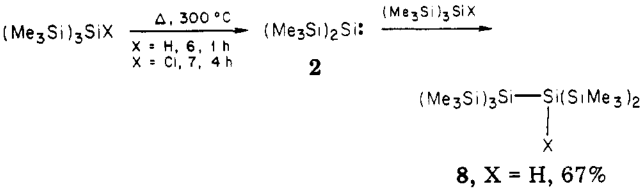
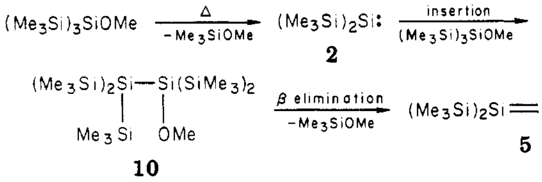
dimerization as the origin of the disilene intermediate in the formation of 4 by both mechanisms suggested above. When tris(trimethylsilyl)silane (6) or chlorotris(trimethylsilyl)silane (7) is employed as the precursor for bis(trimethylsilyl)silylene (2), *no* cyclotetrasilane (4) is formed. Instead 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%

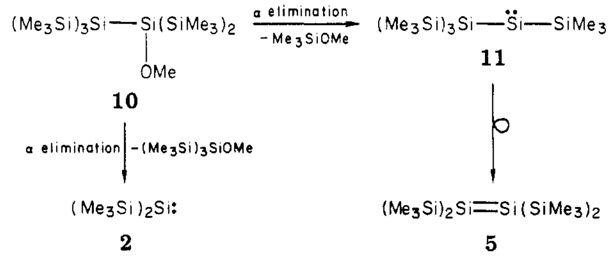
The analogous product is found in only trace quantities when methoxytris(trimethylsilyl)silane is employed as the silylene precursor. This may reflect the differences in reactivity of Si–H, Si–Cl, and Si–OMe bonds toward silylene insertion,[1] with Si–H and Si–Cl bonds competing successfully with silylene 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 β 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 β elimination, for which precedent exists in the literature,[13] would permit the formation of a disilene *without* silylene dimerization by substituting the sequence: an α elimination producing a silylene, silylene insertion, and β elimination, for the sequence: two α eliminations producing two silylene molecules, followed by silylene dimerization.

The second alternative recognizes that methoxypentakis(trimethylsilyl)disilane (10) has available to it *two* α 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 α 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).

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

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Summary: The reaction of $(Me_3Si)_3SiLi$ with *t*-$BuPCl_2$ results initially in $(Me_3Si)_3SiP(Cl)$(*t*-Bu) which undergoes thermal rearrangement to $(Me_3Si)_2(Cl)SiP$(*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_3SiCl 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.

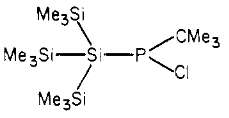
(3) A compound with a P=Si bond has been suggested previously as a reactive intermediate. See: Couret, C.; Escudie, J.; Satge, J.; Andriamizaka, J. D.; Saint-Roch, B. *J. Organomet. Chem.* **1979,** *182,* 9–15.

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

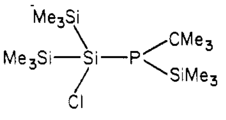
(5) For a review, see: Appel, R.; Knoll, F.; Ruppert, I. *Angew. Chem., Int. Ed. Engl.* **1981,** *20,* 731–744.

thermolysis of bulky silylphosphines of the type $(Me_3Si)_3SiP(R)Cl$.

A THF/Et_2O solution (100 mL, 4:1) of $(Me_3Si)_3SiLi$ (31.2 mmol) was prepared[6] by the reaction of $(Me_3Si)_4Si$ with MeLi and added dropwise to a solution of 4.96 g (31.2 mmol) of t-$BuPCl_2$ in 150 mL of THF at −23 °C. After being gradually warmed to room temperature and stirred overnight, the reaction mixture was concentrated by distillation to ~50-mL volume and the precipitated LiCl removed by filtration. NMR assay of the filtrate was consistent with the presence of **1** as the major product. **1**:



1



2

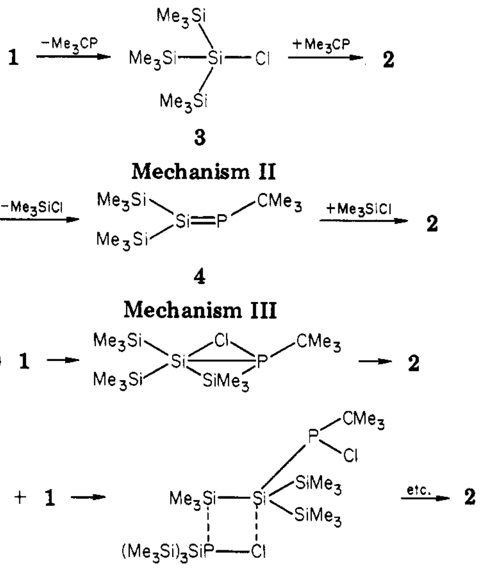
$^{31}P\{^1H\}$ NMR (36.43 MHz)[7] δ +141.5 (s); $^{13}C\{^1H\}$ NMR (20.0 MHz, Me_4Si) δ 2.6 $(Me_3Si)_3Si$, 28.8 (Me_3C, d, J_{PCC} = 17.9 Hz). Continued distillation of **1** (bp 110–115 °C (10^{-2} torr) afforded 5.62 g (15.1 mmol, 48.4% yield) of **2** as a colorless waxy solid. Anal. Calcd for $C_{13}H_{36}ClPSi_4$: C, 42.06; H, 9.78, P, 8.34. Found: C, 42.19; H, 10.59; P, 8.61. The isomerization of **1** to **2** was evident inter alia from the >200-ppm upfield shift in the ^{31}P NMR spectrum. **2**: $^{31}P\{^1H\}$ NMR (36.43 MHz)[7] δ −92.9 (s). The presence of one Me_3Si group directly attached to phosphorus was apparent in both the ^1H and ^{13}C NMR spectra of **2**: ^1H NMR (90 MHz) δ 0.31 $(Me_3Si)_2Si$, s, 18 H), 0.39 (Me_3SiP, d, 9 H, J_{PSiCH} = 4.5 Hz), 1.36 (Me_3C, d, 9 H, J_{PCCH} = 13.5 Hz); ^{13}C NMR (20 MHz, Me_4Si) δ −0.05 $(Me_3Si)_2Si$, s), 4.04 (Me_3SiP, d, J_{PSiC} = 11.7 Hz), 34.93 (Me_3C, d, J_{PCC} = 11.2 Hz). Although we were not able to isolate **1** in a pure state due to the **1** → **2** rearrangement that took place on distillation, it is nevertheless remarkably stable for a P-halogenated silylphosphine. The only previously reported example of this class of compound is t-BuP(Cl)$SiMe_3$ for which $t_{1/2}$ is ~13 min at ambient temperature.[8] All other attempts to prepare P-halo-P-silylphosphines have failed due to the facile elimination of silyl halide.[9]

