Silicon–Carbon Unsaturated Compounds. 19. Nickel-Catalyzed Reactions of Silacyclopropenes and (Phenylethynyl)polysilanes with Phenyl(trimethylsilyl)acetylene and Molecular Structure of 1,4,4-Trimethyl-3,6-diphenyl-1,2,5-tris(trimethylsilyl)-1,4-disilacyclohexa-2,5-diene

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The nickel-catalyzed reactions of silacyclopropenes and (phenylethynyl)polysilanes with phenyl(trimethylsilyl)acetylene have been studied. Both 2-(phenylethynyl)-2-(trimethylsilyl)hexamethyltrisilane (1) and 3-phenyl-1,1,2-tris(trimethylsilyl)-1-silacyclopropene (2) reacted with phenyl(trimethylsilyl)acetylene in the presence of a catalytic amount of dichlorobis(triethylphosphine)nickel(II) to give 3-phenyl-4-[phenyl(trimethylsilyl)methylene]-1,1,2-tris(trimethylsilyl)-1-silacyclobut-2-ene and 1,4,4-trimethyl-3,6-diphenyl-1,2,5-tris(trimethylsilyl)-1,4-disilacyclohexa-2,5-diene (4), respectively. Similar reaction of 1-methyl-3-phenyl-1,2-bis(trimethylsilyl)-1-silacyclopropene (6) with phenyl(trimethylsilyl)acetylene afforded 1-methyl-3,4-diphenyl-1,2,5-tris(trimethylsilyl)silole (7), 1,1,4,4-tetramethyl-3-phenyl-5-[phenyl(trimethylsilyl)methylene]-2-(trimethylsilyl)-1,4-disilacyclopent-2-ene (8) and its isomer (9), and 1-methyl-2-phenyl-4-[phenyl(trimethylsilyl)methylene]-1,2-bis(trimethylsilyl)-1-silacyclobut-2-ene (10), while 2-(phenylethynyl)heptamethyltrisilane (12) yielded 8, 9, and 10, but not silole 7. The reaction of 1,1-dimethyl-3-phenyl-2-(trimethylsilyl)-1-silacyclopropene with a catalytic amount of a nickel catalyst afforded 1,1,4,4-tetramethyl-3,6-diphenyl-2,4-bis(trimethylsilyl)-1,4-disilacyclohexa-2,5-diene, but (phenylethynyl)pentamethyldisilane produced 1,1,3,3-tetramethyl-2,4-[phenyl(trimethylsilyl)methylene]-1,3-disilacyclobutane as the sole product. The reactions of (phenylethynyl)pentamethyldisilane and 1-phenyl-1-(phenylethynyl)tetramethyldisilane with phenyl(trimethylsilyl)acetylene in the presence of the nickel catalyst are also described. The crystal structure of 4 has been determined. Compound 4 crystallizes in the monoclinic space group $P2_1/c$ with cell dimensions $a = 10.500$ (1) Å, $b = 18.073$ (3) Å, $c = 18.156$ (4) Å, $\beta = 106.21$ (1)°, $V = 3308.6$ (9) Å^3, and $D_{calcd} = 1.050$ ($Z = 4$) M g^{-3}.

Introduction

In 1967, Gusel'nikov and Flowers presented evidence that 1,1-dimethylsilene could exist in the thermolysis of 1,1-dimethyl-1-silacyclobutane.[2] Since that time, numerous papers on the chemistry of silenes have been published.[3–5] In spite of these studies, no interest has been shown in the transition-metal-catalyzed formation of the silenes.[6] As part of a systematic study on the chemistry of the unsaturated silicon compounds, we have now investigated the metal-catalyzed reaction of organopolysilanes in the hope of obtaining a silene–transition-metal complex.

We report here some reactions of silacyclopropenes and (phenylethynyl)polysilanes with phenyl(trimethylsilyl)acetylene in the presence of a catalytic amount of dichlorobis(triethylphosphine)nickel(II). These reactions afford the products which can best be explained by assuming the transient formation of nickel-containing reactive intermediates such as 1-silapropadiene–nickel complexes.[8] We also describe the results of an X-ray crystallographic study of 1,4,4-trimethyl-3,6-diphenyl-1,2,5-tris(trimethylsilyl)-1,4-disilacyclohexa-2,5-diene.

Scheme I
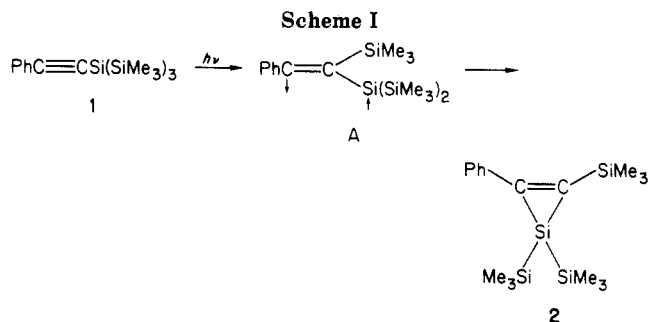
Results and Discussion

Irradiation of a hexane solution of 2-(phenylethynyl)-2-(trimethylsilyl)hexamethyltrisilane (1) with a low-pressure mercury lamp bearing a Vycor filter at room temperature afforded 3-phenyl-1,1,2-tris(trimethylsilyl)-1-silacyclopropene (2) in 36% yield, in addition to 5% yield of phenyl(trimethylsilyl)acetylene. We have proposed the mechanism involving a singlet diradical intermediate for the photochemical formation of the silacyclopropenes from (phenylethynyl)disilanes.[9] It seems likely that the present silacyclopropene 2 would also be formed from the singlet diradical intermediate A (Scheme I). Compound 2 was less sensitive to air than the usual silacyclopropenes reported to date, but it still had to be handled under an inert atmosphere.

