The Dimer of Unsubstituted Silole

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Gas-phase flow pyrolysis of 1-(trimethylsilyl)-1-silacyclopent-3-ene and 1-methoxy-1-(trimethylsilyl)-1-silacyclopent-3-ene leads to the formation of the dimer of silole, 3,8-disila-3a,4,7,7a-tetrahydro-4,7-methano-1*H*-indene. Attempts to isolate or trap the silole monomer by means other than self-reaction have failed. It is suggested that the initially formed intermediate silylene, 1-silacyclopent-3-enylidene, undergoes rearrangement to silole and that silole is not very reactive in 2 + 4 cycloadditions, but does undergo dimerization.

Ever since Thiele demonstrated the acidity of cyclopentadiene,[1] organosilicon chemists have tried to synthesize 1-silacyclopenta-2,4-diene, hereafter called silole 1, and wondered whether it can be deprotonated to a silacyclopentadienide anion stabilized by delocalization. Recent theoretical calculations suggest very modest stabilization of the $SiC_4H_5^-$ anion.[2,3] The chemistry of the $SiC_4H_5^-$ anion has been reviewed.[4]

Experiments in this area have been hindered by the difficulty in preparing lightly encumbered 1-hydridosiloles. Barton and Burns prepared the first C-unsubstituted 1-hydridosilole, 1-methylsilole, in 1979,[5] but an earlier report of the synthesis of unsubstituted silole 1 was later retracted.[6] The first C-unsubstituted silole to be isolated, 1,1-dimethylsilole, was reported by two groups in 1981.[7–9] The chemistry of siloles has recently been reviewed.[10]

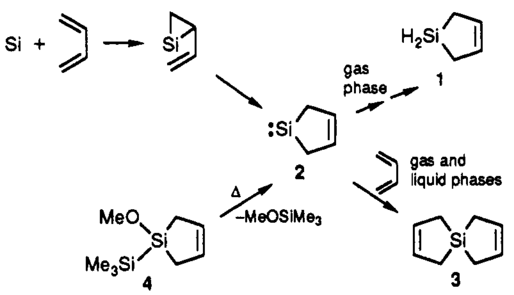
In 1974 we suggested that unsubstituted silole 1 was the major product from the reactions of recoiling ^{31}Si atoms with 1,3-butadiene,[11] and in 1981 we proposed the mechanism shown in Scheme I, in which 1-silacyclopent-3-en-1-ylidene (2) rearranges to silole 1.[12] Only a few million molecules are produced in recoil experiments, and our structure assignment for the product identified as silole 1 was based largely on the gas chromatographic behavior of the product.[11] Our claim to have detected silole 1 in a hot-atom experiment was quite rightly received with skepticism by Barton and Burns.[5]

In the intervening years, evidence has been found for the intermediacy of 1-silacyclopent-3-en-1-ylidene (2) in the reactions of recoiling ^{31}Si atoms with butadiene,[12] and the present report supports the rearrangement of 2 to silole 1. An explanation for the survival of silole 1 in the recoil experiment is also offered.

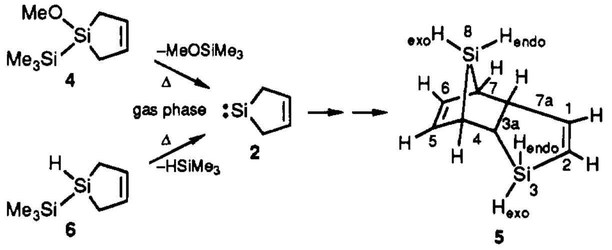
Evidence for the formation of silylene intermediate 2 in the recoil experiment was the detection of the same butadiene adduct 5-silaspiro[4.4]nona-2,7-diene (3) as is obtained when 2 is generated by pyrolytic elimination of MeOSiMe, from 1-methoxy-1-(trimethylsilyl)-1-silacyclopent-3-ene (4).[12] The same spiro-adduct 3 was formed upon cocondensation of thermally evaporated silicon atoms with butadiene.[12]

Evidence for the rearrangement of 1-silacyclopent-3-en-1-ylidene (2) to silole 1 was gained by studying the gas-phase thermolysis of 1-methoxy-1-(trimethylsilyl)-1-silacyclopent-3-ene (4) in the *absence* of butadiene. The only product formed, as shown in Scheme II, was a compound that was identified as 3,8-disila-3a,4,7,7a-tetrahydro-4,7-methano-1*H*-indene (5), the dimer of silole.[13] The same product was obtained from the elimination of trimethylsilane from 1-(trimethylsilyl)-1-silacyclopent-3-ene (6).[14]

Scheme I



Scheme II



Given the checkered history of unsubstituted silole 1, it seemed necessary to characterize its formal dimer 5 carefully and to attempt to gain evidence for the intermediacy of silole 1 in its formation.

