Octahedral metal carbonyls
74*. Estimates of solvent–metal bond strengths in (solvent)$M(CO)_5$ complexes (solvent = benzene (M = Mo, W) and tetrachloromethane (M = Cr))

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Abstract

Desolvation in three (solv)$M(CO)_5$ complexes (M = Cr, Mo, W; solv = solvent) produced after pulsed laser flash photolysis in solv/1-hexene mixtures takes place exclusively via dissociative mechanisms. The enthalpies of activation for solvent dissociation, which should closely approximate the solv–M bond strengths, have been determined for the η^2-benzene–Mo and η^2-benzene–W bonds, in which benzene likely is coordinated to the metal edge-on in a dihapto fashion, and tetrachloromethane–Cr bonds, which involve Cl-to-Cr coordination. These inferred bond strengths are compared to other reported metal–ligand (L) bond strengths derived from kinetics data in solution for $LM(CO)_5$ complexes, and M–alkane bond strengths obtained from time-resolved photoacoustic calorimetric studies.

Introduction

Recent investigations of the rates of solvation of $[M(CO)_5]$ intermediates produced through heterolytic cleavage of M–CO bonds in $M(CO)_6$ molecules (M = Cr [1], W [2]) employing pulsed laser flash photolysis have revealed that solvation takes place on the ps–fs time-scale; it is reasonable to expect this also to be true for the third member of the Group VI-B triad, Mo. Based on these very rapid solvation rates, the corresponding enthalpies of activation are expected to be small. Thus, based upon the principle of microscopic reversibility, the enthalpies of activation for desolvation of (solv)$M(CO)_5$ transients via dissociative pathways should closely approximate the M–solv bond strengths (Fig. 1).

Where a Lewis base (L) displaces a solvent molecule via such a dissociative mechanism

$$(\mathrm{solv})\mathrm{M(CO)_5} \underset{k_{-1}[\mathrm{solv}]}{\overset{k_1}{\rightleftharpoons}} [\mathrm{M(CO)_5}] \xrightarrow{k_2[\mathrm{L}]} \mathrm{LM(CO)_5} \qquad (1)$$

and where $[M(CO)_5]$ is a steady-state intermediate, the rate law will be

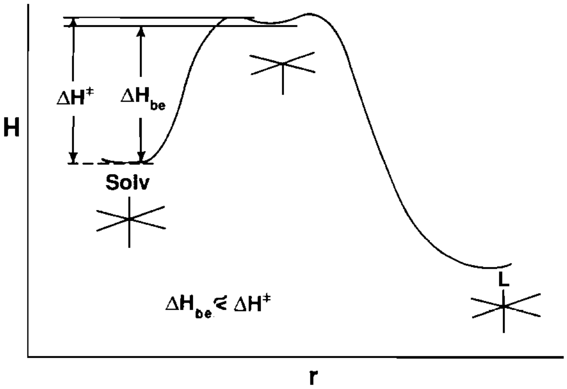

Fig. 1. Qualitative plot of reaction enthalpy vs. reaction coordinate for solvent dissociation from (solv)$M(CO)_5$ in the presence of L to afford $LM(CO)_5$ products. $\Delta H^{\ddagger}_{\mathrm{be}}$ is the solvent–metal bond energy.

$$-\mathrm{d}[(\mathrm{solv})\mathrm{M(CO)_5}]/\mathrm{d}t = \frac{k_1k_2[(\mathrm{solv})\mathrm{M(CO)_5}][\mathrm{L}]}{k_{-1}[\mathrm{solv}]+k_2[\mathrm{L}]} \qquad (2)$$

$[M(CO)_5]$ should be relatively non-discriminating among solv and L ($k_{-1} \approx k_2$), since the enthalpies of activation for interaction of solv and L with $[M(CO)_5]$ will approach zero [3]. Thus, this rate law will adopt a limiting form,

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*For Part 73 see ref. 3.