(1) (a) Kyoto University. (b) Osaka City University.
(2) Gusel'nikov, L. E.; Flowers, M. C. *Chem. Commun.* 1967, 864.
(3) Gusel'nikov, L. E.; Nametkin, N. S. *Chem. Rev.* 1979, 79, 529.
(4) Barton, T. J. *Pure Appl. Chem.* 1980, 52, 615.
(5) Ishikawa, M.; Kumada, M. *Adv. Organomet. Chem.* 1981, 19, 51.
(6) It has been reported that the reaction of transition-metal halides with silylmethyl Grignard reagents gives products which may be explained in terms of a silaethene intermediate (see ref 7).
(7) (a) Tamao, K.; Yoshida, J.; Okazaki, S.; Kumada, M. *Isr. J. Chem.* 1967/1977, 15, 265. (b) Pannell, K. H. *J. Organomet. Chem.* 1970, 21, P17. (c) Cundy, C. S.; Lappert, M. F.; Pearce, R. *Ibid.* 1973, 59, 161.
(8) Preliminary results were communicated earlier: Ishikawa, M.; Matsuzawa, S.; Hirotsuo, K.; Kamitori, S.; Higuchi, T. *Organometallics* 1984, 3, 1930.
(9) Ishikawa, M.; Sugisawa, H.; Fuchikami, T.; Kumada, M.; Yamabe, T.; Kawakami, H.; Fukui, K.; Ueki, Y.; Shizuka, H. *J. Am. Chem. Soc.* 1982, 104, 2872.
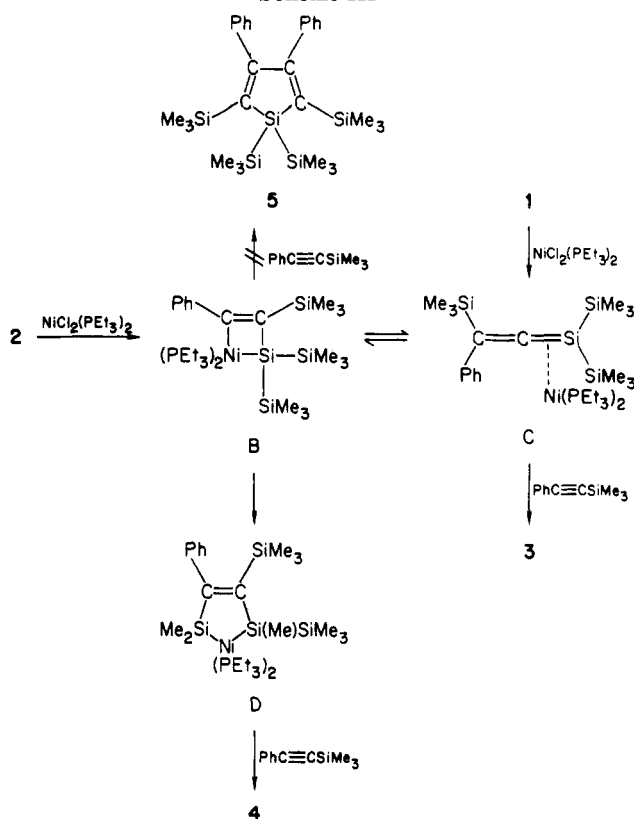
Scheme II
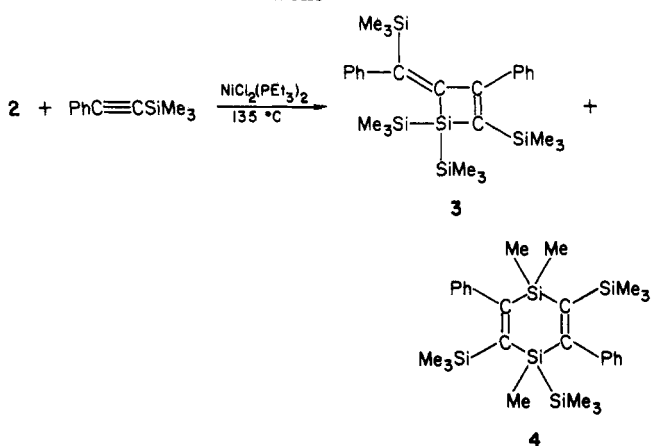
When a mixture of 2 and phenyl(trimethylsilyl)acetylene was heated for 15 h at 135 °C in the presence of a catalytic amount of dichlorobis(triethylphosphine)nickel(II) in a sealed glass tube, two crystalline products identified as 3-phenyl-4-[phenyl(trimethylsilyl)methylene]-1,1,2-tris-(trimethylsilyl)-1-silacyclobut-2-ene (3) and 1,4,4-tri-methyl-3,6-diphenyl-1,2,5-tris(trimethylsilyl)-1,4-disila-cyclohexa-2,5-diene (4) were obtained in the ratio of 1:1.4 in 87% combined yield (Scheme II). Products 3 and 4 could be readily isolated by medium-pressure liquid chromatography.

The structure of 3 was confirmed by IR, mass, and ^{1}H and ^{13}C NMR spectroscopic analysis and an X-ray diffraction study as reported previously.[8] All spectral data obtained for 4 were wholly consistent with the proposed structure (see Experimental Section). The structure of 4 was also determined by an X-ray diffraction study as discussed below.
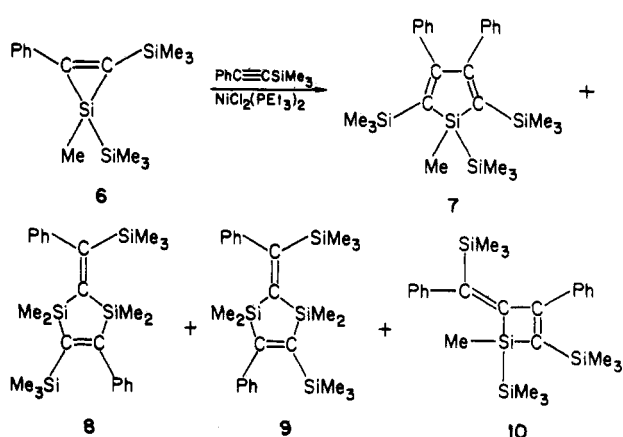
Similar nickel-catalyzed reactions of 1,1-dimethyl-3-phenyl-2-(trimethylsilyl)-, 1-methyl-1,3-diphenyl-2-(tri-methylsilyl)-, and 1,1,3-triphenyl-2-(trimethylsilyl)-1-sila-cyclopropene with phenyl(trimethylsilyl)acetylene always afforded 3,4-diphenyl-2,5-bis(trimethylsilyl)silole deriva-tives in high yields. The present reaction, however, pro-duced no silole derivative such as 3,4-diphenyl-1,1,2,5-tetrakis(trimethylsilyl)silole (5). We proposed a nickela-silacyclobutene as a key intermediate for the formation of the siloles.[10] The formation of such a metal-asilacyclobutene intermediate has also been proposed in the transition-metal-catalyzed reaction of silacyclopropenes with an acetylene.[11,12] In the present case, however, two bulky trimethylsilyl groups on the ring silicon atom in the nickelasilacyclobutene intermediate B presumably prevent the formation of silole 5. Therefore, it seems likely that the intermediate B would isomerize to give another type of intermediates such as silapropadiene–nickel complex C and nickeladisilacyclopentene D, which could serve to explain for the formation of 3 and 4 (Scheme III).

Interestingly, the reaction of 1 with phenyl(trimethyl-silyl)acetylene in the presence of a catalytic amount of NiCl$_2$(PEt$_3$)$_2$ in a degassed glass tube at 200 °C for 20 h gave 3 and 4 in 19 and 58% yield, respectively. The fact that the reactions of 1 and 2 with phenyl(trimethylsilyl)-acetylene in the presence of the nickel catalyst afford the

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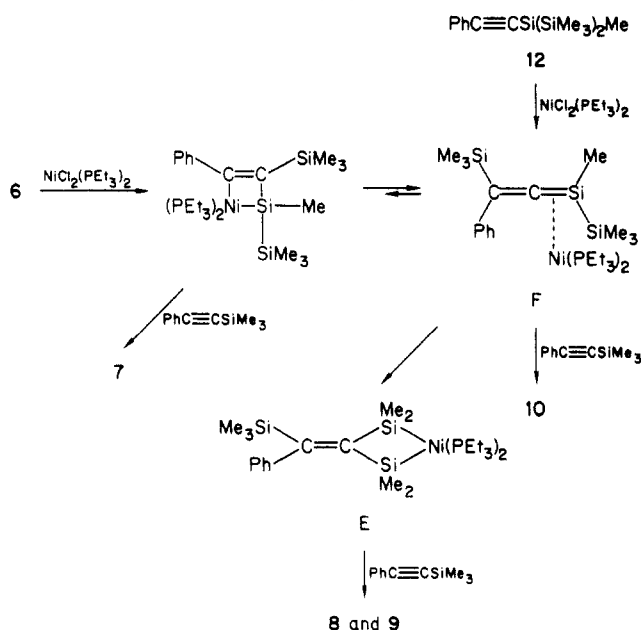
Scheme III

