalpies D_1(M–L) and D_2(M–L) in $M(\eta\text{-}C_5H_5)_2L_2$ complexes (M = Ti, Mo; L = H, Cl, CO, CH_3, SCH_3) have been estimated from using thermochemical data and extended Hückel MO calculations. It is concluded that for the systems studied ligand to metal π-donation results in larger differences $D_2 - D_1$ than σ-donation.

Introduction

Transition metal–ligand bond energies can provide important assistance in understanding the mechanisms of many processes in areas such as catalysis, biochemistry, and coordination chemistry [1,2]. Calorimetric studies of a large variety of organometallic complexes have been made by a number of groups, using several types of calorimeters. The large majority of these studies led to the enthalpies of formation of the crystalline (or liquid) complexes from which the respective gas-phase enthalpies of formation were derived by measuring or estimating enthalpies of sublimation or vaporization. Those gas-phase enthalpies may be used to derive quantities which provide very useful information about the energetics of the metal–ligand bonds but usually do not afford partial bond dissociation enthalpies. Consider the molecule $ML_nL'_m$, where M is a transition metal atom and L and L′ are different types of ligands. The mean bond dissociation enthalpy, $\bar{D}$(M–L′), and the bond enthalpy term, E(M–L′), can be obtained through Scheme 1, in which a star indicates a non-reorganized fragment, i.e., a fragment retaining the geometry it had in the initial complex. ER_1 and ER_2 are reorganization enthalpies and can be tentatively estimated by using e.g. the Extended Hückel Molecular Orbital method. This procedure has been described in previous papers [2–5].



SCHEME 1

The estimation of partial bond dissociation enthalpies, which are clearly more useful data for dealing with reactivity problems, is illustrated in the present paper for complexes of the type MCp_2L_2 (M = Ti, Mo; Cp = η^5-C_5H_5; L = H, Cl, CH_3, CO, SCH_3).

Calculations

The ICON8 program with the modified Wolfsberg–Helmholz method was used to make the extended Hückel MO calculations [6–8]. The basis set for the metal atoms consisted of $(n-1)d$, ns, and np orbitals. Only $3s$ and $3p$ orbitals were considered for the sulphur and chlorine atoms. The s and p orbitals were described by single Slater-type wave-functions and the d orbitals as contracted linear combinations of two Slater-type wave-functions. The orbital exponents and the parameters for molybdenum and titanium are listed in Table 1. The others are standard parameters. Geometrical details are given in the Appendix.

Results and discussion

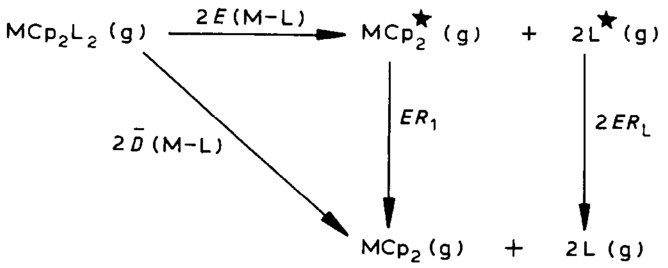
Consider the molecules MCp_2L_2 and MCp_2Cl_2 and Schemes 2 and 3, from which eqs. 1 and 2 can be derived [1,12]. E(M–Cl), the bond enthalpy term in MCp_2Cl_2, is assumed to be equal to E(M–Cl) in MCl_n ($n = 4$ for Ti and $n = 6$ for Mo and W). There is experimental evidence that this assumption is reasonable, particularly for M = Ti [1,2]. If the assumption is not correct this would imply a

TABLE 1

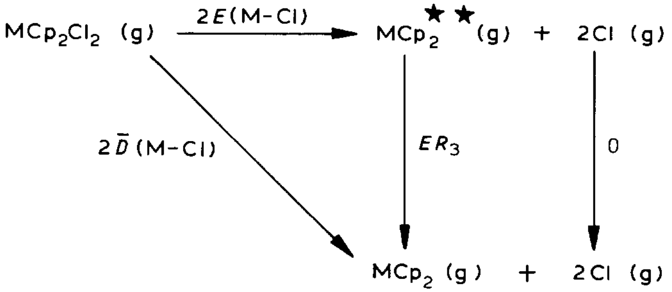
ORBITAL EXPONENTS AND PARAMETERS USED IN THE EXTENDED HÜCKEL MO CALCULATIONS

Orbital	Slater exponent	$-H_{ii}$ (eV) [a]	Ref.
Ti 4s	1.075	8.97	9
Ti 4p	0.675	5.44	9
Ti 3d	[b]	10.81	9,10
Mo 5s	1.96	8.77	11
Mo 5p	1.90	5.60	11
Mo 4d	[c]	11.60	10,11

