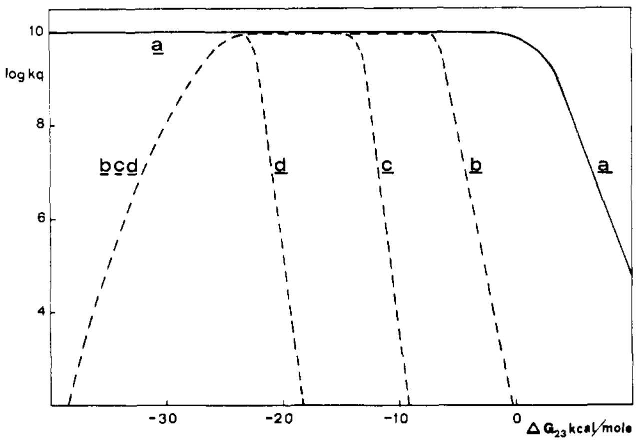

Figure 2. Free-energy correlation of rate constants for electron-transfer quenching calculated[10] from eq 3 and 7 plus eq 6 (curve a) or eq 5 (curves b, c, d); curves b, c, and d refer to $E_{0\text{-}0}$ values in eq 7 of 40, 55, and 70 kcal/mol, respectively.

eq 3, which is "neutral" in this regard, should be used. If this is done, it can be shown that the discrepancy between the correlations predicted using Marcus and RW functions is even more dramatic than that shown in Figure 1.

Equation 3 can be used to calculate k_q as a function of ΔG_{23} by using either Marcus (eq 5) or RW (eq 6) functions for both $\Delta G^{\ddagger}{}_{23}$ and $\Delta G^{\ddagger}{}_{30}$. This is facilitated by the assumption of equal intrinsic barriers for both-electron-transfer processes,[13] and by consideration of the energetics of the system given by

$$\Delta G_{30} + \Delta G_{23} = -E_{0\text{-}0} \qquad (7)$$

where $E_{0\text{-}0}$ is the spectroscopic energy of the excited state.[14] The results of such a calculation[10] are shown in Figure 2. Curve a is calculated with the RW function and is practically independent of the $E_{0\text{-}0}$ value used. Curves b, c, and d are calculated with the Marcus function with $E_{0\text{-}0}$ values of 40, 55, and 70 kcal/mol, respectively. As expected, curve a is almost identical with curve a of Figure 1. Curves b, c, and d, on the other hand, show the "inverted" region in the highly exoergonic part (similarly to curve b in Figure 1). However, they also show a sharp drop in the quenching constants relative to curves a in the "normal" region. The physical reason behind this behavior is that in the "normal" ΔG_{23} region, the back electron transfer to the ground state is, according to the Marcus function, in the "inverted" ΔG_{30} region. In these cases, back electron transfer to the excited state, k_{32}, predominates over that to the ground state, k_{30}, with the consequence of a strongly reduced quenching effect. Obviously, the departure from the well-behaved curves a in the normal region becomes more and more dramatic as the energy of the excited state is increased (curves b, c, and d of Figure 2).

In conclusion, the use of the Marcus model for free-energy correlation of rate constants of excited-state electron-transfer quenching leads to a much more serious disagreement with experimental results than previously believed. In particular, the model predicts unobserved inefficiencies not only in the highly exoergonic "inverted" region, but also in the commonly investigated slightly exo- or endoergonic, "normal" region.

Acknowledgment. We thank Professor V. Balzani and Dr. R. Ballardini for stimulating discussions and Professor F. Pulidori for kind help with the computations.

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(10) The calculation has been performed using the following set of parameters: $k_{12} = 1.0 \times 10^{10}\ M^{-1}\ s^{-1}$, $k_{21} = 8.7 \times 10^{9}\ s^{-1}$, $Z = 6.2 \times 10^{12}\ s^{-1}$, $\Delta G^{\ddagger}{}_{23}(0) = 3.0$ kcal/mol, $T = 298$ K. The qualitative features of Figures 1 and 2 are not affected by varying these values within reasonable ranges.
(11) "Vestiges" of the inverted region have been recently reported for electron-transfer quenching of ruthenium(II) polypyridine complexes,[12] although the observed effect is orders of magnitude too small compared with the expectations of the Marcus model.
(12) C. Creutz and N. Sutin, *J. Am. Chem. Soc.*, **99**, 241 (1977).
(13) The assumption of equal intrinsic barriers for excited-state and ground-state processes is justified as long as the differences in shape, size, and solvation between the states (i.e., the Stokes shift) are small.
(14) Equation 7 holds if the entropy changes associated with the excitation are small,[2,5] a condition met by most of the systems studied so far.