Scheme IV

same products 3 and 4 indicates that both reactions involve the common intermediates. The production of the in-termediate C from 1 may be understood by the nickel-catalyzed isomerization of 1 involving a 1,3-shift of a tri-methylsilyl group. Similar reaction of 1-methyl-3-phenyl-1,2-bis(trimethylsilyl)-1-silacyclopropene (6) with phenyl(trimethylsilyl)acetylene in the presence of NiCl$_2$-(PEt$_3$)$_2$ in a degassed sealed tube at 135 °C afforded 1-methyl-3,4-diphenyl-1,2,5-tris(trimethylsilyl)silole (7) in 41% yield.[10] In this reaction, 1,1,4,4-tetramethyl-3-phenyl-5-[phenyl(trimethylsilyl)methylene]-2-trimethyl-silyl-1,4-disilacyclopent-2-ene (8) and its isomer (9) were obtained in 36% combined yield, in addition to 3% yield of 1-methyl-2-phenyl-4-[phenyl(trimethylsilyl)-methylene]-1,2-bis(trimethylsilyl)-1-silacyclobut-2-ene (10) (Scheme IV). No 1,1,4,4-tetramethyl-3,6-diphenyl-2,5-bis(trimethylsilyl)-1,4-disilacyclohexa-2,5-diene (11), analogous to compound 4 was detected by spectroscopic analysis. Compound 7 and a mixture of 8 and 9 could readily be isolated by medium-pressure liquid chroma-tography. All attempts to separate 8 from 9 by using either

Scheme V

Scheme VI

HPLC or VPC were unsuccessful. However, fractional recrystallization of the mixture from ethanol afforded 8 and 9 in pure form. The structures of 8, 9, and 10 were confirmed by mass, IR, and ^{1}H and ^{13}C NMR spectroscopic analysis.

The fact that the cleavage reaction of a 1:1 mixture of 8 and 9 with hydrogen chloride in benzene at 0 °C, followed by methylation of the resulting products gave 1-phenyl-1-(trimethylsilyl)ethene[13] and (Z)-1-phenyl-1,2-bis(trimethylsilyl)ethene[14] in 70 and 31% yields, was wholly consistent with the proposed structure.

When a mixture of 2-(phenylethynyl)heptamethyltrisilane (12) and phenyl(trimethylsilyl)acetylene in the presence of $NiCl_2(PEt_3)_2$ was heated in a sealed glass tube at 200 °C for 20 h, products 8, 9, and 10 were formed in 23, 23, and 33% yields, respectively. Silole 7, however, could not be detected by either VPC or spectroscopic analysis. The formation of 8 and 9 can be best explained by assuming the production of a nickeladisilacyclobutane (E), followed by the reaction with phenyl(trimethylsilyl)acetylene, while product 10 corresponds to the addition of silapropadiene–nickel complex F which would be formed from the reaction of 12 with the nickel catalyst, to phenyl(trimethylsilyl)acetylene (Scheme V). Here again, common intermediates E and F seem to be involved in both nickel-catalyzed reactions of 6 and 12 in the presence of phenyl(trimethylsilyl)acetylene.

As reported previously, the nickel-catalyzed reaction of 1,1-dimethyl-3-phenyl-2-(trimethylsilyl)-1-silacyclopropene (13) with phenyl(trimethylsilyl)acetylene at 135 °C gave 1,1-dimethyl-3,4-diphenyl-2,5-bis(trimethylsilyl)silole (14) in high yield.[10] The reaction of (phenylethynyl)pentamethyldisilane (15) with phenyl(trimethylsilyl)acetylene in the presence of a catalytic amount of $NiCl_2(PEt_3)_2$ at 200 °C afforded two isomers of 1,1,4,4-tetramethyl-5-(methylphenylmethylene)-3-phenyl-2-(trimethylsilyl)-1,4-disilacyclopent-2-ene (16 and 17), and 1,1,3,3-tetramethyl-2,4-bis(methylphenylmethylene)-1,3-disilacyclobutane (18) in 23, 23, and 15% yields, in addition to 32% yield of silole 14. Products 14, 18, and a mixture of 16 and 17 were readily separated by medium-pressure liquid
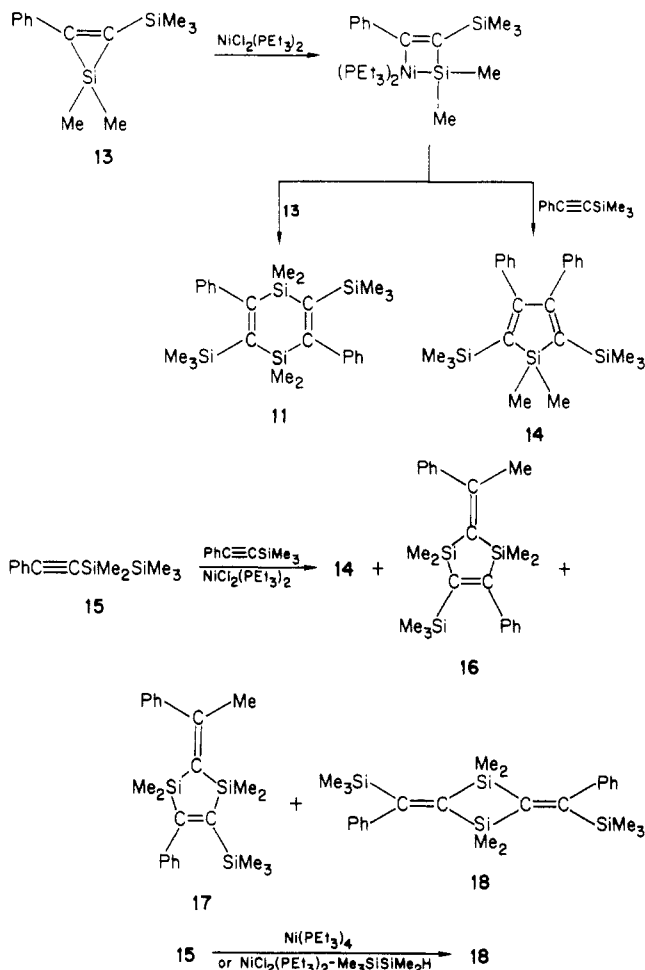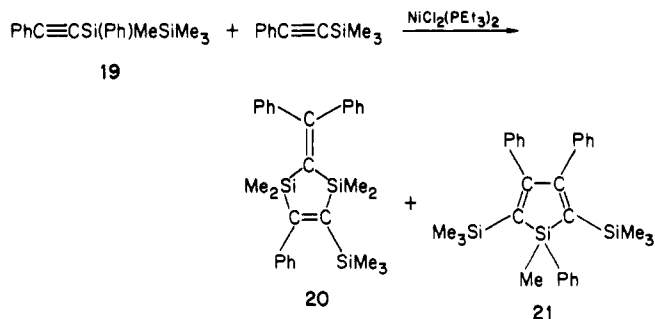
chromatography. Unfortunately, 16 could not be separated from 17 in pure form by either VPC or fractional recrystallization. In the absence of phenyl(trimethylsilyl)-acetylene, 13 yielded a dimer, 1,4-disilacyclohexa-2,5-diene (11), in 45% yield (Scheme VI). In contrast to 13, compound 15 did not react with a catalytic amount of $NiCl_2(PEt_3)_2$ at 200 °C for 20 h in the absence of phenyl(trimethylsilyl)acetylene. The starting 15 was recovered unchanged. Under the same conditions, however, 15 did react with a nickel(0) catalyst to give a dimer. Thus, heating 15 with a catalytic amount of tetrakis(triethylphosphine)nickel(0) in a sealed glass tube gave a dimer, 1,3-disilacyclobutane (18), in 64% yield, but not 1,4-disilacyclohexa-2,5-diene (11). Similarly, heating 15 with a catalytic amount of $NiCl_2(PEt_3)_2$–$Me_3SiSiMe_2H$ at 180 °C for 20 h afforded 18 in 78% yield, as the sole product. The results indicate that the active catalyst in the present system is not a nickel(II) compound but a nickel(0) species. Careful analysis of the reaction product showed that no stereoisomer for 18 was detected by either VPC or spectroscopic analysis.