[a] 1 eV = 96.4845 kJ mol^{-1}. [b] $\xi_1 = 4.55$, $\xi_2 = 1.40$, $C_1 = 0.4206$, and $C_2 = 0.7839$. [c] $\xi_1 = 4.54$, $\xi_2 = 1.90$, and $C_1 = C_2 = 0.5899$.



SCHEME 2



SCHEME 3

$$E(\text{M–L}) = E(\text{M–Cl}) + \Delta H_f^\circ(\text{L}^\star,\text{g}) - \Delta H_f^\circ(\text{Cl,g}) - [\Delta H_f^\circ(\text{MCp}_2\text{L}_2,\text{g}) - \Delta H_f^\circ(\text{MCp}_2\text{Cl}_2,\text{g})]/2 + (ER_3 - ER_1)/2 \quad (1)$$

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

systematic error in all the obtained E(M–L) and $\bar{D}$(M–L) values, and so the conclusions would not be invalidated.

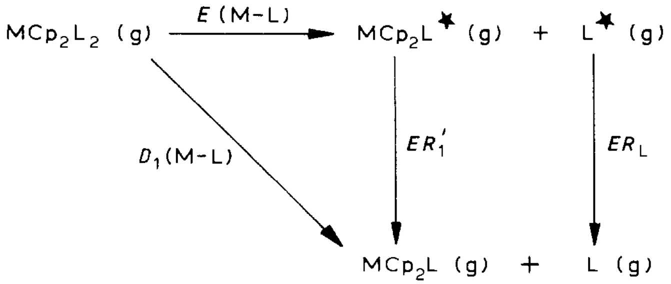
The calculation of ER_1 and ER_3 by the extended Hückel method has been described elsewhere [1–3,5]. All the remaining input data for eqs. 1 and 2 are available for a number of ligands, with exception of $\Delta H_f^\circ(\text{L}^\star, \text{g})$, which has to be estimated [1,12]. It should be noticed, however, that this value is not important for the present purpose of evaluating the partial bond dissociation enthalpies, as discussed below.

Scheme 4 represents the cleavage of one M–L bond. The stars have the usual meaning, i.e. they indicate non-reorganized fragments. The first bond dissociation enthalpy is therefore given by eq. 3, where ER_1' is the reorganization enthalpy of the fragment MCp_2L. The value of D(M–L) does not depend on the value assigned to ER_L because this quantity is cancelled when E(M–L), calculated through eq. 1, is introduced into 3 [$\Delta H_f^\circ(\text{L}^\star,\text{g}) = \Delta H_f^\circ(\text{L,g}) - ER_L$].

$$D_1(\text{M–L}) = E(\text{M–L}) + ER_1' + ER_L \quad (3)$$

The second M–L bond dissociation enthalpy, D_2(M–L), can be obtained from $\bar{D}$(M–L) and D_1(M–L):

$$D_2(\text{M–L}) = 2\bar{D}(\text{M–L}) - D_1(\text{M–L}) \quad (4)$$



SCHEME 4

Table 2 summarizes the bond enthalpy terms and the mean bond dissociation enthalpies for the complexes chosen to illustrate the estimation of D_1 and D_2. Values for $(ER_3 - ER_1)$ and ER_3 are also listed in the Table.

The reorganization enthalpies ER_1 and ER_3 are mainly a function of the Cp–M–Cp angle (θ) and they represent the enthalpy (or energy) change when the non-reorganized fragment MCp_2 relaxes to its stable geometry [1,3]. For the titanium complexes those values are small because the most stable geometry is achieved with $\theta \simeq 140°$, an angle which is close to the one observed for many MCp_2L_2 complexes. For metals with four d electrons [M = Mo^{II}, W^{II}], the relaxed state has θ 180°, implying large reorganization enthalpies and large corrections to E(M–L) and $\bar{D}$(M–L).