Reported in the Experimental Section are ^1H and ^{13}C NMR spectroscopic and mass spectrometric data that

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(1) Thiele, J. *Chem. Ber.* **1901**, *34*, 68.
(2) Gordon, M. S.; Boudjouk, P.; Anwari, F. *J. Am. Chem. Soc.* **1983**, *105*, 4972.
(3) Damewood, J. R., Jr. *J. Org. Chem.* **1986**, *51*, 5028.
(4) Colomer, E.; Corriu, R. J. P.; Lheureux, M. *Chem. Rev.* **1990**, *90*, 265.
(5) Barton, T. J.; Burns, G. T. *J. Organomet. Chem.* **1979**, *179*, C17.
(6) Benkeser, R. A.; Grossman, R. F.; Stanton, G. M. *J. Am. Chem. Soc.* **1962**, *84*, 4723. Benkeser, R. A.; Nagai, Y.; Noe, J. L.; Cunico, R. F.; Gund, P. H. *Ibid.* **1964**, *86*, 2446.
(7) Laporterie, A.; Mazerolles, P.; Dubac, J.; Iloughmane, H. *J. Organomet. Chem.* **1981**, *206*, C25.
(8) Burns, G. T.; Barton, T. J. *J. Organomet. Chem.* **1981**, *209*, C25.
(9) Laporterie, A.; Dubac, J.; Mazerolles, P.; Iloughmane, H. *J. Organomet. Chem.* **1981**, *216*, 321.
(10) Dubac, J.; Laporterie, A.; Manuel, G. *Chem. Rev.* **1990**, *90*, 215.
(11) Gaspar, P. P.; Hwang, R.-J.; Eckelman, W. C. *J. Chem. Soc., Chem. Commun.* **1974**, 242.
(12) Gaspar, P. P.; Chen, Y.-S.; Helfer, A. P.; Konieczny, S.; Ma, E. C.-L.; Mo, S.-H. *J. Am. Chem. Soc.* **1981**, *103*, 7344.
(13) Chen, Y.-S. Unpublished results.
(14) Boo, B. H. The Chemistry of Silylsilylenes: Generation and Reactions of Trimethylsilylsilylene and Silylsilylene. Doctoral dissertation, Washington University, St. Louis, MO, Dec 1984.

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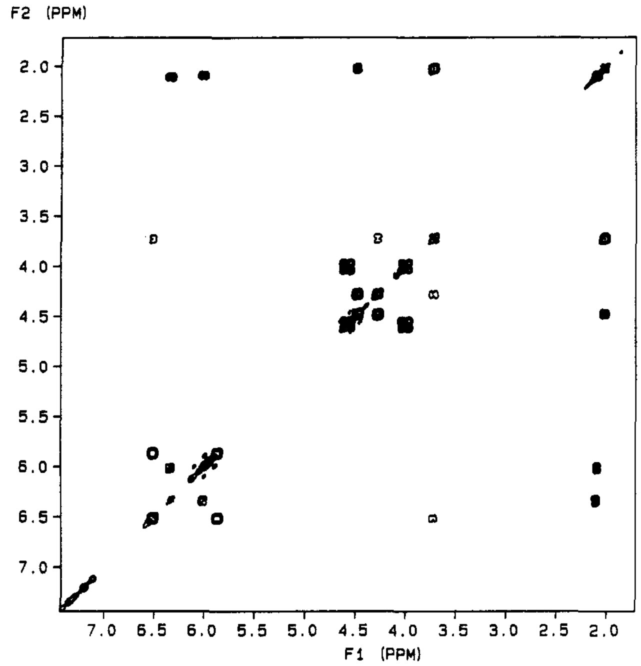
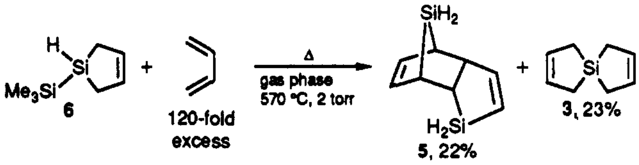


Figure 1. COSY 2D ^1H NMR spectrum of the silole dimer 3,8-disila-3a,4,7,7a-tetrahydro-4,7-methano-1*H*-indene (5).

Scheme III



characterize the silole dimer 5. The NMR data include the results of decoupling and 2D (COSY) experiments.

These data can be summarized briefly: (1) The decoupled and fully coupled ^{13}C NMR spectra indicate the presence of eight nonequivalent carbon atoms, four sp^2 and four sp^3, each of which carries one hydrogen. (2) All the resonances in the ^1H NMR spectrum are resolved. From the 1D ^1H NMR spectra, coupling constants could be obtained for pairs of protons at Si_3, Si_8, Si_3 and C_{3a}, the other proton at Si_3 and C_{7a}, C_1 and C_2, C_1 and C_{7a}, C_{3a} and C_{7a}, C_4 and C_5, C_5 and C_6, and C_6 and C_7. These spin–spin couplings were confirmed by a 2D COSY spectrum (Figure 1) and by the use of 1D decoupling experiments. (3) The mass spectra indicate a correct molecular weight and correct elementary composition for the parent ion and a prominent fragment at half the parent mass.

The NMR data do not guarantee the stereochemistry at the 3a- and 7a-positions of 5 shown in Scheme II, but the similarity of the ^1H NMR spectra of 5 and those of other reported silole dimers[5,7–9] lends confidence to the assignment.

That 1-silacyclopent-3-en-1-ylidene (2) is a common intermediate in the formation of silole dimer 5 and spirosilanonadiene (3) was suggested by an experiment in which silylene 2 was generated in the gas phase in the presence of a large excess of butadiene. As shown in Scheme III, when a mixture of trimethylsilylsilacyclopentene 6 and butadiene was subjected to flow pyrolysis, the yield of the silole dimer 5 decreased to 22% from the 55% yield obtained in the absence of butadiene, and spirosilanonadiene (3) was obtained in 23% yield.