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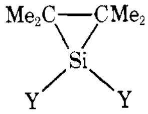
1,1-Difluoro-2,2,3,3-tetramethyl-1-silirane: Synthesis and Novel Chemistry. Reinterpretation of Difluorosilylene Reaction Mechanisms

Sir:

We reported the preparation of hexamethylsilirane (**1a**) in 1975 and in subsequent research have studied its chemistry in some detail.[1] Its thermolysis at 75 °C proceeds by reversible extrusion of dimethylsilylene.[1c] A concomitant, irreversible process is the insertion of Me_2Si into an Si–C bond of **1a** to give octamethyl-1,2-disilacyclobutane.[1f] The dimethylsilylene thus generated also may be intercepted with other reactants such as silicon hydrides, methoxysilanes, other olefins, and acetylenes.[1b-d] The synthesis and study of other siliranes of type **1**, as well as of similar siliranes with two different substituents on the silicon atom, would be of interest, especially if they also underwent silylene extrusion on thermolysis.

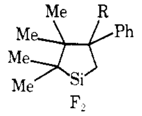
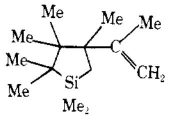
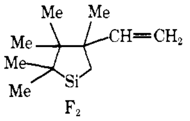
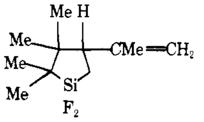
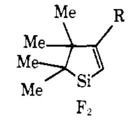
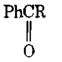
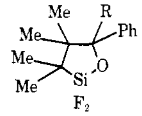
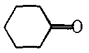
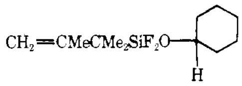


1a, Y = CH_3
b, Y = F

The generation of difluorosilylene as currently practised requires the reaction of gaseous SiF_4 with elemental silicon at 1100–1200 °C at low pressures.[2] The availability of an SiF_2 precursor which would release this intermediate in solution below 100 °C would be an obviously attractive improvement. In view of the intriguing results reported by Margrave and his co-workers on the reactions on SiF_2 with organic and inorganic substrates,[2] we directed our attention to the synthesis and investigation of 1,1-difluoro-2,2,3,3-tertramethyl-1-silirane (**1b**).

The synthesis of **1b** was effected using an adaptation of our procedure for hexamethylsilirane.[1a] Diisopropyldifluorosilane[3] was brominated at 95–100 °C to give bis(α-bromoisopropyl)difluorosilane (**2**), mp 33–35 °C, in 75% yield. Ring closure was effected under an atmosphere of argon by reaction of the latter with 1 molar equiv of magnesium in a THF/dimethyl

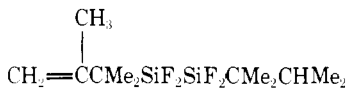
Table I. Two-Atom Insertion Reactions of 1,1-Difluoro-2,2,3,3-tetramethyl-1-silirane

substrate	products	% yield[a]
PhC(R)=CH$_2$ (R = H, Me)		54 (R = H) 44 (R = Me)
CH$_2$=CMeCMe=CH$_2$ (followed by MeLi)		71
CH$_2$=CMeCH=CH$_2$		36
		20
RC≡CH (R = Ph, CH$_2$=CMe)		55 (R = Ph) 91 (R = CH$_2$=CMe)
	[Me$_2$CHCMe$_2$SiF$_2$C≡CPh]	8
 $PhC(=O)R$ (R = H, Me)		21 (R = H) 55 (R = Me)
	[CH$_2$=CMeCMe$_2$SiF$_2$OCHMePh]	12
		55
Me$_3$CCH=O	CH$_2$=CMeCMe$_2$SiF$_2$OCH$_2$CMe$_3$	69

[a] GLC yield, using the internal standard method, based on silirane **1b**.

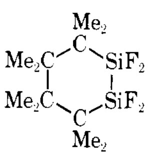
ether solvent system.[4] Subsequent slow evaporation of the dimethyl ether was followed by trap-to-trap distillation of the remaining volatiles in vacuo into a receiver cooled with liquid nitrogen. Yields of **1b** (by NMR) in the resulting concentrated THF solution were in the 40–80% range.

1,1-Difluoro-2,2,3,3-tetramethyl-1-silirane is less stable and more reactive than hexamethylsilirane. Its half-life at 60 °C in THF solution is ~1.75 h (vs. $t_{1/2} \sim 5$ h at 63 °C in THF for **1a**). The products of its thermolysis at 50–60 °C were found to be **3** and **4**;[5] in one experiment these were obtained in yields of 23 and 35%, respectively, based on available SiF$_2$ groups.



$CH_2{=}C(CH_3)CMe_2SiF_2SiF_2CMe_2CHMe_2$

3

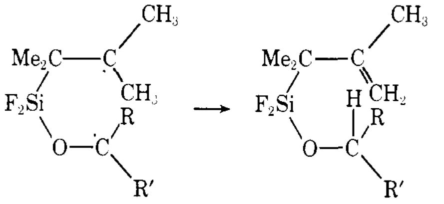


4, mp 203–205 °C (GLC sample)

Attempted isolation of **1b** as a pure compound has been unsuccessful so far: its high volatility precludes selective removal of the THF at reduced pressure and its thermal instability prohibits fractional distillation or the application of gas chromatography. (More specialized procedures may be applicable but have not been tried as yet.) However, both the spectroscopy and the chemistry of **1b** may be studied using the concentrated THF solution. Its ^{1}H NMR spectrum shows the methyl protons as a triplet with a small ($J_{HF} = 3.2$ Hz) coupling constant, as would be expected for a four-bond F–H interaction. The ^{19}F NMR spectrum shows a multiplet (at least seven lines) centered at −47.7 ppm (upfield) from CF$_3$CO$_2$H.

