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HEATS OF REACTION OF $HMo(CO)_3C_5H_5$ WITH CCl_4 AND CBr_4 AND OF $NaMo(CO)_3C_5H_5$ WITH I_2 AND CH_3. SOLUTION THERMOCHEMICAL STUDY OF THE Mo–X BOND FOR X = H, Cl, Br, I AND CH_3

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Summary

The heats of reaction of $HMo(CO)_3C_5H_5$ with CX_4 (X = Cl, Br) producing $XMo(CO)_3C_5H_5$ have been measured by solution calorimetry and are -31.8 ± 0.9 and -34.4 ± 2.0 kcal/mole, respectively. The heats of reaction of $NaMo(CO)_3C_5H_5$ with I_2 and CH_3I producing $IMo(CO)_3C_5H_5$ and $H_3CMo(CO)_3C_5H_5$ are -32.3 ± 1.3 and -7.7 ± 0.3 kcal/mole. Oxidation with Br_2/CCl_4 yielding $Br_3Mo(CO)_2C_5H_5$ was measured for the following complexes: $(C_5H_5(CO)_3Mo)_2$, (-92.0 ± 1.0 kcal/mole), $BrMo(CO)_3C_5H_5$ (-24.9 ± 2.0 kcal/mole) and $HMo(CO)_3C_5H_5$ (-60.7 ± 2.0 kcal/mole). These and other data are used to calculate the Mo–X bond strength for X = H, Cl, Br, I, and CH_3. These bond strength estimates are compared to those reported for $X_2Mo(C_5H_5)_2$. Iodination of $H_3CMo(CO)_3C_5H_5$, reported in the literature to yield CH_3I and $IMo(CO)_3C_5H_5$, actually produces $CH_3C(O)I$ and $I_3Mo(CO)_2C_5H_5$.

Introduction

Knowledge of the transition metal–ligand bond strengths is fundamental to understanding organometallic chemistry [1]. We have recently reported thermochemical data and bond strength estimates for organomolybdenum complexes of arenes and olefins [2], phosphines and phosphites [3] and other two electron donors [4]. These data are of utility in calculating enthalpies of ligand exchange and estimating equilibrium constants for a number of reactions. There are less data available for homolytic cleavage of the M–X bond to produce radical fragments. A series of papers on the complexes $X_2Mo(C_5H_5)_2$ has led to generation of Mo–X bond strength estimates for X = H, I [5], Br [6], CH_3, Cl [7] and OOCR [8]. We now report new thermochemical data which allow estimation of the Mo–X bond strength in the complexes $XMo(CO)_3C_5H_5$ and comparison of bond strengths between the two systems.

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Experimental

General

All operations involving air-sensitive organometallic complexes were done using standard Schlenk tube and high vacuum techniques or in a Vacuum/Atmospheres glove box filled with argon and containing less than one ppm O_2 and H_2O. Solvents were distilled under argon from an appropriate drying agent and into flame-dried glassware. Organometallic complexes were prepared by standard methods and subjected to at least two purification steps including a combination of fractional recrystallization and/or high vacuum sublimation. Infrared spectra were run on either a Perkin–Elmer 267 or 599 spectrophotometer. NMR spectra were obtained using a Varian FT-80-A spectrometer. Calorimetric measurements of heats of reaction were obtained using either a Setaram C-80 Calvet calorimeter or a Guild solution calorimeter. Both systems have been described previously [2–4] and typical procedures are described below for each system.

Heat of reaction of $HMo(CO)_3C_5H_5$ with CCl_4 and CBr_4

The mixing cells of the C-80 calorimeter were dried in an oven at 150°C for 2 h and taken into the glove box. A sample of approximately 0.15 g of freshly sublimed $HMo(CO)_3C_5H_5$ was loaded in the lower chamber, the cell assembled and filled with 1.5 ml of Hg. The upper chamber was then filled with 4.0 ml of a solution containing CCl_4 (distilled from P_2O_5) in THF (distilled from sodium benzophenone ketyl) at about 25% concentration CCl_4. After sealing the cell it was taken from the glove box and loaded in the calorimeter. After about 2 h it had equilibrated to 50°C and the reaction was initiated by rotating the calorimeter. After the signal had returned to the baseline, about 2 h for this reaction, the cell was removed from the calorimeter. A clear red-orange solution showed no signs of precipitation. Examination of the IR and NMR spectra showed the sole product to be $ClMo(CO)_3C_5H_5$. The heat of the reaction, -29.7 ± 0.9 kcal/mole, is the average of six separate determinations. To convert this to the heat of reaction in solution, the heat of solution of $HMo(CO)_3C_5H_5$ in THF ($+2.1 \pm 0.1$ kcal/mole) must be subtracted to yield the enthalpy of reaction with all components in solution yielding a net value of -31.8 ± 0.9 kcal/mole.

Reaction with CBr_4 was performed in a similar fashion with the important difference that a stoichiometric amount of CBr_4 was used. In experiments where excess CBr_4 was used, slight oxidation of $BrMo(CO)_3C_5H_5$ occurred leading to high values. The experimental heats were corrected for the extent of reaction which was determined quantitatively by IR spectroscopy. The heat of reaction, -32.3 ± 2.0 kcal/mole, refers to reaction of solid $HMo(CO)_3C_5H_5$, subtraction of the heat of solution of $HMo(CO)_3C_5H_5$ (2.1 kcal/mole), leads to a value of -34.4 kcal/mole for the heat of reaction in solution.