Since silole dimer 5 contains two SiC_4 units, clearly both rearrangement and dimerization steps must occur for conversion of silylene 2 to silole dimer 5. The finding that formation of silole dimer 5 is not totally suppressed when its precursor, silacyclopentenylidene (2), is generated in the presence of a large excess of an efficient silylene trapping agent, butadiene, suggests that a unimolecular reaction of silacyclopentenylidene (2) rather than its dimerization plays a key role in the conversion of 2 to silole 1.

We therefore dismiss the possibility that silacyclopentenylidene dimerization followed by rearrangement is the mechanism for the formation of silole dimer 5. Instead, we favor the rearrangement of silacyclopentenylidene (2) to silole 1, *followed* by dimerization of 1 as the mechanism for the formation of silole dimer 5.

This interpretation is supported by the observation that the pyrolysate from (trimethylsilyl)silacyclopentene (6) and methoxy(trimethylsilyl)silacyclopentene (4) condensed just downstream from the hot zone in a trap cooled with liquid nitrogen can be readily volatilized and recondensed in a vacuum line. Upon standing at room temperature for a few minutes, however, the pyrolysate becomes significantly less volatile. This can be understood if the initially condensed pyrolysate contains monomeric silole 1 that dimerizes over a time scale of minutes. Laporterie and coworkers observed that the dimerization of dimethylsilole, initially 1% in CCl_4, was complete in 2 h at room temperature.[9]

Given the successful trapping by Barton and Burns of 1-methylsilole,[5] it was disappointing to us that attempts to trap monomeric silole 1 by cycloaddition to perfluoro-2-butyne and maleic anhydride failed. These experiments were carried out by placing the trapping agent (perfluorobutyne or maleic anhydride) in the trap, directly below the hot zone, in which the pyrolysate from neat 1-methoxy-1-(trimethylsilyl)-1-silacyclopent-3-ene (4) was condensed in a liquid nitrogen bath. The trap was warmed to room temperature and kept overnight. Following trap-to-trap distillation the less volatile fraction was found to contain the silole dimer 5, but no other cyloaddition product, while the more volatile fraction was found to contain the $MeOSiMe_3$ coproduct but no silole adduct.

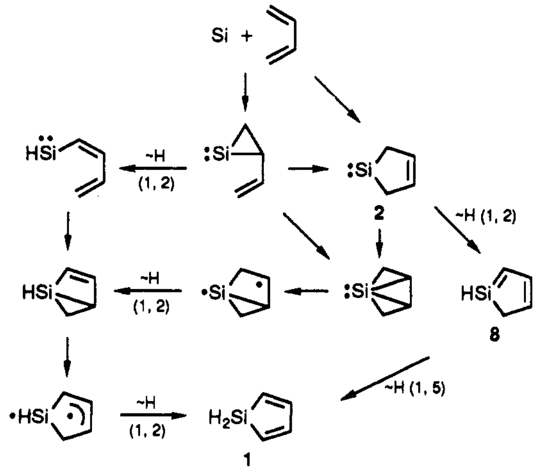
The failure to trap monomeric silole 1 with perfluoro-2-butyne or maleic anhydride may point to a sluggish reactivity for 1 in cycloaddition reactions other than dimerization. This would explain the detection of ^{31}Si-silole ^{31}Si-1 by radio gas chromatography following the reaction of high-energy silicon atoms recoiling from the $^{31}P(n,p)^{31}Si$ nuclear transformation in mixtures of phosphine PH_3 and butadiene.[11]

The formation of monomeric silole ^{31}Si-1 can be explained by addition of a ^{31}Si atom to a butadiene molecule and rearrangement of the resulting adduct to silole 1. In such a hot-atom experiment the maximum mole fraction of monomeric silole 1 would not exceed 10^{-14} (i.e. ca. 10^6 silole molecules in a reaction mixture containing ca. 10^{20} molecules). If monomeric silole 1 is as lethargic in its nongeminate cycloaddition reactions as is indicated by our unsuccessful trapping experiments with $CF_3C{\equiv}CCF_3$ and maleic anhydride, then its survival in the presence of a large mole fraction of butadiene is plausible.

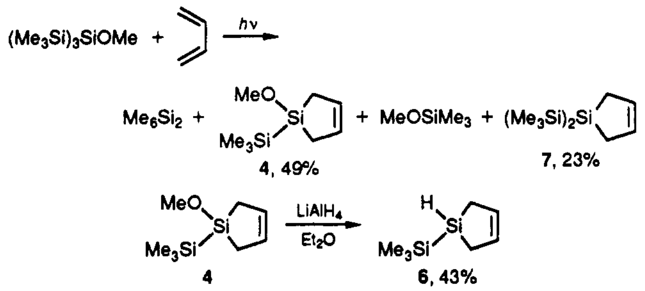
While the intermediacy of silacyclopentenylidene (2) in the recoil experiments was indicated by the formation of silaspirononadiene (3), it must be pointed out that the gas-phase formation of silole 1 from addition of a high-energy silicon atom to butadiene could follow other pathways. Several are shown in Scheme IV.