The geometry optimization of the fragments MCp_2L is required for the evaluation of ER'_1. Two parameters were used in this optimization (Fig. 1): the angle Cp–M–Cp (θ) and the angle between L and the z axis (α). Instead of computing a whole potential surface for each fragment we looked for a local minimum, changing α and θ successively, in an iterative way. Lowest energy values were obtained for the structures described in Table 3.

The value of θ varies slightly from the non-reorganized to the optimized geometry (less than 10°). A decrease in θ in MCp_2 means a larger amount of mixing

TABLE 2

BOND ENTHALPY AND REORGANIZATION ENTHALPY DATA FOR SOME MCp_2L_2 COMPLEXES (in kJ mol^{-1})

Complex	E(M–L) [a]	$\bar{D}$(M–L) [b]	$ER_3 - ER_1$	ER_3	Ref.
$TiCp_2Cl_2$	431	431	0	−11	3
$TiCp_2(CH_3)_2$	274	298	−4 [c]	−11	13
$TiCp_2(CO)_2$	165 [d]	152	−11	−11	14
$MoCp_2Cl_2$	304	304	0	−82	5
$MoCp_2H_2$	251	251	−66	−82	1,15
$MoCp_2(CH_3)_2$	142 [e]	166 [e]	−36 [c]	−82	1

[a] Values not affected by $(ER_3 - ER_1)/2$. [b] Values not affected by $ER_3/2$. [c] The molecular structures of the complexes are not available. Values of Cp–M–Cp angles were estimated as 132.5° (M = Ti), leading to ER_1 −6 kJ mol^{-1}, and 136° (M = Mo), yielding ER_1 −46 kJ mol^{-1}. [d] This is a provisional value, based on the assumption that E(Ti–I) has the same value in $TiCp_2I_2$ and TiI_4. [e] These values differ slightly from those quoted in ref. 1, owing to a correction made to take account of acid dilution (see ref. 2).

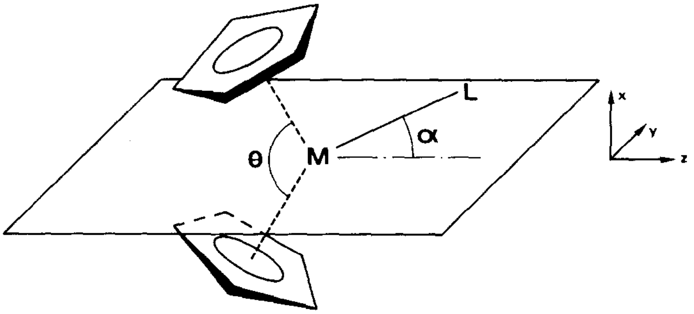


Fig. 1. Geometry of the fragment MCp_2L.

TABLE 3

OPTIMIZED STRUCTURES OF MCp_2L (angles in degrees) AND VALUES OF THE REORGANIZATION ENTHALPIES (kJ mol^{-1})

Complex	MCp_2L		$MCp_2L^{\star}$ [a]			ER'_1
	α	θ	α	θ	Ref.	
$TiCp_2Cl_2$	0	134	47.3	130.97	16	−41
$TiCp_2(CH_3)_2$	32	136	(45)	(132.5)	–	−11
$TiCp_2(CO)_2$	38	140	44.0	138.6	17	−2
$TiCp_2(SCH_3)_2$	22 [b]	134 [b]	46.8	131.4	18	−59
$MoCp_2Cl_2$	0	138	41.0	130.5	19	−65
$MoCp_2H_2$	17	146	37.8	145.8	20	−11
$MoCp_2(CH_3)_2$	1	146	(40)	(136)	–	−17
$MoCp_2(SCH_3)_2$	1 [c]	138 [c]	(42)	(130)	–	−81

[a] Parameters for the fragment in the complex. Estimated values in parentheses. [b] Optimized torsion angle: 64° (see text). [c] Optimized torsion angle: 82° (see text).

