

were isolated and identified as the following (in order of their elution) on the basis of the data presented.

(1) 0.574 g (3.1 mmol, 20%) of ferrocene: mp 171–173 °C; ^1H NMR (CDCl_3) δ 4.09 (s).

(2) 0.242 g (0.5 mmol, 6%) of diferrocenylphenylphosphine, $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_4)\text{-}]\text{PPh}$: mp 188–190 °C (lit.¹⁰ 191–193 °C); ^1H NMR (CDCl_3) δ 3.88–4.30 (m, 8 H, Cp), 4.04 (s, 10 H, Cp), 7.24–7.58 (m, 5 H, Ph); mass spectrum, m/e 478 (M^+ , 42.6).

(3) 0.735 g (17% conversion) of oligomers **6** as a fluffy, glassy, yellow solid: IR (CH_2Cl_2) 3100 (m), 3080 (m), 3050 (m), 2968 (w), 1586 (w), 1482 (m), 1436 (m), 1412 (w), 1386 (m), 1310 (w), 1195 (m), 1164 (s), 1110 (m), 1098 (w), 1071 (w), 1059 (w), 1031 (s), 1004 (w), 913 (s), 890 (sh), 865 (w), 830 (vs), 635 (w) cm^{-1} .

Reaction of 1,1'-Dilithioferrocene-Tetramethylethylenediamine with Phenylidichlorophosphine in DME at -40, 0, and 25 °C and Subsequent Reaction with Phenyllithium. The standard procedure used for all three temperatures is as follows.

A 300-mL three-necked, round-bottomed flask was charged with 2.00 g (6.3 mmol) of dilithioferrocene and then equipped with a magnetic stir-bar, a pressure-equalizing dropping funnel, a gas inlet tube, and two no-air stoppers in the glovebox. The apparatus was connected to a Schlenk manifold, and 75 mL of DME was added to give an orange solution. A solution of PhPCl_2 (0.855 mL, 6.3 mmol) in 50 mL of DME was added to the dilithioferrocene/DME solution, which was maintained at the appropriate temperature, over a 1.25–1.5-h period. The reaction mixture was stirred an additional hour at the same temperature and then at room temperature for 2 h. The reaction mixture was then cooled to 0 °C, 10 mL (7.6 mmol) of 0.76 M PhLi in diethyl ether was added, and the mixture was then stirred for 45 min at 0 °C. The mixture was hydrolyzed to the "dry end point" with sat. aq. NH_4Cl solution. MgSO_4 was added to ensure drying, and the mixture was filtered, followed by removal of the solvent on a rotary evaporator to give a brown oil. The precipitation method described previously was used to purify the polymer. The results of each temperature run and characterization of the polymers is listed as follows.

(10) Sollott, G. P.; Mertwoy, H. E.; Portnoy, S.; Snead, J. L. *J. Org. Chem.* **1963**, *28*, 1090.

(11) Measurements made at the University of Michigan NMR facilities funded under NSF Grant CHE-7909108.

A. Reaction at 25 °C: 1.256 g (68% conversion) of polymer; IR (CH_2Cl_2) 3078 (m), 3048 (m), 2965 (w), 1480 (m), 1435 (m), 1417 (w), 1384 (m), 1308 (m), 1257 (w), 1191 (s), 1162 (vs), 1108 (m), 1095 (m), 1070 (m), 1058 (w), 1030 (vs), 1002 (m), 887 (w), 832 (vs), 688 (w), 630 (m) cm^{-1} ; $^{31}\text{P}\{^1\text{H}\}$ NMR (CH_2Cl_2) δ_p -25.1 (m, P(Ph)OH), -31.7 (m, internal P atoms), -32.3 (m, internal P atoms).

B. Reaction at 0 °C: 1.269 g (69% conversion) of polymer; IR (CH_2Cl_2) 3078 (m), 3048 (m), 2965 (w), 1480 (m), 1435 (m), 1417 (w), 1384 (m), 1308 (m), 1257 (w), 1191 (s), 1163 (vs), 1108 (m), 1095 (m), 1070 (m), 1058 (w), 1030 (vs), 1002 (m), 887 (w), 832 (vs), 688 (w), 630 (m) cm^{-1} ; $^{31}\text{P}\{^1\text{H}\}$ NMR (CH_2Cl_2) δ_p -25.2 (m, P(Ph)OH), -32.3 (m, internal P atoms).

C. Reaction at -40 °C: 1.307 g (71% conversion) of polymer; IR (CH_2Cl_2) 3078 (m), 3048 (m), 2965 (w), 1480 (m), 1435 (m), 1417 (w), 1384 (m), 1308 (m), 1257 (w), 1191 (s), 1162 (vs), 1108 (m), 1095 (m), 1070 (m), 1058 (w), 1020 (vs), 1002 (m), 887 (w), 832 (vs), 688 (w), 630 (m) cm^{-1} ; $^{31}\text{P}\{^1\text{H}\}$ NMR (CH_2Cl_2) δ_p -26.2 (m, P(Ph)OH), -32.4 (m, internal P atoms).

The molecular weights, M_w , of the polymers obtained in experiments A, B, and C were 43 500, 90 000 and 131 000 amu, respectively.

Acknowledgment. The research performed at the Massachusetts Institute of Technology was supported by the U.S. Air Force Office of Scientific Research (NC)-AFSC. We are grateful for this assistance. The award of a fellowship to H.P.W. by the Dow Chemical Co. also is acknowledged. Thanks also are due to Dr. L. Messerle¹¹ for assistance in obtaining the high-field NMR spectra of the oligomers, to Dr. C. W. Jung for the high-resolution NMR spectrum of the dimer, and to Dr. Catherine Costello (M.I.T. Mass Spectrometry Facility, Dr. K. Biemann, Principal Investigator) for mass spectral data on the oligomers.

Registry No. **6** $x = 2$, 82311-92-0; **6** $x = 3$, 82311-93-1; **6** $x = 4$, 82322-77-8; **6** $x = 5$, 82311-94-2; (1,1'-ferrocenediyl)phenylphosphine, 72954-06-4; 1-lithio-1'-(diphenylphosphino)ferrocene, 82311-95-3; phenylidichlorophosphine, 644-97-3; bis(1'-(diphenylphosphino)ferrocenyl)phenylphosphine, 82311-96-4; (1,1'-dilithioferrocene)(dichlorophenyl)phosphine copolymer, 82322-78-9.

Hexamethylsilirane. 3. Dimethylsilylene-Transfer Chemistry¹

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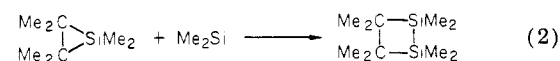
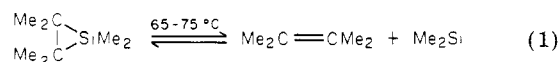
Received April 15, 1982

The thermolysis of hexamethylsilirane at ca. 65–75 °C results in the extrusion of trappable dimethylsilylene. Dimethylsilylene generated in this manner inserted into the Si–H bonds of organosilicon hydrides and into the Si–O bonds of methoxysilanes, hexamethylcyclotrisiloxane, and 2,2,5,5-tetramethyl-2,5-disila-1-oxacyclopentane, and it added to the C=C bonds of various olefins to yield new siliranes. Evidence is presented which indicates that such Me_2Si addition to the C=C bond occurs stereospecifically with retention of configuration.