Of the species shown in Scheme IV, only silole 1 is expected to have a chemical lifetime sufficiently long for detection in a hot-atom experiment.

Scheme IV



Scheme V



Finally, while some reactions of 1-methoxy-1-(trimethylsilyl)-1-silacyclopent-3-ene (4) have been reported[7] and 1-(trimethylsilyl)-1-silacyclopent-3-ene (6) has been characterized as an addition product from (trimethylsilyl)silylene (Me_3SiSiH:) and butadiene,[15] their synthesis has not been reported, nor has that of their ultimate precursor in Scheme V, methoxytris(trimethylsilyl)silane. The details of these syntheses are included in the Experimental Section.

Publication of the silole dimer 5 has been delayed for several years by the hope that more definite information could be included about the monomer 1. Further delay seems counterproductive of this goal, since dimer 5 may itself become a useful precursor for the generation of monomeric silole 1 via retrocycloaddition, when it is synthesized in quantity. Publication seems appropriate now in light of the matrix experiments of Michl and Khabashesku in which photochemical rearrangement of silacyclopentenylidene (2) to silole 1 via isosilole 8 and dimerization of silole 1 to dimer 5 have been observed.[16] We believe that the thermal rearrangement of 1-silacyclopent-3-en-1-ylidene (2) to silole 1 occurs via isosilole 8.

Experimental Section

General Data. ^{1}H NMR spectra were recorded on Hitachi Perkin-Elmer R-24B 60 MHz, JEOL JNM-FX-100 FT, and Varian XL-300 and XL-500 spectrometers. ^{13}C NMR spectra and ^{1}H COSY 2D NMR spectra were recorded on the Varian XL-300 spectrometer. All chemical shifts are reported as ppm downfield from TMS, and coupling constants are in hertz. C_6D_6 and $CDCl_3$ were used as alternate internal standards and internal lock solvents.

Combined gas chromatography–mass spectrometry was performed on a Finnegan 3200 mass spectrometer operating at an ionizing energy of 70 eV or on a Varian CH-7 mass spectrometer interfaced with a Biemann-Watson Separator to a Varian Aerograph Moduline 2700 Series gas chromatograph. High-resolution mass spectra were recorded on a VG-ZAB-SE double-focusing mass spectrometer. Mass spectra were calibrated against perfluoroalkane internal standards.

For separation of product mixtures and for yield determinations, a preparative gas chromatograph was employed that was constructed in this laboratory employing dual rhenium tungsten filaments (Code 13-002, Gow-Mac Instrument Co.) in the thermal conductivity detector and fitted with $^1/_4$ in. o.d. columns. Absolute yields were determined on the basis of the amount of unrecovered precursor using isomeric products as internal standards in order to correct for differences in chromatographic response factors.

Infrared spectra were recorded on a Perkin-Elmer Model 238B infrared spectrophotometer as neat liquids between sodium chloride plates and calibrated against the 1601.3-cm^{-1} band of polystyrene.

Ultraviolet spectra were recorded on a Carey 219 spectrophotometer using 1-cm silica cells.

Materials. 1,3-Butadiene was from Matheson Gas Products, no purity given, purified by trap-to-trap distillation. Butadiene was passed through U-traps cooled with a toluene slush bath and liquid N_2, respectively. The butadiene was condensed in the liquid N_2 trap, and heavy impurities were retained in the toluene slush trap.

Perfluoro-2-butyne was from PCR Inc., 99.5%.

Maleic anhydride was from Aldrich, 99%.

Chlorotris(trimethylsilyl)silane was synthesized by the method of Gilman and Harrell.[17]

Methoxytris(trimethylsilyl)silane was synthesized by the method of Chen.[19] A 250-mL round-bottomed flask containing 18.7 g (0.066 mol) of chlorotris(trimethylsilyl)silane in 80 mL of cyclohexane was cooled in an ice bath. To this mixture a solution of 10 mL (0.25 mol) of absolute methanol and 13.4 g (0.133 mol) of triethylamine in 40 mL of cyclohexane was added dropwise. After being stirring at room temperature overnight, the reaction mixture was filtered to remove triethylamine hydrochloride. Cyclohexane was then removed by distillation and the residue distilled under vacuum to yield 16.1 g (88%) of methoxytris(trimethylsilyl)silane, bp 68–70 °C (0.5–0.6 Torr) (lit. 63 °C [0.5 Torr]).[18] ^{1}H NMR (CCl_4, 60 MHz): δ 0.14 (s, 27 H, SiMe), 3.35 (s, 3 H, OMe).[18] IR (neat): 2950 (s), 2895 (s), 2825 (s), 1445 (m), 1400 (m), 1320 (w), 1265 (s), 1250 (s), 1185 (w), 1085 (s), 840 (s), 750 (w), 715 (m), 690 (m), 625 (m) cm^{-1}. MS *m/e* (relative intensity): 278 (M^+, 3), 263 (62), 205 (34), 189 (48), 175 (base, 100), 159 (39), 147 (18), 145 (10), 131 (51), 129 (24), 117 (44), 115 (22), 101 (12), 89 (50), 73 (93), 59 (47), 45 (35), 43 (18). UV (C_6H_{12}): λ_{max} (nm) 219 (ϵ = 7000), 245 (ϵ = 1360), 265 (ϵ = 880).

