Table I. Superhyperfine Coupling Constants ($\times 10^{-4}$ cm^{-1})

	^{1}H	^{17}O
cis-[MoO(OH)L]	13.7	7 ± 2[f]
"MoO(OH)$(O_b)_4$"	9-10[a]	
desulfo XO (slow signal)	13.7-14.9[b]	9[c]
active XO (rapid type 1)	11.7-12.8[b]	9-13[c]
spinach NR (signal A)	12.0[d]	
SO (aquo, low pH)	9.1[b]	5.5[c]
E. coli NR (aquo, low pH)	8.5[e]	

[a] References 20, 21: The osberved signals are generated by photolysis of single crystals of $A_6[Mo_7O_{24}]\cdot 3H_2O$ (A = NH_3Pr, NH_3-*i*-Pr). O_b are bridging oxygen atoms. [b] Reference 5: The ranges quoted are those observed for signals generated in the presence of different anions and buffers. [c] References 12, 22. [d] Reference 9. [e] Reference 8. [f] Estimated for the OH ligand, assuming a coupling constant of 2×10^{-4} cm^{-1} for the oxo ligand; see text.

different enzymes in Table I.

Incubation of I in THF solutions containing ^1H_2O (52.1 atom % ^{17}O; $I = {}^5/_2$) allows oxygen exchange. Careful drying, followed by electrolysis at −42 °C in the presence of 0.1 M $^2H_2{}^{16}O$ generates the ESR spectrum (Figure 1c) of II (100 atom % ^{2}H; 52.1 atom % ^{17}O).[23] In comparison with that of II (100 atom % $^2H^{16}O$; Figure 1b), this signal exhibits larger central[24] and hyperfine line widths and partially resolved structure is apparent on the central line. This structure is attributed to ^{17}O-superhyperfine coupling with a coupling constant of 7 (±2) $\times 10^{-4}$ cm^{-1} for the OH ligand. This value can be compared with those derived for the enzymes (Table I).

The data strongly support the presence of an OH ligand at the ESR-active site in SO and desulfo XO, at least. Closer comparison will be possible when anisotropic data for II become available.

Electrolysis of I at −42 °C in carefully dried CH_2Cl_2 solution generates a broad signal at *g* 1.89 characteristic[25] of $[Mo^VO_2L]^-$ (III), which converts to that of II in the presence of a proton source. The existing data are consistent with the following mechanism:

$$\underset{\mathrm{I}}{[\mathrm{Mo^{VI}O_2L}]} \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} \underset{\mathrm{III}}{[\mathrm{Mo^{V}O_2L}]^-} \underset{-\mathrm{H}^+}{\overset{+\mathrm{H}^+}{\rightleftharpoons}} \underset{\mathrm{II}}{[\mathrm{Mo^{V}O(OH)L}]} \qquad E^\circ = -1.3\ \mathrm{V}$$

The observation of this chemically reversible coupled electron-proton transfer relates to similar processes[26-28] in the enzymes of interest and suggests that the exact nature of the peripheral (cofactor?)[29] ligands can control the pK of the $[MoO_2]$ and [MoOS] centers. Interestingly, a pH-dependent equilibrium exists in SO[30] and NR[31] but has not been detected in XO.[32]

Finally, estimation of ^{17}O coupling to the OH ligand in II (Table I) is complicated by the possible presence of ^{17}O coupling to the oxo ligand. The latter was assumed to be about 2×10^{-4} cm^{-1} and justification of this assumption rests upon the observation of the ESR spectrum of $[MoO(SPh)_4]^-$ (98.23 atom % ^{98}Mo; 51.2 atom % ^{17}O) at four frequencies (1.9, 2.9, 3.8, and 9.1 GHz).[33,34] ^{17}O coupling is resolved at the lower frequencies and simulation at all frequencies permits extraction of the ^{17}O-superhyperfine constants: *a*, 2.12; $A_\parallel$, 0.64; $A_\perp$, 2.86 $\times 10^{-4}$ cm^{-1}. Intriguingly, these parameters span the range ((0.6-2.9) $\times 10^{-4}$ cm^{-1}) observed for the two inequivalent oxygen atoms detected[12] in the "inhibited" signal of XO.

