followed. However, the reactions of 1,1-difluoro-2,2,3,3-tetramethyl-1-silirane with cyclohexanone and *tert*-butylcarboxaldehyde have no counterpart in hexamethylsilirane chemistry. The exceptional reactivity of silirane **1b** must result in formation of diradical **5** on collision with a molecule of carbonyl compound. This species then must undergo hydrogen-atom transfer as shown in eq 1.

(1)

5
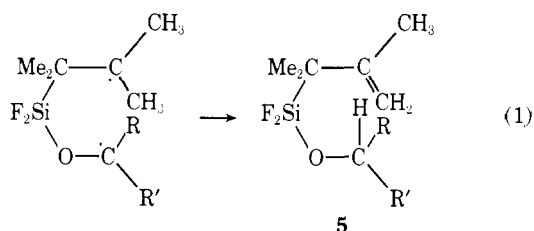
The decreased stability and enchanced reactivity of **1b**, compared with these of **1a**, is interesting, and we note that recent CNDO/2 calculations by Jones and White[7] have predicted that a 1,1-difluorosilirane should have comparable or greater thermodynamic stability relative to those siliranes without Si–F bonds, but a much higher reactivity. The results of our study thus far, together with those of previous studies in which were discovered the addition of silylenes to olefins and acetylenes to give siliranes[1c,8] and silirenes,[1d,9] respectively, and the insertions of dimethylsilylene into siliranes and silirenes to give 1,2-disilacyclobutanes and butenes,[1f] lead us to a reinterpretation of the postulated mechanisms of the reactions of difluorosilylene with olefins, 1,3-dienes, allene, and acetylenes.[2] For instance, SiF$_2$ was found to react with ethylene to produce **6** and **7** and with acetylene to produce compounds **8–11**.[10,11] An interpretation in terms of addition reactions of the ·SiF$_2$SiF$_2$· diradical was given by Margrave and his co-workers[2] and recently was reiterated.[12] Only in the case of fluorinated ethylenes did reactions with SiF$_2$ give products whose formation possibly could be rationalized unambiguously
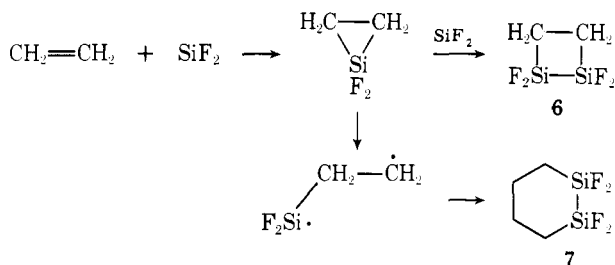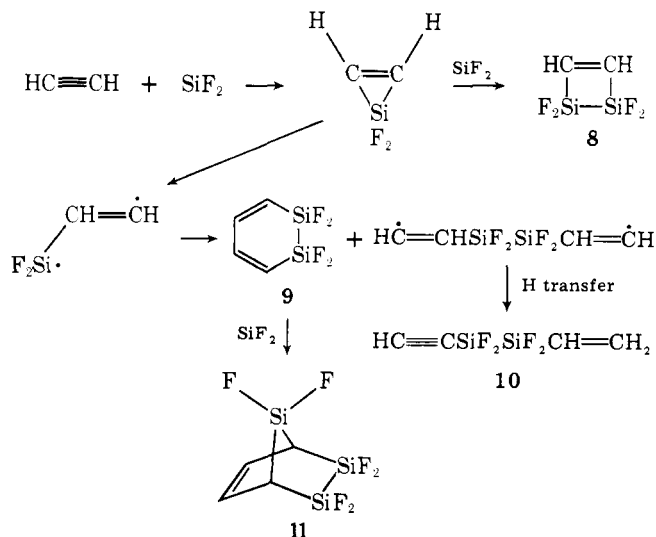
in terms of silirane intermediates.[13,14] We suggest that most of the products of the reactions of SiF$_2$ with olefins and acetylenes are readily explicable in terms of initial formation of difluorosiliranes and difluorosilirenes (see Schemes I and II). These considerations do not exclude comcomitant reaction paths involving ·(SiF$_2$)$_n$· oligomeric diradicals, but we see no need to postulate more complex mechanisms in the absence of compelling evidence in their favor when simpler mechanisms are possible, as our results have shown.