1-Methoxy-1-(trimethylsilyl)-1-silacyclopent-3-ene (4) and 1,1-bis(trimethylsilyl)-1-silacyclopent-3-ene (7) were synthesized by the method of Chen.[19] A 10-g (36 mmol) sample of methoxytris(trimethyl)silane, 600 mL of cyclohexane, and a few boiling chips, were placed in a cylindrical quartz vessel equipped with a nitrogen inlet and outlet and with a Friedrich condenser through which a 70% MeOH–30% H_2O cooling agent was circulated. The assembled apparatus was placed in a Rayonet photochemical reactor and thoroughly degassed by bubbling dry prepurified nitrogen through the reaction mixture for 2 h. When the temperature of the cooling agent reached −10 °C, 25 g (0.46 mol) of butadiene was condensed into the reaction vessel. With the nitrogen flowing through the reaction mixture at a rate of a bubble every 5 s, the low-pressure mercury lamps were turned on and the mixture was irradiated for 24 h. This procedure was repeated three times and a total of 35 g of methoxytris(trimethylsilyl)silane was subjected to photolysis, with ca. 70%

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[15] Boo, B. H.; Gaspar, P. P. *Organometallics* **1986**, *5*, 698.

[16] Khabashesku, V. N.; Balaji, V.; Boganov, S. E.; Bashkirova, S. A.; Matveichev, P. M.; Chernyshev, E. A.; Nefedov, O. M.; Michl, J. Matrix Isolation and Photochemical Interconversion of Silacyclopentadienes. Submitted for publication.

[17] Gilman, H.; Harrell, R. *J. Organomet. Chem.* **1966**, *5*, 199.

[18] Nakadaira, Y.; Kobayashi, T.; Otsuka, T.; Sakurai, H. *J. Am. Chem. Soc.* **1979**, *101*, 486.

[19] 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, 1981.

conversion. Gas chromatographic analysis of the reaction mixture indicated that 1-methoxy-1-(trimethylsilyl)-1-silacyclopent-3-ene (4) was formed in 49% yield, accompanied by a 23% yield of 1,1-bis(trimethylsilyl)-1-silacyclopent-3-ene (7), and the coproducts of silylene extrusion, hexamethyldisilane and methoxytrimethylsilane. The reaction mixtures were combined, and the solvent was removed by simple distillation. The crude product mixture was distilled under reduced pressure to yield 7.5 g of 1-methoxy-1-(trimethylsilyl)-1-silacyclopent-3-ene (4) (90% purity, 41% yield) which was further purified by preparative gas chromatography (3 ft. × 1/4 in. o.d. aluminum, 20% DC-200 on ABS Anakrom 60/80 mesh). ^{1}H NMR (C_6D_6, 60 MHz): δ 0.19 (s, 9 H, SiMe), 1.48 (bs, 4 H, CH_2), 3.26 (s, 3 H, OMe), 5.95 (s, 2 H, =CH–). IR (neat): 3050 (m), 2945 (m), 2890 (m), 2825 (m), 1625 (m), 1340 (w), 1245 (m), 1200 (w), 1095 (s), 1075 (s), 945 (w), 865 (m), 805 (m), 735 (m), 680 (m), 615 (s) cm^{-1}. MS *m/e* (relative intensity): 186 (M$^+$, 13), 171 (19), 143 (20), 117 (83), 112 (24), 73 (base, 100), 59 (66), 45 (19). 1,1-Bis(trimethylsilyl)-1-silacyclopent-3-ene (7) was isolated by preparative gas chromatography and identified from the following spectral data: ^{1}H NMR (CCl_4, 60 MHz) δ 0.15 (s, 18 H, SiMe), 1.60 (m, 4 H, CH_2), 5.87 (m, 2 H, =CH–); IR (neat) 3040 (w), 2850 (m), 2800 (m), 1620 (m), 1440 (w), 1405 (w), 1250 (s), 1100 (m), 950 (w), 835 (bs), 800 (m), 745 (w), 690 (m), 650 (m) cm^{-1}; MS *m/e* (relative intensity) 228 (M$^+$, 7), 213 (11), 174 (19), 159 (28), 155 (41), 154 (50), 139 (30), 129 (22), 127 (24), 116 (12), 115 (11), 113 (13), 95 (26), 73 (base, 100), 59 (41), 45 (42), 43 (14).

1-(Trimethylsilyl)-1-silacyclopent-3-ene (6) was synthesized by the method of Boo.[14] Into a dry, 100-mL, three-necked round-bottomed flask equipped with a reflux condenser and a pressure-equalizing dropping funnel containing 400 mg (2.2 mmol) of 1-methoxy-1-(trimethylsilyl)-1-silacyclopent-3-ene (4) in 30 mL of dry ethyl ether was placed 350 mg (9.2 mmol) of $LiAlH_4$ and 40 mL of ethyl ether. The suspension of $LiAlH_4$ was stirred for 15 min with dry N_2 gas flowing through the apparatus. Then the solution of methoxy(trimethylsilyl)silacyclopentene (4) was added dropwise over 30 min. The reaction mixture was stirred for 20 h at room temperature, and then ethyl acetate was added to destroy excess $LiAlH_4$. After filtration of the reaction mixture to remove the appreciable amount of salts formed, the filtrate was cooled with an ice–acetone bath and the solvent evaporated at reduced pressure. Final purification was by preparative gas chromatography (10 ft. × 1/4 in. o.d. glass, 20% tricresyl phosphate on ABS Ankrom 60/80 mesh), giving 143 mg (43% yield) of 6. The chromatogram indicated that 100% conversion of 4 had occurred. The ^{1}H NMR and mass spectra of 6 were identical with those reported previously for a sample obtained from the addition of Me_3SiSiH: to butadiene.[15]