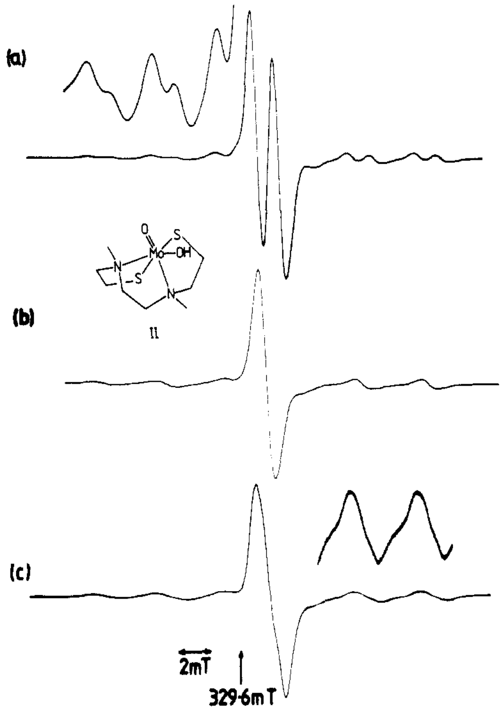

Figure 1. X-band ESR signals generated by electrolysis of 0.01 M $[MoO_2L]$ (I) in THF (0.1 M Bu_4NBF_4) at −1.4 V (vs. SCE) and −42 °C in the presence of (a) 0.1 M ^1H_2O, (b) 0.1 M ^2H_2O, and (c) 0.1 M ^2H_2O after previous incubation of I with 0.1 M ^1H_2O (52.1 atom % ^{17}O) followed by drying (see text).

Acknowledgment. A.G.W. thanks the Australian Research Grants Scheme for financial support of this work.

Registry No. I, 80287-02-1; II, 99797-95-2; SO, 9029-38-3; XO, 9002-17-9; NR, 9013-03-0.

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[23] Oxygen exchange in I occurs with a half-life of several hours in THF solutions containing 0.1 M H_2O, while that in II is much slower than hydrogen exchange at −42 °C.

[24] The apparent peak-to-peak half-width of the cental resonance increases from 11 to 20 mT.

[25] Hinshaw, C. C.; Spence, J. T. Fifth International Conference on the Chemistry and Uses of Molybdenum, Newcastle-upon-Tyne, U.K., July, 1985.

[26] Stiefel, E. I. *Proc. Natl. Acad. Sci. U.S.A.* **1973**, *70*, 988-992.

[27] Porros, A. G.; Palmer, G. *J. Biol. Chem.* **1982**, *257*, 11 617-11 626.

[28] Barber, M. J.; Siegel, L. M. *Biochemistry* **1982**, *21*, 1638-1647.

[29] Johnson, J. L.; Hainline, B. E.; Rajagopalan, K. V.; Arison, B. H. *J. Biol. Chem.* **1984**, *259*, 2414-5422 and references therein.

[30] Cohen, H. J.; Fridovich, I.; Rajagopalan, K. V. *J. Biol. Chem.* **1971**, *246*, 374-382.

[31] George, G. N.; Bray, R. C.; Morpeth, F. F.; Boxer, D. H. *Biochem. J.* **1985**, *227*, 925-931.

[32] Tsopanakis, A. D.; Tanner, S. J.; Bray, R. C. *Biochem. J.* **1978**, *175*, 879-885.

[33] Hanson, G. R.; Brunette, A. A.; McDonell, A. C.; Murray, K. S.; Wedd, A. G. *J. Am. Chem. Soc.* **1981**, *103*, 1953-1959.

[34] Hanson, G. R.; Wilson, G. L.; Bailey, T. D.; Pilbrow, J. R.; Wedd, A. G. *Inorg. Chem.*, submitted for publication.