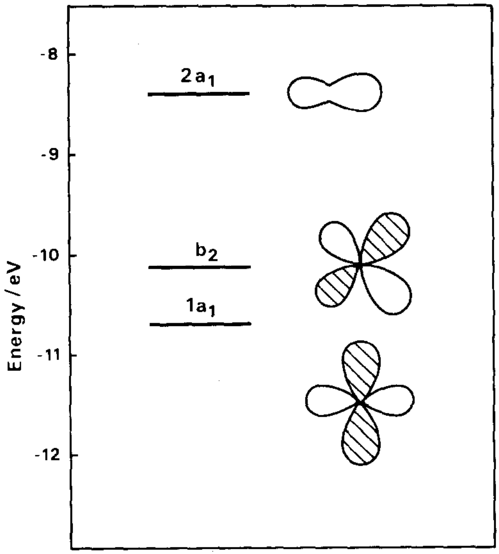
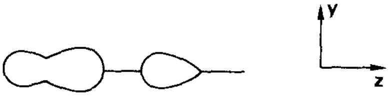
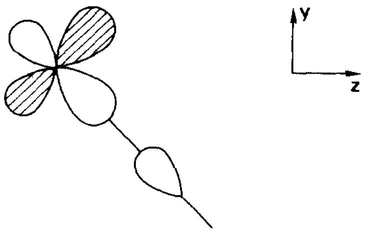


Fig. 2. Frontier orbitals of a MCp_2 fragment.



(1)



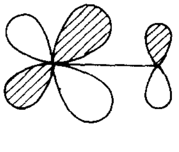
(2)

of high lying empty orbitals in a bonding fashion (hybridizing the frontier orbitals towards incoming ligands and thus allowing better overlap). At very small θ values, repulsive interactions between the hydrogens and between p orbitals on carbons in each ring become dominant. The α values fall in two groups: $\alpha \approx 0$ and α large (17–38°). We can understand these values qualitatively by looking at the frontier orbitals of a MCp_2 fragment (Fig. 2) described before [9], and analysing its interaction with the ligand L orbitals. Different behaviour is to be expected when the electron count in MCp_2 is varied or the ligand is changed from one that is only a σ donor to one that is also a π donor or a π acceptor.

Two of the MCp_2 fragment frontier orbitals point in the z axis direction ($1a_1$ and $2a_1$), $2a_1$ being well suited to overlap with a ligand coming from that direction, **1**. This orbital is empty for d^0, d^2, and d^4 metals. $1a_1$ is essentially developed around the y axis. A ligand is not expected to approach along this direction owing to steric repulsions from the cyclopentadienyl ligands. The remaining orbital, b_2, has zero or negligible overlaps with orbitals from ligands approaching in either z or y directions, but a good overlap can be achieved at $\sim 45°$, **2**. This orbital is empty for d^0 and d^2 metals, that is, for Ti^{IV} and Mo^{IV}. A σ donor ligand will approach so that the interaction with both $2a_1$ and b_2 is maximized, and α may be large ($TiCp_2Me$ and $MoCp_2H$ in Table 3). π-Interaction can occur with $1a_1$ with large α (**3**) or with b_2 at $\alpha = 0$ (**4**).

The metal electron count is the factor which determines the preferred geometry, as $1a_1$ is empty for d^0 Ti^{IV} and filled for d^2 Mo^{IV} and Ti^{II}. A π donor ligand

(3)



(4)

should avoid a four electron destabilizing interaction such as **3** (typically in $MoCp_2Cl$). The reverse is expected to be the case for π-acceptors, as with $TiCp_2(CO)$.

On the whole, there is a balance between several interactions. Even for ligands of the same type, the overlap integrals with $2a_1$ and b_2 depend on the orbital (for instance H 1*s* orbital is very different from the C "sp^3 hybrid" in CH_3).

Another problem was posed by the SCH_3 ligand owing to the possibility of rotation of the methyl group around the M–S bond. Even in the absence of electronic effects, rotation is restricted to some extent by the neighbouring cyclopentadienyl rings. It was thus necessary to optimize the methyl position (the torsion angle mentioned in Table 3 is the angle between the M–S–C plane and *yz*). The final geometry also reflects these steric constraints.

The curves shown in Fig. 3 illustrate the above discussion for $TiCp_2L$ (L = Cl, CO, CH_3).