Gas-Phase Pyrolyses. The pyrolyses were carried out in a vacuum flow system whose hot zone was a 10 mm i.d. × 18 cm quartz tube wrapped with ca. 22 ft. of 26-guage nichrome heating wire with an inner and outer layer of asbestos ribbon. The temperature of the hot zone was measured with an iron–constantan thermocouple placed between the outer surface of the quartz tube and the inner layer of asbestos. The flow system was throttled downstream from the hot zone with a copper disk with a 0.036 in. diameter orifice. Products were trapped ca. 12 cm from the hot zone in a U-trap immersed in liquid nitrogen. The reactants were delivered from a storage tube or from a 1-L reservoir through ball-type flow meters (Fisher and Porter Co., Crest Division). The pressure was measured just upstream from the hot zone by a calibrated thermocouple gauge. Preliminary fractionation of the products of a flow pyrolysis experiment was carried out by trap-to-trap distillation in the vacuum line to which the flow pyrolysis system was attached. Further purification was by preparative gas chromatography.

Gas-Phase Flow Pyrolysis of 1-Methoxy-1-(trimethylsilyl)-1-silacyclopent-3-ene (4). An 80-mg sample (0.46 mmol) of 1-methoxy-1-(trimethylsilyl)-1-silacyclopent-3-ene (4) was pyrolyzed over 5 min at 570 °C, 0.4 Torr, residence time 0.07 s. The orange pyrolysate was separated by trap-to-trap distillation using traps cooled by acetone–dry ice and by liquid N_2. The more volatile fraction was transferred from the liquid N_2 trap to an ampule mounted on the vacuum line. The ampule was sealed and held overnight at room temperature, and the contents were separated by preparative gas chromatography (3 ft. × 1/4 in. o.d. aluminum, 20% DC-200 on ABS Anakrom 60/80 mesh, injection port 120 °C, column 70 °C, 75 mL of He/min). The silole dimer 5 was obtained in 61% yield based on the starting material consumed (100%). ^{1}H NMR (C_6D_6, 500 MHz): δ 1.97 (ddd, 1 H, $J_{3exo,3a} = 3.3$, $J_{3endo,3a} = 2.7$, $J_{7a,3a} = 8.7$, $C_{3a}H$), 2.03 (bd, 1 H, $J_{5,4} = 6.1$, C_4H), 2.05 (bd, 1 H, $J_{6,7} = 6.9$, C_7H), 3.67 (ddd, 1 H, $J_{3a,7a} = 8.7$, $J_{3endo,7a} = 2.7$, $J_{1,7a} = 2.4$, $C_{7a}H$), 3.93 (bd, 1 H, $J_{gem} = 21$, Si_8H_{exo}), 4.20 (ddd, 1 H, $J_{gem} = 11.1$, $J_{3a,3endo} = 2.7$, $J_{7a,3endo} = 2.7$, Si_3H_{endo}), 4.40 (dd, 1 H, $J_{gem} = 11.1$, $J_{3a,3exo} = 3.3$, Si_3H_{exo}), 4.52 (bd, 1 H, $J_{gem} = 21$, Si_8H_{endo}), 5.80 (ddd, 1 H, $J_{1,2} = 10.2$, $J_{3exo,2} = 2.4$, $J_{3endo,2} = 1.2$, C_2H), 5.94 (dd, 1 H, $J_{6,5} = 6.1$, $J_{4,5} = 6.3$, C_5H), 6.27 (dd, 1 H, $J_{5,6} = 6.3$, $J_{7,6} = 6.9$, C_6H), 6.45 (dd, 1 H, $J_{2,1} = 10.2$, $J_{7a,1} = 2.4$, C_1H). ^{13}C NMR (C_6D_6, 125 MHz): δ 22.02 (d, C_{3a}), 31.26 (d, C_4), 33.69 (d, C_7), 53.73 (d, C_{7a}), 125.12 (d, C_1), 132.33 (d, C_6), 132.62 (d, C_5), 158.35 (d, C_2). MS *m/e* (relative intensity): 164 (M$^+$, 28), 163 (24), 149 (23), 137 (14), 136 (68), 135 (17), 134 (26), 133 (93), 132 (31), 131 (base, 100), 130 (15), 123 (11), 119 (22), 117 (17), 110 (16), 109 (27), 108 (20), 107 (57), 106 (44), 105 (85), 103 (13), 95 (11), 94 (16), 93 (99), 91 (11), 86 (34), 84 (11), 83 (23), 82 (100), 81 (50), 80 (35), 79 (22), 78 (18), 77 (24), 73 (29), 69 (15), 67 (50), 66 (11), 56 (18), 55 (53), 54 (32), 53 (61). Exact mass determination for $C_8H_{12}Si_2$ (M$^+$): calcd 164.047; found 164.046.