Heat of reaction of $NaMo(CO)_3C_5H_5$ with I_2 and CH_3I

A solution of $NaMo(CO)_3C_5H_5$ in THF was prepared by slow addition of solid NaH (50% dispersion in mineral oil) to 25 g of $HMo(CO)_3C_5H_5$ in about 500 ml THF. After complete addition of NaH and evolution of hydrogen had stopped, the solution was filtered into a clean flask, and taken into the glove box. Approximately 400 ml of this solution was used in the calorimetric measurements. Sealed ampoules of alternatively I_2 or CH_3I were broken. Approximately 0.15 g samples were used in the ampoules. Before and after breaking each ampoule, a series of electrical calibrations were performed to match the heat of reaction with equivalent electrical energy. The heat of reaction with I_2 was -31.8 ± 1.3 kcal/mole which must be corrected for the heat of solution of I_2 in THF which we determined to be $+0.5$ kcal/mole, leading to a heat of reaction in solution of -32.3 ± 1.3 kcal/mole. The heat of reaction with CH_3I was found to be -7.7 ± 0.3 kcal/mole and we assumed that the heat of solution of CH_3I in THF was negligible leading to the heat of reaction in solution as -7.7 ± 0.3 kcal/mole.

Heats of reaction of $[Mo(CO)_3C_5H_5]_2$*,* $BrMo(CO)_3C_5H_5$*, and* $HMo(CO)_3C_5H_5$ *with* Br_2/CCl_4

These reactions were performed in a calorimeter installed in a stainless steel hood and equipped to work under an argon atmosphere. The calorimeter vessel is identical to the Guild calorimeter used in the glove box and it is controlled by the same electrical system. The calorimeter was loaded under a flush of argon with a solution of 10 ml Br_2 in 400 ml of freshly distilled CCl_4. Sealed ampoules of the crystalline organometallic complex were broken in a rotating fashion for the three compounds studied. The heats of reaction were: $[Mo(CO)_3C_5H_5]_2$ (-92.0 ± 1.0 kcal/mole), $BrMo(CO)_3C_5H_5$ (-24.9 ± 2.0 kcal/mole) and $HMo(CO)_3C_5H_5$ (-60.7 ± 1.0 kcal/mole). These heats of reaction refer to solid transformations and we assume that heats of solution cancel. Since these results were used primarily as a check on the Mo–Br bond strength, further refinement was not needed.

Heat of solution of $[Mo(CO)_3C_5H_5]_2$ *in THF*

The heats of reaction of the complexes $HMo(CO)_3C_5H_5$ and $[Mo(CO)_3C_5H_5]_2$ with I_2 in THF had been previously reported as -18.0 ± 0.6 and -31.8 ± 1.0 kcal/mole respectively [9]. In order to convert these to solution phase values the heats of solution of the molybdenum hydride and dimer in THF were measured in the Guild calorimeter in the glove box. The heats of solution were 2.1 ± 0.1 and 4.0 ± 0.2 kcal/mole respectively. This leads to heats of reaction with I_2 in solution of -20.1 ± 0.6 and -35.8 ± 1.1 kcal/mole for the two complexes.

Reaction of $H_3CMo(CO)_3C_5H_5$ *with* I_2

In a Schlenk tube under an argon atmosphere, a solution of I_2 in CH_2Cl_2 was added slowly by syringe to a solution of $H_3CMo(CO)_3C_5H_5$. Following each incremental addition, an IR spectrum was run to monitor the reaction. The only peaks present in the carbonyl region were those due to starting material and $I_3Mo(CO)_2C_5H_5$ [15], no peaks due to $IMo(CO)_3C_5H_5$ were seen. Similar behaviour was observed in THF and C_6D_6. In C_6D_6 NMR spectra showed no formation of H_3CI, only $H_3CC(O)I$ and its hydrolysis product H_3CCO_2H.

Results

The Mo–H bond

Thermochemical study of the substitution of cyclopentadiene for toluene (reaction 1) led to assignment of the Mo–H bond strength as 66 ± 7 kcal/mole [2]. A

$$\text{tolMo(CO)}_3 + C_5H_6 \rightarrow HMo(CO)_3C_5H_5 + \text{tol} \qquad (1)$$

later study of the heat of hydrogenation of the metal–metal dimer shown in eq. 2

$$[Mo(CO)_3C_5H_5]_2 + H_2 \rightarrow 2HMo(CO)_3C_5H_5 \qquad (2)$$

led to an independent determination of the bond strength as 65 ± 6 kcal/mole [9]. This value was based on the kinetic determination of the Mo–Mo bond strength as 32.5 kcal/mole [10]. As discussed below, bromination studies yield results in agreement with these assignments and we consider the absolute values of these bond strengths estimates to be accurate to within ±5 kcal/mole. These values of the Mo–H and Mo–Mo bond strengths are the basis for all other Mo–X bond strength estimates reported. Any errors in the Mo–H and Mo–Mo values will affect only the absolute but not the relative positions of the other bond strength estimates.