Introduction

In previous papers we have described the preparation and properties of hexamethylsilirane, its mode of thermal decomposition, and some of its reactions with simple reagents in which the SiC_2 ring is opened.^{2,3} As noted in

part 1,² hexamethylsilirane decomposes thermally by extrusion of dimethylsilylene (eq 1). The process is rever-



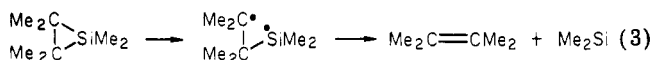
sible, but there are two irreversible pathways which involve consumption of dimethylsilylene: its polymerization to form poly(dimethylsilylene) and its reaction with as yet

(1) Preliminary communications: Seyferth, D.; Annarelli, D. C. *J. Am. Chem. Soc.* **1975**, *97*, 7162; Seyferth, D.; Annarelli, D. C. *J. Organomet. Chem.* **1976**, *117*, C51.

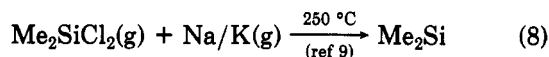
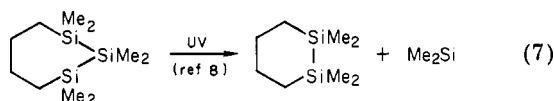
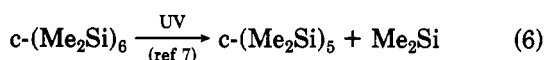
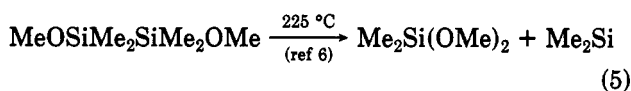
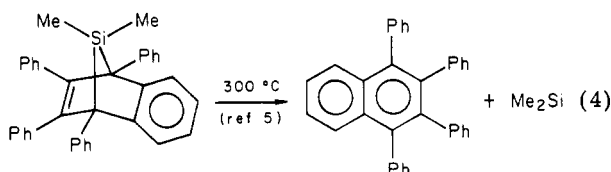
(2) Seyferth, D.; Annarelli, D. C.; Vick, S. C.; Duncan, D. P. *J. Organomet. Chem.* **1980**, *201*, 179.

(3) Seyferth, D.; Annarelli, D. C.; Shannon, M. L.; Escudie, J.; Duncan, D. P. *J. Organomet. Chem.* **1982**, *225*, 177.

undecomposed hexamethylsilirane (eq 2). No information is available on the nature of the Me_2Si extrusion process. It could be a concerted, one-step reaction, or it could proceed in two steps via a diradical intermediate (eq 3).



Since hexamethylsilirane thermolysis takes place at a reasonable rate at temperatures as low as 65–75 °C, this process possibly could serve as a useful method for the generation of dimethylsilylene. Dimethylsilylene has proven to be a useful reagent in organosilicon syntheses. Its reactivity parallels that of organic carbenes, R_2C ; thus it undergoes insertion into various single bonds and addition to multiple bonds.⁴ Dimethylsilylene has been generated by a number of different procedures, most of which involve either the application of higher temperatures (200 °C or above) or activation with ultraviolet radiation.⁴ The principal procedures are summarized in eq 4–8.

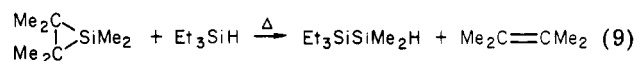


Although it generally is assumed that all of these processes proceed by way of extrusion of free Me_2Si , this is by no means proven. As Gaspar has pointed out,^{4b} "chemical criteria for the formation of free silylenes are still rather vague".¹⁰ The disadvantages associated with high temperature procedures are obvious. The major problems arising in applications of the photolytic procedures are those of further chemistry involving excited states of the initial products and photoinduced secondary reactions. In either case, the products which are isolated will not be the initially formed products. Although these methods of dimethylsilylene generation have been applied with good success in many instances (in particular, those using $\text{MeOSiMe}_2\text{SiMe}_2\text{OMe}$ thermolysis and $c\text{-(Me}_2\text{Si)}_6$ photolysis), we felt that an exploration of the application of

hexamethylsilirane as a dimethylsilylene source would be worthwhile. We report here concerning results of such studies.

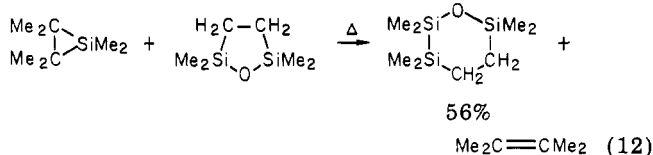
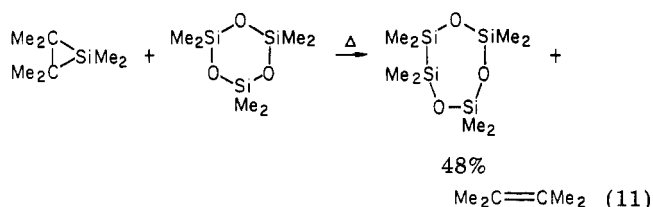
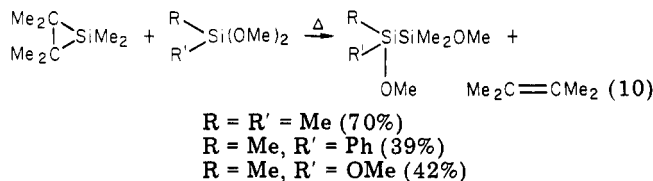
Results and Discussion

A known and often applied reaction of silylenes is their insertion into the Si–H bond,⁴ and this reaction was chosen as the first one to study. When a tetrahydrofuran (THF) solution of hexamethylsilirane was heated (100 °C oil bath) in the presence of an excess of triethylsilane, the expected pentaalkyldisilane was formed in 40% yield (eq 9).



Tetramethylethylene was present in 61% yield at the end of the reaction time of 15 h. Best results were obtained when most of the THF solvent was removed from the hexamethylsilirane after its preparation, and the Me_2Si transfer was carried out in neat triethylsilane. In this manner, a 68% yield of $\text{Et}_3\text{SiSiMe}_2\text{H}$ was obtained (together with a 100% yield of tetramethylethylene) in a reaction time of 16 h at 75 °C. Similar decomposition of hexamethylsilirane in dimethylisopropylsilane and in diethylsilane gave $i\text{-PrMe}_2\text{SiSiMe}_2\text{H}$ (40%) and $\text{HEt}_2\text{SiSiMe}_2\text{H}$ (48%), respectively.

Another characteristic reaction of dimethylsilylene is its insertion into the Si–O bonds of methoxydisilanes¹¹ and the Si–O–Si bonds of the strained and reactive hexamethylcyclotrisiloxane¹² and 2,2,5,5-tetramethyl-1-oxa-2,5-disilacyclopentane.¹³ Hexamethylsilirane-derived dimethylsilylene showed similar reactivity (eq 10–12).



Of some interest has been the addition of silylenes to olefins to form silacyclopropanes (siliranes). Although the results of some attempts to effect this conversion had been rationalized in terms of the formation of an intermediate silirane,⁴ it was an experiment with methylphenylsilylene by Ishikawa and Kumada¹⁴ which provided clear evidence for such a product (eq 13). The photolysis route to silylenes, however, as pointed out in the Introduction,

(11) Atwell, W. H.; Weyenberg, D. R. *J. Am. Chem. Soc.* 1968, 90, 3438.