Pregeneration, Spectroscopic Detection, and Chemical Reactivity of (Trifluoromethyl)copper, an Elusive and Complex Species[1]

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Pharmaceutical and agricultural chemicals that contain a trifluoromethyl group have been the subject of increased research activity in recent years.[2] Concomitant with these applications have been increased efforts to develop a cheaper and more efficient synthetic methodology for the introduction of the trifluoromethyl group into organic compounds. An adjunct of this strategy has been numerous attempts to incorporate the trifluoromethyl group directly into the molecule via in situ generation and coupling of CF_3Cu with aryl halides.[3] Although some modest success has

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[1] Presented in part at the 11th International Symposium On Fluorine Chemistry, East Berlin, Germany, Aug, 1985, Abstract B-4.

[2] Filler, R., Ed. *ACS Symp. Ser.* **1976**, *No. 28*. "Biomedicinal Aspects of Fluorine Chemistry"; Filler, R., Kobayashi, Y., Eds.; Kodasha/Elsevier: New York, 1982. "Organofluorine Compounds and Their Industrial Applications"; Banks, R. E., Ed.; Ellis Horwood Ltd.: Chichester, 1979.

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been achieved in this work, these previous methods have either utilized expensive reagents [CF_3I, $(CF_3)_2Hg$] or required high temperatures and/or have been plagued with competing Ullmann coupling and reduction of the aryl halide.

We report herein the preliminary results of a novel, high-yield, low-temperature pregenerative route to (trifluoromethyl)copper via in situ metathesis of (trifluoromethyl)cadmium and -zinc reagents with soluble copper(I) salts, such as CuCl, CuBr, CuI, and CuCN.

$$2M + 2CF_2X_2 \xrightarrow[\text{room temperature}]{\text{DMF}}$$

M=Cd, Zn
X=Br, Cl

$$[CF_3MX + (CF_3)_2M] \xrightarrow[\text{Y=I, Br, Cl, CN}]{\text{CuY/-80 °C-room temperature}} [CF_3Cu]$$

80-95% 90-100%

Since the requisite cadmium and zinc reagents can be produced in situ from difluorodihalomethanes,[4] the overall process yields a simple, one-pot preparation of (trifluoromethyl)copper from cheap Freon precursors. The metathesis reaction with [CF_3CdX] occurs rapidly even at −30 °C, whereas the exchange reaction with [CF_3ZnX] is much slower, since at −20 °C no exchange is observed between [CF_3ZnX] and CuBr over 24 h.

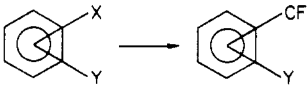
When the metathesis process is followed by ^{19}F NMR spectroscopy, an interesting and unexpected phenomenon is observed.[5] If CuBr is added to a solution of [CF_3CdX] in DMF at −50 °C, only one ^{19}F NMR signal for [CF_3Cu][6] is observed at −28.8 ppm (relative to $CFCl_3$). If HMPA is added to stabilize this [CF_3Cu] reagent, warming to room temperature shows no change, with only the signal at −28.8 ppm detected. However, in the absence of HMPA, warming of the [CF_3Cu] solution to room temperature causes a remarkable change. Analysis of this solution by ^{19}F NMR indicates two new [CF_3Cu] species at −32.3 and −35.5 ppm. These two peaks begin to grow, with a diminution in intensity of the initial [CF_3Cu] species.[7]

$$[CF_3Cu]\ ([A], -28.8\text{ ppm}) \xrightarrow[\text{DMF}]{\text{room temperature}} [CF_3Cu]\ ([B], -32.3\text{ ppm}) + [CF_3Cu]\ ([C], -35.5\text{ ppm}) + [CF_3CF_2Cu]$$

Subsequently, signals for [CF_3CF_2Cu] at −84.7 (CF_3) and −113.7 ppm (CF_2) also begin to grow into the spectrum.[8] After 11 h at room temperature only [CF_3CF_2Cu] remains.[9] Heating to 50–70 °C accelerates these conversions. Our data suggest that species [A] and [B] are slowly converted to [C] and [CF_3CF_2Cu], and in a slower event, [C] is also converted to [CF_3CF_2Cu]. Crude estimates suggest that the amount of [CF_3CF_2Cu] formed is quantitative, based on the assumption that 2 equiv of [CF_3Cu] produce 1 equiv of [CF_3CF_2Cu].