Having optimized the geometry of the MCp_2L fragments as far as possible, we then compared its energy with that of the same fragment having the geometry of the parent compound, MCp_2L_2; as mentioned above, this energy difference is denoted by ER'_1 in Table 3. Since α values for MCp_2L^* are always large (> 37.8°), ER'_1 will have its highest value for $MoCp_2Cl$, which is more stable for $\alpha = 0$ after relaxation. The opposite holds for $TiCp_2(CO)$; in this case, CO is a moderate σ donor and good π acceptor ligand, and the preferred relaxed geometry is characterized by a large α. Other values fall in between, depending on the interplay of all the factors discussed before.

The ER'_1 values, together with E(M–L) and ER_L, were introduced in eq. 3, to yield D_1(M–L) (Table 4). As noted above, these results are independent of the reorganization enthalpies of the ligands L. Therefore, the values of ER_L quoted in Table 4 are the same as those used for calculating E(M–L). The values of D_2(M–L), obtained from eq. 4, and the difference $D_1 - D_2$ (see eq. 5) are also presented in the Table.

$$D_1 - D_2 = 2ER'_1 - ER_1 \tag{5}$$

For L = SCH_3 there are no experimental data for use in deriving $\bar{E}$(M–L) and $\bar{D}$(M–L). Values for several SR (R = alkyl) ligands suggest, however, $\bar{E}(Ti\text{–}SCH_3)$ ~ 325 and $\bar{E}(Mo\text{–}SCH_3)$ ~ 215 kJ mol^{-1} [2,21]. Taking ER_L ~ $D(CH_3S\text{–}H) - E(CH_3S\text{–}H)$ 19 kJ mol^{-1} [22,23], one obtains $D_1(Ti\text{–}SCH_3)$ ~ 285, $D_2(Ti\text{–}SCH_3)$ ~ 403, $D_1(Mo\text{–}SCH_3)$ ~ 153, and $D_2(Mo\text{–}SCH_3)$ ~ 315 kJ mol^{-1}; only the differences D_1–D_2, which do not rely on experimental data, are given in Table 4.

Caution must be used when drawing conclusions from the data in Table 4. All the values were derived by use of a semi-empirical method, the extended Hückel MO calculations, and must therefore be discussed almost in a qualitative way only. It could be argued that calculations at a more sophisticated level would produce more significant results; this is probably so, but it must also be recognized that sophistication of the method of calculation does not always lead to more reliable results.

The data in Table 4, used together with eq. 5, indicate that the first bond dissociation enthalpy is lower than the second for the complexes studied. This is a direct consequence of eq. 5, in which $2ER'_1$ is more negative than ER_1. Some of the differences $D_1 - D_2$ are, however, considerably more negative for ligands such as Cl and SCH_3 than for CH_3, H, and CO. For Mo–CH_3 it can be seen that D_1 is