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(5) All new compounds have been characterized by combustion analysis and ¹H NMR spectroscopy, some additionally by mass spectroscopy.
(6) In our initial report[1c] of the hexamethylsilirane–2,3-dimethyl-1,3-butadiene reaction, which was carried out at 70 °C, we reported only the Me$_2$Si addition product, 1,1,3,4-tetramethylsilacyclopent-3-ene, the two-atom insertion product having been missed in the GLC analysis.
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Scheme I

6

7

Scheme II

8

9

+ HC≡CHSiF$_2$SiF$_2$CH≡ĊH

| H transfer

SiF$_2$ ↓   HC≡CSiF$_2$SiF$_2$CH≡CH$_2$

10

11

Triple-Bonded Ethane-like M$_2$L$_6$ Transition Metal Complexes Should be Eclipsed

Sir:

A number of remarkable d^3–d^3 binuclear complexes of type **1** have been prepared, and the structural and chemical consequences of triple bonding in these molecules explored in detail

1   **2**
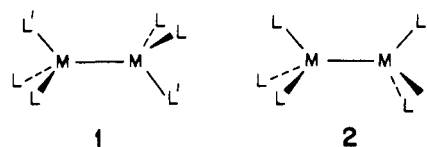
M = Cr, Mo, W

L = Me$_2$N, Et$_2$N, CH$_2$SiMe$_3$

L' = Cl, Me, Me$_2$N, CH$_2$SiMe$_3$

by the Chisholm and Cotton groups.[1,2] In every case known to date the structural studies show an approximate staggered, D_{3d}, ethane-like core conformation. We believe this geometry to be the consequence of the steric bulk of the ligands. With smaller substituents these molecules should prefer the eclipsed conformation **2**.

The argument runs as follows. The frontier orbitals of an ML_3 fragment[3] are shown schematically. They consist of a low-lying $1a_1 + 1e$, remnants of the octahedral t_{2g} set, and a high-lying $2a_1 + 2e$. In both e sets there is an intermixing of
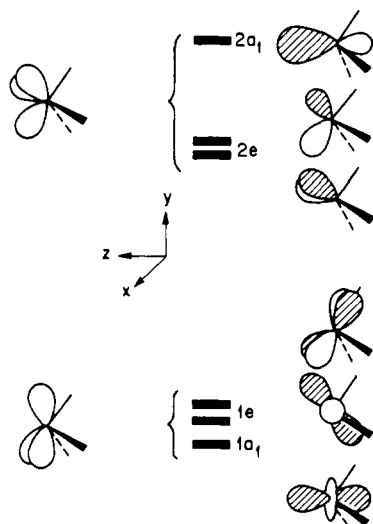
$\delta(x^2-y^2, xy)$ and $\pi(xz, yz)$ character (with respect to the M–M z axis to be formed). In both there is some admixture of metal p; more so in the upper set. Directional character is introduced by this orbital mixing, in such a way that the upper $a_1 + e$ set can be thought of as the delocalized equivalent of a set of three hybrids completing the octahedron, i.e., staggered with respect to the ML_3 directions, while the lower set concentrates electron density over the ML_3 directions, i.e. completes a trigonal prism.[4,5] This is shown schematically in **3**, and forms the basis for a general understanding of rotational barriers in ML_3–polyene complexes.[3c]

3
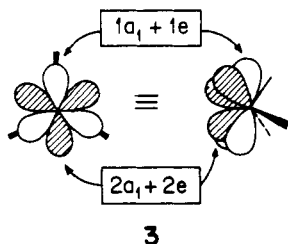
In the d^3–d^3 dimers only the lower $1a_1 + 1e$ set is involved, to a first approximation. A partial interaction diagram for staggered and eclipsed geometries is shown in Figure 1. The level ordering of $1e_u$ below $1e_g$ for the staggered geometry has also been found in $X\alpha$ calculations on $Mo_2(OH)_6$ and $Mo_2(NH_2)_6$.[2] The dimer a levels are cylindrically symmetrical and do not lead to a conformational preference. The e levels are split by a greater amount in the eclipsed case than the staggered—a result of their better overlap, which in turn is a consequence of the above-mentioned hybridization. The six-electron d^3–d^3 case favors an eclipsed geometry by 11 kcal/mol in M_2H_6, 4 kcal/mol in M_2Cl_6, 9 kcal/mol in $M_2(CO)_6$, the quantitatively not very reliable numbers coming from an extended Hückel calculation.[6]

Our mode of reasoning is akin to the one-electron rationalization of the ethane rotational barrier,[7] with interesting distinctions in detail. In ethane both the bonding and antibonding combinations of two methyl group e type orbitals are occupied,
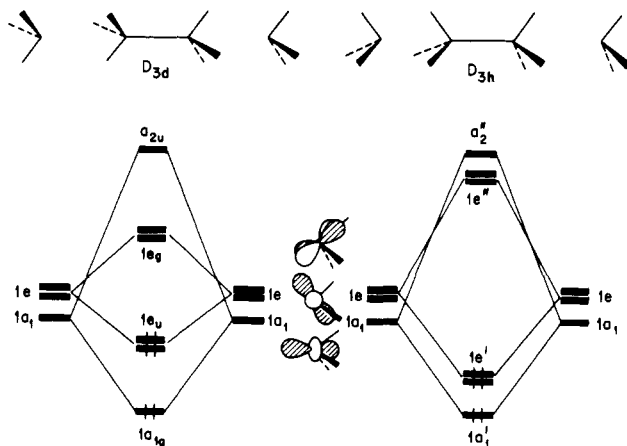
Figure 1. Schematic interaction diagram for a M_2L_6 dimer in eclipsed and staggered geometry.