$$2[CF_3Cu] \rightarrow [CF_3CF_2Cu] + CuF$$

Table I. Coupling of [CF_3Cu][12] with



Y	X	% of CF_3–aromatic[a]
H	I	100
NO_2	*o*-I	95 (75)
NO_2	*m*-I	88 (72)
NO_2	*p*-I	81 (75)
CH_3	*o*-I	95 (76)
OCH_3	*p*-I	78
Br	*p*-I	95
Cl	*o*-I	96 (84)

[a] ^{19}F NMR yield vs. $PhCF_3$, isolated yield is in parentheses.

Even more remarkable is the astonishing difference in chemical reactivity between species [A] and [C].[10] Hydrolysis at room temperature of a mixture of [A] and [C] with either H_2O or aqueous HCl destroys [A] within minutes, whereas [C] is unaffected by these reagents. Also, when oxygen is bubbled through a mixture of [A] and [C] for 6 h at room temperature, *only* [A] is consumed, whereas [C] is unaffected by oxygen.

To further elucidate the difference in chemical reactivity of [A] and [C], a mixture of these two copper species was treated at room temperature with allyl chloride. Species [A] reacted immediately to produce $CF_3CH_2CH{=}CH_2$. Only after [A] was totally consumed did [C] slowly react with allyl chloride to give the butene product. Similar differences in reactivity between [A] and [C] were also observed in reactions with (*E*)-2-phenyl-1-iodo-*F*-propene. Species [A] reacted immediately to give (*Z*)-CF_3-(Ph)C=CFCF$_3$, whereas [C] reacted slowly to give this olefin *only* after [A] was totally consumed. Thus, it is evident that reagent [A] is the reactive species and, obviously, the reagent to be employed in subsequent coupling-type chemistry. Reactions which require long reaction times or higher temperatures produce the less reactive copper species [C] and/or [CF_3CF_2Cu], thereby diminishing the probability of a successful high-yield trifluoromethylation process.

However, if stabilization of the reactive species [A] is effected, even trifluoromethylation of aryl iodides at higher temperatures (70 °C) can be achieved in excellent yield.[11] Table I summarizes these preliminary results.

In summary, this work describes the *first unequivocal* pregenerative route to [CF_3Cu]. The reagent is produced in situ from readily available, cheap, commercial precursors, is easily scaled up,[12] and can be directly utilized for the preparation of useful quantities of trifluoromethylated products. Thermal decomposition of the initially formed [CF_3Cu] demonstrates that [CF_3Cu] solutions[3] are much more complex than previously appreciated and that control of the species formed can have significant conse-

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(3) (a) McLoughlin, V. C. R.; Thrower, J. *Tetrahedron* **1969**, *25*, 5921. (b) Kobayashi, Y.; Kumadaki, I. *Tetrahedron Lett.* **1969**, 4095. (c) Kobayashi, Y.; Kumadaki, I.; Sato, S.; Hara, N.; Chidami, E. *Chem. Pharm. Bull.* **1970**, *18*, 2334. (d) Kobayashi, Y.; Kumadaki, I.; Hanzawa, Y. *Chem. Pharm. Bull.* **1977**, *25*, 3009. (e) Kobayashi, Y.; Yamamoto, K.; Kumadaki, I. *Tetrahedron Lett.* **1979**, 4071. (f) Kobayashi, Y.; Kumadaki, I.; Ohsawa, A.; Yamada, T. *Chem. Pharm. Bull.* **1972**, *20*, 1839. (g) Kobayashi, Y.; Kumadaki, I. *J. Chem. Soc., Perkin Trans. 1* **1980**, 661. (h) Kobayashi, Y.; Yamamoto, K.; Asai, T.; Nakano, M.; Kumadaki, I. *J. Chem. Soc., Perkin Trans. 1* **1980**, 2755. (i) Kondratenko, N. V.; Vechirko, E. P.; Yagupolskii, L. M. *Synthesis* **1980**, 932. (j) Suzuki, H.; Yoshida, Y.; Osuka, A. *Chem. Lett.* **1982**, 135. (k) Matsui, K.; Tobita, E.; Ando, M.; Kondo, K. *Chem. Lett.* **1981**, 1719. (l) Leroy, J.; Rubinstein, M.; Wakselman, C. *J. Fluorine Chem.* **1985**, *27*, 291.