(12) Soysa, H. S. D.; Okinoshima, H.; Weber, W. P. *J. Organomet. Chem.* 1977, 133, C17.

(13) Okinoshima, H.; Weber, W. P. *J. Organomet. Chem.* 1978, 150, C25.

(14) Ishikawa, M.; Kumada, M. *J. Organomet. Chem.* 1974, 81, C3.

(4) Gaspar, P. P. In "Reactive Intermediates"; Jones, M., Jr., Moss, R. A., Ed. Wiley-Interscience: New York, 1978, Vol. 1, pp 229–277; 1981, Vol. 2, pp 335–385.

(5) Gilman, H.; Cottis, S. G.; Atwell, W. H. *J. Am. Chem. Soc.* 1964, 86, 1596, 5584.

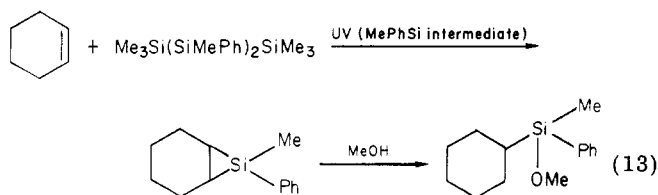
(6) Atwell, W. H.; Weyenberg, D. R. *Angew. Chem., Int. Ed. Engl.* 1969, 8, 469; *J. Am. Chem. Soc.* 1968, 90, 3438.

(7) Ishikawa, M.; Kumada, M. *J. Organomet. Chem.* 1972, 42, 325.

(8) Sakurai, H.; Kobayashi, Y.; Nakadaira, Y. *J. Am. Chem. Soc.* 1971, 93, 5272.

(9) Skell, P. S.; Goldstein, E. J. *J. Am. Chem. Soc.* 1964, 86, 1442.

(10) Note, however, the spectroscopic and chemical trapping evidence in favor of free dimethylsilylene which was obtained in a matrix isolation experiment: Drahanak, T. J.; Michl, J.; West, R. *J. Am. Chem. Soc.* 1979, 101, 5427.

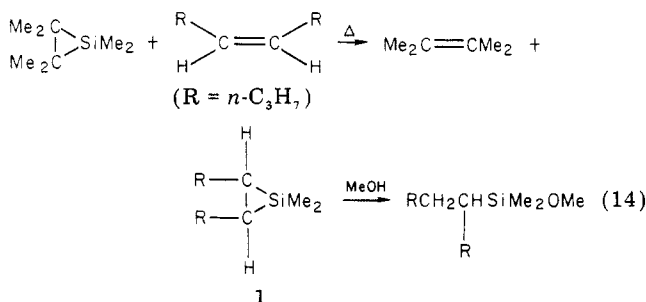


presents complications, and these workers found that such siliranes undergo photoinduced ring opening via 1,2 and 1,3 hydrogen shifts.⁴

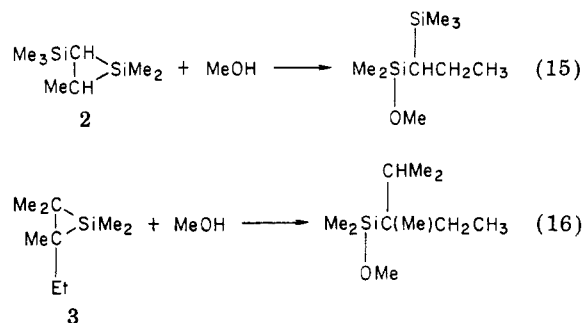
In our initial paper of this series,² we reported that hexamethylsilirane, which decomposes as described in the Introduction, is completely stable when heated at 63 °C in tetramethylethylene solution for 20 h. This implies that the dimethylsilylene extrusion from the silirane is a reversible process, i.e., that Me_2Si can add to the $\text{C}=\text{C}$ bond of tetramethylethylene to regenerate hexamethylsilirane. Further experiments demonstrated the generality, albeit limited, of this process.

For the transfer of Me_2Si from hexamethylsilirane to the $\text{C}=\text{C}$ bond of an external olefin to form a new silirane and tetramethylethylene to be successful, the new silirane must have a thermal stability comparable to or greater than that of hexamethylsilirane. To ensure success, hexamethylsilirane (THF concentrate) was heated in the presence of a large excess of the neat olefin. This approach would not be successful if the new silirane underwent facile decomposition by some process other than reversible dimethylsilylene extrusion. In the absence of knowledge about the thermal stability of simple siliranes other than hexamethylsilirane, we examined both internal olefins and terminal olefins as potential Me_2Si acceptors.

After a solution of hexamethylsilirane in *cis*-4-octene, which showed δ_{Si} at -49.5 for the silirane,² had been heated under nitrogen at 71 °C for 18 h, a ²⁹Si NMR spectrum of the reaction mixture showed that the original silirane had been consumed and that a new silirane with δ_{Si} -59.8 was present. (The ²⁹Si resonances of the known siliranes are in the range ca. -50 to -54 ppm,^{2,15} far upfield from those of all other organosilicon compounds, cyclic and acyclic, with four Si-C bonds.) A preparative experiment in which such a reaction mixture obtained by hexamethylsilirane thermolysis in *cis*-4-octene was treated with methanol gave the expected acyclic methoxysilane in 69% yield (eq 14), thus confirming the formation of silirane 1



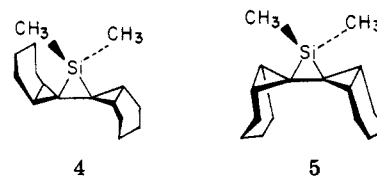
in fairly good yield. Such dimethylsilylene-transfer reactions were successful with other internal olefins as indicated by the formation of the methanolysis products of the expected siliranes. Thus similar experiments gave the methanolysis products from the siliranes derived from the following olefins in the indicated yields: *trans*-4-octene, 25%; cyclooctene, 35%; 1-propenyltrimethylsilane (isomer mixture), 68%; trimethylisopropylethylene, 48%. It is noteworthy that in the case of the unsymmetrically substituted siliranes, 2 and 3, reaction with methanol results in cleavage of the less hindered Si-C bond (eq 15 and 16).



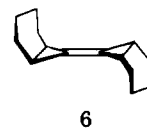
No evidence for the formation of siliranes was obtained when hexamethylsilirane was thermolyzed in the presence of 1-decene and allyltrimethylsilane, although in each case tetramethylethylene was produced in high yield. It may be that the siliranes derived from terminal olefins are less stable than those formed by Me_2Si addition to internal olefins.

The stereochemistry of dimethylsilylene addition to the $\text{C}=\text{C}$ bond is of interest, and this question also was investigated. Two different approaches indicated that the addition is stereospecific and suggested that the addition is a *cis* process.

In previous work¹⁵ we had prepared silirane 4 whose structure had been determined by an X-ray diffraction study.¹⁶ The other isomeric silirane, 5, also had been



prepared.¹⁵ Both 4 and 5 were found to react with methanol to give ring-opened methoxysilanes which differed slightly in their proton NMR and IR spectra and whose refractive indexes were different. Thermolysis of hexamethylsilirane in a benzene solution of the anti isomer of bi-7-norcaranylidene, 6,¹⁷ at 73 °C for 18 h, followed by



methanolysis of the reaction mixture, gave a high-boiling methoxysilane in 35% yield. Its refractive index (n_{D}^{25} 1.5090) was close to that of the methanolysis product of 4 (n_{D}^{25} 1.5100), and its proton NMR and IR spectra were identical with those of the methanolysis product of 4. Thus the addition of dimethylsilylene to 6 appears to be a stereospecific process.

