homogeneous catalytic hydrogenation of Th or U acyls leads to the corresponding alkoxide (eq 5). This is a

$$[M\eta^2\text{-}C(O)R] + H_2 \xrightarrow{\text{cat.}} [M\text{-}OCH_2R] \qquad (5)$$

precise analogue of the conversion that we have now shown to occur with a manganese acyl carbonyl in the absence of added catalyst. The addition of $H_2$ to the acylmanganese carbonyl, especially when the carbonyl is written in the resonance form **4**, is reminiscent of the proposed mechanism for the hydrogenation of Cr and W carbene complexes.[9] The hydrogenation of a carbonyl group of a transition-metal acyl to a transition-metal oxymethylene may be quite general and may have implications for catalytic synthesis gas chemistry including the Fischer–Tropsch process. Since $R\text{-}M(CO)_n$ readily undergoes CO insertion, it was expected that we could convert $Ph(CH_2)_2Mn(CO)_5$ into **2** on treatment with $CO/H_2$ in hexane solution, and indeed this proved to be the case (Table I).

**Acknowledgment.** The authors wish to thank The Standard Oil Company of Ohio for financial assistance.

**Registry No.** 1, 82849-27-2; 2, 82849-28-3; $RMn(CO)_5$ (R = $PhCH_2CO$), 15022-57-8; $RMn(CO)_5$ (R = $CH_2Ph$), 14049-86-6; $RMn(CO)_5$ (R = $PhCH_2CH_2CO$), 82849-25-0; $RMn(CO)_5$ (R = $PhCH_2CH_2$), 82849-26-1; $PhCH_2CHO$, 122-78-1; $PhCH_2CH_2OH$, 60-12-8; $PhCH_2CH_2CHO$, 104-53-0; CO, 630-08-0; $H_2$, 1333-74-0; sulfolane, 126-33-0.

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(8) $PhCH_2CH_2Mn(CO)_5$ was made by refluxing a solution of $PhCH_2CH_2C(O)Mn(CO)_5$ in hexanes under $N_2$ for 0.5 h. Recrystallization from hot hexanes gave a 61% yield of pure crystals: mp 84.6–85.0 °C; IR (hexanes) 2120 (m), 2022 (s), 2000 (s), 1958 (w); $^1H$ NMR ($CDCl_3$) $\delta$ 1.27 (t, alkyl, 2), 2.98 (t, benzyl, 2), 7.20 (s, aromatic, 5). Anal. Calcd for $[PhCH_2CH_2Mn(CO)_5]$: C, 52.00; H, 3.00. Found: C, 51.97, H, 3.17.

(9) Casey, C. P.; Neumann, S. M. *J. Am. Chem. Soc.* 1977, *99*, 1651.

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# Octakis(trimethylsilyl)cyclotetrasilane. A Stable Cyclotetrasilane from a Silylene Precursor†

**Yue-Shen Chen and Peter P. Gaspar***

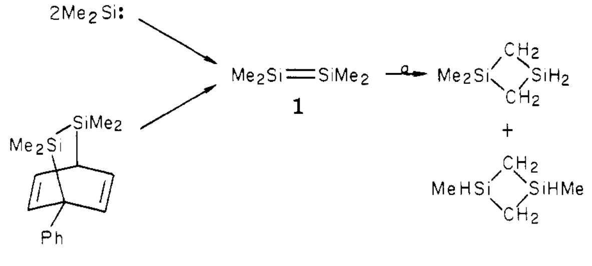
*Department of Chemistry, Washington University*
*Saint Louis, Missouri 63130*

*Received April 21, 1982*

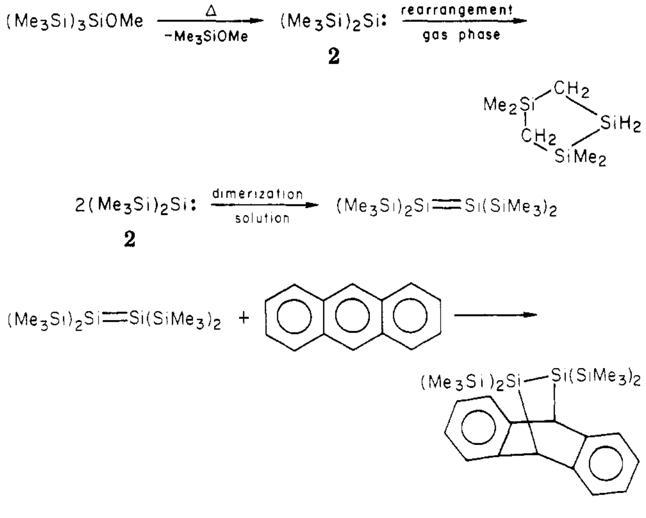
*Summary:* Liquid-phase pyrolysis of neat methoxytris(trimethylsilyl)silane leads to the formation of octakis(trimethylsilyl)cyclotetrasilane. This stable molecule has been characterized, and the preliminary results of the X-ray structure determination indicate that the four-membered ring is planar. The intermediacy of tetrakis(trimethylsilyl)disilene is strongly indicated, but several alternatives are considered for its conversion to the cyclotetrasilane and for its formation. It is suggested that insertion of a silylene into its own precursor, followed by direct $\beta$ elimination to the disilene or by $\alpha$ elimination to a new silylene followed by rearrangement to the disilene, should both be considered in addition to silylene dimerization as the mechanism for disilene formation under these conditions.

