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Thermochemistry of Some Metal-to-Metal Triple Bonds

Sir:

Although multiple bonds between transition metal atoms have now become very well known[1-4] and compounds containing them are quite well characterized structurally and spectroscopically, as well as chemically, there have been no thermochemical data bearing on the strengths of these presumably very strong bonds. There have, indeed, been coarse bond energy estimates ranging from too high,[5] to plausibly intermediate,[6,7] to too low,[8] but no heats of formation of pertinent compounds have heretofore been reported. Some heats of formation have now been measured and are reported here. From these it is, *in principle*, possible to evaluate the energies of the multiple metal-to-metal ($M\underset{}{\overset{n}{-}}M$) bonds,[9] but, *in practice*, there are ambiguities. These too will be considered and the question of what may be credible $M\underset{}{\overset{n}{-}}M$ bond energies, and with what ranges of uncertainty, will be discussed. The measurements themselves and other technical points will be the subject of specialized reports to appear elsewhere.

All species containing $M\underset{}{\overset{n}{-}}M$ bonds with $n \geq 3$ are of at least the complexity represented by the general formula $[X_xM\underset{}{\overset{n}{-}}MX_x]^{\pm y}$. In such a species there are only two kinds of bond and, if we consider only neutral molecules ($y = 0$), the problem of determining $D(M\underset{}{\overset{n}{-}}M)$, the bond enthalpy of the $M\underset{}{\overset{n}{-}}M$ bond, is reduced to the following two steps: (1) measuring the enthalpy of formation of $X_xMMX_n(g)$; (2) estimating the value of $\overline{D}(M-X)$. The first of these steps is the less troublesome, though by no means trivial. The second poses insidious difficulties.

A review of all available compounds showed that the most attractive candidates for study are the triply-bonded molecules X_3MMX_3 where M = Mo or W. Species of this type with X = alkyl-, alkoxy-, or dialkylamide are known. In order to have any chance of success in step 2, it is required that there exist for each X_3MMX_3 at least one MX_z molecule, the heat of formation of which can also be measured. On this basis, our selection was reduced to $Mo_2(NMe_2)_6$ and $Mo(NMe_2)_4$ for molybdenum and to $W_2(NMe_2)_6$ and $W(NMe_2)_6$ for tungsten. For each of these four compounds the structure is known,[10-14] establishing it to be molecular in character, with equivalent M–N bonds. In addition, each one can be volatilized and all are available in appropriate quantity and purity to allow accurate thermochemical measurements.

The thermochemical data[15] are presented in Table I. From the ΔH_f° data for the two mononuclear compounds and using standard[16] values of $\Delta H_f^\circ[\text{Mo, g}] = 658.1$, $\Delta H_f^\circ[\text{W, g}] = 859.9$, and $\Delta H_f^\circ[\text{NMe}_2, \text{g}] = 123.4$ kJ mol^{-1}, one may straightforwardly deduce the following $\overline{D}(M-N)$ values (± 5 kJ mol^{-1}): $\overline{D}(\text{Mo}-\text{NMe}_2) = 255$ kJ mol^{-1} in $Mo(NMe_2)_4$ and $\overline{D}(\text{W}-\text{NMe}_2) = 222$ kJ mol^{-1} in $W(NMe_2)_6$.

We now employ the equation

Table I. Standard Enthalpy of Formation[a] of Dimethylamido Compounds of Molybdenum and Tungsten

	$\Delta H_f^\circ(c)$	ΔH^{298}_{sub}	$\Delta H_f^\circ(g)$
$Mo(NMe_2)_4$	59.0	72.4	131.4
$Mo_2(NMe_2)_6$	17.2	111	128.2
$W(NMe_2)_6$	178.9	89.1	268.0
$W_2(NMe_2)_6$	19.2	113.3	132.5

[a] In kJ mol^{-1}.

Table II. $\overline{D}(\text{M}-\text{NMe}_2)$ and Corresponding $D(\text{M}\overset{3}{-}\text{M})$[a] for Various Formal Oxidation Numbers of the Metal Atom

	formal oxidation number			
	3	4	5	6
$\overline{D}(\text{Mo}-\text{NMe}_2)$	288	255[b]	223	190
$D(\text{Mo}\overset{3}{-}\text{Mo})$	200	396	592	788
$\overline{D}(\text{W}-\text{NMe}_2)$	331	295	258	222[b]
$D(\text{W}\overset{3}{-}\text{W})$	340	558	775	995

[a] In kJ mol^{-1}. [b] Experimental value.