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$$-\mathrm{d}[(\mathrm{solv})\mathrm{M(CO)_5}]/\mathrm{d}t=\frac{k_1k_2[(\mathrm{solv})\mathrm{M(CO)_5}][\mathrm{L}]}{k_{-1}[\mathrm{solv}]} \qquad (3)$$

or

$$-d[(\mathrm{solv})\mathrm{M(CO)_5}]/\mathrm{d}t=k[(\mathrm{solv})\mathrm{M(CO)_5}][\mathrm{L}] \qquad (4)$$

where $k=k_1k_2/k_{-1}[\mathrm{solv}]$, since in dilute solution [solv] is approximately constant and $[\mathrm{solv}]\gg[\mathrm{L}]$ $(k_{-1}[\mathrm{solv}]\gg k_2[\mathrm{L}])$. Rate behavior consistent with eqn. (4) has been observed [3–7]. Since the rate is dependent on [L], the mechanistic possibilities are by no means limited to a dissociative pathway; the rate behavior given in eqn. (4) could also be interpreted in terms of an associative, or even competing dissociative and associative pathways [8]. Some effort has gone into unravelling the mechanistic possibilities; attention has been focussed in particular on the interpretation of entropies and volumes of activation [4, 6].

This situation is to be contrasted to observations for metal carbonyl substitution reactions, e.g.

$$\mathrm{M(CO)_6}+\mathrm{L}\longrightarrow \mathrm{LM(CO)_5}+\mathrm{CO} \qquad (5)$$

for which the dissociative rate law analogous to that given in eqn. (2) is

$$-\mathrm{d}[\mathrm{M(CO)_6}]/\mathrm{d}t=\frac{k_1k_2[\mathrm{M(CO)_6}][\mathrm{L}]}{k_{-1}[\mathrm{CO}]+k_2[\mathrm{L}]} \qquad (6)$$

In this case, usually, $[\mathrm{CO}]\ll[\mathrm{L}]$ and thus, in practice, this rate law adopts the limit opposite to that observed for the solvation reactions (eqn. (3))

$$-\mathrm{d}[\mathrm{M(CO)_6}]/\mathrm{d}t=k_1[\mathrm{M(CO)_6}] \qquad (7)$$

In this limit associative and dissociative reaction pathways are distinguishable on the basis of the dependence (or lack of it) of the rate on the concentration of L [9, 10].

In a recent study of the displacement of benzene from (η^2-benzene)Cr(CO)$_5$ by 1-hexene (hex)

$$(\eta^2\text{-benzene})\mathrm{Cr(CO)_5}+\text{hex}\longrightarrow (\text{hex})\mathrm{Cr(CO)_5}+\text{benzene} \qquad (8)$$

which in dilute solution obeyed the rate law given in eqn. (4), the concentrations of benzene and 1-hexene were varied widely enough so that the non-limiting form of that rate law (eqn. (2)) was observed, strongly supporting the dissociative nature of the desolvation process [11]. Rate constants and, from studies at various temperatures, the activation enthalpy for Cr–benzene bond fission (governed by k_1, eqn. (2)), was obtained; this enthalpy of activation, 9.4(3) kcal/mol, was taken as an approximation of the η^2-benzene–Cr bond strength.

These methods have now been applied to several other (solv)M(CO)$_5$ systems, (solvent/M = benzene/Mo, W, and tetrachloromethane/Cr). It is demonstrated that for these systems desolvation pathways also are dissociative. Thus, estimates of the strengths of the solvent–metal bonding interactions also have been obtained.

Experimental

Materials

Cr(CO)$_6$, W(CO)$_6$ (Pressure Chemical Co.) and Mo(CO)$_6$ (Climax Molybdenum Co.) were vacuum-sublimed before use. Benzene (Mallinckrodt Chemical Co.) was fractionally distilled from sodium under nitrogen. Tetrachloromethane (Fisher Scientific) was distilled from P_4O_{10} under nitrogen.

Kinetics studies

The pulsed laser flash photolysis studies were carried out employing a Tachisto 800 XR excimer laser (Xe/F$_2$/He gas mixture at 351 nm, 200 mJ maximum energy per pulse and 20 ns fwhi). Other details of the flash photolysis apparatus have been given elsewhere [12].