Like carbene chemistry before it, the investigation of molecules containing a divalent silicon atom, silylenes, has produced both amusing molecules and challenging mechanistic problems.[1] The purpose of this communication is to report a silylene reaction that leads to the formation of a cyclotetrasilane and to describe its structure. While this finding strongly indicates the intermediacy of a disilene, the route by which the disilene is formed under these conditions is not yet clear. It is this mechanistic uncertainty and its implied warning, as well as the novelty of the product, that has prompted publication.

In 1976 Conlin was led to suggest that dimethylsilylene undergoes dimerization to tetramethyldisilene (**1**) by the observation that the same products were isolated following generation of the silylene in the gas phase[2] as had been obtained by Roark and Peddle from rearrangement of the disilene.[3]



Sakurai subsequently found a number of examples in solution in which generation of a silylene in the presence of anthracene led to the formation of a product that could reasonably be attributed to cycloaddition by a disilene that was believed to be formed by silylene dimerization.[4] The example of bis(trimethylsilyl)silylene (**2**) is pertinent to the work reported here and was also found in our laboratory.[5] It has been shown that in the gas phase, rearrangement of **2** is much more rapid than dimerization.[6]



That silylenes do indeed dimerize has been most vividly demonstrated by the work of West, Fink, and Michl, who have isolated a stable disilene from the thawing of a matrix

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† This work was carried out with financial support from the U.S. Department of Energy. This is technical report no. COO-1713-107.

(1) Gaspar, P. P. "Reactive Intermediates"; Jones, M., Jr., Moss, R. A., Eds.; Wiley-Interscience: New York, 1978; Vol. 1, p 229; 1981; Vol. 2, p 335.

(2) Conlin, R. T.; Gaspar, P. P. *J. Am. Chem. Soc.* **1976**, *98*, 868.

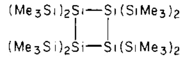
(3) Roark, D. N.; Peddle, G. J. D. *J. Am. Chem. Soc.* **1972**, *94*, 5837.

(4) Nakadaira, Y.; Kobayashi, T.; Otsuka, T.; Sakurai, H. *J. Am. Chem. Soc.* **1979**, *101*, 486.

(5) Chen, Y.-S. "The Chemistry of Silylsilylenes. Generation and Reactions of Bis(trimethylsilyl)silylene and Methoxy(trimethylsilyl)silylene", Doctoral dissertation, Washington University, St. Louis, MO, Aug 1981.

(6) Chen, Y.-S.; Cohen, B. H.; Gaspar, P. P. *J. Organomet. Chem.* **1980**, *195*, C1.

Table I. Properties of Octakis(trimethylsilyl)cyclotetrasilane (4), Pentakis(trimethylsilyl)disilane (8), and Chloropentakis(trimethylsilyl)disilane (9)



4

$^1$H NMR ($CS_2$) δ 0.28 (s)
$^{13}$C NMR ($CS_2$) δ 4.27 (q, $J_{^{13}C-H}$ = 120 Hz)
$^{29}$Si NMR ($CS_2$) δ −8.88 ($Si[CH_3]_3$), −91.05 ($Si[Si(CH_3)_3]_2$)
IR (KBr) 2950 (m), 2900 (m), 1400 (w), 1260 (m), 1245 (s), 842 (vs), 735 (m), 680 (m) 620 (m), 400 (w) cm$^{-1}$
MS (70 eV) *m/e* (rel intens) 696 (27, M$^+$), 73 (100, base)
mp (uncorrd) 332–334 °C dec
Anal. Calcd for $C_{24}H_{72}Si_{12}$: C, 41.31; H, 10.40; Si, 48.29. Found: C, 41.07; H, 10.38; Si, 48.44.
Mol wt ($CHCl_3$) for $C_{24}H_{72}Si_{12}$: calcd, 696; found, 682, 715.