Attempted Trapping by Perfluoro-2-butyne and Maleic Anhydride of the Pyrolysis Products from 1-Methoxy-1-(trimethylsilyl)-1-silacyclopent-3-ene (4). An 80-mg (0.46 mmol) sample of 1-methoxy-1-(trimethylsilyl)-1-sila-cyclopent-3-ene (4) was passed through the hot zone as described above at 570 °C over 5 min at 0.3 Torr, residence time 0.07 s, and condensed in a U-trap containing 400 mg of perfluoro-2-butyne, cooled by liquid N_2. The trap was allowed to warm to room temperature and kept overnight. Then the contents were fractionated by trap-to-trap distillation in the vacuum line, to traps cooled by dry ice–acetone and by liquid N_2. The contents of the dry ice–acetone trap were diluted with 200 μL of C_6D_6, and the resulting solution was analyzed by ^{1}H NMR spectroscopy. Only the silole dimer 5 was detected. The liquid N_2 trap was found to contain perfluoro-2-butyne and methoxytrimethylsilane. When maleic anhydride was employed as a trapping agent, using the same procedure, no silole dimer 5 was obtained nor was any product attributable to reaction of monomeric silole 1 with maleic anhydride.

Gas-Phase Flow Pyrolysis of 1-(Trimethylsilyl)-1-silacyclopent-3-ene (6). A 50-mg (0.32 mmol) sample of 1-(trimethylsilyl)-1-silacyclopent-3-ene (6) was subjected to flow pyrolysis over 15 min at 500 °C, 0.3 Torr, residence time 0.3 s. Immediately afterward the pyrolysate condensed in the U-trap immersed in liquid N_2 was subjected to fractionation by trap-to-trap distillation employing two traps cooled by dry ice–2-propanol and liquid N_2, respectively. The less volatile fraction stopped by dry ice–2-propanol contained 15% recovered 1-(trimethylsilyl)-1-silacyclopent-3-ene (6), identified by gas chromatography and ^{1}H NMR spectroscopy. The more volatile fraction stopped by liquid N_2 was transferred again by trap-to-trap distillation to a tube which was sealed and maintained at room temperature for several hours and finally opened and analyzed by gas chromatography. The products were trimethylsilane, 86% yield, and silole dimer 5, 55% yield. When the pyrolysis temperature was reduced to 460 °C, only 47% of the 1-(trimethylsilyl)-1-silacyclopent-3-ene (6) was converted, and the products obtained were trimethylsilane, in 83% yield, and silole dimer 5, in 57% yield.

Gas-Phase Flow Pyrolysis of 1-(Trimethylsilyl)-1-silacyclopent-3-ene (6) in the Presence of 1,3-Butadiene. A mixture of 30 mg (0.19 mmol) of 1-(trimethylsilyl)-1-silacyclopent-3-ene (6) and 1.23 g (23 mmol, 120-fold excess) of 1,3-butadiene was passed through the hot zone at 570 °C, 2 Torr over a 5.7-min period, residence time 0.008 s. Immediately after the flow pyrolysis was completed, the pyrolysate condensed in a U-trap with the aid of liquid N_2 was fractionated by trap-to-trap distillation as described above. The fraction stopped by dry ice–2-propanol contained the 10% unreacted starting 1-(trimethylsilyl)-1-silacyclopent-3-ene (6). The more volatile fraction stopped by liquid N_2 was kept in a 1-L reservoir for 1 day and then analyzed by gas chromatography. In addition to 1,3-butadiene and trimethylsilane the products datected were 5-silaspiro-

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[4.4]nona-2,7-diene (**3**), obtained in 23% yield, and silole dimer **5**, obtained in 22% yield.

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Supplementary Material Available: Figures of original NMR, infrared, ultraviolet, and mass spectra for methoxytris(trimethylsilyl)silane, NMR, infrared, and mass spectra for 1-methoxy-1-(trimethylsilyl)-1-silacyclopent-3-ene and 1,1-bis(trimethylsilyl)-1-silacyclopent-3-ene, and NMR and mass spectra for the silole dimer 3,8-disila-3a,4,7,7a-tetrahydro-4,7-methano-1*H*-indene and a table of gas chromatographic mass spectral data for the silole dimer (24 pages). Ordering information is given on any current masthead page.