The formation of 18 may be understood formally by head-to-tail dimerization of 1,1-dimethyl-3-phenyl-3-(trimethylsilyl)-1-silapropadiene produced by the nickel-catalyzed isomerization of 15, via a 1,3-silyl shift.

The nickel-catalyzed reaction of 1-phenyl-1-(phenylethynyl)tetramethyldisilane (19) with phenyltrimethylsilyl)acetylene for 20 h at 200 °C gave 1,1,4,4-tetramethyl-3-phenyl-5-(diphenylmethylene)-2-(trimethylsilyl)-1,4-disilacyclopent-2-ene (20) and 1-methyl-1,3,4-triphenyl-2,5-bis(trimethylsilyl)silole (21) in 52 and 10% yields, respectively. The structure of 20 was confirmed by spectroscopic method and also by chemical reaction.

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PhC≡CSi(Ph)MeSiMe₃ + PhC≡CSiMe₃ →[NiCl₂(PEt₃)₂]→

19

Ph\C/Ph
‖
C
Me₂Si   SiMe₂
   \   /
    C=C
   /   \
 Ph   SiMe₃

20

+

Ph   Ph
 \   /
  C=C
 /   \
Me₃Si—Si—C–SiMe₃
     |
    Me Ph

21

Figure 1. Molecular structure of 1,4,4-trimethyl-3,6-diphenyl-1,2,5-tris(trimethylsilyl)-1,4-disilacyclohexa-2,5-diene (4).

The fact that cleavage reaction of **20** with dry hydrogen chloride in benzene at room temperature produces 1,1-diphenylethene and phenyltris(trimethylsilyl)ethene[15] in 74 and 49% yields, respectively, indicates that a 1,3-phenyl shift from an internal silicon atom to alkynyl carbon bearing a phenyl group in the starting compound **19** would be involved. Again, we propose the intermediacy of the nickeladisilacyclobutane analogous to E, as a key intermediate for the formation of **20**.

The structure of **4** was verified by an X-ray diffraction study. The crystals obtained by recrystallization from ethanol are monoclinic of space group $P2_1/c$ with cell dimensions a = 10.500 (1) Å, b = 18.073 (3) Å, c = 18.156 (4) Å, and β = 106.21 (1)°, V = 3308.6 (9) Å³, and D_{calcd} = 1.050 (Z = 4). A total of 3823 symmetry-independent reflections were collected on a Philips PW1100 automatic four-circle diffractometer with graphite-monochromatized Mo radiation within a 2θ range of 3–42°. The ω scanning mode was used with scan speed 2° min⁻¹. Intensities were corrected for Lorentz and polarization factors and converted to structure factors. No corrections were made for absorption (μ = 0.812 cm⁻¹ and $\mu t \simeq 0.02$). The structure was solved by MULTAN[16] and refined by a least-squares procedure[17] for the 2066 reflections with $I > 3\sigma(I)$, to give R and $R\omega$ ($\omega = 1/(\sigma F_o)^2$) values of 0.047 and 0.051, respectively, for all atoms. An ORTEP drawing of the molecular structure of **4**[18] and the atom labeling scheme are shown in Figure 1. Atomic coordinates, bond distances, and bond angles are listed in Tables I–III.

To our knowledge, 1,4-disilacyclohexa-2,5-dienes reported to date, 1,1,4,4-tetramethyl-2,3,5,6-tetraphenyl-1,4-disilacyclohexa-2,5-diene[19] and *trans*-1,4-dimethyl-1,3,4,6-tetraphenyl-2,5-bis(trimethylsilyl)-1,4-disilacyclohexa-2,5-diene[20] have a chair-like conformation. The 1,4-disilacyclohexa-2,5-diene ring of **4**, however, is a boat form which has no center of symmetry. Two phenyl rings in the 3- and 6-positions of the heterocyclic ring of **4** are parallel to each other with the dihedral angle of 13.9 (5)°. Similar relationship between two phenyl rings on the carbon atoms in the 1,4-disilacyclohexa-2,5-diene ring have also been observed for two other compounds which have a chair-like conformation. In the present compound **4**, two planes involving each one of phenyl groups are sloped to the plane A consisting of four carbon atoms in the six-membered heterocyclic ring with 91.5 (5) and 80.1 (5)°, respectively, and the silicon atoms in this ring deviate fairly
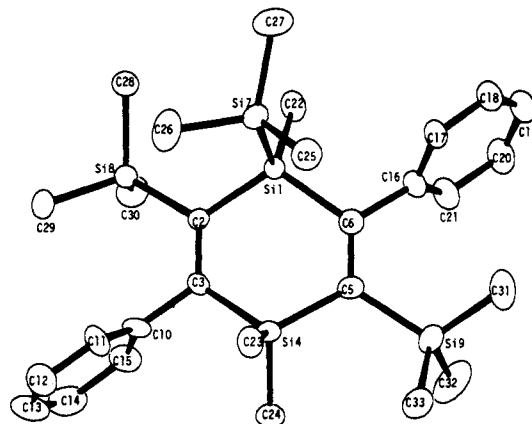
from the plane A, +0.37 (1) for Si1 and +0.30 (1) Å for Si4. The distance from one silicon to the other in the heterocyclic ring of **4** is 3.343 (3) Å, whereas this nonbonded distance in *trans*-1,4-dimethyl-1,3,4,6-tetraphenyl-2,5-bis(trimethylsilyl)-1,4-disilacyclohexa-2,5-diene whose conformation is the chair form, is determined to be 3.416 (1) Å. The distances of Si—C bonds (average 1.889 Å) and C=C bonds (average 1.346 Å) in the heterocyclic ring of **4** correspond to those of 1,1,4,4-tetraphenyl-2,3,5,6-tetraphenyl-1,4-disilacyclohexa-2,5-diene and *trans*-1,4-dimethyl-1,3,4,6-tetraphenyl-2,5-bis(trimethylsilyl)-1,4-disilacyclohexa-2,5-diene. The endocyclic bond angles of Si1 and Si4 with tetrahedral arrangement are 112.5 (3) and 111.7 (3)°, respectively. The endocyclic bond angles (average 125.5°) of carbon atoms bearing a phenyl group are larger than those of ones attached to a trimethylsilyl group (average 118.5°).

Experimental Section

General Data. ¹H NMR spectra were determined with a JEOL Model JNM-MH-100 spectrometer in carbon tetrachloride with the use of cyclohexane as an internal standard. ¹³C NMR spectra were obtained on a JEOL Model JNM-GX-400 spectrometer in deuteriochloroform as a solvent. ²⁹Si NMR spectra were determined with a JEOL Model JNM-PFT-100 spectrometer in deuteriochloroform as a solvent. Mass spectra were measured on a JEOL Model JMS-D 300 equipped with a JMA-2000 data processing system.