The Mo–Cl bond

Estimation of the Mo–Cl bond is based on reaction of the hydride with carbon tetrachloride as shown in reaction 3:

$$HMo(CO)_3C_5H_5 + CCl_4 \rightarrow ClMo(CO)_3C_5H_5 + CHCl_3 \qquad (3)$$

In the presence of excess CCl_4 this reaction proceeds quantitatively as shown [11]. The enthalpy of this reaction in THF solution (−31.8 ± 0.9 kcal/mole) leads directly to an estimate of 72.4 kcal/mole for the Mo–Cl bond strength [12].

The Mo–Br bond

Three independent routes were used to estimate the strength of the $Br{-}Mo(CO)_3C_5H_5$ bond. Reaction with CBr_4 as shown in reaction 4 is exothermic

$$HMo(CO)_3C_5H_5 + CBr_4 \rightarrow BrMo(CO)_3C_5H_5 + HCBr_3 \qquad (4)$$

by 34.4 ± 2.0 kcal/mole. This leads to a Mo–Br bond strength value of 60.6 kcal/mol [14a].

In the presence of a large excess of CBr_4, additional oxidation takes place. The enthalpy of reaction 4 was therefore determined in the presence of a stoichiometric amount of CBr_4 (see experimental section for additional details). As an additional check on the Mo–Br bond strength, we determined the heats of reaction of $[Mo(CO)_3C_5H_5]_2$ and $BrMo(CO)_3C_5H_5$ with Br_2 in CCl_4. These reactions proceed as shown in eq. 5 and 6 [11,15]:

$$[Mo(CO)_3C_5H_5]_2 + 3Br_2 \rightarrow 2Br_3Mo(CO)_2C_5H_5 + 2CO \qquad (5)$$

$$BrMo(CO)_3C_5H_5 + Br_2 \rightarrow Br_3Mo(CO)_2C_5H_5 + CO \qquad (6)$$

Subtracting twice reaction 6 from reaction 5 leads directly to reaction 7, the enthalpy of bromination of the metal–metal bonded dimer.

$$[Mo(CO)_3C_5H_5]_2 + Br_2 \rightarrow 2BrMo(CO)_3C_5H_5 \qquad (7)$$

It is not possible to measure the enthalpy of reaction 7 directly since, at room temperature at least, even in the presence of a limited amount of Br_2, oxidation of the initially formed $BrMo(CO)_3C_5H_5$ always occurs to some extent. The enthalpy of reaction 5 is −92.0 ± 1.0 kcal/mole. The enthalpy of reaction 6 is −24.9 ± 2.0 kcal/mole. The enthalpy of reaction 7 is then calculated as −42.2 ± 3.0 kcal/mole. This leads to an estimation of the Mo–Br bond strength, based on the Mo–Mo bond, of 60.5 kcal/mole [14b]. This is in excellent agreement with the value from reaction 4 based on the Mo–H bond strength. It is clear that these values have internal consistency.

As a final check on this sytem, we investigated the reaction of $HMo(CO)_3C_5H_5$ with Br_2 (eq. 8):

$$HMo(CO)_3C_5H_5 + 2Br_2 \rightarrow Br_3Mo(CO)_2C_5H_5 + HBr + CO \tag{8}$$

The enthalpy of this reaction was -60.7 ± 2.0 kcal/mole. Subtraction of reaction 6 from reaction 8 leads directly to reaction 9. Using the data mentioned above we

$$HMo(CO)_3C_5H_5 + Br_2 \rightarrow BrMo(CO)_3C_5H_5 + HBr \tag{9}$$

calculate the enthalpy of reaction 9 as -35.8 kcal/mole. This leads to estimation of the Mo–Br bond strength as 60.7 kcal/mole [14c]. The average value obtained from the three independent determinations is 60.6 kcal/mole. Since the estimated values for the Mo–Br bond strength, based on eq. 4, 7 and 9, are in good agreement, confidence is added to the assignments for the Mo–Mo and Mo–H bond strengths.

The Mo–I bond

The Mo–I bond strength can be evaluated from previously available data. The enthalpies of reactions 10 and 11 are -35.8 ± 1.0 and -20.1 ± 0.6 kcal/mole respectively [9]. These data lead to a Mo–I bond strength value of 52.4 kcal/mole

$$[Mo(CO)_3C_5H_5]_2 + I_2 \rightarrow 2IMo(CO)_3C_5H_5 \tag{10}$$

$$HMo(CO)_3C_5H_5 + I_2 \rightarrow IMo(CO)_3C_5H_5 + HI \tag{11}$$

based on eq. 10 and 51.2 kcal/mole based on eq. 11 [16]. The average value, 51.8 kcal/mole shows good agreement between the two methods.