The other approach used to answer the question of stereochemistry is based on the proton NMR analysis of hexamethylsilirane/*cis*- (or *trans*-) propenyltrimethylsilane reaction mixtures before and after methanolysis. In each case, an excess of the individual *cis*- and *trans*-propenyltrimethylsilane isomer was heated with hexamethylsilirane (THF concentrate) in an NMR tube at 70 °C for 16 h. After ¹H and ¹³C NMR spectra of the reaction mixture had been obtained, methanol was added. ¹H and ¹³C NMR spectra of the methanol-treated solution were

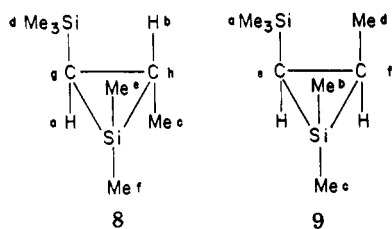
(15) Seyferth, D.; Lambert, R. L. Jr.; Annarelli, D. C. *J. Organomet. Chem.* 1976, 122, 311.

(16) Delker, G. L.; Wang, Y.; Stucky, G. D.; Lambert, R. L., Jr.; Haas, C. K.; Seyferth, D. *J. Am. Chem. Soc.* 1976, 98, 1779.

(17) Seyferth, D.; Massol, M.; Barrau, J.; Satgé, J. *J. Organomet. Chem.* 1980, 185, 307.

measured, and the $\text{Me}_2(\text{MeO})\text{SiCH}(\text{SiMe}_3)\text{CH}_2\text{CH}_3$, 7, formed was isolated by gas chromatography (GLC) and quantified. In the NMR spectra of the methanol-treated solutions the resonances which appeared could be assigned to methoxysilane 7, the product of the addition of methanol to both possible isomeric siliranes, 8 and 9. The resonances which disappeared from the NMR spectrum of the original reaction mixture then could be assigned to siliranes 8 and 9 or to octamethyl-1,2-disilacyclobutane, a minor byproduct resulting from Me_2Si insertion into a Si-C bond of hexamethylsilirane.² Not all signals which were observed could be assigned, and some of the resonances in the ^1H NMR spectra were obscured by the solvent resonances (i.e., those of the starting propenylsilane isomer) or by the tetramethylethylene which was formed. In the ^{13}C NMR spectra, all silirane lines could be identified and tentative assignments of the ring-carbon lines were made.

The signals which were found to disappear (not including the octamethyl-1,2-disilacyclobutane signals) from the proton NMR spectrum of the hexamethylsilirane/*trans*-propenyltrimethylsilane reaction mixture were those occurring at and assigned to the following in compound 8: δ -0.10 (s, presumably half of the doublet due to proton



H_a ; the other half was obscured by the propenylsilane solvent), 0.01 (s, a large peak; integration was impossible because of its nearness to the SiMe_3 resonance of the solvent; assigned to H_d), 0.19 and 0.23 (both s, smaller peaks than the 0.01 resonance; assigned to H_e and H_f), 1.05 (d, $J = 17$ Hz, assigned to H_c). The peaks that were found to disappear from the ^{13}C NMR spectrum of this reaction mixture were those occurring at and assigned to the following in 8: δ_{C} -7.54 (C_e), -5.65 (C_f), 0.32 (C_d), 9.02 (C_c), 9.35 (C_g), 18.74 (C_b).

The signals which were found to disappear from the proton NMR spectrum of the hexamethylsilirane/*cis*-propenyltrimethylsilane reaction mixture were those occurring at and assigned to the following in compound 9: δ 0.09 (s, H_a), 0.21 (s, H_b), 0.26 (s, H_c), 0.94 (d, $J = 12.5$ Hz, H_d). The resonances which were found to disappear from the ^{13}C NMR spectrum upon methanolysis were those occurring at and assigned to the following in 9: δ_{C} -9.00 (C_b), -4.28 (C_c), 2.48 (C_a), 5.85 (C_d), 9.36 (C_e), 14.90 (C_f).

These assignments were made based on the following considerations. The ^1H NMR spectra of both silirane solutions were fairly predictable: the expected three SiCH_3 resonances could be identified in each case, and signals appearing in the spectrum of the *trans*-propenylsilane reaction mixture did not appear in that of the *cis*-propenylsilane reaction mixture (and vice versa). The ring protons were expected to resonate in the region associated with cyclopropyl protons (δ 0.0-0.4)¹⁸ or perhaps at somewhat higher field due to the influence of the nearby silicon atoms. These proton signals could not be clearly assigned in either case due to their low intensity with respect to the nearby SiCH_3 signal of the solvent and because their multiplicity (a doublet for one and a doublet

of quartets for the other) renders them even less likely to be observed. The $\text{C}(\text{ring})-\text{CH}_3$ group, could, however, be easily assigned in both cases due to its fortunate chemical shift position in an area relatively free of interfering signals. Clearly, the $\text{C}(\text{ring})-\text{CH}_3$ doublet of the silirane derived from the *trans*-propenylsilane does not appear in the NMR spectrum of the silirane derived from the *cis*-propenylsilane (and vice versa). The ^{13}C NMR spectra also provided telling evidence in demonstrating the stereochemical purity of the respective silirane solutions and also provided evidence that dimethylsilylene addition to the propenylsilane isomers occurred with retention of stereochemistry. None of the signals assigned to the silirane derived from the *cis*-propenylsilane appear in the spectrum of the silirane derived from the *trans* olefin (and vice versa). Also, the $\text{Si}(\text{ring})-\text{CH}_3$ carbon atom signals were found in a fairly normal position, with all four carbon atoms, two each from the two siliranes, resonating between 4.3 and 9 ppm upfield from tetramethylsilane. The SiCH_3 ^{13}C resonance of hexamethylsilirane was observed at δ_{Si} -9.67.² The evidence that the addition of Me_2Si to the $\text{C}=\text{C}$ bond proceeds with retention of configuration is found in the position of the $\text{Si}(\text{ring})-\text{CH}_3$ and $\text{C}(\text{ring})-\text{CH}_3$ ^{13}C signals, as well as in the position of the $\text{C}(\text{ring})-\text{CH}_3$ proton resonances. The presence of three nongeminal substituents on a three-membered ring, all *cis* to each other, would be expected to result in slightly higher field resonances for these nuclei due to the increased shielding effects caused by their neighbors. Thus, one $\text{Si}(\text{ring})-\text{CH}_3$ resonance of the silirane derived from the *cis*-propenylsilane is observed at a higher field than any other $\text{Si}(\text{ring})-\text{CH}_3$ resonance in either silirane. Similarly, the $\text{C}(\text{ring})-\text{CH}_3$ resonances in both the ^1H and ^{13}C NMR spectra occur at higher field in the spectrum of the silirane derived from the *cis*-propenylsilane than in that of the silirane obtained from *trans*-propenyltrimethylsilane. Also, one of the $\text{Si}(\text{ring})-\text{CH}_3$ resonances in the ^{13}C NMR spectrum of the silirane prepared from the *cis*-propenylsilane resonates at a lower field (less shielded position) than any other $\text{Si}(\text{ring})-\text{CH}_3$ resonance in the ^{13}C NMR spectra of either silirane. This signal, therefore, is assigned to the $\text{Si}(\text{ring})-\text{CH}_3$ carbon atoms *trans* to the other ring substituents (CH_3 and SiMe_3). These arguments are consistent with the observation that the $\text{Si}(\text{ring})-\text{CH}_3$ resonance in the ^{13}C NMR spectrum of hexamethylsilirane occurs at δ_{Si} -9.67. Both of the CH_3 groups on silicon are *cis* to two adjacent CCH_3 groups, contributing to the shielding observed.