and the four-electron repulsion favors the conformer with least overlap. In the d^3–d^3 M_2L_6 dimers, only the bonding e type combination is filled, and the barrier is set by two-electron attractions. Maximum overlap is sought out, being achieved in the eclipsed conformation.[8]

If the ML_3 fragment orbitals were pure π, pure δ, or pure p, the resultant barrier would be negligible. But the orbitals mix, in such a way as to give hybrids "tied" to the ML_3 frame of the fragment. The net bonding picture of **4** may be ov-

4
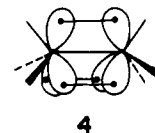
ersimplified.[2,4c] Nevertheless, we look forward to a test of the risky prediction that with small ligands d^3–d^3 L_3MML_3 dimers will be eclipsed. Unfortunately, as the steric bulkiness of the ligands decreases, polynuclear or cluster compounds may be preferred relative to the dimer.[9]

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(8) Although there have been many interpretations of the origin of the rotational barrier in ethane, most have singled out closed-shell interactions between the hydrogens or between the C–H bonds.[7c] In our calculations deleting al

non-nearest-neighbor interactions in ethane gives rise to a very small barrier. However, when these interactions are neglected for the M_2L_8 series, there is essentially no change in the magnitude of the barrier. This supports our contention that the rotational barrier in these dimers is due to the tilting or hybridization of the orbitals at the metal itself.

(9) We are grateful to the National Science Foundation for the support of this work through Research Grant CHE-7606099.

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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$\overset{n}{-}$M) bonds,[9] but, *in practice*, there are ambiguities. These too will be considered and the question of what may be credible M$\overset{n}{-}$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$\overset{n}{-}$M bonds with $n \geq 3$ are of at least the complexity represented by the general formula $[X_xM\overset{n}{-}MX_x]^{\pm y}$. In such a species there are only two kinds of bond and, if we consider only neutral molecules ($y = 0$), the problem of determining $D(M\overset{n}{-}M)$, the bond enthalpy of the M$\overset{n}{-}$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 $\Delta H_f°$ data for the two mononuclear compounds and using standard[16] values of $\Delta H_f°[Mo, g] = 658.1$, $\Delta H_f°[W, g] = 859.9$, and $\Delta H_f°[NMe_2, g] = 123.4$ kJ mol^{-1}, one may straightforwardly deduce the following $\overline{D}(M-N)$ values (± 5 kJ mol^{-1}): $\overline{D}(Mo-NMe_2) = 255$ kJ mol^{-1} in $Mo(NMe_2)_4$ and $\overline{D}(W-NMe_2) = 222$ 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

	$\Delta H_f°(c)$	$\Delta H^{298}{}_{sub}$	$\Delta H_f°(g)$
$Mo(NMe_2)_4$	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. $\overline{D}(M-NMe_2)$ and Corresponding $D(M\overset{3}{-}M)$[a] for Various Formal Oxidation Numbers of the Metal Atom

	formal oxidation number			
	3	4	5	6
$\overline{D}(Mo-NMe_2)$	288	255[b]	223	190
$D(Mo\overset{3}{-}Mo)$	200	396	592	788
$\overline{D}(W-NMe_2)$	331	295	258	222[b]
$D(W\overset{3}{-}W)$	340	558	775	995

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

$$D(M-M) + 6\overline{D}(M-NMe_2) = \Delta H_D \qquad (1)$$

to evaluate $D(M-M)$, where ΔH_D represents the sum of all D values, a quantity obtainable from the $\Delta H_f°$ values. The ambiguity arises because there is no unequivocal way to decide what values are to be used for $\overline{D}(M-NMe_2)$. 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 $\overline{D}(M-X)$ varies with the oxidation number of M. From the known correlations for these other sorts of bonds, and using the two measured $\overline{D}(M-NMe_2)$ values, we can estimate the dependence of $\overline{D}(M-NMe_2)$ values on oxidation number.[17]

We thus finally arrive at the figures in Table II, where we present $\overline{D}(M-NMe_2)$ values for oxidation numbers 3–6 and the $\overline{D}(M\overset{3}{-}M)$ values which result when each of these is employed in eq 1. Even though $\overline{D}(M-NMe_2)$ values vary only moderately with oxidation number, the factor of 6 in eq 1 causes the $D(M\overset{3}{-}M)$ values to span a considerable range.

We are not prepared positively to exclude any of the $\overline{D}(M\overset{3}{-}M)$ 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 $\overline{D}(M-NMe_2)$ value in all cases, then the highest $D(M\overset{3}{-}M)$ 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 $D(M\overset{3}{-}M)$ values are lower. Perhaps formal oxidation numbers as low as 4 are appropriate. Our tentative suggestion is to assign $D(M\overset{3}{-}M)$ 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 $D(Mo\overset{4}{-}Mo)$ and 560 ± 120 kJ mol^{-1} for $D(Re\overset{4}{-}Re)$. 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. $D(N\equiv N) = 946$ kJ mol^{-1}). The experimental work is being extended to other compounds with M$\overset{n}{-}$M bonds.[18]

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