1-Hexene (hex) was chosen as the 'trapping' ligand for several reasons: (i) it is a sterically-demanding, weak nucleophile [4, 11] whose use thus should suppress a possible competitive interchange pathway (eqn. (10), path (b), *vide infra*), the accessibility of which would severely complicate the interpretation of activation data; (ii) the λ_{max} for the (hex)M(CO)$_5$ products of the overall reaction (eqn. (1)), are considerably blue-shifted relative to λ_{max} observed for the (solv)M(CO)$_5$ intermediates produced in predominant concentration after the flash [11], and thus relatively large changes in absorbance accompany conversion of (solv)M(CO)$_5$ to (hex)M(CO)$_5$; (iii) upon photolysis, the (hex)M(CO)$_5$ products regenerate (solv)M(CO)$_5$ intermediates, allowing the use of data-averaging for successive flashes of the same reaction solution [11]. Solutions *c.* 3×10^{-3} M in M(CO)$_6$ containing large (weighed) excesses of both solv and hex were employed so that pseudo first-order reaction conditions were obtained. Concentrations of solv and hex were varied widely, 1.6 M < [solv] < 9 M; 1.4 M < [hex] < 6.8 M, so that the influences of the concentrations of both solv and hex on the rates could be evaluated. The disappearance of the photogenerated (solv)M(CO)$_5$ intermediates was monitored at observation wavelengths (see Table 1) which were selected to afford the largest change in absorbance as these species were converted to the (hex)M(CO)$_5$ products. Values

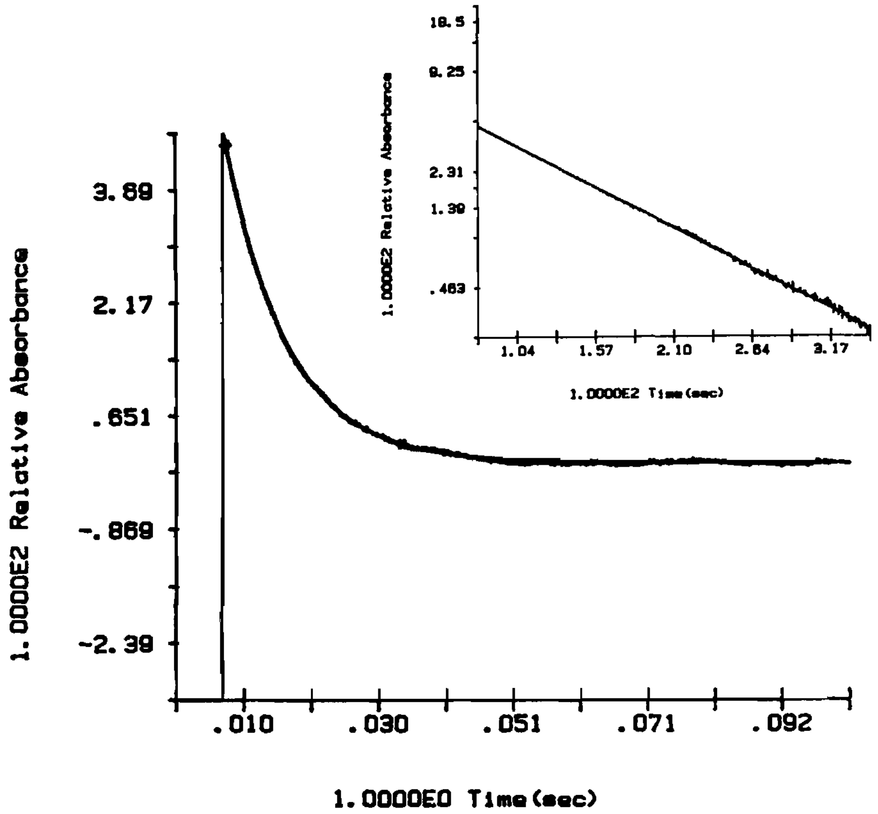

Fig. 2. Plot of relative absorbance vs. time for displacement of benzene from (η^2-benzene)W(CO)$_5$ 1-hexene/benzene solution (4.65 M) at 15.0 °C; the inset is of a plot of $\ln(A_t - A_\infty)$ vs. time for these data (A_t and A_∞ are relative absorbances at time t and infinite time, respectively).

of the pseudo first-order rate constants, k_{obs}, were determined from data from 1–10 kinetics traces, depending on the observed signal-to-noise ratio. Data were analyzed employing Asyst®-based computer programs developed in-house. The limits of error, given in parentheses as the uncertainties of the last digit(s) of the cited experimental values, are one standard deviation. See also 'Supplementary material'.