(4) Burton, D. J.; Wiemers, D. M. *J. Am. Chem. Soc.* **1985**, *107*, 5014.

(5) In some of the earlier reports a preformed solution of a (trifluoromethyl)copper or copper complex solution was suggested or claimed; however, no spectroscopic evidence or data were presented.[3e,i]

(6) The organocopper species are shown as monomeric for simplicity. The extent and nature of aggregation of these species are not known. The chemical shift of these (trifluoromethyl)copper reagents is consistent with other previously reported trifluoromethyl organometallics.[4]

(7) After 9 min at room temperature, the percentage of [A]/[B]/[C]/[CF_3CF_2Cu] is 63:6:15:5, after 22 min the percentage is 48:4:22:9, after 85 min the percentage is 33:4:22:13, and after 211 min the percentage is 12:0:22:28.

(8) These signals for [CF_3CF_2Cu] were confirmed by preparation of an authentic sample of [CF_3CF_2Cu] from CF_3CF_2I and Cu bronze. We are indebted to P. L. Heinze for this experiment.

(9) Similar detection of three [CF_3Cu] species via exchange of [CF_3ZnX] and CuBr at room temperature has also been observed with subsequent decomposition to [CF_3CF_2Cu] after prolonged reaction time or heating to higher temperatures.

(10) [CF_3Cu] species [B] is generally formed in such small amounts that quantitative data are difficult to obtain with this reagent and our initial focus has been on the two major species [A] and [C].

(11) The reaction of [CF_3Cu] with ArI is slow at room temperature, and with nonstabilized [CF_3Cu] solutions the main product is the pentafluoroethyl aromatic—unpublished work of D. M. Jones.

(12) An equal volume of HMPA was added to the cadmium reagent solution prepared from 0.1 mol of CF_2BrCl as previously described.[4] CuBr (0.05 mol) was added to this solution at 0 °C, the aryl iodide (0.035 mol) added to the preformed [CF_3Cu], and the reaction mixture then heated at 60–70 °C for 4–6 h. The reaction mixture was then steam distilled, the organic layer separated, the aqueous layer extracted with pentane, and the organic material dried over anhydrous $MgSO_4$, filtered, and fractionally distilled to give the isolated trifluoromethyl aromatic compound.

quences in further elaborative chemistry of this reagent. Our work continues with this reagent and future efforts will be directed toward elucidation of the full scope of the reagent as well as the mechanistic process for the production of [CF_3CF_2Cu] from [CF_3Cu].

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Kinetics of the Isomerization of 1-Methylsilene to Dimethylsilylene

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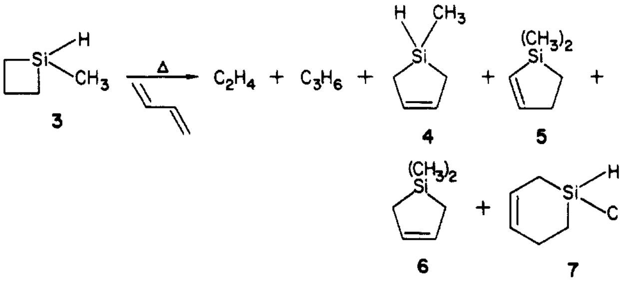
The activation barrier for the transfer of hydrogen atoms between a metal and a carbon atom is currently a subject of wide interest. In particular, the hydrogen shift that converts hydridosilenes to methylsilylenes has been the focus of numerous experimental[1-4] and theoretical studies.[5-7] The energy required for the silene isomerization has been calculated from theory[8,9] but the result is without experimental verification. We now report results of a kinetic study of the temperature dependence for butadiene trapping of 1-methylsilene (**1**) and dimethylsilylene (**2**)

$$\underset{\mathbf{1}}{H(CH_3)Si{=}CH_2} \rightarrow \underset{\mathbf{2}}{CH_3\ddot{S}i{-}CH_3}$$

which allow an experimental measure of the activation enthalpy and entropy of the 1,2-hydrogen shift from a silene to a silylene.