The arguments that *trans*-propenyltrimethylsilane reacts with hexamethylsilirane-derived dimethylsilylene to give a silirane in which the *trans* relationship of CH_3 and SiMe_3 groups of the olefin is preserved and that *cis*-propenyltrimethylsilane gives a silirane with the CH_3 and SiMe_3 substituents on the carbon atoms in *cis* relationship are, admittedly, not as strong as would be liked. However, the evidence that the stereochemically pure olefins yield stereochemically pure siliranes (within the inherent limitations of these NMR experiments) is clear. That such Me_2Si additions to the $\text{C}=\text{C}$ bond would occur with inversion of geometric configuration rather than with retention is an idea which is difficult to rationalize. Furthermore, the experiment with *anti*-bi-7-norcaranylidene provides strong support for addition with retention of configuration.

A similar conclusion was reached by Tortorelli and Jones¹⁹ on the basis of a study of the reaction of di-

(18) Silverstein, R.; Bassler, G. C.; Morrill, T. C. "Spectrometric Identification of Organic Compounds"; Wiley: New York, 1974; p 212.

(19) Tortorelli, V. J.; Jones, M., Jr. *J. Am. Chem. Soc.* 1980, 102, 1425.

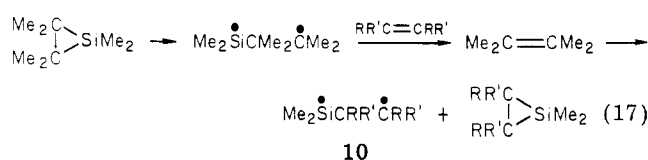
methylsilylene (via Me_2Si)₆ photolysis) with *cis*- and *trans*-2-butene followed by treatment of the siliranes formed with CH_3OH and CH_3OD . ^1H and ^2H NMR spectroscopy of the methanolysis products served to indicate that the Me_2Si addition and the silirane/methanol reaction are at least 95% stereospecific, but an experimental choice between retention and inversion in the Me_2Si addition reaction could not be made. The stereochemistry of the siliranes formed in these reactions was not investigated directly. Also, Ishiwaka et al.²⁰ have reported that the addition of phenyl(trimethylsilyl)silylene to *cis*- and *trans*-2-butene occurs with high stereoselectivity.

In conclusion, we note that the very useful property of hexamethylsilirane to extrude a trappable dimethylsilylene on mild heating is not a general property of siliranes. We have already reported that siliranes such as 4 and 5 and others which have a 7-siladispiro[2.0.2.1]heptane basic structure are very stable thermally and do not release Me_2Si when they do decompose.¹⁵ We have also examined the thermal decomposition of the silirane derived by Me_2Si addition to *cis*-4-octene. After this silirane had been prepared by hexamethylsilirane thermolysis in an excess of *cis*-4-octene, a large excess of tetramethylethylene was added to the reaction mixture and the resulting solution was heated at 66 °C for 22 h. Had 1,1-dimethyl-2,3-di-*n*-propyl-1-silirane decomposed via Me_2Si extrusion, hexamethylsilirane should have been formed and should have accumulated in the reaction mixture. However, methanolysis of the reaction mixture after the heating period showed that about half of the starting silirane had remained undecomposed but that no hexamethylsilirane was present at the time of methanolysis. In another experiment, 1,1-dimethyl-2,3-di-*n*-propyl-1-silirane prepared in this manner failed to give the expected $\text{Et}_3\text{SiSiMe}_2\text{H}$ when heated with triethylsilane for 21 h at 73 °C. Methanolysis of the reaction mixture in this case also indicated that a substantial portion of the silirane had been present at the end of the heating period. Apparently 1,1-dimethyl-2,3-di-*n*-propyl-1-silirane is more stable than hexamethylsilirane, and when it does decompose, it apparently does not do so via extrusion of Me_2Si . This point requires further investigation.

Hexamethylsilirane thus is a very useful source of dimethylsilylene. It may be prepared on a reasonably large scale from simple starting materials.²¹ Although it must be handled and utilized with great care with total exclusion of air and moisture, stock solutions of hexamethylsilirane in organic solvents may be prepared and these enjoy long-term stability.² Finally, the extrusion of dimethylsilylene occurs at a moderate rate at temperatures of 65–75 °C, conditions under which the initial Me_2Si insertion or addition products usually are stable. Other Me_2Si -transfer chemistry is possible with hexamethylsilirane, and in a later paper of this series we will report details of our preparations of highly reactive silacyclopropenes by Me_2Si transfer from hexamethylsilirane to acetylenes.

Finally, we note that the details of the mechanism of Me_2Si transfer from hexamethylsilirane to silicon hydrides and to silicon-oxygen compounds are not known. However, some conclusions about the mechanism of Me_2Si transfer from the silirane to olefins are possible. The fact that the Me_2Si transfer is stereospecific indicates that a "silylenoid" process, i.e., direct, bimolecular transfer of Me_2Si to substrate from an initially formed diradical as

shown in eq 17, is not operative. In this case, the inter-



mediate product must be another diradical, 10 (rigorously demanded only for $\text{Me}_2\text{C}=\text{CMe}_2$ substrate). For such a process to be stereospecific, the diradical intermediate lifetime would have to be shorter than the time required for rotation about the C–C bond in diradical 10. This would be more likely for 10 than for the all-carbon diradical intermediates in triplet carbene additions to olefins. However, that Me_2Si transfer from hexamethylsilirane is stereospecific and that all available evidence speaks in favor of a singlet ground state for dimethylsilylene^{4,10} suggest strongly that a concerted addition of free Me_2Si to the olefinic double bond occurs in the reactions which are reported here.

Experimental Section

General Comments. Infrared spectra were recorded by using a Perkin-Elmer Model 457A infrared spectrophotometer and proton magnetic resonance spectra by using either a Varian Associates T60, a Perkin-Elmer R-20, or a Perkin-Elmer R-22 spectrometer. Chemical shifts are reported in δ units, ppm downfield from internal tetramethylsilane. Chloroform and dichloromethane often were used as alternative internal standards. ^{13}C NMR spectra were obtained with a JEOL FNM HFX-60Q spectrometer; ^{29}Si NMR spectra with a Bruker HFX-90 spectrometer which was interfaced with a Digilab FTS/NMR-3 computer. Gas-liquid chromatography (GLC) was used routinely for isolation of pure samples, determination of purity of distilled samples, and yield determinations by the internal standard method. All columns were packed on acid-washed, dimethyldichlorosilane-treated Chromosorb W.

All solvents used were rigorously dried. All reactions were carried out under an atmosphere of prepurified nitrogen or argon. All glassware was flame-dried under a stream of nitrogen before use. Reactive reagents were transferred by syringe or cannula.