Preparation of 2-(Phenylethynyl)-2-(trimethylsilyl)-hexamethyltrisilane (1). To a solution of (phenylethynyl)-lithium prepared from 4.0 g (39 mmol) of phenylacetylene and 20 mL (32 mmol) of 1.6 M butyllithium–hexane solution in 30 mL of hexane was added 7 g (25 mmol) of chlorotris(trimethylsilyl)silane[21] dissolved in 30 mL of THF at room temperature. The mixture was refluxed for 20 min and then hydrolyzed with water. The organic layer was washed with water and dried over potassium carbonate. The solvent was evaporated, and the residue was fractionally distilled by using a short column under reduced pressure to give 7.4 g (86% yield) of **1**: bp 136 °C (2 mm); mp 37–38 °C; exact mass, m/e 348.1579 (calcd 348.1581); IR 2160 cm⁻¹; ¹H NMR δ 0.25 (s, 27 H, Me₃Si), 7.1–7.5 (m, 5 H, ring protons). Anal. Calcd for $C_{17}H_{32}Si_4$: C, 58.54; H, 9.25. Found: C, 58.25; H, 9.17.

Preparation of 3-Phenyl-1,1,2-tris(trimethylsilyl)-1-sila-cyclopropene (2). A solution of 0.2612 g (0.75 mmol) of **1** in 25 mL of dry benzene was photolyzed with a low-pressure mercury lamp bearing a Vycor filter for 1 h with a slow stream of purified nitrogen bubbling through the solution. After evaporation of the solvent under an atmosphere of nitrogen, the residue of the flask was evaporated under reduced pressure (1 mm) to give 63 mg (24% yield) of **2**: ¹H NMR δ (in C_6D_6) 0.20 (s, 18 H, Me₃Si), 0.38

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Table I. Fractional Coordinates and Temperature Factors for 4[a]

atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Si(1)	0.8509 (2)	−0.0700 (1)	0.7227 (1)	0.051 (1)	0.059 (2)	0.042 (1)	−0.005 (1)	0.016 (1)	−0.002 (1)
Si(4)	0.5309 (2)	−0.1156 (1)	0.6873 (1)	0.045 (1)	0.062 (2)	0.056 (1)	−0.011 (1)	0.015 (1)	0.001 (1)
Si(7)	0.9602 (2)	−0.1648 (1)	0.8064 (1)	0.060 (2)	0.071 (2)	0.062 (2)	0.007 (2)	0.002 (1)	−0.004 (1)
Si(8)	0.8138 (2)	0.0591 (1)	0.8416 (1)	0.052 (1)	0.065 (2)	0.063 (2)	−0.004 (1)	0.015 (1)	−0.012 (1)
Si(9)	0.5327 (3)	−0.1856 (2)	0.5210 (1)	0.083 (2)	0.103 (2)	0.061 (2)	−0.026 (2)	0.016 (1)	−0.016 (2)
C(2)	0.7413 (6)	−0.0196 (4)	0.7722 (3)	0.041 (4)	0.049 (5)	0.037 (4)	−0.002 (4)	0.007 (4)	0.008 (4)
C(3)	0.6144 (6)	−0.0416 (4)	0.7573 (4)	0.047 (5)	0.050 (5)	0.051 (5)	−0.002 (4)	0.023 (4)	0.008 (4)
C(5)	0.6251 (7)	−0.1353 (4)	0.6143 (4)	0.050 (6)	0.062 (6)	0.059 (5)	−0.003 (4)	0.009 (4)	0.014 (5)
C(6)	0.7534 (7)	−0.1152 (4)	0.6300 (4)	0.061 (5)	0.056 (5)	0.055 (5)	0.012 (5)	0.012 (4)	0.015 (5)
C(10)	0.5214 (7)	−0.0081 (4)	0.8003 (4)	0.037 (5)	0.062 (6)	0.080 (6)	−0.002 (4)	0.019 (4)	0.014 (5)
C(11)	0.4963 (8)	−0.0456 (5)	0.8595 (5)	0.090 (7)	0.099 (7)	0.102 (7)	−0.018 (6)	0.063 (6)	−0.025 (6)
C(12)	0.4135 (9)	−0.0186 (6)	0.9001 (6)	0.108 (8)	0.14 (1)	0.135 (9)	−0.049 (7)	0.067 (7)	−0.043 (8)
C(13)	0.3514 (9)	0.0447 (6)	0.8757 (7)	0.062 (7)	0.18 (1)	0.21 (1)	−0.012 (8)	0.047 (7)	−0.06 (1)
C(14)	0.3640 (9)	0.0850 (5)	0.8155 (6)	0.082 (7)	0.108 (9)	0.18 (1)	0.026 (7)	−0.002 (7)	−0.037 (8)
C(15)	0.4541 (8)	0.0551 (5)	0.7749 (5)	0.068 (6)	0.093 (7)	0.120 (8)	0.014 (6)	0.021 (6)	−0.007 (6)
C(16)	0.8327 (7)	−0.1262 (4)	0.5728 (4)	0.070 (6)	0.084 (6)	0.053 (5)	0.002 (5)	0.034 (4)	0.012 (5)
C(17)	0.9380 (8)	−0.1741 (5)	0.5880 (4)	0.077 (6)	0.104 (7)	0.062 (5)	0.012 (6)	0.029 (5)	−0.008 (5)
C(18)	1.0156 (8)	−0.1774 (5)	0.5388 (5)	0.081 (6)	0.103 (8)	0.089 (7)	0.003 (6)	0.036 (5)	−0.019 (6)
C(19)	0.9940 (9)	−0.1321 (5)	0.4753 (5)	0.100 (7)	0.122 (8)	0.100 (7)	−0.034 (6)	0.063 (6)	−0.030 (7)
C(20)	0.8895 (9)	−0.0830 (5)	0.4614 (5)	0.124 (8)	0.110 (8)	0.080 (6)	−0.007 (7)	0.056 (6)	0.007 (6)
C(21)	0.8114 (8)	−0.0788 (5)	0.5109 (4)	0.094 (7)	0.095 (7)	0.076 (6)	0.009 (6)	0.045 (5)	0.013 (6)
C(22)	0.9685 (8)	−0.0047 (5)	0.6952 (4)	0.091 (7)	0.087 (7)	0.077 (6)	−0.021 (6)	0.046 (5)	−0.012 (5)
C(23)	0.5170 (8)	−0.2004 (4)	0.7427 (4)	0.097 (7)	0.080 (7)	0.074 (6)	−0.025 (6)	0.041 (5)	−0.002 (5)
C(24)	0.3612 (7)	−0.0818 (5)	0.6385 (4)	0.054 (6)	0.109 (8)	0.095 (7)	−0.003 (5)	0.017 (5)	−0.018 (6)
C(25)	0.8967 (8)	−0.2576 (5)	0.7712 (5)	0.101 (7)	0.078 (7)	0.093 (7)	−0.002 (6)	0.027 (6)	0.003 (6)
C(26)	0.927 (1)	−0.1524 (5)	0.9025 (4)	0.18 (1)	0.107 (8)	0.053 (6)	0.026 (7)	0.017 (6)	0.027 (6)
C(27)	1.1433 (8)	−0.1630 (5)	0.8193 (6)	0.072 (7)	0.104 (8)	0.16 (1)	0.020 (6)	−0.007 (7)	−0.006 (8)
C(28)	0.9970 (7)	0.0511 (5)	0.8808 (4)	0.058 (6)	0.114 (8)	0.084 (6)	−0.006 (6)	0.019 (5)	−0.024 (6)