Results and discussion

Data were taken after flash photolysis of the metal hexacarbonyl in the following solvent/hex mixtures: Mo(CO)$_6$/benzene and W(CO)$_6$/benzene (for comparison to data reported for the Cr(CO)$_6$/benzene/hex system [11]) and Cr(CO)$_6$/CCl$_4$. The analogous Mo and W systems for tetrachloromethane were not investigated since previous studies strongly suggest that where bonding to the metal atom through Cl takes place, displacement of such solvents by L is likely to proceed via competitive dissociation and interchange mechanisms (the two pathways illustrated in eqn. (10), *vide infra*) [6].

Data for thermal reactions taking place after flash photolysis of M(CO)$_6$/solv/hex solutions are illustrated in Figs. 2–4. The data shown, for W(CO)$_6$/benzene/hex solutions, are typical and illustrative of those obtained for all three systems. For the Mo/benzene reaction, a second, much slower decay ($k_{obs} = 20$ s^{-1}), to be studied employing flash photolysis with infrared detection [13], also was observed.

Figure 2 shows a plot of absorbance versus time, monitoring 410 nm (disappearance of photogenerated (solv)M(CO)$_5$); the inset shows the corresponding plot of $\ln(A_t - A_\infty)$ versus time (A_t and A_∞ are the absorbances measured at time t and at infinite time, respectively), which demonstrates that

$$-\mathrm{d}[(\mathrm{solv})\mathrm{M(CO)_5}]\mathrm{d}t = k_{obs}[(\mathrm{solv})\mathrm{M(CO)_5}] \qquad (9)$$

Figure 3 exhibits plots of k_{obs} versus [hex]/[benzene] from data taken at four temperatures; the curvature of these plots is suggestive of a contribution to the

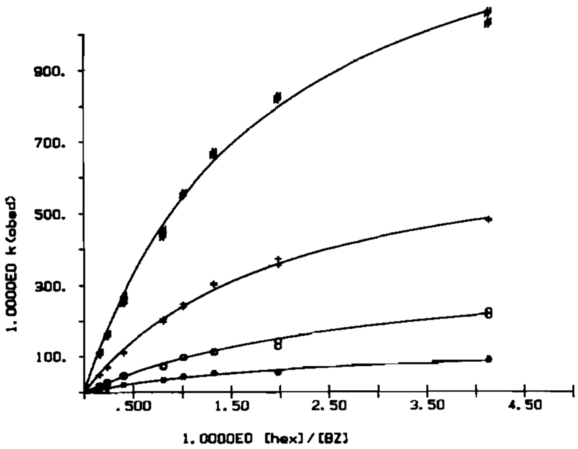

Fig. 3. Plots of k_{obs} vs. [1-hexene]/[benzene] for displacement of benzene from (η^2-benzene)W(CO)$_4$ at four temperatures (bottom to top: 5.0, 15.0, 25.0, 35.0 °C).

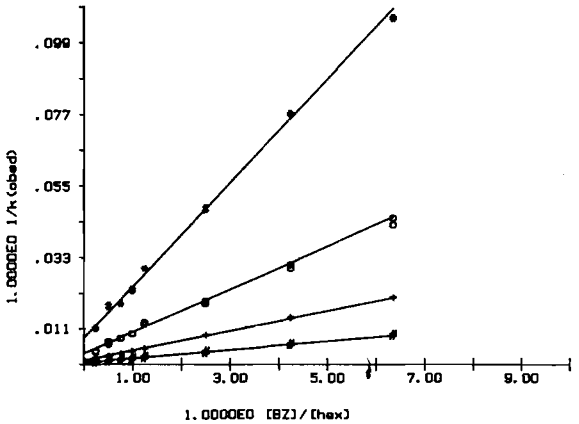

Fig. 4. Plots of $1/k_{obs}$ vs. [benzene]/[1-hexene] for displacement of benzene from (η^2-benzene)W(CO)$_5$ at four temperatures (bottom to top: 35.0, 25.0, 15.0, 5.0 °C).