In part 1² the preparations of hexamethylsilirane and its precursors are described in detail, as are the methods used for the determination of the yield of hexamethylsilirane, for the preparation of solutions of hexamethylsilirane in solvents other than THF, and for the handling of hexamethylsilirane and its solutions. We stress again the high reactivity of hexamethylsilirane toward atmospheric oxygen and moisture and the absolute need to perform all operations involving this compound with complete exclusion of air in rigorously dried glassware using rigorously dried and degassed solvents.

For thermolysis reactions which were carried out in benzene or neat trapping reagent, the following procedure was used. The reaction vessel, usually a 25-mL one-necked flask equipped with a magnetic stir bar and a reflux condenser with an argon inlet tube, was purged with argon and flame-dried. The substrate then was added to the flask by syringe, followed by a weighed amount of the concentrated hexamethylsilirane solution. The reaction vessel then was heated in a preheated oil bath. Reaction temperatures are uncorrected.

Thermolysis of Hexamethylsilirane in the Presence of Organosilicon Hydrides. (a) **Triethylsilane.** A solution of 1.27 mmol of hexamethylsilirane (concentrated THF solution) in 4 mL of triethylsilane (Silar) was stirred and heated under argon for 16 h at 75 °C. Subsequent GLC analysis indicated that one product had been formed which was collected and identified as 1,1-dimethyl-2,2,2-triethylidisilane, $\text{Et}_3\text{SiSiMe}_2\text{H}$ (68% yield): n_{D}^{20} 1.4578 (lit.²² n_{D}^{20} 1.4589); IR (neat film) $\nu(\text{Si-H})$ 2090 (vs) cm^{-1} ;

(20) Ishikawa, M.; Nakagawa, K.-I.; Kumada, M. *J. Organomet. Chem.* 1979, 178, 105.

(21) Goure, W. F.; Barton, T. J. *J. Organomet. Chem.* 1980, 199, 33.

(22) Gladyshev, E. N.; Andruvichev, V. S.; Klimov, A. A.; Vyazakin, N. S.; Razuvaev, G. A. *J. Organomet. Chem.* 1971, 28, C42; *Zh. Obshch. Khim.* 1972, 42, 1077.

NMR (CCl_4) δ 0.17 (d, $J = 5$ Hz, 6 H, Me_2Si), 0.38–1.23 (m, 15 H, Et_3Si), 3.50–3.90 (m, 1 H, SiH). Tetramethylethylene was present in quantitative yield.

(b) **Isopropylidimethylsilane.** A solution of 1.69 mmol of hexamethylsilirane (THF concentrate) in 9 mL (71 mmol) of *i*-Pr Me_2SiH (Silar) was stirred and heated for 15 h at 71 °C. The product (40% yield), *i*-Pr $\text{Me}_2\text{SiSiMe}_2\text{H}$, n_D^{25} 1.4417, was collected by GLC: IR (neat film) $\nu(\text{Si-H})$ 2100 (vs) cm^{-1} ; NMR (CCl_4) δ 0.03 (s, 6 H, Me_2Si), 0.12 (d, $J = 5$ Hz, 6 H, HMe_2Si), 0.99 (br s, 7 H, CHMe_2), 3.49–3.82 (m, 1 H, SiH). The tetramethylethylene yield was 97%. Anal. Calcd for $\text{C}_7\text{H}_{20}\text{Si}_2$: C, 52.40; H, 12.57. Found: C, 52.10; H, 12.49.

(c) **Diethylsilane.** A small Pyrex bomb-tube equipped with a magnetic stir bar was charged (under argon) with 1.47 mmol of hexamethylsilirane (THF concentrate) and 10 mL of diethylsilane (Alfa). The tube was cooled in liquid nitrogen, evacuated, sealed, and then heated for 17 h at 73 °C. The tube was cooled to room temperature and opened, and the contents were transferred to a one-necked flask and trap-to-trap distilled in vacuum into a receiver cooled to -78 °C. GLC examination of the distillate showed the presence of $\text{HEt}_2\text{SiSiMe}_2\text{H}$ (48% yield): n_D^{25} 1.4449; IR (neat film) $\nu(\text{SiH})$ 2100 (vs) cm^{-1} ; NMR (CCl_4) δ 0.23 (d, $J = 6$ Hz, 6 H, Me_2Si), 0.67–0.91 (m, 4 H, SiCH_2), 1.08 (t, $J = 6$ Hz, 6 H, CCH_3), 3.44–3.89 (m, 2 H, SiH). Anal. Calcd for $\text{C}_8\text{H}_{18}\text{Si}_2$: C, 49.22; H, 12.39. Found: C, 49.20; H, 12.36.

Thermolysis of Hexamethylsilirane in the Presence of Methoxysilanes. (a) **Dimethyldimethoxysilane.** A solution of 1.18 mmol of hexamethylsilirane (THF concentrate) in 12 mL (75 mmol) of $\text{Me}_2\text{Si}(\text{OMe})_2$ was stirred and heated under argon for 15 h at 73 °C. Trap-to-trap distillation was followed by GLC analysis of the distillate. The product, 1,2-dimethoxytetramethyldisilane, n_D^{25} 1.4230 (lit.²³ n_D^{25} 1.4207), was present in 71% yield: NMR (CCl_4) δ 0.23, 3.40 (s). Tetramethylethylene was present in 95% yield.

(b) **Methylphenyldimethoxysilane.** A solution of 1.26 mmol of hexamethylsilirane (THF concentrate) in 3.64 g (20 mmol) of $\text{MePhSi}(\text{OMe})_2$ was stirred and heated for 16 h at 73 °C. GLC analysis showed that 1-phenyl-1,2,2-trimethyl-1,2-dimethoxydisilane, $\text{PhMe}(\text{OMe})\text{SiSiMe}_2\text{OMe}$, n_D^{25} 1.4987, was present in 39% yield: NMR (CCl_4) δ 0.22 (s, 6 H, SiMe_2), 0.47 (s, 3 H, SiMePh), 3.36 (s, 3 H, OMe), 3.47 (s, 3 H, OMe), 7.2–7.5 (m, 5 H, Ph). Anal. Calcd for $\text{C}_{11}\text{H}_{20}\text{O}_2\text{Si}_2$: C, 54.72; H, 8.76. Found: C, 54.91; H, 8.34.

(c) **Methyltrimethoxysilane.** A solution of 1.48 mmol of hexamethylsilirane (THF concentrate) in 2.7 g (20 mmol) of $\text{MeSi}(\text{OMe})_3$ (Petrarch) was heated and stirred for 16 h at 75 °C. Subsequent GLC analysis showed the presence of 1,1,2-trimethyl-1,2,2-trimethoxydisilane (42% yield). The IR and proton NMR spectra of a collected sample were identical with those of authentic material.²⁴

(d) **Trimethylmethoxysilane and Trimethylphenoxy-silane.** A solution of 1.54 mmol of hexamethylsilirane (THF concentrate) in 2.1 g (20 mmol) of Me_3SiOMe was heated for 17 h at 70 °C in an evacuated, sealed Pyrex bomb-tube. Subsequent examination of the reaction mixture by GLC showed that no volatile products other than tetramethylethylene (90%) had been formed.