The Mo–CH_3 bond

In order to determine the Mo–CH_3 bond strength, we attempted to measure the heat of reaction 12. Despite the report in the literature [17] that iodination of the

$$H_3CMo(CO)_3C_5H_5 + I_2 \rightarrow IMo(CO)_3C_5H_5 + CH_3I \tag{12}$$

methylmolybdenum complex proceeds as shown in eq. 12, we found that the reaction proceeds according to eq. 13.

$$H_3CMo(CO)_3C_5H_5 + I_2 \rightarrow H_3C(O)I + I_3Mo(CO)_2C_5H_5 \tag{13}$$

The enthalpy of reaction 12 cannot be measured directly since reaction 13 occurs. It can be calculated, since both eq. 14 and 15 are rapid and quantitative [18].

$$NaMo(CO)_3C_5H_5 + I_2 \rightarrow IMo(CO)_3C_5H_5 + NaI \tag{14}$$

$$NaMo(CO)_3C_5H_5 + ICH_3 \rightarrow H_3CMo(CO)_3C_5H_5 + NaI \tag{15}$$

Subtraction of eq. 15 from eq. 14 yields eq. 12. The enthalpy of reaction 14 in THF solution is -32.3 ± 1.3 kcal/mole. The enthalpy of reaction 15 in solution is -7.7 ± 0.3 kcal/mole leading to a calculated enthalpy of eq. 12 of -24.6 ± 1.6 kcal/mole. Estimation of the H_3C–Mo bond strength as 47.0 kcal/mole is straightforward [19], based on the calculated enthalpy of eq. 12.

Discussion

The heats of reaction and bond strength estimates discussed above are part of a program of solution thermochemical study of organometallic reactions. The majority of this work has dealt with organomolybdenum complexes. A goal of our work is to be able to predict the reactions which are thermodynamically favored for as wide a range of complexes as possible. A notable feature of molybdenum is the accessibility of a wide range of oxidation states. This work reports new estimates for Mo–X bond strengths in the formally divalent complexes $XMo(CO)_3C_5H_5$ and allows comparison to the bond strength estimates in the literature for the formally tetravalent complexes $X_2Mo(C_5H_5)_2$. To our knowledge no such comparison exists for organometallic complexes in solution. In addition, some of the oxidative reactions described here lay the foundation for coupling our earlier work on Mo^0 and Mo^{II} to the Mo^{IV} state. Such studies should be of use in understanding the oxidative addition and redox chemistry of these organomolybdenum compounds, and are currently under more detailed consideration in our laboratory.

The bond strength estimates generated as described above are collected in Table 1. For comparison, data for the $X_2Mo(C_5H_5)_2$ system are included. It was anticipated that the bond strengths in the Mo^{II} system would be stronger than those for the Mo^{IV} system. For example the average Mo–Br bond strength in $MoBr_2$, corresponding to one half the enthalpy of reaction 16 is 115.8 kcal/mole [20a].

$$MoBr_2(g) \rightarrow Mo(g) + 2Br(g) \qquad (16)$$

The average Mo–Br strength in $MoBr_4$, defined as one fourth the enthalpy of the gas phase reaction shown in eq. 17 is 75.2 kcal/mole [20b]. On this basis considerable difference in the bond strength estimates for the two systems was expected. Despite this expectation, the agreement between the two systems is remarkable. The average values deviate by roughly 2 kcal/mole, with the Mo^{II} bond strength estimates being on average higher, but not generally outside the limits of experimental error.

$$MoBr_4(g) \rightarrow Mo(g) + 4Br(g) \qquad (17)$$

It is also of interest that the bonds to the halides are generally weaker than estimates that would be made for simple inorganic complexes. For example, the

TABLE 1

ESTIMATES OF THE Mp-X BOND STRENGTH FOR THE $XMo(CO)_3C_5H_5$ AND $X_2Mo(C_5H_5)_2$ SYSTEMS

X	$XMo(CO)_3C_5H_5$ [a]	$X_2Mo(C_5H_5)_2$ [b]	Average
H	66.0 (1.5)	60.0	63
Cl	72.4 (0.9)	72.9	73
Br	60.5 (2.0)	57.8	59
I	51.8 (1.0)	49.4	51
H_3C	47.0 (1.6)	36.9	42
$C_5H_5(CO)_3Mo$	32.5 (0.5)	–	32.5

[a] This work, all units are in kcal/mole; error limits are based on relative values, and are subject to change in absolute value relative to the kinetic determination of Mp–Mp bond strength [13]. [b] Literature values taken from ref. 5–8.

Mo–Br bond strength estimates discussed above for $MoBr_2$ and $MoBr_4$ are both considerably higher than the bond strength estimates in the organometallic systems. These data can be interpreted in several ways. The simplest is to conclude that the relatively "hard" metal–halogen bond is not as stable in the relatively "soft" organometallic environment. An alternative interpretation is that addition of ligands to the metal results in destabilization of the M–X bond. Thus for a divalent species MX_2, dissociation to form MX and X might require more energy than dissociation of MX_2Ln to MXLn and X since the ligands might be able to stabilize MXLn, reducing the effect of loss of the M–X bond. Finally we should examine briefly the assumptions made in making these isolated bond strength assignments.