atom	x	y	z	U, Å^2	atom	x	y	z	U, Å^2
H(30)	1.034 (6)	0.095 (4)	0.922 (4)	0.128 (28)	H(39)	0.577 (6)	−0.278 (4)	0.434 (4)	0.113 (25)
H(31)	1.024 (6)	0.007 (4)	0.909 (4)	0.110 (25)	H(40)	0.709 (7)	−0.220 (4)	0.463 (4)	0.144 (30)
H(32)	0.766 (6)	0.010 (4)	0.956 (4)	0.115 (25)	H(41)	0.491 (7)	−0.083 (4)	0.435 (4)	0.135 (28)
H(33)	0.792 (7)	0.102 (4)	0.961 (4)	0.129 (28)	H(42)	0.384 (7)	−0.149 (4)	0.402 (4)	0.158 (32)
H(34)	0.649 (6)	0.073 (3)	0.918 (3)	0.093 (22)	H(43)	0.379 (7)	−0.092 (4)	0.466 (4)	0.152 (31)
H(35)	0.679 (6)	0.156 (4)	0.770 (4)	0.106 (24)	H(44)	0.345 (6)	−0.228 (4)	0.558 (4)	0.118 (26)
H(36)	0.824 (6)	0.190 (4)	0.820 (3)	0.106 (24)	H(45)	0.352 (7)	−0.271 (4)	0.490 (4)	0.132 (28)
H(37)	0.812 (6)	0.147 (4)	0.748 (4)	0.119 (27)	H(46)	0.454 (7)	−0.289 (4)	0.576 (4)	0.144 (30)
H(38)	0.689 (7)	−0.285 (4)	0.522 (4)	0.150 (31)					

[a] Standard deviations of the least significant figures are given in parentheses. Hydrogens are assigned the same numbers as the heavy atoms to which they are bonded. U_{ij} coefficients are given by the expression $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + [U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

Table II. Bond Distances (Å) of 4[a]

Si(1)–Si(7)	2.363 (3)	Si(9)–C(33)	1.834 (11)
Si(1)–C(2)	1.882 (7)	C(2)–C(3)	1.344 (9)
Si(1)–C(6)	1.895 (6)	C(3)–C(10)	1.536 (11)
Si(1)–C(22)	1.873 (9)	C(5)–C(6)	1.347 (10)
Si(4)–C(3)	1.884 (7)	C(6)–C(16)	1.515 (11)
Si(4)–C(5)	1.896 (8)	C(10)–C(11)	1.358 (12)
Si(4)–C(23)	1.862 (9)	C(10)–C(15)	1.353 (11)
Si(4)–C(24)	1.858 (7)	C(11)–C(12)	1.375 (15)
Si(7)–C(25)	1.853 (9)	C(12)–C(13)	1.331 (15)
Si(7)–C(26)	1.884 (10)	C(13)–C(14)	1.351 (17)
Si(7)–C(27)	1.872 (9)	C(14)–C(15)	1.455 (15)
Si(8)–C(2)	1.911 (6)	C(16)–C(17)	1.370 (11)
Si(8)–C(28)	1.860 (7)	C(16)–C(21)	1.382 (11)
Si(8)–C(29)	1.866 (9)	C(17)–C(18)	1.369 (13)
Si(8)–C(30)	1.840 (9)	C(18)–C(19)	1.379 (12)
Si(9)–C(5)	1.929 (7)	C(19)–C(20)	1.378 (13)
Si(9)–C(31)	1.874 (13)	C(20)–C(21)	1.378 (14)
Si(9)–C(32)	1.837 (10)		

[a] The standard deviation of the least significant figure of each distance is given in parentheses.

(s, 9 H, Me$_3$Si), 6.9–7.9 (m, ring protons); exact mass for C$_{17}$H$_{32}$Si$_4$, m/e 348.1583 (found 348.1581).

Reaction of 2 with Phenyl(trimethylsilyl)acetylene in the Presence of NiCl$_2$(PEt$_3$)$_2$. In a 500-mL reaction vessel fitted internally with a low-pressure mercury lamp bearing a Vycor filter was placed a solution of 5.0578 g (14.5 mmol) of 1 and 0.4843 g (2.14 mmol) of cetane as an internal standard in ca. 500 mL of dry hexane. The mixture was irradiated for 6 h at room temperature with a slow stream of purified nitrogen bubbling through the mixture. After the solvent was evaporated off, the residue

was analyzed by GLC as being 2 (5.22 mmol, 36% yield), phenyl(trimethylsilyl)acetylene (5% yield) and 20% of the unchanged 1. The residue was distilled under reduced pressure (1 mm) directly into a 1.0 cm × 20 cm glass tube containing 1.2723 g (7.03 mmol) of phenyl(trimethylsilyl)acetylene and 27.8 mg (7.6 × 10^{-2} mmol) of NiCl$_2$(PEt$_3$)$_2$ as a catalyst. The tube was sealed under reduced pressure and heated for 15 h at 135 °C. Nonvolatile products were removed from the mixture by flash column chromatography, and the volatile products were chromatographed at medium pressure over silica gel to give 0.983 g (36% yield) of 3-phenyl-4-[phenyl(trimethylsilyl)methylene]-1,1,2-tris(trimethylsilyl)-1-silacyclobut-2-ene (3) and 1.391 g (51% yield) of 1,4,4-trimethyl-3,6-diphenyl-1,2,5-tris(trimethylsilyl)-1,4-disilacyclohexa-2,5-diene (4). For 3: mp 70 °C; IR 1245, 1400, 1440, 1465, 1490, 1560, 1575, 1598 cm^{-1}; MS, m/e 522 (M$^+$); ^{1}H NMR δ −0.42 (s, 9 H, Me$_3$Si), −0.19 (s, 9 H, Me$_3$Si), 0.02 (s, 18 H, Me$_3$Si), 6.8–7.4 (m, 10 H, ring protons); ^{13}C NMR δ −0.4 (Me$_3$Si), 0.5 (Me$_3$Si), 1.2 (Me$_3$Si), 125.2, 127.2, 127.6, 127.8, 127.9, 128.8, 143.2, 145.1 (phenyl ring carbons), 149.4, 158.3, 160.2, 174.2 (olefinic carbons); ^{29}Si NMR δ −16.5 (Si(SiMe$_3$)$_2$), −16.3 (Me$_3$SiSi), −12.0 (Me$_3$Si), −9.0 (Me$_3$Si). Anal. Calcd for C$_{28}$H$_{46}$Si$_5$: C, 64.29; H, 8.86. Found: C, 64.23; H, 9.10. For 4: mp 80 °C; IR 1245, 1395, 1440, 1463, 1560, 1575, 1595 cm^{-1}; MS, m/e 522 (M$^+$); ^{1}H NMR δ −0.23 (s, 9 H, Me$_3$Si), 0.01 (s, 9 H, Me$_3$Si), 0.31 (s, 18 H, Me$_3$Si, Me$_2$Si and MeSi), 6.4–7.3 (m, 10 H, ring protons); ^{13}C NMR δ −0.3 (Me$_3$Si), 0.5 (Me$_3$Si and Me$_2$Si), 0.9 (Me$_3$Si), 2.6 (MeSi), 124.4, 125.2, 126.6, 126.8, 127.9, 128.5, 142.8, 142.9 (phenyl ring carbons), 146.0, 150.2, 158.8, 176.7 (olefinic carbons); ^{29}Si NMR δ −19.8 (SiSiMe$_3$), −15.7 (Me$_3$SiSi), −12.2 (Me$_3$Si), −5.5 (Me$_2$Si). Anal. Calcd for C$_{28}$H$_{46}$Si$_5$: C, 64.29; H, 8.86. Found: C, 64.20; H, 9.11.