A similar experiment (at atmospheric pressure) with Me_3SiOPh gave similar results. A minor product was identified as octamethyl 1,3-disila-2-oxacyclopentane, the oxidation product of the compound formed by insertion of dimethylsilylene into the Si–C bond of hexamethylsilirane.²

Thermolysis of Hexamethylsilirane in the Presence of Hexamethylcyclotrisiloxane. A solution of 1.54 mmol of hexamethylsilirane (THF concentrate) in 2.2 g (10 mmol) of the title cyclosiloxane (Petrarch) was stirred and heated for 16 h at 70 °C. GLC analysis of the reaction mixture showed the presence of 1,1,2,2,4,4,6,6-octamethyl-3,5,7-trioxa-1,2,4,6-tetrasilacycloheptane (see eq 11). A GLC-collected sample had IR and NMR spectra which matched those as described for this compound in the literature.¹² The product was present in 48% yield. A small amount of octamethyl-1,2-disilacyclobutane² also was observed.

Thermolysis of Hexamethylsilirane in the Presence of 2,2,5,5-Tetramethyl-2,5-disila-1-oxacyclopentane (Experiment by M. L. Shannon²⁵). A solution of 3.88 mmol of hexamethylsilirane (THF concentrate) in 2.50 mL (ca. 13.5 mmol) of the title disiloxane (Silar) was stirred and heated for 18 h at 68 °C under an argon atmosphere. GLC analysis of the reaction mixture showed the presence of 2,2,3,3,6,6-hexamethyl-2,3,6-trisila-1-oxacyclohexane (see eq 12), n_D^{25} 1.4519, in 56% yield: NMR (CCl_4) δ 0.05, 0.07, 0.18 (s, 6 H, each, SiMe_2) and 0.73, 0.77 (AA' multiplet, 4 H total, CH_2CH_2).¹³ Anal. Calcd for $\text{C}_8\text{H}_{22}\text{OSi}_3$: C, 43.96; H, 10.15. Found: C, 44.22; H, 10.20. Tetramethylethylene was present in 74% yield.

Thermolysis of Hexamethylsilirane in the Presence of Olefins. (a) **cis-4-Octene.** A solution of 1.70 mmol of hexamethylsilirane (THF concentrate) in 5 mL of the title olefin (Chem Samples) was stirred and heated for 15 h at 75 °C under an argon atmosphere. The solution was cooled to room temperature, and 0.5 mL of absolute MeOH was added. An exothermic reaction resulted. GLC analysis of the reaction mixture indicated the presence of one product, 4-octyldimethylmethoxysilane (69%): n_D^{25} 1.4260; NMR (CCl_4) δ 0.11 (s, 6 H, Me_2Si), 0.60–1.53 (m, octyl CH), 3.40 (s, 3 H, OMe). Anal. Calcd for $\text{C}_{11}\text{H}_{22}\text{OSi}$: C, 65.27; H, 12.95. Found: C, 65.11; H, 12.96. Tetramethylethylene was present in 95% yield.

In another experiment, about 5 mmol of hexamethylsilirane in 4 mL of *cis*-4-octene was prepared. A portion of this solution was added to a 10-mm NMR tube, and a proton-decoupled ^{29}Si NMR spectrum was obtained: δ_{Si} –49.5. The remainder of the solution was heated for 18 h at 71 °C. The solution then was cooled, and another portion was used to record the ^{29}Si NMR spectrum after this heating period: δ_{Si} –59.8. When fully coupled, this resonance was observed as a complex multiplet. The addition of methanol to the NMR tube produced a strong exotherm; NMR analysis indicated that 4-octyldimethylmethoxysilane had been formed.

(b) **trans-4-Octene.** A solution of 1.8 mmol of hexamethylsilirane (THF concentrate) in 4 mL of the title olefin (Aldrich) was stirred and heated for 18 h at 74 °C. The reaction mixture was cooled to room temperature, and 0.5 mL of absolute MeOH was added. GLC analysis followed. The product (25% yield) was identified (n_D^{25} 1.4280 and IR spectrum) as 4-octyldimethylmethoxysilane. Tetramethylethylene was present in 89% yield.

(c) **2,3-Dimethyl-2-pentene.** A solution of 1.62 mmol of hexamethylsilirane in 4 mL of the title olefin (Chem Samples) was stirred and heated for 15 h at 75 °C. Subsequent methanolysis (0.5 mL of MeOH; exothermic reaction) gave 3-(3,4-dimethylpentyl)dimethylmethoxysilane (see eq 16), n_D^{25} 1.4395, in 48% yield: NMR (CCl_4) δ –0.14 (s, 6 H, SiMe_2), 0.80–1.02 (m, 12 H, CCH_3), 1.32 (q, $J = 7$ Hz, 2 H, CH_2), 1.67–2.04 (m, 1 H, methine H), 3.42 (s, 3 H, OMe). Anal. Calcd for $\text{C}_{10}\text{H}_{24}\text{OSi}$: C, 63.75; H, 12.84. Found: C, 63.76; H, 12.71. Tetramethylethylene was present in 90% yield.

(d) **Cyclooctene.** A solution of 2.0 mmol of hexamethylsilirane (THF concentrate) in 5 mL of cyclooctene was stirred and heated for 20 h at 63 °C. Methanolysis (0.5 mL of MeOH; exothermic reaction) of the reaction mixture gave cyclooctyldimethylmethoxysilane, n_D^{25} 1.4620, in 35% yield: NMR (CCl_4) δ 0.08 (s, 6 H, Me_2Si), 0.68–1.95 (m, 15 H, cyclooctyl H), 3.41 (s, 3 H, OMe). The mass spectrum (70 eV) showed the molecular ion m/e 200. Anal. Calcd for $\text{C}_{11}\text{H}_{24}\text{OSi}$: C, 65.92; H, 12.07. Found: C, 65.76; H, 12.12. Tetramethylethylene was formed in 94% yield.

(e) **Propenyltrimethylsilane.** A solution of 1.60 mmol of hexamethylsilirane (THF concentrate) in 5 mL of $\text{Me}_3\text{SiCH}=\text{CHCH}_3$ (58% *cis*, 42% *trans*)²⁶ was stirred and heated for 18 h at 75 °C. Subsequent methanolysis (0.5 mL of MeOH; exothermic reaction) gave 1-(1-(trimethylsilyl)propyl)dimethylmethoxysilane (see eq 15), n_D^{25} 1.4341, in 68% yield: NMR (CCl_4) δ –0.20 (t, $J = 7$ Hz, 1 H, Si_2CH), 0.06 (s, 9 H, Me_3Si), 0.12 (s, 6 H, Me_2Si), 1.00 (t, $J = 7$ Hz, 3 H, CCH_3), 1.56 (m, 2 H, CH_2), 3.39 (s, 3 H, OMe). Anal. Calcd for $\text{C}_9\text{H}_{24}\text{OSi}_2$: C, 52.86; H, 11.83. Found: C, 52.93; H, 11.77. Tetramethylethylene was present in 99% yield.

(23) Atwell, W. H.; Weyenberg, D. R. *J. Organomet. Chem.* 1967, 7, 71.

(24) Hengge, E.; Holtschmidt, N. *Monatsh. Chem.* 1968, 99, 340.

(25) Shannon, M. L. Ph.D. Thesis, Massachusetts Institute of Technology, 1980.

(26) Seyferth, D.; Vaughan, L. G. *J. Organomet. Chem.* 1963, 1, 138.