The Mo–Br bond strength assignment is based on analysis of reactions like eq. 18. The enthalpy of this reaction in solution, discussed earlier, is −37.1 kcal/mole.

$$HMo(CO)_3C_5H_5 + Br_2 \rightarrow BrMo(CO)_3C_5H_5 + HBr \qquad (18)$$

This reaction can be broken down into the sum of the two reactions shown (eq. 19 and 20). The enthalpy of eq. 19 is −41.5 kcal/mole [21].

$$H\bullet + Br_2 \rightarrow HBr + Br\bullet \qquad (19)$$

The enthalpy of eq. 20 is therefore estimated to be endothermic by 4.4 kcal/mole.

$$HMo(CO)_3C_5H_5 + Br\bullet \rightarrow BrMo(CO)_3C_5H_5 + H\bullet \qquad (20)$$

The assignment of bond strengths in reactions of diatomic molecules such as that shown in eq. 19 is relatively straightforward. The endothermic nature of eq. 20, if taken at face value, implies that the Mo–Br bond is actually 4.4 kcal/mole weaker than the Mo–H bond. This is the approach that we take. It assumes that since only the Mo–X bond is changing, all other bond strengths, e.g. the Mo–CO and Mo–C_5H_5 bonds, have the same bond energy in $HMo(CO)_3C_5H_5$ as they do in $BrMo(CO)_3C_5H_5$. This is known as the principle of transferability and it has generally been upheld for organometallic systems [22]. So long as one system is adhered to, the use of bond strength estimates to calculate heats of reaction will be reliable [23].

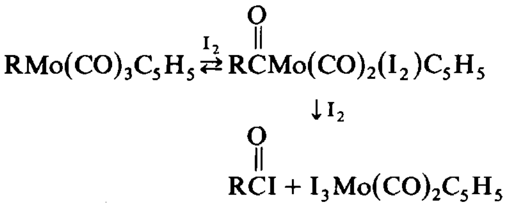
There is no reason to believe that the Mo–CO bond strength in $HMo(CO)_3C_5H_5$ is the same as it is in $BrMo(CO)_3C_5H_5$. There is a shift in the carbonyl stretching frequency of about 25 cm^{-1} to higher frequency for the MoBr complex. This could be interpreted as a weakening of the Mo–CO bond in the MoBr complex. An alternative interpretation of eq. 20 would be that the Mo–Br bond strength is about 75 kcal/mole (the same as in $MoBr_4$ [20b]) and that the Mo–CO bonds are an average of 6 kcal/mole weaker in the MoBr complex than in the MoH complex. It has been estimated that the average bond strength in $Cr(CO)_6^+$ is about 5 kcal/mole weaker than in $Cr(CO)_6$ [24]. This demonstrates the effect of removing electron density from the metal on the metal–ligand bond. The carbon monoxide ligand is especially sensitive to this since an important component of its bonding is back donation from the metal to the antiboding CO orbitals.

Detailed partitioning of energy in such complexes is beyond the scope of this paper and will require the blending of both theory and experiment [25]. The bond strength estimates in Table I assume that the $Mo(CO)_3C_5H_5$ group has the same ancillary bond strengths for each complex. Thus the net effect of converting Mo–H to Mo–Br in reaction 20 is a decrease in energy for the system of 4.4 kcal/mole which we attribute to the influence of the Mo–Br versus the Mo–H bond. However the "influence", particularly where oxidations take place, may involve important contributions from ancillary ligands. Additional experimental work is planned to determine heats of binding of CO to higher valent Mo complexes and this should help clarify some aspects of the partitioning of energy in these complexes.

Thermochemical data on the $MoCH_3$ complex was more difficult to generate than anticipated. Thus reaction 12 which had been reported in the literature [17] was found to proceed as shown in eq. 13, producing acetyl iodide rather than methyl iodide. This is in keeping with recent work which has shown that iodination of alkylcobalt tetracarbonyls can proceed in similar fashion generating acyl rather than alkyl iodides [26]:

$$RCo(CO)_4 + I_2 \xrightarrow{CO} IC(O)R + ICo(CO)_4 \qquad (21)$$

The reaction mechanism of $RMo(CO)_3C_5H_5$ complexes [27] with phosphines and other reagents has shown the importance of solvated acyl intermediates $RC(O)Mo(CO)_2(D)C_5H_5$ where D is a donor or solvent ligand. The reaction with I_2 is much faster than reaction with, for example THF [27], and hence direct attack of I_2 similar to that in eq. 22 is a possible mechanism.



$$RMo(CO)_3C_5H_5 \overset{I_2}{\rightleftarrows} R\overset{\overset{O}{\|}}{C}Mo(CO)_2(I_2)C_5H_5 \qquad (22)$$

$$\downarrow I_2$$

$$R\overset{\overset{O}{\|}}{C}I + I_3Mo(CO)_2C_5H_5$$

While direct measurement of reaction 12 could not be made due to unanticipated side reactions, calorimetric measurement of reactions 14 and 15 does allow indirect determination of the enthalpy of this reaction. This represents the first use of metal carbonyl anions in organometallic thermochemistry and we are currently extending this to other systems [28].