$$D(\text{M}-\text{M}) + 6\overline{D}(\text{M}-\text{NMe}_2) = \Delta H_D \qquad (1)$$

to evaluate $D(\text{M}-\text{M})$, where ΔH_D represents the sum of all D values, a quantity obtainable from the ΔH_f° values. The ambiguity arises because there is no unequivocal way to decide what values are to be used for $\overline{D}(\text{M}-\text{NMe}_2)$. Those obtained experimentally in the mononuclear molecules, where formal oxidation numbers are different, are not necessarily appropriate. It is well established for other sorts of M–X bonds (X = C, F, Cl, Br, I, for example) that $\overline{D}(\text{M}-\text{X})$ varies with the oxidation number of M. From the known correlations for these other sorts of bonds, and using the two measured $\overline{D}(\text{M}-\text{NMe}_2)$ values, we can estimate the dependence of $\overline{D}(\text{M}-\text{NMe}_2)$ values on oxidation number.[17]

We thus finally arrive at the figures in Table II, where we present $\overline{D}(\text{M}-\text{NMe}_2)$ values for oxidation numbers 3–6 and the $\overline{D}(\text{M}\overset{3}{-}\text{M})$ values which result when each of these is employed in eq 1. Even though $\overline{D}(\text{M}-\text{NMe}_2)$ values vary only moderately with oxidation number, the factor of 6 in eq 1 causes the $D(\text{M}\overset{3}{-}\text{M})$ values to span a considerable range.

We are not prepared positively to exclude any of the $\overline{D}(\text{M}\overset{3}{-}\text{M})$ values in Table II, but we believe that some are more plausible than others. The metal atoms in $Mo_2(NMe_2)_6$ have formal oxidation numbers of 3, but each metal atom actually has a valence of 6. If it is assumed that a valence of 6 implies the same $\overline{D}(\text{M}-\text{NMe}_2)$ value in all cases, then the highest $D(\text{M}\overset{3}{-}\text{M})$ values are the best estimates, and this would make these triple bonds among the strongest chemical bonds known. The Mo–Mo and W–W quadruple bonds would be even stronger—perhaps the strongest bonds known. If, on the other hand, this equating of valence number with formal oxidation number overestimates the value of the latter to be used in Table II, the true $D(\text{M}\overset{3}{-}\text{M})$ values are lower. Perhaps formal oxidation numbers as low as 4 are appropriate. Our tentative suggestion is to assign $D(\text{M}\overset{3}{-}\text{M})$ values in the range 592 ± 196 and 775 ± 218 kJ mol^{-1} for Mo and W, respectively. These values are reasonably concordant with the plausibly intermediate estimates made earlier for some quadruple bonds, viz., 640 ± 120 kJ mol^{-1} for $D(\text{Mo}\overset{4}{-}\text{Mo})$ and 560 ± 120 kJ mol^{-1} for $D(\text{Re}\overset{4}{-}\text{Re})$. In short, $M\overset{3}{-}M$ and $M\overset{4}{-}M$ bonds are very strong ones, though probably not the strongest homonuclear bonds known (cf. $D(\text{N}\equiv\text{N}) = 946$ kJ mol^{-1}). The experimental work is being extended to other compounds with $M\underset{}{\overset{n}{-}}M$ bonds.[18]

References and Notes

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(15) All of the thermochemical measurements were made at the University of Manchester and they will be reported fully in forthcoming papers. Briefly, the following methods were used to measure enthalpies from which enthalpies of formation could then be calculated. For W(NMe₂)₆ the heat of hydrolysis in 0.1 M aqueous HCl was measured; the products were [NMe₂H₂]Cl and H₂WO₄. For W₂(NMe₂)₆ both combustion-bomb calorimetry and an oxidative hydrolysis reaction employing acidic dichromate were used. The same type of oxidative hydrolysis reaction was also used for Mo(NMe₂)₄ and Mo₂(NMe₂)₆. The enthalpies of sublimation of all compounds were measured using the vacuum-sublimation, drop-microcalorimeter technique previously described by F. A. Adedeji et al., *J. Organomet. Chem.*, **97**, 221 (1975).
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(17) The arguments on which these estimates are based are not particularly controversial and will be explained in detail elsewhere.
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Perturbation Molecular Orbital Treatment of Free-Radical Hydrogen-Abstraction Reactions

Sir:

The successful PMO treatment[1] of the reactivity and regioselectivity in dicyanomethyl radical additions to alkenes and of the reactivity in $CF_3\cdot$ radical additions to alkenes using MINDO/3 data[2-4] prompted us to extend this approach to hydrogen-abstraction reactions for which kinetic data are available,[5] e.g., the reactions of $CF_3\cdot$ and $CH_3\cdot$ radicals with alkanes.[6]