Three mechanisms can be considered for the transformation of **1** to **2**. Mechanism I involves the elimination of the phosphinidene, Me_3CP, followed by its insertion into a silicon–silicon bond of $(Me_3Si)_3SiCl$ (**3**). Mechanism II features the formation of a silicon–phosphorus double-bonded compound, **4**, which, in turn, reacts with the extruded Me_3SiCl to form **2**. The third mechanism addresses the possibility that silicon–chlorine exchange could proceed via an intramolecular process (Mechanism IIIa) or via a sequence of intermolecular, four-centered processes, one of which is indicated in Mechanism IIIb. The phosphinidene extrusion process suggested in Mechanism I is disfavored because thermolysis of $(Me_3Si)_3SiP(Me)Cl$ (**5**), the methyl analogue of **1**, in the presence of a large excess of the phosphinidene trapping agent, 2,3-dimethylbutadiene, failed to yield any trapped products (vide *infra*). Moreover, in previous work[10] we have demonstrated that CF_3P groups do not insert into silicon–silicon bonds. Exchange via the silicon–phosphorus double-bonded species, **4**, cannot be excluded rigorously; however, we regard is as unlikely because (i) under the vacuum pyrolysis conditions, Me_3SiCl should be removed as soon as it is formed and (ii) there was no NMR spectroscopic evidence for the existence of oligomers of **3** such as $[(Me_3Si)_2SiPCMe_3]_2$ and $[(Me_3Si)_2SiPCMe_3]_3$. On the basis of the present evidence, therefore, we believe that the **1** → **2** conversion proceeds via an intra- or intermolecular silicon–chlorine exchange process.

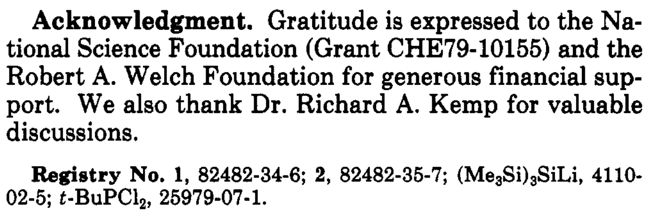
Mechanism I

Mechanism II

Mechanism III



It is not possible to detect analogues of **2** with phosphorus substituents less bulky than Me_3C. In the case of the reaction of $(Me_3Si)_3SiLi$ with $MePCl_2$ in THF at −50 °C it is possible to detect a $^{31}P\{^1H\}$ NMR singlet at +100.0 ppm which we attribute to **5**. However, when the reaction mixture was warmed $(Me_3Si)_3SiCl$ and the cyclopentaphosphine, $(MeP)_5$, were formed. Since $(MeP)_5$ is still formed in the presence of excess 1,3-dimethylbutadiene, a phosphinidene trap, this suggests that **5** decomposes via a condensation pathway[11] such as



Finally, the reaction of $(Me_3Si)_3SiLi$ with PCl_3 yielded only $(Me_3Si)_3SiCl$ and an intractable phosphorus polymer.

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Registry No. 1, 82482-34-6; **2**, 82482-35-7; $(Me_3Si)_3SiLi$, 4110-02-5; t-$BuPCl_2$, 25979-07-1.

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[6] For the preparation of $(Me_3Si)_3SiLi$, see: Gilman, H.; Smith, C. L. *J. Organomet. Chem.* **1968**, *14*, 91–101.

[7] Positive ^{31}P chemical shifts are in ppm downfield from external 85% H_3PO_4 and vice versa.

[8] Appel, R.; Paulen, W. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 869–870.

[9] (a) Ebsworth, E. A. V.; Glidewell, C.; Sheldrick, G. M. *J. Chem. Soc. A* **1969**, 352–353. (b) Baudler, M.; Zarkadas, A. *Chem. Ber.* **1971**, *104*, 3519–3524. (c) Baudler, M.; Hallab, M.; Zarkadas, A.; Tolls, E. *Ibid.* **1973**, *106*, 3962–3969.

[10] Cowley, A. H.; Dierdorf, D. S. *J. Am. Chem. Soc.* **1969**, *91*, 6609–6613.

[11] A similar pathway has been suggested[8] for the production of $(t\text{-}BuP)_4$ from $Me_3SiP(t\text{-}Bu)Cl$.