The $Mo–CH_3$ bond strength estimate for $H_3CMo(CO)_3C_5H_5$ of 47 kcal/mole is considerably higher than the estimate of 37.8 kcal/mole for $(H_3C)_2Mo(C_5H_5)_2$ and shows the largest deviation of the bond strength values in Table 1. A recent general estimate for the metal–alkyl bond strength for first row transition metals was 25 kcal/mole. This compares to their estimate of the metal–hydride bond strengths of 60 kcal/mole [1]. A second row metal such as molybdenum would be expected to form stronger bonds than first row metals, nevertheless the metal–alkyl bond strength estimate is 22 kcal/mole stronger than the first row estimate and the metal hydride only 6 kcal/mole stronger. This discrepancy has caused us to examine this value more closely. Two research groups have come to the conclusion that the metal–methyl bond is similar in strength to the metal–iodine bond in organometallic complexes of Ir [29] and Pt [30]. In fact, for both systems the metal–methyl bond was judged as slightly stronger. The molybdenum–iodine bond strength estimate agrees well for both systems in Table 1, and by analogy with the work on Ir and Pt one would expect a bond strength slightly greater than 50 kcal/mole. In this light our value of 47 kcal/mole appears reasonable.

In addition to estimation of bond strengths, the data obtained in this work can be used directly to calculate the enthalpies of a number of important organometallic reactions. An example is reductive elimination of methane as shown in eq. 23:

$$HMo(CO)_3C_5H_5 + H_3CMo(CO)_3C_5H_5 \rightarrow CH_4 + [Mo(CO)_3C_5H_5]_2 \qquad (23)$$

The enthalpy of reaction 23 can be estimated from the bond strength estimates in Table 1 to be -23.5 kcal/mole [31]. Calculation of the enthalpy of eq. 23 can be made entirely independent of any errors in assignment of bond strengths and based only on experimental data and heats of formation [32]. The same value is obtained, as should be the case if all bond strength assignments are made consistently [23].

The reverse of reaction 21, methane activation, is of current interest since several active metal complexes have been shown to add methane [33]. No example of activation by a dinuclear complex has been observed. It is clear that for the molybdenum dimer this process would not be thermodynamically allowed. Unlike the mononuclear coordinatively unsaturated complexes which have been shown to add methane, reaction 23 requires the additional energy of breaking the metal–metal bond. Thus binuclear reductive elimination is strongly favored but methane activation is thermodynamically disfavored for this binuclear system. A second application is calculation of the enthalpy of reaction 24, formation of the metal–metal bonded complex from the metal carbonyl anion and a metal halide. Such "salt elimination" routes have proven to be a general method of synthesis of metal–metal bonded complexes [34].

$$NaMo(CO)_3C_5H_5 + IMo(CO)_3C_5H_5 \rightarrow NaI + [Mo(CO)_3C_5H_5]_2 \qquad (24)$$

As part of a study of the electrochemical behaviour of organometallic complexes it was shown that reaction 24 did not occur [35]. It is not clear whether this was for kinetic or thermodynamic reasons. The enthalpy of reaction 24 can be estimated by considering the two iodination experiments shown in eq. 25 and 26 below.

$$NaMo(CO)_3C_5H_5 + I_2 \rightarrow NaI + IMo(CO)_3C_5H_5 \qquad (25)$$

$(\Delta H\ -32.3\ \text{kcal/mole})$

$$[Mo(CO)_3C_5H_5]_2 + I_2 \rightarrow 2IMo(CO)_3C_5H_5 \qquad (26)$$

$(\Delta H\ -35.8\ \text{kcal/mole})$

Subtraction of eq. 26 from eq. 25 leads directly to eq. 24, calculated to be endothermic by 3.5 kcal/mole. This is in keeping with the failure to observe eq. 24 even though the molybdenum carbonyl anion will undergo similar nucleophilic displacements. It should be noted that the reverse of eq. 24, cleavage of the Mo–Mo dimer by halide anions has been observed both thermally and photochemically [36]. Thus thermodynamic as well as kinetic factors apparently control the reactivity of these metal carbonyl anions. Additional work on the thermochemistry of these reactions is in progress.

Conclusion

The heats of reaction and interconversion of a number of $XMo(CO)_3C_5H_5$ complexes have been measured for X = H, Cl, Br, I and CH_3. These data have been used to calculate individual bond strength estimates assuming that all other bond strengths are unaffected by changes in the nature of X. The order of bond strengths as a function of X is Cl > H > Br > I > CH_3 > $Mo(CO)_3(C_5H_5)$. These estimates are in excellent agreement with data in the literature for $X_2Mo(C_5H_5)_2$ and the average bond strengths can be used to calculate the enthalpies of a number of important organometallic reactions. While the use of bond strength estimates within a given system can lead to accurate values for heats of reaction, comparison to simple inorganic compounds shows that bonds to the halogens are weaker in the organometallic system. This is probably due to a balance of factors including the weakening of terminal metal–carbon monoxide bond strengths in the halogen complexes. This highlights the importance of using original data, where possible, to estimate heats of reaction rather than relying on bond strength estimates [23]. Additional calorimetric measurements are in progress, the goal of which is obtaining a complete thermodynamic surface describing the reactions of these and related complexes.