$[(CH_3)_3Si]_3Si\text{-}Si(H)[Si(CH_3)_3]_2$

8

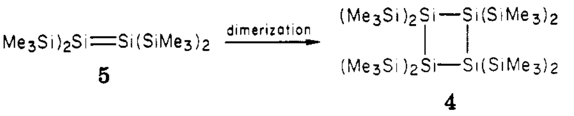
$^1$H NMR ($CS_2$) δ 2.62 (s, 1 H, Si-H), 0.30 (s, 18 H, $[Si(CH_3)_3]_2$), 0.29 (s, 27 H, $[Si(CH_3)_3]_3$)
IR (KBr) 2945 (m), 2890 (m), 2040 (m), 1440 (w), 1395 (w), 1260 (m), 1245 (s), 1060 (m), 835 (s), 750 (w) cm$^{-1}$
MS (70 eV), *m/e* (rel intens) 422 (0.5, M$^+$), 349 (90), 73 (100, base), 201 (75)

$[(CH_3)_3Si]_3Si\text{-}Si(Cl)[Si(CH_3)_3]_2$

9

$^1$H NMR ($CS_2$) δ 0.29 (s)
$^1$H NMR ($C_6D_6$) δ 0.35 (s, 27 H, $[Si(CH_3)_3]_3$), 0.34 (s, 18 H, $[Si(CH_3)_3]_2$)
IR (KBr) 2950 (m), 2890 (m), 1440 (w), 1395 (w), 1260 (m), 1240 (s), 830 (s), 740 (w), 680 (m), 620 (m), 470 (m) cm$^{-1}$
mp (uncorrd) 168–170 °C
MS (70 eV), *m/e* (rel intens) 456 (1, M$^+$), 348 (100, base), 73 (90)

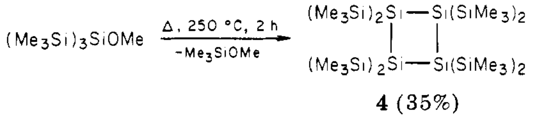
Scheme I



containing dimesitylsilylene (3; mes = mesityl) generated photochemically in situ.[7]

$$Me_3SiSi(mes)_2SiMe_3 \xrightarrow[-Me_6Si_2]{h\nu} \underset{3}{(mes)_2Si:} \xrightarrow{\text{dimerization}} (mes)_2Si{=}Si(mes)_2$$

We have found that when bis(trimethylsilyl)silylene (2) is produced in the liquid phase by pyrolysis of neat precursor, the cooled reaction mixture deposits crystals of a white solid whose spectroscopic properties and molecular weight, reported in Table I, left little doubt that it was octakis(trimethylsilyl)cyclotetrasilane (4).



An X-ray crystal structure determination is under way, and the preliminary results,[8] depicted in Figure 1, indicate that the molecule is planar, in contrast to the highly folded structure found for 1,2,3,4-tetra-*tert*-butyltetramethylcyclotetrasilane.[9]

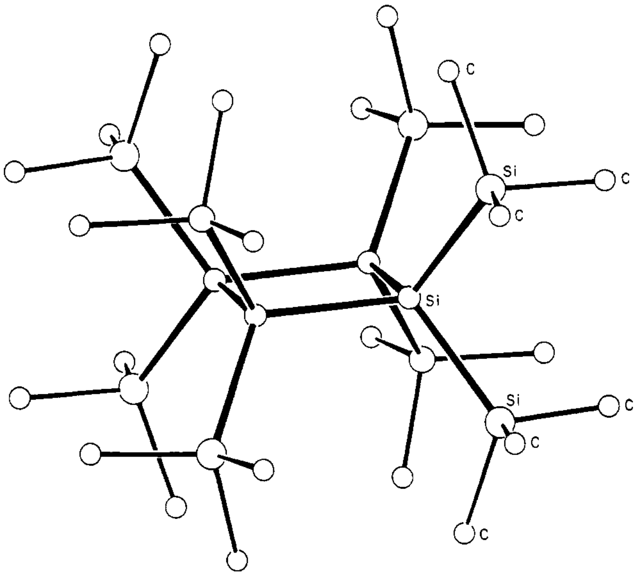
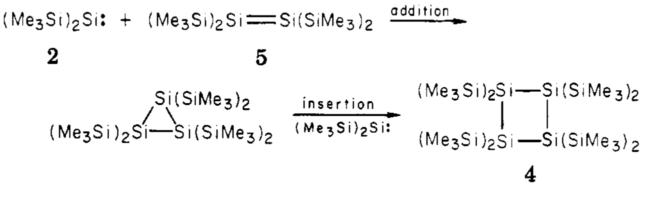


**Figure 1.** A computer-generated perspective drawing of an X-ray model of octakis(trimethylsilyl)cyclotetrasilane (4). Hydrogens are omitted.