In further experiments, *cis*- and *trans*-propenyltrimethylsilane were separated by GLC (6 ft \times 0.25 in. 20% by weight of a 14% AgNO₃ solution in tetraethylene glycol; F&M 700 gas chromatograph). Each isomer (3.6 and 2.6 mmol, respectively) was added separately to an argon-purged 5-mm NMR tube capped with a rubber septum, and then 15 μ L of C₆D₆ (lock sample and reference sample for ¹³C NMR) and 0.49 mmol of hexamethylsilirane (THF concentrate) were added by syringe. The NMR tubes were cooled, evacuated, sealed off, and heated for 17 h at 70 °C. After ¹H and ¹³C NMR spectra had been obtained, 100 μ L of MeOH was added to each tube (exothermic reaction). ¹H and ¹³C NMR measurements were repeated. Subsequent GLC analysis of the solutions showed the presence of Me₂(OMe)SiCH(Et)SiMe₃ (GLC retention time and IR spectrum) in each case. The yield of this methoxysilane was 68% in the case of the *cis*-propenylsilane experiment and 55% in the case of the experiment with the *trans* isomer.

(f) *anti*-Bi-7-norcaranylidene, **6**. A solution of 0.90 mmol of hexamethylsilirane (THF concentrate), 2.40 g (12.6 mmol) of *anti*-bi-7-norcaranylidene¹⁷ and 5 mL of benzene was stirred and heated for 18 h at 73 °C. The solution was cooled to room temperature, and 0.5 mL of methanol was added (mild exotherm). An additional 5 mL of MeOH was added to precipitate most of the unreacted olefin. Filtration was followed by concentration of the filtrate at reduced pressure. GLC analysis of the residue indicated that one major product had been formed. This material was collected by GLC and identified (*n*_D²⁵ and IR) as the methanolysis product of silirane **4**.¹⁵ The yield of this product was 35%;

tetramethylethylene was present in 76% yield.

Acknowledgment. We are grateful to the U.S. Air Force Office of Scientific Research (NC)-AFSC for generous support of this work and to Dr. Michel Massol for a sample of *anti*-bi-7-norcaranylidene. We are indebted to a reviewer for very useful comments concerning the mechanistic aspects of this work.

Registry No. Et₃SiSiMe₂H, 31732-54-4; *i*-PrMe₂SiSiMe₂H, 58023-36-2; HEt₂SiSiMe₂H, 34202-97-6; PhMe(OMe)SiSiMe₂OMe, 82281-37-6; hexamethylsilirane, 55644-09-2; triethylsilane, 617-86-7; tetramethylethylene, 563-79-1; isopropyltrimethylsilane, 18209-61-5; diethylsilane, 542-91-6; dimethyldimethoxysilane, 1112-39-6; 1,2-dimethoxytetramethyldisilane, 10124-62-6; methylphenyldimethoxysilane, 3027-21-2; methyltrimethoxysilane, 1185-55-3; 1,1,2-trimethyl-1,2,2-trimethoxydisilane, 18107-31-8; trimethylmethoxysilane, 1825-61-2; trimethylphenoxysilane, 1529-17-5; hexamethylcyclotrisiloxane, 541-05-9; 1,1,2,2,4,4,6,6-octamethyl-3,5,7-trioxo-1,2,4,6-tetrasilacycloheptane, 17865-99-5; 2,2,5,5-tetramethyl-2,5-disila-1-oxacyclopentane, 7418-20-4; 2,2,3,3,6,6-hexamethyl-2,3,6-trisila-1-oxacyclohexane, 66977-50-2; *cis*-4-octene, 7642-15-1; 4-octyldimethylmethoxysilane, 61753-24-0; *trans*-4-octene, 14850-23-8; 2,3-dimethyl-2-pentane, 10574-37-5; 3-(3,4-dimethylpentyl)dimethylmethoxysilane, 61753-26-2; cyclooctene, 931-88-4; cyclooctyldimethylmethoxysilane, 61753-23-9; propenyltrimethylsilane, 17680-01-2; 1-(1-(trimethylsilyl)propyl)dimethylmethoxysilane, 61753-25-1; *anti*-bi-7-norcaranylidene, 18688-18-1; dimethylsilane, 1111-74-6.

Preparation and Properties of (μ_3 -Thio)(μ_3 -organophosphido)tris(tricarbonyliron)(2Fe-Fe) Complexes

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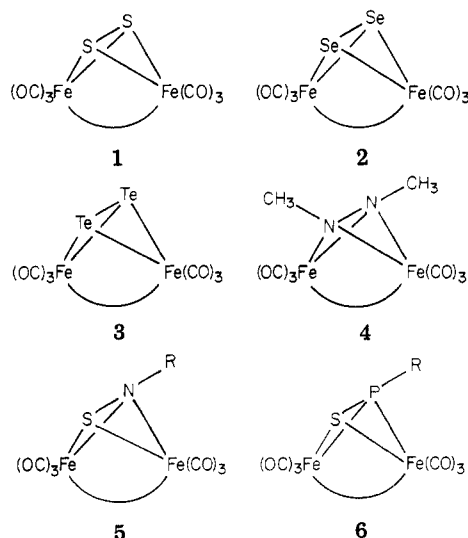
Received June 7, 1982

The reactions of Fe₃(CO)₁₂ with RP(S)Cl₂ gave (μ_3 -S)(μ_3 -RP)Fe₃(CO)₉ and not the desired (μ -RPS)Fe₂(CO)₆ complexes.

Introduction

Our studies have shown that (μ -dithio)bis(tricarbonyliron),¹ **1**, has a very reactive S-S bond.² The analogous selenium compound **2**¹ shows similar reactivity,³ and the tellurium analogue **3** recently has been isolated and characterized.⁴ The RN, RP, RAs, and RSb moieties are isoelectronic with the corresponding chalcogen atoms, O, S, Se, and Te, respectively, and so it is not surprising that **4**,⁵ a group 5 analogue of complexes **1-3**, and **5**,⁶ an analogous mixed group 5/group 6 complex, are known. It would be of interest to study in detail the chemistries of **4** and **5**, but, unfortunately, the known preparative routes

to these complexes are unsatisfactory, giving only very low yields. A Fe₂(CO)₆ complex of the group 5/group 6 bridge type which has not yet been reported is **6**, and we report here concerning our attempts to prepare compounds of this type.



(1) (a) Brendel, G. Ph.D. Dissertation, Technische Hochschule München, 1956. (b) Hieber, W.; Gruber, J. *Z. Anorg. Allg. Chem.* **1958**, *296*, 91.

(2) (a) Seyferth, D.; Henderson, R. S.; Song, L.-C. *Organometallics* **1982**, *1*, 125. (b) Seyferth, D.; Henderson, R. S.; Gallagher, M. K. *J. Organomet. Chem.* **1980**, *193*, C75.

(3) Seyferth, D.; Henderson, R. S. *J. Organomet. Chem.* **1981**, *204*, 333.

(4) Lesch, D. A.; Rauchfuss, T. B. *Inorg. Chem.* **1981**, *20*, 3583.

(5) Dekker, M.; Knox, G. R. *J. Chem. Soc., Chem. Commun.* **1967**, 1234.

(6) (a) Meij, R.; Stufkens, D. J.; Vrieze, K.; Brouwers, A. M. F.; Schagen, J. D.; Zwinselman, J. J.; Overbeek, A. R.; Stam, C. H. *J. Organomet. Chem.* **1979**, *170*, 337. (b) Gast, C. H.; Nooitgedacht; Kraak, J. C. *Ibid.* **1980**, *184*, 221. (c) Otsuka, S.; Yoshida, T.; Nakamura, A. *Inorg. Chem.* **1968**, *7*, 1833.