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12 Estimation of the Mo–Cl bond strength is based on the following analysis (Mp = $Mo(CO)_3C_5H_5$)

$$\begin{array}{llll} MpH + & ClCCl_3 \rightarrow & MpCl + & HCCl_3 \\ 66 & 70.4 & x & 95.8 \end{array}$$

$$\Delta H_{react.} = -31.8 \text{ kcal/mole}$$

$$\begin{array}{lll} \Delta H_{react.} = D(Mp\text{–}H) + & D(Cl-CCl_3) - & D(Mp\text{–}Cl) - D(H\text{–}CCl_3) \\ -31.8 = 66 & +70.4 & -D(Mp\text{–}Cl) - 95.8 \end{array}$$

$$D(Mp\text{–}Cl) = -72.4 \text{ kcal/mole}$$

See ref. 13

13a The following bond strength estimates were obtained from the literature:

Bond	Bond strength (kcal/mole)	Reference
$Cl{-}CCl_3$	70.4	13b
$H{-}CCl_3$	95.8	13b
$Br{-}CBr_3$	56.2	13b
$H{-}CBr_3$	96.0	13b
$Br{-}Br$	46.3	13b
$I{-}I$	36.5	13b
$I{-}CH_3$	56.3	13b
Mp–H	66.0	2,9
Mp–Mp	32.5	10

The rest of the bond strength estimates used in this work are discussed in the text.

13b R.C. Weast (Ed.), Handbook of Chemistry and Physics, 58th edition, CRC press, Cleveland, Ohio, 1977, p. 231 etc.

14a Estimation of the Mp–Br bond strength is based on the following analysis:

$$\begin{array}{llll} \mathrm{Mp{-}H} + & \mathrm{Br{-}CBr_3} \rightarrow & \mathrm{Mp{-}Br} + & \mathrm{H{-}CBr_3} \\ 66 & 56.2 & x & 96.0 \end{array}$$

$\Delta H_{\mathrm{react.}} = -34.4$ kcal/mole

$$\begin{array}{lllll} \Delta H_{\mathrm{react}} = & D(\mathrm{Mp{-}H}) + & D(\mathrm{Br{-}CBr_3}) - & D(\mathrm{Mp{-}Br}) - & D(\mathrm{H{-}CBr_3}) \\ -34.4 = & 66 & +56.2 & -D(\mathrm{Mp{-}Br}) & -96.0 \end{array}$$

$D(\mathrm{Mp{-}Br}) = 60.6$ kcal/mole

14b Estimate based on analysis of the following reaction:

$$\begin{array}{lll} \mathrm{Mp{-}Mp} + & \mathrm{Br{-}Br} \rightarrow & 2\mathrm{Mp{-}Br} \\ 32.5 & 46.3 & x \end{array}$$

$\Delta H_{\mathrm{react.}} = -42.2$ kcal/mole

$$\begin{array}{llll} \Delta H_{\mathrm{react}} = & D(\mathrm{Mp{-}Mp}) + & D(\mathrm{Br{-}Br}) - & 2D(\mathrm{Mp{-}Br}) \\ -42.4 = & 32.5 & +46.3 & -2D(\mathrm{Mp{-}Br}) \end{array}$$

$D(\mathrm{Mp{-}Br}) = 60.5$ kcal/mole

14c Estimate based on analysis of the following reaction:

$$\begin{array}{llll} \mathrm{H{-}Mp} + & \mathrm{Br{-}Br} \rightarrow & \mathrm{Mp{-}Br} + & \mathrm{H{-}Br} \\ 66 & 46.4 & x & 87.4 \end{array}$$

$\Delta H_{\mathrm{react}} = -35.8$ kcal/mole

$$\begin{array}{lllll} \Delta H_{\mathrm{react}} = & D(\mathrm{H{-}Mp}) + & D(\mathrm{Br{-}Br}) - & D(\mathrm{Mp{-}Br}) - & \mathrm{D}(\mathrm{H{-}Br}) \\ -35.8 = & 66 & +46.4 & -\mathrm{D}(\mathrm{Mp{-}Br}) & -87.4 \end{array}$$

$D(\mathrm{Mp{-}Br}) = 60.7$ kcal/mole.

See ref. 13.

15 See, for example, ref. 11, p. 1186 and references therein.

16a This estimate of the Mp–I bond strength is based on the following data:

$$\begin{array}{lll} \mathrm{Mp{-}Mp} + & \mathrm{I{-}I} \rightarrow & 2\mathrm{Mp{-}I} \\ 32.5 & 36.5 & x \end{array}$$

$\Delta H_{\mathrm{react.}} = -35.8$ kcal/mole

$$\begin{array}{llll} \Delta H_{\mathrm{react.}} = & D(\mathrm{Mp{-}Mp}) + & D(\mathrm{I{-}I}) - & 2D(\mathrm{Mp{-}I}) \\ -35.8 = & 32.5 & +36.5 & -2\mathrm{D}(\mathrm{Mp{-}I}) \end{array}$$

$D(\mathrm{Mp{-}I}) = -52.4$ kcal/mole

16b Estimate of the Mp–I bond strength based on the following data:

$$\begin{array}{llll} \text{H–Mp} + & \text{I–I} \rightarrow & \text{H–I} + & \text{I–Mp} \\ 66 & 36.1 & 71.3 & x \end{array}$$

$\Delta H_{\text{react.}} = -20.1$ kcal/mole

$$\begin{array}{lllll} \Delta H_{\text{react.}} = & D(\text{H–Mp}) + & D(\text{I–I}) - & D(\text{Mp–I}) - & D(\text{H–I}) \\ -20.1 = & 66 & +36.1 & -71.3 & -D(\text{Mp–I}) \end{array}$$

$D(\text{Mp–I}) = 51.2$ kcal/mole

See ref. 13.