Reaction of 1 with Phenyl(trimethylsilyl)acetylene. In a 10-mL glass tube was placed 1.0058 g (2.89 mmol) of 1, 1.88 g

Table III. Bond Angles (deg) of 4[a]

Si(7)–Si(1)–C(2)	107.2 (2)	C(32)–Si(9)–C(33)	107.8 (5)
Si(7)–Si(1)–C(6)	107.7 (2)	Si(1)–C(2)–Si(8)	119.4 (3)
Si(7)–Si(1)–C(22)	113.0 (3)	Si(1)–C(2)–C(3)	117.7 (5)
C(2)–Si(1)–C(6)	112.5 (3)	Si(8)–C(2)–C(3)	123.0 (5)
C(2)–Si(1)–C(22)	111.0 (4)	Si(4)–C(3)–C(2)	126.5 (6)
C(6)–Si(1)–C(22)	105.5 (3)	Si(4)–C(3)–C(10)	112.4 (4)
C(3)–Si(4)–C(5)	111.7 (3)	C(2)–C(3)–C(10)	121.1 (6)
C(3)–Si(4)–C(23)	108.2 (3)	Si(4)–C(5)–Si(9)	118.0 (4)
C(3)–Si(4)–C(24)	107.0 (3)	Si(4)–C(5)–C(6)	119.2 (5)
C(5)–Si(4)–C(23)	110.9 (4)	Si(9)–C(5)–C(6)	122.8 (6)
C(5)–Si(4)–C(24)	110.3 (3)	Si(1)–C(6)–C(5)	124.4 (6)
C(23)–Si(4)–C(24)	108.6 (4)	Si(1)–C(6)–C(16)	113.7 (5)
Si(1)–Si(7)–C(25)	111.8 (3)	C(5)–C(6)–C(16)	121.9 (6)
Si(1)–Si(7)–C(26)	109.1 (3)	C(3)–C(10)–C(11)	119.8 (7)
Si(1)–Si(7)–C(27)	111.4 (3)	C(3)–C(10)–C(15)	120.4 (7)
C(25)–Si(7)–C(26)	106.6 (4)	C(11)–C(10)–C(15)	119.5 (8)
C(25)–Si(7)–C(27)	108.5 (4)	C(10)–C(11)–C(12)	122.5 (8)
C(26)–Si(7)–C(27)	109.4 (5)	C(11)–C(12)–C(13)	116.9 (10)
C(2)–Si(8)–C(28)	111.9 (4)	C(12)–C(13)–C(14)	125.6 (11)
C(2)–Si(8)–C(29)	114.9 (4)	C(13)–C(14)–C(15)	115.7 (9)
C(2)–Si(8)–C(30)	108.5 (3)	C(10)–C(15)–C(14)	119.5 (8)
C(28)–Si(8)–C(29)	103.8 (4)	C(6)–C(16)–C(17)	120.8 (7)
C(28)–Si(8)–C(30)	108.2 (4)	C(6)–C(16)–C(21)	118.8 (7)
C(29)–Si(8)–C(30)	109.2 (4)	C(17)–C(16)–C(21)	119.6 (8)
C(5)–Si(9)–C(31)	114.6 (4)	C(16)–C(17)–C(18)	119.4 (7)
C(5)–Si(9)–C(32)	110.0 (4)	C(17)–C(18)–C(19)	122.0 (8)
C(5)–Si(9)–C(33)	110.0 (4)	C(18)–C(19)–C(20)	118.2 (9)
C(31)–Si(9)–C(32)	110.7 (5)	C(19)–C(20)–C(21)	120.3 (8)
C(31)–Si(9)–C(33)	103.3 (5)	C(16)–C(21)–C(20)	120.4 (8)

[a] The standard deviation of the least significant figure of each angle is given in parentheses.

(10.8 mmol) of phenyl(trimethylsilyl)acetylene, and 21.4 mg (5.85 × 10⁻² mmol) of NiCl₂(PEt₃)₂. The tube was sealed under reduced pressure and heated for 20 h at 200 °C. After flash chromatography of the reaction mixture, the resulting products were isolated by medium-pressure liquid chromatography to give 289.4 mg (19% yield) of 3 and 876.3 mg (58% yield) of 4. All spectral data for 3 and 4 were identical with those of authentic samples.

Reaction of 6 with Phenyl(trimethylsilyl)acetylene. A solution of 5.55 g (19.1 mmol) of 2-(phenylethynyl)heptamethyltrisilane and 0.44 g (2.2 mmol) of tetradecane as an internal standard dissolved in 500 mL of dry hexane was irradiated with a low-pressure mercury lamp at room temperature for 6 h. VPC analysis of the resulting mixture showed the presence of 7.3 mmol (38% yield) of silacyclopropene 6. Most of the solvent was evaporated under a nitrogen atmosphere, and the residue of the flask was distilled under reduced pressure (1 mm) directly to a 10-mL glass tube containing 1.3 g (7.4 mmol) of phenyl(trimethylsilyl)acetylene and 32.0 mg (8.8 × 10⁻² mmol) of NiCl₂-(PEt₃)₂. The glass tube was sealed under reduced pressure and then heated for 10 h at 135 °C. The mixture was chromatographed at medium pressure over silica gel to give 1.39 g (41% yield) of silole 7, 1.22 g (36% yield) of a mixture of 8 and 9, and 0.10 g (3% yield) of 10. Products 8 and 9 were separated by fractional recrystallization from ethanol–benzene (5:1). All spectral data for 7 were identical with those of an authentic sample.[10] For 8: mp 154–156 °C; MS, *m/e* 464 (M⁺); IR 1593, 1470, 1432, 1260, 1242 cm⁻¹; ¹H NMR δ −0.27 (s, 9 H, Me₃Si), −0.17 (s, 6 H, Me₂Si), 0.05 (s, 9 H, Me₃Si), 0.26 (s, 6 H, Me₂Si), 6.75–7.35 (m, 10 H, ring protons); ¹³C NMR δ 0.2 (Me₂Si), 1.0 (Me₃Si), 1.6 (Me₃Si), 1.9 (Me₂Si), 125.3, 125.5, 126.5, 126.8, 127.5, 127.6, 147.0, 149.5, (phenyl ring carbons), 159.4, 163.3, 176.8, 180.9 (olefinic carbons). Anal. Calcd for C₂₆H₄₀Si₄: C, 67.16; H, 8.67. Found: C, 67.32; H, 8.76. For 9: mp 173–175 °C; MS, *m/e* 464 (M⁺); IR 1596, 1470, 1435, 1245 cm⁻¹; ¹H NMR δ −0.43 (s, 6 H, Me₂Si), −0.16 (s, 9 H, Me₃Si), 0.11 (s, 9 H, Me₃Si), 0.49 (s, 6 H, Me₂Si), 6.65–7.30 (m, 10 H, ring protons); ¹³C NMR δ −0.4 (Me₂Si), 1.1 (Me₃Si), 1.8 (Me₃Si), 2.4 (Me₂Si), 125.1, 125.5, 126.3, 126.8, 127.46, 127.50, 146.8, 149.7 (phenyl carbons), 160.3, 163.5, 176.6, 181.2 (olefinic carbons). Anal. Calcd for C₂₆H₄₀Si₄: C, 67.16, H, 8.67. Found: C, 67.08; H, 8.59.