For the reaction of each radical we calculated Fukui's delocalizabilities $D_r^{(R)}$,[7,8] according to

$$D_r^{(R)} = \sum_i^{occ} \frac{c_{ri}^2}{\alpha - \epsilon_i}(-\beta) + \sum_i^{unocc} \frac{c_{ri}^2}{\epsilon_i - \alpha}(-\beta)$$

This treatment implies that only the mutual interactions of the radical SOMO and the AO of the hydrogen to be abstracted in all occupied and unoccupied MO's of the alkane are considered. The resonance integral β for each series of abstractions
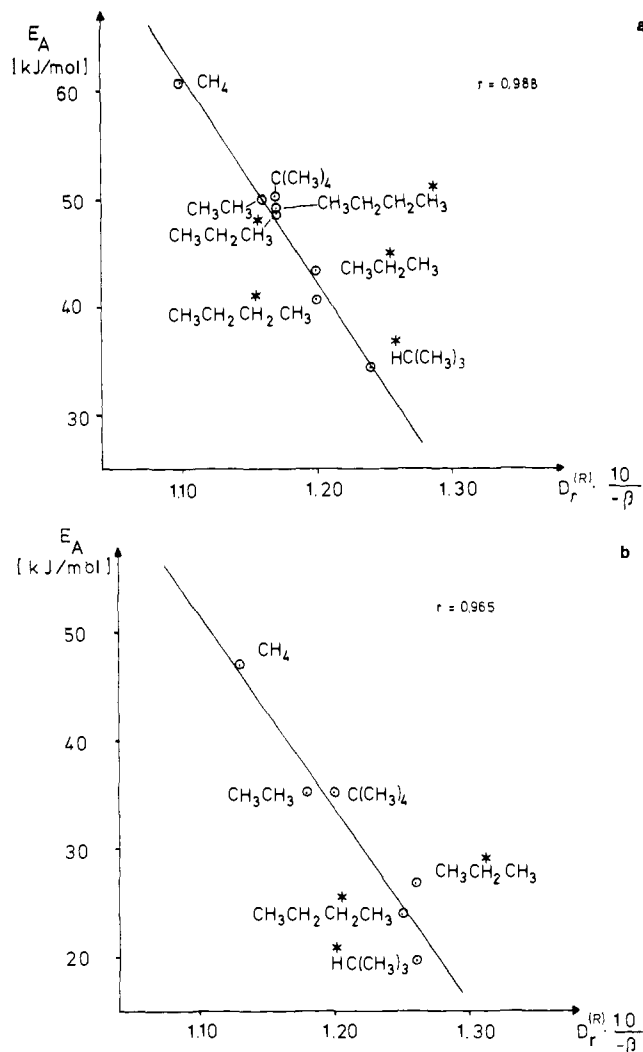

Figure 1. Activation energy (E_a) for hydrogen abstraction from various alkanes at the marked positions (a) by $CH_3\cdot$[10] and (b) by $CF_3\cdot$[11] radicals vs. delocalizabilities $D_r^{(R)}$ (in units of β).
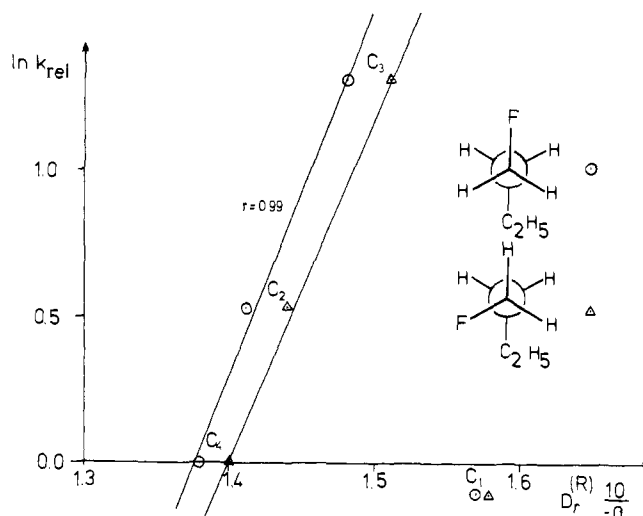

Figure 2. Logarithm of relative rates of hydrogen abstraction[13] (ln k_{rel}) from 1-fluorobutane by chlorine atoms vs. delocalizability ($D_r^{(R)}$) (in units of β) as calculated for the shown conformations.

was taken as constant. This approximation may be justified on employing the same reagent (radical) and similar substrates.[9] The results of the calculations are listed in Table I.

As can be seen from Figures 1a and 1b there is a fairly good