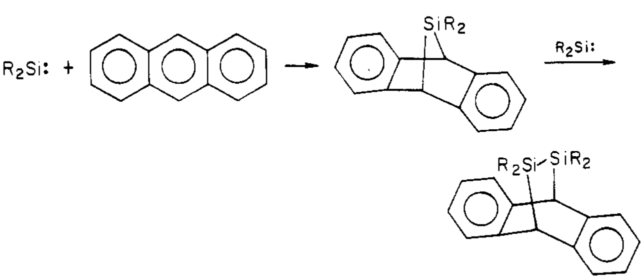
Scheme II



How was the cyclotetrasilane 4 formed? It is tempting to suggest the dimerization of tetrakis(trimethylsilyl)disilene (5) as shown in Scheme I.

Alternatively one could conceive of the formation of the four-membered ring via successive reactions of silylene 2 with disilene 5 (Scheme II). The addition is the inverse of a recently discovered reaction of a stable cyclotrisilane,[10] and the insertion of silylenes into strained silicon–silicon bonds has also been described.[11]

Whichever mechanism operates, the formation of cyclotetrasilane 4 does seem to indicate clearly the intermediacy of disilene 5. This was *not* demanded by Sakurai's experiments, in which the products suggested as arising from cycloadditions of silylene dimers[4] could have resulted from stepwise reactions of the silylene with anthracene.



How does disilene 5 arise in the present experiments? One observation suggests caution in accepting silylene

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[7] West, R.; Fink, M. J.; Michl, J. *Science (Washington, DC)* **1981**, *214*, 1343.

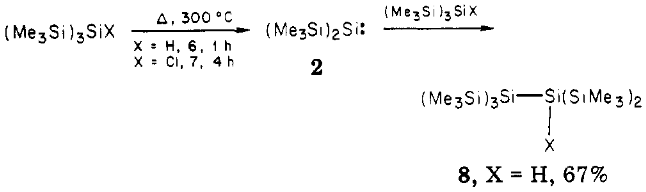
[8] Private communication from Professor Jon Clardy, Stewart R. Leftow, and Edward Arnold.

[9] Hunt, C. J.; Calabrese, T. C.; West, R. *J. Organomet. Chem.* **1975**, *91*, 273.

[10] Masamune, S.; Hanzawa, Y.; Murakami, S.; Bally, T.; Blount, J. F. *J. Am. Chem. Soc.* **1982**, *104*, 1150.

[11] Sakurai, H.; Kobayashi, T.; Nakadaira, Y. *J. Organomet. Chem.* **1978**, *162*, C43.

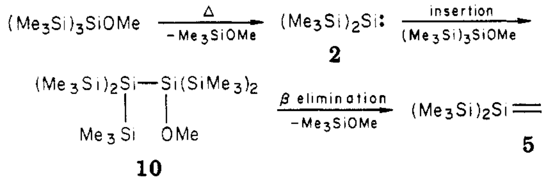
dimerization as the origin of the disilene intermediate in the formation of **4** by both mechanisms suggested above. When tris(trimethylsilyl)silane (**6**) or chlorotris(trimethylsilyl)silane (**7**) is employed as the precursor for bis(trimethylsilyl)silylene (**2**), *no* cyclotetrasilane (**4**) is formed. Instead the major product in both reactions is that of insertion of the silylene into the Si–H or Si–Cl bond, respectively, of its precursor. The spectroscopic properties of pentakis(trimethylsilyl)disilane (**8**) and chloropentakis(trimethylsilyl)disilane (**9**) are given in Table I.[12]



**8**, X = H, 67%
**9**, X = Cl, 30%

The analogous product is found in only trace quantities when methoxytris(trimethylsilyl)silane is employed as the silylene precursor. This may reflect the differences in reactivity of Si–H, Si–Cl, and Si–OMe bonds toward silylene insertion,[1] with Si–H and Si–Cl bonds competing successfully with silylene dimerization. It could be, however, that the formation of cyclotetrasilane (**4**) and the low yield of methoxypentakis(trimethylsilyl)disilane have a common cause in the thermal instability of the latter compound.

We are suggesting two alternative possibilities. The first is that tetrakis(trimethylsilyl)disilene (**5**) may be formed by $\beta$ elimination of methoxytrimethylsilane from the product of insertion of bis(trimethylsilyl)silylene (**2**) into the Si–O bond of methoxytris(trimethylsilyl)silane.