mechanism of a pathway consisting of consecutive steps, one or more of which is reversible; such a mechanism (eqn. (10)) has been observed for the

$$\begin{tikzcd}
[(solv)M(CO)_5] \arrow[rr, shift left, "k_1"] \arrow[dr, "k_3[hex]" ', "(b)"] & & {[M(CO)_5]} \arrow[ll, shift left, "k_{-1}\,[solv]"] \arrow[dl, "k_2[hex]", "(a)" '] \\
& (hex)M(CO)_5 &
\end{tikzcd} \qquad (10)$$

previously-reported and closely-related Cr(CO)$_6$/benzene/L systems [11].

The steady-state rate law for this mechanism ([M(CO)$_5$] is the steady-state intermediate), expressed in terms of k_{obs}, pseudo first-order rate constant ([(solv)M(CO)$_5$] ≪ [solv], [hex]) is

$$k_{obs} = k_3[hex] + k_1k_2[hex]/(k_{-1}[solv] + k_2[hex]) \qquad (11)$$

which, upon rearrangement, becomes

$$1/(k_{obs} - k_3[hex]) = 1/k_1 + (k_{-1}/k_1k_2)[solv]/[hex] \qquad (12)$$

The best fit of the data to eqn. (12), shown in Fig. 4, demonstrates, as do the data for all systems, that k_3[hex] is less than 0.2% of the value of k_{obs}; thus the data indicate that these reactions all take place exclusively via the dissociative pathway (eqn. (10), path (a)) and that [M(CO)$_5$] is the intermediate produced upon desolvation, which is governed by k_1.

Based on eqn. (12), where $k_3[hex] \ll k_{obs}$ values of k_{-1}/k_1k_2 and $1/k_1$ can be obtained from the slopes and intercepts, respectively, of plots of $1/k_{obs}$ versus [solv]/[hex]. The reciprocal of the intercept is k_1, the rate of M–solv bond dissociation, while intercept/slope is k_2/k_{-1}, the 'competition ratio' of the rate constants for reaction of hex and solv, respectively, with [M(CO)$_5$].

TABLE 1. Rate constants for reactions of (solvent)M(CO)$_5$ complexes with 1-hexene (M = Cr, Mo, W)[a]

M/solvent T (°C)	$10^{-4} \times k_1$ (s^{-1})	k_2/k_{-1}
Cr/benzene[b]		
25.0	27.0(2)	0.35(4)
Mo/benzene		
6.5	0.76(4)	0.52(4)
15.2	1.64(10)	0.45(3)
25.0	3.5(3)	0.47(5)
35.0	7.2(4)	0.44(3)
W/benzene		
5.0	0.0123(8)	0.51(6)
15.0	0.030(3)	0.51(5)
25.0	0.082(5)	0.40(3)
35.0	0.183(10)	0.41(3)
Cr/tetrachloromethane		
5.8	3.1(2)	0.79(7)
15.8	6.4(3)	0.85(5)
25.0	14.3(3)	0.72(2)

[a] Observation wavelengths: Mo/benzene, 420 nm; W/benzene, 400, 410 nm; Cr/tetrachloromethane, 465, 480 nm. [b] Ref. 11.

Table 1 presents the rate constants (k_1, k_2/k_{-1}) for reactions proceeding according to eqn. (1) and the mechanism given in eqn. (10), pathway (a). The rate constants, k_1, for dissociation of benzene from (η^2-benzene)M(CO)$_5$ vary Cr > Mo > W, which is not the usual order for dissociation of CO from this series of metals (Mo > Cr > W [14, 15]; *vide infra*), and may be related to the bulkiness of benzene relative to that of CO. For Cr, the rate of dissociation of solv is slower for CCl_4 than for benzene, an effect attributable to the differing mode of bonding for benzene to Cr (via an isolated C=C bond [11]) than for CCl_4 (via a coordinate covalent bond through Cl).