Gas-phase pyrolysis[10] at 477.5 °C of 1-methylsilacyclobutane (**3**) (3 torr) and a 5-fold excess of butadiene in a 250-mL quartz vessel yielded ethylene and propylene in a ratio of ca. 10:1 and four different silicon-containing products: 1-methyl-1-silacyclopent-3-ene (**4**) (3%), 1,1-dimethyl-1-silacyclopent-2-ene (**5**) (4%), 1,1-dimethyl-1-silacyclopent-3-ene (**6**) (18%), and 1-methyl-1-silacyclohex-3-ene (**7**) (74%). The relevant reaction paths for the isomerization kinetics are outlined in Scheme I.[11] Under pseudo-first-order conditions the ratio of silylene to silene adducts (six- and five-membered rings, respectively) is time invariant beween 200–400 s. The equation that relates the influence of temperature to the concentration of silene and silylene products is given below:[12]



Scheme I

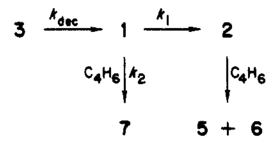


Table I. Ratio of **7**/(**5** + **6**)

T, °C	453.3	460.2	470.6	477.5[a]	485.4
7/(**5** + **6**)	5.55	4.01	3.70	3.32	2.79

[a] If this value is omitted, the correlation coefficient R = 0.999.

Table II. Rate Constants for Decomposition of **3**

T, °C	453.3	460.2	470.6	477.5	485.4
K_{overall}, $10^3\ s^{-1}$	1.09	1.69	2.86	4.29	6.19

$$\mathbf{7}/(\mathbf{5} + \mathbf{6}) = A(\mathbf{2})[\text{butadiene}]/A(\mathbf{1})e^{-(E(\mathbf{1}) - E(\mathbf{2}))/RT} \quad (1)$$

Product ratios, **7**/(**5** + **6**), from the pyrolysis of **3** and butadiene at five different temperatures from 453.3 to 485.4 °C are listed in Table I. A least-squares plot of eq 1 against $1/T$ provides the slope, $E(\mathbf{1}) - E(\mathbf{2}) = 23.4 \pm 0.7$ kcal mol^{-1}, and the intercept, $\ln A(\mathbf{1})[\text{butadiene}]/A(\mathbf{2}) = -14.5 \pm 0.5$. With the assumption that the activation energy $E(\mathbf{2})$ is ca. 7 kcal mol^{-1} and the preexponential $A(\mathbf{2}) = 10^7$ dm^3 mol^{-1} s^{-1} for the cycloaddition of methylsilene to butadiene,[14] the Arrhenius parameters would be $E(\mathbf{1}) = 30.4 \pm 0.7$ kcal mol^{-1} ($\Delta H^\ddagger = 28.9 \pm 0.7$ kcal mol^{-1}) and $A(\mathbf{1}) = 9.6 \pm 0.2$ s^{-1} ($\Delta S^\ddagger = -18.5 \pm 0.9$ cal/(mol deg)).[15]

The preexponential term for the silene to silylene isomerization is surprisingly lower than previous experimental estimates[4,7] thus suggesting an unusually "tight" transition state for the H-shift. This observation, however, is consistent with the theoretical prediction that rotation about the Si═C bond of the silene involves pyramidalization of the hydrogens on the trigonal Si.[7] The large decrease in entropy during the hydrogen shift from Si to C may be attributed to the geometry of the vibrationally excited silene or possibly to the participation of the triplet state of the silene.[16] The lack of other data for the entropic demands of 1,2-H shifts leaves the interpretation open.