Insertion of Acetylenes into *trans,trans*-$\mathrm{WH(CO)_2(NO)(PMe_3)_2}$

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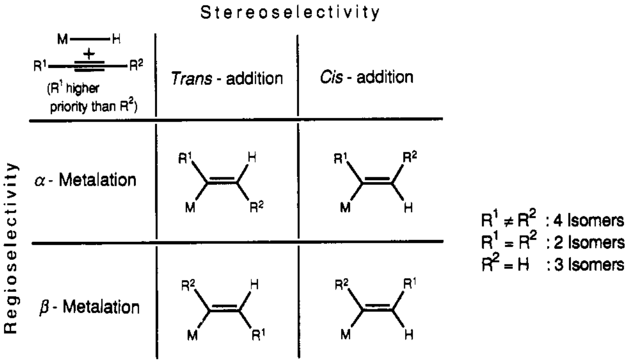
The insertion reactions of *trans,trans*-$\mathrm{WH(CO)_2(NO)(PMe_3)_2}$ with activated acetylenes of the type $\mathrm{RC{\equiv}CCO_2R'}$ (R = H, Me, Ph, $\mathrm{R'O_2C}$) were investigated. In all cases selective α-metalation occurs, affording tungsten–vinyl compounds, and except for R = Ph, selective trans insertion is observed as well. Thus, from the reaction of $\mathrm{RC{\equiv}CCO_2Me}$ (R = H, Me) the products W[*Z*-$\mathrm{C(CO_2Me){=}CH(R)](CO)_2(NO)(PMe_3)_2}$, where R = H (**1**) and Me (**2**), were isolated in high yield. The reaction with $\mathrm{PhC{\equiv}CCO_2Et}$ initially yields the trans- and cis-insertion products W[*Z*-$\mathrm{C(CO_2Me){=}CH(Ph)](CO)_2(NO)(PMe_3)_2}$ (**3a**) and W[*E*-$\mathrm{C(CO_2Me){=}CH(R)](CO)_2(NO)(PMe_3)_2}$ (**3b**) in a 85:15 ratio. Compound **3a** slowly and reversibly loses CO affording the four-membered metallacycle $\overline{\mathrm{W\{}Z\mathrm{\text{-}C[C(O}}\mathrm{)OEt]{=}CH(Ph)\}(CO)(NO)(PMe_3)_2}$ (**3c**). Heating equilibrium solutions of **3a** and **3c** and CO results in complete, irreversible conversion of these compounds to **3b**. Insertion reactions of $\mathrm{RO_2CC{\equiv}CCO_2R}$ initially afford W[*Z*-$\mathrm{C(CO_2R){=}CH(CO_2R)](CO)_2(NO)(PMe_3)_2}$, where R = Me (**4a**) and tBu (**5a**). These compounds have half-lives of ca. 10 min at room temperature, as irreversible CO loss produces the isolable five-membered-ring compounds $\overline{\mathrm{W\{}Z\mathrm{\text{-}C(CO_2R){=}CH[C(O}}\mathrm{)OR]\}(CO)(NO)(PMe_3)_2}$ (**4b**, **5b**). Remarkably enough, these compounds are also only metastable, since a $\mathrm{PMe_3}$-catalyzed isomerization occurs in which the NO and CO ligands switch positions, affording **4c** and **5c**, respectively. The X-ray structures of three complexes were determined: **3c**, orthorhombic, space group $P2_12_12_1$, a = 15.985 (5) Å, b = 16.000 (4) Å, c = 9.167 (3) Å, Z = 4; **5b**, monoclinic, space group $P2_1/c$, a = 12.282 (5) Å, b = 11.238 (4) Å, c = 19.463 (8) Å, β = 98.87 (3)°; **5c**, monoclinic, space group $P2_1/c$, a = 10.537 (4) Å, b = 12.319 (4) Å, c = 21.606 (8) Å, β = 95.20 (3)°. Comparison of structures **5b** and **5c** provides direct insight into the difference in electronic effects between CO and NO ligands.

Introduction

The insertion of activated acetylenes into metal–hydride bonds represents a general route to metal–vinyl complexes.[1] Statistically, the insertion of asymmetrically substituted acetylenes can give rise to four different isomers (Scheme I).

Usually, however, these reactions produce only one stereoisomer, and much effort has gone into the elucidation of the factors influencing the regio- and stereoselectivity. Several insertion reactions, which were initially thought to proceed in a cis fashion,[2,3] are now being recognized as trans insertions, followed by a cis/trans isomerization of the kinetic product to a more stable thermodynamic product.[4-6] For asymmetrically substituted acetylenes the regioselective choice between α- and β-metalation is less well understood. Reaction of the monosubstituted acetylenes $\mathrm{HC{\equiv}CCO_2R}$, $\mathrm{HC{\equiv}CCF_3}$, or $\mathrm{HC{\equiv}CCN}$ with $\mathrm{MnH(CO)_5}$,[7] $\mathrm{ReH(CO)_5}$,[8] $\mathrm{Cp_2ReH}$,[9] $\mathrm{[Os(\eta^6\text{-}C_6H_6)(PiPr_3)\text{-}}$

Scheme I



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[1] Otsuka, S.; Nakamura, A. *Adv. Organomet. Chem.* **1976,** *14,* 245. Bianchini, C.; Meli, A.; Perruzini, M.; Vizza, F.; Frediani, P. *Organometallics* **1990,** *9,* 1146 and references cited therein.

[2] Dubeck, M.; Schell, R. A. *Inorg. Chem.* **1964,** *3,* 1757.

[3] Nakamura, A.; Otsuka, S. *J. Am. Chem. Soc.* **1972,** *94,* 1886.

[4] Herberich, G. E.; Hessner, B.; Okuda, J. *J. Organomet. Chem.* **1983,** *254,* 317.

[5] Herberich, G. E.; Barlage, W. *Organometallics* **1987,** *6,* 1924.

[6] Herberich, G. E.; Mayer, H. *J. Organomet. Chem.* **1988,** *347,* 93.

[7] Booth, B. L.; Hargreaves, R. G. *J. Chem. Soc. A* **1969,** 2766.

[8] Wilford, J. B.; Stone, F. G. A. *Inorg. Chem.* **1965,** 93. Harbourne, D. A.; Stone, F. G. A. *J. Chem. Soc. A* **1968,** 1765.

0276-7333/92/2311-0563$03.00/0