The competition ratios, k_2/k_{-1}, are less than one for all systems. Thus, rate constants for solvation are larger than are rate constants for attack at $[M(CO)_5]$ by hex despite the greater strengths of hex–M than solv–M bonds. These relative rates may be attributable to statistical or steric factors (multiple bonding sites in the solvents or, for CCl_4, a greater probability of correct orientation for bonding). The competition ratios are relatively constant with temperature, suggesting similar enthalpic barriers to reaction of $[M(CO)_5]$ with hex and solv.

Activation parameters

Activation parameters for solvent dissociation from (solv)$M(CO)_5$ intermediates calculated from data taken at three or four temperatures over a 20–30° temperature range are presented in Table 2. The values of $\Delta H^{\ddagger}$ for solvent dissociation from the (solv)$M(CO)_5$ complexes studied here all lie within the range of 12.5–14.9 kcal/mol.

The value of $\Delta H^{\ddagger}$ obtained for dissociation of CCl_4 from $(CCl_4)Cr(CO)_5$, 12.5(7) kcal/mol, may be contrasted to the reported enthalpy of activation for dissociation of chlorobenzene (CB) from (η^1-CB)$Cr(CO)_5$, in which CB also is coordinated to Cr via a Cl–Cr bond [3], 9.8(1) kcal/mol [5]. This lower value for H_1 was observed for CB despite the fact that CCl_4 dissociation from $(CCl_4)Cr(CO)_5$ is significantly faster than is CB dissociation from its solvate [5]. These relative rates might be anticipated on the basis of weaker Cl-to-Cr bonding in $(CCl_4)Cr(CO)_5$ as a consequence of the greater electron-withdrawing ability of $-CCl_3$ relative to $-C_6H_5$.

The addition of the 'inert' solvent, hexanes, into the solvent mixture employed in the (CB)$Cr(CO)_5$ study to effect variation of the concentration of CB [5] might be responsible for the low enthalpy of activation and correspondingly negative entropy of activation, −2.9(4) eu versus 7.0(24) eu for CCl_4, observed for CB dissociation. The possibility exists that CB displacement in CB/hexanes solution proceeds, at least in part, via (hexane)$Cr(CO)_5$ intermediates; that scenario was considered and rejected based upon the lack of discriminating ability of the intermediate(s), among incoming nucleophiles [5]. However, it has recently been shown that displacement of n-heptane from photogenerated (n-heptane)$Cr(CO)_5$ takes place via competitive dissociative and interchange pathways (eqn. (10); [8]).

The entropies of activation obtained here for the dissociative process governed by k_1 are positive, as is to be expected. One may contrast these values to the entropy of activation observed for dissociation of benzene from (η^2-benzene)$Cr(CO)_5$ (Table 2), which is slightly negative [11]. In that system isotopic labelling studies suggest an 'agostic' [17] C–H–Cr interaction in the transition state, which would be consistent with such an entropy of activation. The more positive values observed for the Mo and W analogues of (η^2-benzene)$Cr(CO)_5$ suggest that such an agostic interaction involving these metals is diminished or absent.

Estimates of bond strengths

(Solv)$M(CO)_5$ molecules may be regarded as 'normal' coordination complexes in which solv functions as a Lewis base (L) which is weakly bonded to the transition metal. As such, the complexes studied here constitute several of the relatively few $LM(CO)_5$ complexes for which enthalpies of activation are known which undergo ligand-exchange via fission of an M–L, rather than an M–CO bond. They thus are of particular interest since, for a given metal atom, the dissociation of L affords a common $[M(CO)_5]$ intermediate (eqn. (13)), the energy of which

$$LM(CO)_5 \xrightarrow{k_1} [M(CO)_5] + L \qquad (13)$$

should be quite similar to those for the transition states for M–L bond fission (Fig. 1) [18]*. In contrast,