The occurrence of the $\beta$ elimination, for which precedent exists in the literature,[13] would permit the formation of a disilene *without* silylene dimerization by substituting the sequence: an $\alpha$ elimination producing a silylene, silylene insertion, and $\beta$ elimination, for the sequence: two $\alpha$ eliminations producing two silylene molecules, followed by silylene dimerization.

The second alternative recognizes that methoxypentakis(trimethylsilyl)disilane (**10**) has available to it *two* $\alpha$ eliminations, one regenerating bis(trimethylsilyl)silylene (**2**) but the other producing a new silylene **11** that seems capable of rearranging to disilene **5**.[14]

Thus the insertion of silylene **2** into its own precursor followed by a second $\alpha$ elimination and a silylene rearrangement may also produce disilene **5** without silylene dimerization.

These alternative mechanistic hypotheses must be tested not only for the present system but also for other cases in which formation of a disilene has been proposed to occur by dimerization at high temperatures of a silylene whose precursor is subject to silylene insertion.[2,4]

**Acknowledgment.** This work has been made possible by financial support from the United States Department of Energy. This is technical report no. COO-1713-107. We are grateful for helpful discussions with Professors Thomas J. Barton and Hideki Sakurai. The X-ray crystal structure determination is being carried out at Cornell University by Professor Jon Clardy, Stewart R. Leftow, and Edward Arnold. The molecular weight determination was kindly performed by Mrs. Alice Gutsche.

**Registry No. 2**, 75567-79-2; **4**, 82615-12-1; **6**, 1873-77-4; **7**, 5565-32-2; **8**, 82615-13-2; **9**, 82615-14-3.

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(12) Pentakis(trimethylsilyl)disilane (**8**) is converted quantitatively into chloropentakis(trimethylsilyl)disilane (**9**) when heated in carbon tetrachloride solution for 1 h. Chloroform is the other product.

(13) Barton, T. J.; Burns, G. T.; Arnold, E. V.; Clardy, J. *Tetrahedron Lett.* **1981**, *22*, 7. Burns, G. T.; Barton, T. J. *J. Organomet. Chem.* **1981**, *216*, C5. Barton, T. J.; Vuper, M. *J. Am. Chem. Soc.* **1981**, *103*, 6788.

(14) Professor H. Sakurai has found rearrangement of a pyrolytically generated disilanylsilylene to a disilene (private communication).

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# Reaction of (Tris(trimethylsilyl)silyl)lithium with Halophosphines. A Novel Silicon–Halogen Exchange Reaction

**A. H. Cowley* and T. H. Newman**
*Department of Chemistry*
*The University of Texas at Austin*
*Austin, Texas 78712*

*Received June 28, 1982*

*Summary:* The reaction of (Me$_3$Si)$_3$SiLi with *t*-BuPCl$_2$ results initially in (Me$_3$Si)$_3$SiP(Cl)(*t*-Bu) which undergoes thermal rearrangement to (Me$_3$Si)$_2$(Cl)SiP(*t*-Bu)(SiMe$_3$) via a novel silicon–chlorine exchange reaction.

There is considerable current interest in compounds which feature multiple bonding between the heavier main-group elements. The recent reports of kinetically stabilized species involving Si═Si[1] and P═P[2] bonds encouraged us to pursue the synthesis of compounds with double bonds between phosphorus and silicon.[3]

Since 1,2-elimination of Me$_3$SiCl from silyl-substituted alkylphosphorus chlorides represents a useful synthetic pathway to compounds containing P═C and P≡C bonds,[4,5] we undertook the synthesis and subsequent

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(1) West, R.; Fink, M. J.; Michl, J. *Science (Washington, DC)* **1981**, *214*, 1343–1344.

(2) (a) Yoshifuji, M.; Shima, I.; Inamoto, N.; Hirotsu, K.; Higuchi, T. *J. Am. Chem. Soc.* **1981**, *103*, 4587–4589. (b) Cowley, A. H.; Kilduff, J. E.; Newman, T. H.; Pakulski, M. *J. Am. Chem. Soc.*, in press.

(3) A compound with a P═Si bond has been suggested previously as a reactive intermediate. See: Couret, C.; Escudie, J.; Satge, J.; Andriamizaka, J. D.; Saint-Roch, B. *J. Organomet. Chem.* **1979**, *182*, 9–15.

(4) Issleib, K.; Schmidt, H.; Wirkner, C. *Z. Anorg. Allg. Chem.* **1981**, *473*, 85–90.

(5) For a review, see: Appel, R.; Knoll, F.; Ruppert, I. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 731–744.