In theoretical studies, $\Delta G^\ddagger$ of the isomerization has been calculated to be 40.6 kcal mol^{-1} for $H_2Si{=}CH_2$[8] and 42.2 kcal mol^{-1} for $H(Me)Si{=}CH_2$.[9] The experimental measure of $\Delta G^\ddagger$, 42.5 kcal mol^{-1} at 470.6 °C, is in excellent but probably fortuitous agreement since it is based on an experimental *estimate* of kinetic parameters for a silene cycloaddition to butadiene.[14]

Despite the limited temperature range required by the thermal instability of the methylsilene adduct **7**, excellent first-order behavior is found for the decomposition of **3**. Rate constants over the same temperatures as above (Table II) provide the activation parameters: $A = 10^{14.9 \pm 0.3}$ s^{-1} and $E(\mathbf{3}) = 59.1 \pm 0.1$ kcal mol^{-1}. Previously, an approximate measure of the Arrhenius plot for the decomposition of **3** has been reported[17] as $A = 10^{14.0}$ s^{-1} and $E(\mathbf{3})$

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(1) Conlin, R. T.; Wood, D. L. *J. Am. Chem. Soc.* **1981**, *103*, 1843.

(2) Conlin, R. T.; Kwak, Y.-W. *Organometallics*, **1984**, *3*, 918 and previous references to experimental work therein.

(3) Davidson, I. M. T.; Hughes, K. J.; Scampton, R. J. *J. Organomet. Chem.* **1984**, *272*, 11.

(4) Davidson, I. M. T.; Ijadi-Magsoodi, S.; Barton, T. J.; Tillman, N. *J. Chem. Soc., Chem. Commun.* **1984**, 478.

(5) Schaefer, H. F., III. *Acc. Chem. Res.* **1982**, *15*, 283.

(6) Bell, T. N.; Kieran, A. F.; Perkins, K. A.; Perkins, P. G. *J. Phys. Chem.* **1984**, *88*, 1334.

(7) Schmidt, M. W.; Gordon, M. S.; Dupuis, M. *J. Am. Chem. Soc.* **1985**, *107*, 2585. For previous references to theoretical calculations, see ref 2.

(8) Yoshioka, Y.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1981**, *103*, 7644.

(9) Nagase, S.; Kudo, T. *J. Chem. Soc., Chem. Commun.* **1984**, 1392.

(10) The kinetics apparatus has been described previously: Conlin, R. T.; Kwak, Y.-W. *Organometallics*, in press.

(11) At the high end of the temperature range, 485.4 °C, pyrolysis of **7** showed no detectable decomposition between 200 and 400 s. Dimerization of butadiene was <3%. Absolute yields of Si-containing products **4** to **7**, determined with cyclohexane as an internal standard, were >95%.

(12) Walsh, R. *J. Chem. Soc., Chem. Commun.* **1982**, 1415. It is assumed in eq 1 that the isomerization of **1** to **2** is not reversible. This assumption appears valid as pyrolysis of the known dimethylsilylene precursor, 1,1,2,2-tetramethyldisilane,[13] with a fivefold excess of butadiene, under the same conditions described in this work, yields no methylsilene adduct.

(13) Gaspar, P. P. In "Reactive Intermediates"; Jones, M., Jr., Moss, R. A., Eds.; Wiley-Interscience: New York, 1978; Vol. 1, pp 229–277.

(14) Frey, H. M.; Kashoulis, A.; Lee, M.-L.; Lodge, S. P.; Pidgeon, I. M.; Walsh, R. *J. Chem. Soc.* **1981**, 915.

(15) It has recently been suggested[4] that $E(\mathbf{2})$ = ca. 2.4 kcal/mol. $E(\mathbf{1})$ then becomes 25.8 kcal/mol. Also, it is most probable that kinetic data for the isomerization were not obtained at the high-pressure limit. However, the corrections to the Arrhenius plot would be small and not significantly alter the kinetic parameters.

(16) Kohler, H. J.; Lishka, H. *J. Am. Chem. Soc.* **1982**, *104*, 5886. Goddard, J. D.; Yoshioka, Y.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1980**, *102*, 7644.

(17) Davidson, I. M. T.; Fenton, A.; Ijadi-Maghsoodi; Scampton, R. J.; Auner, N.; Tillman, N.; Barton, T. J. *Organometallics* **1984**, *3*, 1593.

0002-7863/86/1508-0834$01.50/0