TABLE 2. Activation parameters for reactions of (solvent)$M(CO)_5$ complexes with 1-hexene (M = Cr, Mo, W)

M/solvent	$\Delta H_1^{\ddagger}$ (kcal/mol)	$\Delta S_1^{\ddagger}$ (eu)	$\Delta H_2^{\ddagger} - \Delta H_{-1}^{\ddagger}$ (kcal/mol)	$\Delta S_2^{\ddagger} - \Delta S_{-1}^{\ddagger}$ (eu)
Cr/benzene[a]	9.4(1)	−2.4(3)	−0.8(3)	−1.4(10)
Mo/benzene	12.49(5)	4.1(2)	−0.9(5)	−4.4(16)
W/benzene	14.9(4)	4.8(13)	−1.5(6)	−6.9(20)
Cr/tetrachloromethane	12.5(7)	7.0(24)	−0.7(9)	−2.8(30)

[a] Ref. 11.

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*Activation parameters for dissociation of $P(OMe)_3$, $P(OPh)_3$, PPh_3 and $AsPh_3$ (= L′) from *trans*-(P-n-Bu_3)(L′)$Cr(CO)_4$, which reactions also should proceed via very similar transition states, have also been reported.

TABLE 3. Estimated M–L bond enthalpies (kcal/mol) in $LM(CO)_5$ complexes

L	Cr	Mo	W	Reference
CO	40.2(6)	31.7(4)	39.9(16)	9
PPh_3	36.3(10)			10
$AsPh_3$	36.3(2)			10
$P(OPh)_3$	31.9(6)			10
$SbPh_3$			19.8(16)	20
$C_6H_5NH_2$	26.4(5)		22.1(4)	20, 21
$C_5H_{10}NH$	25.7(6)	23.1(6)		21
CCl_4	12.5(14)			this work
C_6H_5Cl	9.8(1)			5
C_6H_6	9.6(3)	12.49(5)	14.9(4)	this work
n-C_7H_{16}	9.6(23)	8.7(27)	13.4(28)	22

CO dissociation for a series of $LM(CO)_5$ complexes takes place via a mechanism (eqn. (14)), the enthalpies of activation for which are

$$LM(CO)_5 \xrightarrow{k'_1} LM(CO)_4 + CO \qquad (14)$$

affected by influences of L both in the ground state and the transition state. The influences of L on rates of dissociation of CO from $LM(CO)_5$ (eqn. (14)) have been widely studied, and have been rationalized by Atwood and Brown in terms of stabilization of the transition state by L [14, 19].

Table 3 compares the enthalpies of activation for M–L bond fission obtained here with those of other M–L bonds, derived similarly as activation enthalpies, for dissociative reactions proceeding according to eqn. (13). Where L = n-heptane (hep), hep–M bond strengths have been estimated from time-resolved photoacoustic calorimetry studies*; these values also are presented in Table 3. The data represent a range of rates of M–L bond fission of some 21 orders of magnitude [14]. In contrast to observations for ligand exchange via CO loss from $LM(CO)_5$ complexes (eqn. (14)) there does not seem to be a pattern for variation of the bond strengths as a function of the identity of the metal atom among these very different ligands; as suggested above, this may be attributable, at least in part, to the varying steric properties of L. The M–hep bond strengths are not too different from the inferred solv–M bond strengths reported here, despite the much faster (*c.* 2–4 orders of magnitude) rates of displacement of hep [6, 8].

Now that it has been recognized that solvent–metal bonding may be viewed within the context of 'ligand'–metal bonding, it will be important to extend and compare bond strength studies which apply the methods described here, or photoacoustic calorimetry, to other 'solvents'; where competition ratios of *c.* 1 are observed, that is, for relatively non-discriminating coordinatively-unsaturated metal carbonyl fragments, the procedures employed in this study should be widely applicable.

Supplementary material

Values of k_{obs} are available from the authors on request.

Acknowledgements

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*There is no *a priori* reason to assume that time-resolved photoacoustic calorimetric measurements will provide better values for M–L bond strengths than will activation enthalpies for dissociative reactions because of the several assumptions required in that method; see refs. 4 and 22.

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