Some "two-atom" insertion reactions[1e,g] of silirane **1b** are summarized in Table I. This silirane is more reactive in these reactions than in hexamethylsilirane. Thus, hexamethylsilirane reacted slowly at room temperature with styrene, phenylacetylene, benzaldehyde, and acetophenone. On the other hand, **1b** reacted exothermally with these substrates. Hexamethylsilirane reacted with 2,3-dimethylbutadiene only at 70 °C to give the two-atom insertion product, as well as some Me$_2$Si-derived 1,1,3,4-tetramethyl-1-silacyclopent-3-ene as a minor product.[6] In contrast, **1b** reacted with 1,3-dienes at room temperature. Hexamethylsilirane did not react with aliphatic aldehydes and ketones except under UV irradiation, and then it gave only the two-atom insertion products. Silirane **1b** reacted with aliphatic carbonyl compounds at room temperature or below in the absence of UV irradiation to give acyclic products.

The reactions in Table I as well as the thermal decomposition of silirane **1b** may be understood in terms of radical chemistry. In its thermolysis, we suggest that the ·F$_2$SiCMe$_2$CMe$_2$· diradical is formed initially. A radical coupling process then gives a new diradical, ·CMe$_2$CMe$_2$SiF$_2$SiF$_2$CMe$_2$CMe$_2$·, which can cyclize to **4** or undergo hydrogen-atom transfer to produce **3**. In the two-atom insertion reactions the radical pathway which we suggested earlier[1g] appears to be 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.

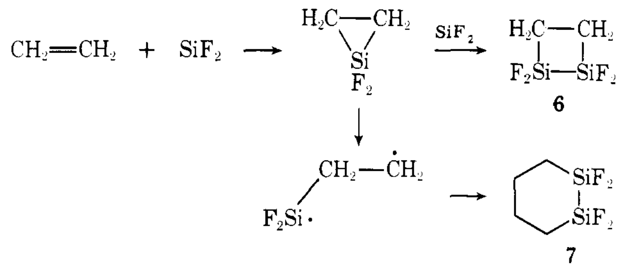


5

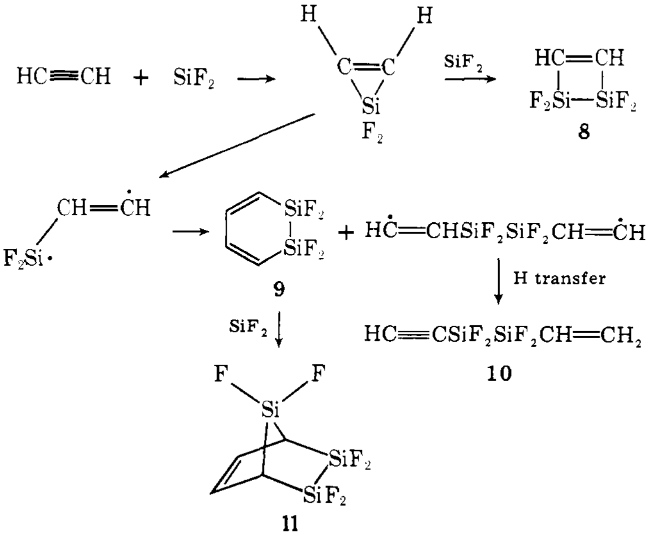
(1)

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 $\cdot SiF_2SiF_2 \cdot$ diradical was given by Margrave and his coworkers[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 $\cdot(SiF_2)_n\cdot$ 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.

Scheme I



Scheme II



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(4) In a typical reaction, 12.7 mmol of **2**, 4 mL of THF, and 25 mL of dimethyl ether was used. The reaction was initiated in THF and then Me_2O was condensed into the reaction vessel which was equipped with a cold condenser. Addition of **2** to the Mg–THF–Me_2O mixture (which was maintained at ca. −25 °C) over a 2-h period was followed by a 3-h period of stirring under argon.

(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_2Si 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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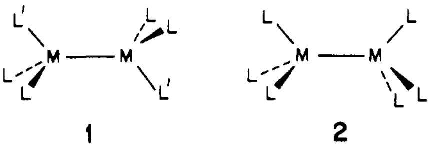
Triple-Bonded Ethane-like M_2L_6 Transition Metal Complexes Should be Eclipsed

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_2N, Et_2N, CH_2SiMe_3
L′ = Cl, Me, Me_2N, CH_2SiMe_3

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