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19 This estimate is based on the following data:

$$\begin{array}{llll} \text{H}_3\text{C–Mp} + & \text{I–I} \rightarrow & \text{H}_3\text{C–I} + & \text{I–Mp} \\ x & 36.5 & 56.3 & 51.8 \end{array}$$

$\Delta H_{\text{react.}} = -24.6$ kcal/mole

$$\begin{array}{lllll} \Delta H_{\text{react.}} = & D(\text{H}_3\text{C–Mp}) + & D(\text{I–I}) - & D(\text{H}_3\text{C–I}) - & D(\text{I–Mp}) \\ -24.6 = & D(\text{H}_3\text{C–Mp}) & +36.5 & -56.3 & -51.8 \end{array}$$

$D(\text{H}_3\text{C–Mp}) = -47.0$ kcal/mole

See ref. 13.

20a Bond strength estimate based on the following data:

$\text{MoBr}_2(\text{g}) \rightarrow \text{Mo(g)} + 2\text{Br(g)}$

$$\begin{array}{llll} \Delta H_{\text{react.}} = & \Delta H_{\text{f}}\text{Mo(g)} & + 2\Delta H_{\text{f}}\text{Br(g)} & - \Delta H_{\text{f}}\text{MoBr}_2(\text{g}) \\ \Delta H_{\text{react.}} = & +157.4 & +2(26.74) & -(-20.8) \end{array}$$

$\Delta H_{\text{react.}} = +231.6$ kcal/mole

$D(\text{Mo–Br}) = \Delta H_{\text{react.}}/2$

$D(\text{Mo–Br}) = 115.8$ kcal/mole

20b Bond strength estimate based on the reaction:

$\text{MoBr}_4 \rightarrow \text{Mo(g)} + 4\text{Br(g)}$

$$\begin{array}{llll} \Delta H_{\text{react.}} = & \Delta H_{\text{f}}\text{Mo(g)} & + 4\Delta H_{\text{f}}\text{Br(g)} & - \Delta H_{\text{f}}\text{MoBr}_4(\text{g}) \\ \Delta H_{\text{react.}} = & +157.4 & +4(26.74) & -(-36.7) \end{array}$$

$\Delta H_{\text{react.}} = +301$ kcal/mole

$D(\text{Mp–Br}) = \Delta H_{\text{react.}}/4$

$D(\text{Mp–Br}) = 75.2$ kcal/mole

The heats of formation of MoBr_2(g), MoBr_4(g) and Mo(g) were taken from ref. 21. The heat of formation of Br(g) was taken from ref. 13b.

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21 The heat of this reaction is based on the heats of formation shown:

$\text{H}\cdot + \text{Br}_2(\text{g}) \rightarrow \text{HBr(g)} + \text{Br}\cdot$

$$\begin{array}{lllll} \Delta H_{\text{react.}} = & \Delta H_{\text{f}}\text{HBr(g)} + & \Delta H_{\text{f}}\text{Br}\cdot - & \Delta H_{\text{f}}H\cdot - & \Delta H_{\text{f}}\text{Br}_2(\text{g}) \\ \Delta H_{\text{react.}} = & -8.7 & +26.7 & -52.1 & -7.4 \end{array}$$

$\Delta H_{\text{react.}} = -41.5$ kcal/mole

Heats of formation of all species are taken from D.D. Wagman, H.H. Evans et al., J. Phys. and Chem. Reference Data., 11 (1982) supplement no. 2.

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$$\begin{array}{cccc} H_3C{-}Mp\ + & H{-}Mp \rightarrow & Mp{-}Mp\ + & H{-}CH_3 \\ 47 & 66 & 32.5 & 104 \end{array}$$

The estimated enthalpy for this reaction as written is -23.5 kcal/mole.

32 The enthalpy of reaction 22 is the sum of the following:

$$\begin{array}{lll} H_3C{-}Mp + I_2 & \rightarrow H_3C{-}I + I{-}Mp & -24.6 \\ H{-}Mp \quad + I_2 & \rightarrow H{-}I \quad + I{-}Mp & -20.1 \\ \quad 2I{-}Mp & \rightarrow Mp_2 \quad + I_2 & +35.8 \\ H_3C{-}I \quad + HI & \rightarrow CH_4 \quad + I_2 & -15.1 \\ \hline H_3C{-}Mp + H{-}Mp & \rightarrow CH_4 \quad + Mp_2 & -24.0 \end{array}$$

The enthalpies of iodination of the molybdenum complexes are reported in this work. The heat of iodination of methane is $+18.6$ kcal/mole (data taken from ref 23.) where HI and CH_4 are gases, CH_3I is a liquid and I_2 is a solid. We estimate the enthalpy of solution of HI in THF to be -4.0 kcal/mole based on our value of -3.0 kcal/mole in CH_2Cl_2 [9]. The enthalpy of solution of I_2 in THF is $+0.5$ kcal/mole. assuming the heat of solution of CH_4 and CH_3I in THF is negligible, leads to the value of -15.1 kcal/mole for the last reaction shown. This estimate, which rests on experimental data and well known heats of formation, agrees with the bond strength estimate, as it must since the bond strength data rests ultimately on the heats of formation for the compounds involved.

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