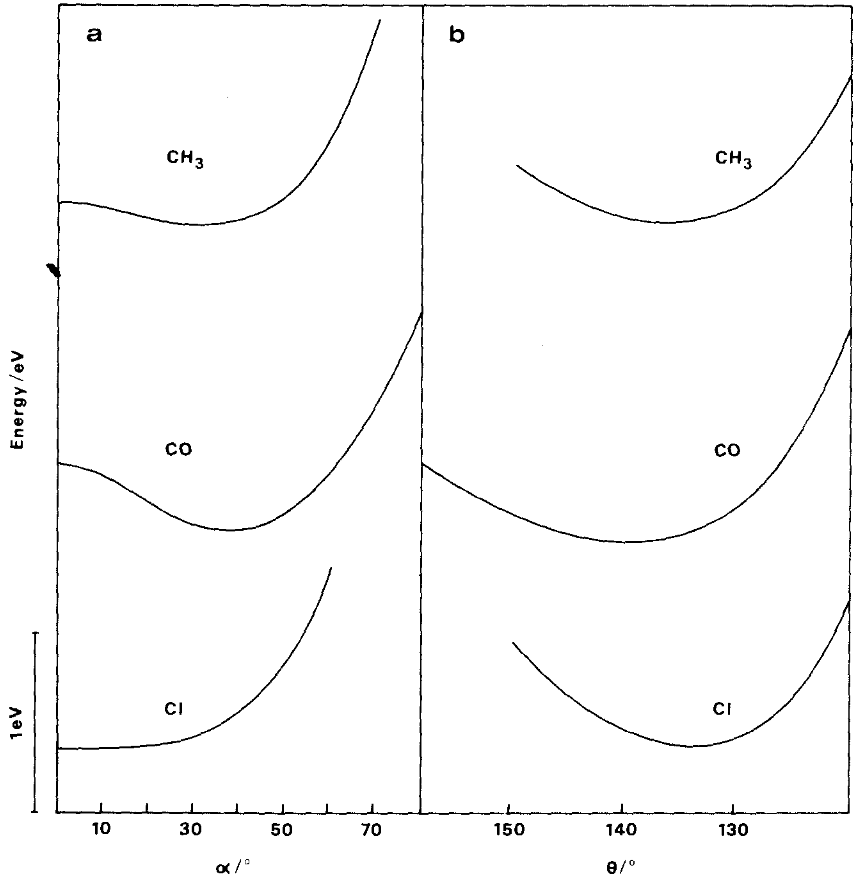


Fig. 3. Total energy of the fragments MCp_2L as a function of α (a) and θ (b).

actually $> D_2$ when the reorganization enthalpy ER_1 is considered. As discussed earlier, the values in Table 4 reflect the π donor character of ligands such as Cl and SCH_3, which leads to a different geometry from the one observed with σ donor ligands.

TABLE 4

ESTIMATED VALUES OF THE FIRST AND SECOND BOND DISSOCIATION ENTHALPIES IN MCp_2L_2 COMPLEXES (kJ mol^{-1})

MCp_2L_2	ER_L	$D_1(M-L)$ [a]	$D_2(M-L)$ [a]	$D_1 - D_2$ [a]
$TiCp_2Cl_2$	0	390 (390)	471 (460)	−81 (−70)
$TiCp_2(CH_3)_2$	23.9	287 (285)	309 (300)	−22 (−15)
$TiCp_2(CO)_2$	−13	150 (144)	154 (149)	−4 (−5)
$TiCp_2(SCH_3)_2$	–	–	–	−118
$MoCp_2Cl_2$	0	238 (238)	369 (287)	−131 (−49)
$MoCp_2H_2$	0	240 (207)	262 (213)	−22 (−6)
$MoCp_2(CH_3)_2$	23.9	149 (131)	182 (118)	−33 (+13)
$MoCp_2(SCH_3)_2$	–	–	–	−162

[a] Data in parenthesis were obtained by using $E(M-L)$ and $\bar{D}(M-L)$ values corrected with $(ER_3 - ER_1)/2$ and $ER_3/2$, respectively (see Table 2).

We were unable to find any unambiguous experimental data reflecting the difference between D_1 and D_2. This was mainly due to the lack of knowledge about the mechanisms of ligand replacement reactions involving MCp_2L_2 complexes. Furthermore many of these processes are thought to begin with heterolytic bond cleavages and, in addition, no direct measurements of partial bond dissociation enthalpies involving transition metal complexes are available. It is possible that techniques such as the recently developed laser-powered homogeneous pyrolysis [24,25] will lead to an increase in the amount of such energy data, which are badly needed in the area of chemical reactivity. The present method is obviously not an alternative to such experiments, but at the present stage it provides useful insights into the reactivity of transition metal–ligand bonds.

Appendix

The structural data used for the extended Hückel calculations were taken from the literature [16–20], except those for the complexes $TiCp_2(CH_3)_2$, $MoCp_2(CH_3)_2$, and $MoCp_2(SCH_3)_2$, which were estimated. *$TiCp_2(CH_3)_2$*: Ti–Cp 208, Ti–CH_3 219 pm, Cp–Ti–Cp 132.5, and CH_3–Ti–CH_3 90°. *$MoCp_2(CH_3)_2$*: Mo–Cp 201, Mo–CH_3 231 pm, Cp–Mo–Cp 136, and CH_3–Mo–CH_3 80°. *$MoCp_2(SCH_3)_2$*: Mo–Cp 199, Mo–S 251, S–C 181.6 pm, Cp–Mo–Cp 129.5, S–Mo–S 81, and Mo–S–C 110°. Carbon–carbon and carbon–hydrogen bond lengths were taken as 140 and 108 pm respectively.

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