Reaction of 12 with Phenyl(trimethylsilyl)acetylene. A mixture of 0.3331 g (1.2 mmol) of 12, 0.2406 g (1.4 mmol) of phenyl(trimethylsilyl)acetylene, and 10.8 mg (3.0 × 10⁻² mmol) of NiCl₂(PEt₃)₂ was placed in a carefully dried 4-mL glass tube,

previously flushed with dry argon. The glass tube was sealed under reduced pressure and then heated for 20 h at 200 °C. VPC analysis of the mixture showed the presence of a mixture of 8 and 9 (46% combined yield) and 10 (33% yield). A 1:1 mixture of 8 and 9 and 10 were isolated by preparative VPC. Product 8 was separated from 9 by fractional recrystallization from ethanol–benzene (5:1). All spectral data for 8 and 9 were identical with those of authentic samples prepared from 6 and phenyl(trimethylsilyl)acetylene. For 10: mp 86–88 °C; MS, *m/e* 464 (M⁺); IR 1470, 1440, 1240, 945 cm⁻¹; ¹H NMR δ −0.22 (s, 9 H, Me₃Si), 0.00 (s, 9 H, Me₃Si), 0.25 (s, 9 H, Me₃Si), 0.63 (s, 3 H, MeSi), 6.40–6.80 (m, 10 H, phenyl ring protons); ¹³C NMR δ −0.7 (MeSi), −0.6 (Me₃Si), −0.4 (Me₃Si), 0.3 (Me₃Si), 124.4, 125.2, 126.5, 126.7, 127.3, 128.3, 142.3, 142.5 (phenyl ring carbons), 145.1, 154.0, 162.6, 175.9 (olefinic carbons). Anal. Calcd for C₂₆H₄₀Si₄: C, 67.16; H, 8.67. Found: C, 67.23; H, 8.88.

Reaction of a 1:1 Mixture of 8 and 9 with Hydrogen Chloride. In a 100-mL two-necked flask fitted with an inlet tube for hydrogen chloride was placed 0.2020 g (0.44 mmol) of a 1:1 mixture of 8 and 9 and 0.0258 g (0.17 mmol) of undecane as an internal standard dissolved in 30 mL of dry ether. Hydrogen chloride gas was passed into the solution for 2 h at 0 °C. The solvent was evaporated under reduced pressure, and then 2 mL (4 mmol) of methyllithium was added to the flask. The mixture was stirred for 2 h at room temperature and then hydrolyzed with water. VPC analysis of the organic layer showed the presence of (*E*)-1,2-bis(trimethylsilyl)phenylethene[14] (31%) and 1-phenyl-1-(trimethylsilyl)ethene[13] (70%). Both compounds were separated by preparative VPC. All spectral data for (*E*)-1,2-bis(trimethylsilyl)phenylethene and 1-phenyl-1-(trimethylsilyl)-ethene were identical with those reported in the literature.

Reaction of 15 with Phenyl(trimethylsilyl)acetylene. A mixture of 0.3990 g (1.72 mmol) of 15, 0.4137 g (2.38 mmol) of phenyl(trimethylsilyl)acetylene, and 8.1 mg (2.2 × 10⁻² mmol) of NiCl₂(PEt₃)₂ was heated for 20 h at 200 °C in a sealed glass tube. The reaction mixture was analyzed by VPC as being products 16 and 17 (46% combined yield) which were shown to be a 1:1 mixture by ¹H NMR spectroscopic method, 1,3-disilacyclobutane 18 (15%) and silole 14 (32%). A mixture of 16 and 17, 18, and 14 was isolated by medium-pressure liquid chromatography. For a mixture of 16 and 17: MS, *m/e* 406 (M⁺); ¹H NMR for 16, δ −0.28 (s, 9 H, Me₃Si), −0.13 (s, 6 H, Me₂Si), 0.18 (s, 6 H, Me₂Si), 2.28 (s, 3 H, MeC), 6.75–7.45 (m, 10 H, phenyl ring protons), and for 17, δ −0.37 (s, 6 H, Me₂Si), −0.20 (s, 9 H, Me₃Si), 0.42 (s, 6 H, Me₂Si), 2.31 (s, 3 H, MeC), 6.75–7.45 (m, 10 H, phenyl ring protons). Anal. Calcd for C₂₄H₃₄Si₃: C, 70.86; H, 8.42. Found: C, 70.57; H, 8.33.

All spectral data obtained for 14 were indentical with those of an authentic sample.[10]

Reaction of a Mixture of 16 and 17 with Hydrogen Chloride. In a 25-mL two-necked fask fitted with an inlet tube was placed a solution of 0.1536 g (0.38 mmol) of a 1:1 mixture of 16 and 17 in 20 mL of dry benzene. Dry hydrogen chloride gas was introduced into the solution for 10 min at room temperature. The solvent benzene was evaporated under reduced pressure. To this residue was added 2 mL of methyllithium (4 mmol), and the mixture was stirred for 2 h at room temperature. VPC analysis using octadecane as an internal standard indicated the presence of 2-phenylpropene and phenyltris(trimethylsilyl)ethene[15] in 37 and 56% yields. Both compounds were isolated by preparative TLC. All data for 2-phenylpropene and phenyltris(trimethylsilyl)ethene were identical with those of authentic samples.

Reaction of 15 with a Catalytic Amount of Ni(PEt₃)₄. A mixture of 0.3332 g (1.44 mmol) of 15 and 32 mg (16.1 × 10⁻² mmol) of Ni(PEt₃)₂ was heated at 200 °C in a sealed glass tube for 20 h. VPC analysis using 80.0 mg (0.44 mmol) of tridecane as an internal standard showed the presence of 18 (64% yield). Product 18 was isolated by preparative TLC; mp 204–205 °C; MS, *m/e* 464 (M⁺); ¹H NMR δ −0.04 (s, 6 H, Me₂Si), −0.02 (s, 9 H, Me₃Si), 6.84–7.41 (m, 5 H, ring protons); ¹³C NMR δ 0.3 (Me₃Si), 1.7 (Me₂Si), 125.4, 126.5, 127.6, 149.9 (ring carbons), 170.4, 176.2 (olefinic carbons). Anal. Calcd for C₂₆H₄₀Si₄: C, 67.16; H, 8.68. Found: C, 67.07; H, 8.81.

Reaction of 15 with a Catalytic Amount of NiCl₂-(PEt₃)–Me₃SiSiMe₂H. A mixture of 0.2597 g (1.12 mmol) of 15,

9.4 mg (2.6×10^{-2} mmol) of $NiCl_2(PEt_3)_2$, and 4.3 mg (3.2×10^{-2} mmol) of pentamethyldisilane was heated for 20 h at 180°C in a sealed glass tube. The mixture was chromatographed on silica gel using hexane to give 0.2034 g (78% yield) of 18.

Reaction of 19 with Phenyl(trimethylsilyl)acetylene. A mixture of 0.4827 g (1.64 mmol) of 19, 0.3345 g (1.92 mmol) of phenyl(trimethylsilyl)acetylene, 11.7 mg (3.2×10^{-2} mmol) of $NiCl_2(PEt_3)_2$, and 0.1628 g (0.52 mmol) of docosane as an interanal standard was heated in a sealed glass tube for 20 h at 200 °C. The mixture was analyzed by VPC as being 20 (52%) and 21 (10%). Pure 20 was obtained from recrystallization of the mixture from ethanol. Compound 21 in the filtrate was isolated by preparative VPC. For 20: mp 157.0–157.5 °C; MS, m/e 468 (M$^+$); ^{1}H NMR δ −0.23 (s, 15 H, Me$_2$Si and Me$_3$Si), 0.01 (s, 6 H, Me$_2$Si), 6.72–7.31 (m, 15 H, phenyl ring protons); ^{13}C NMR δ −0.7 (Me$_2$Si), 1.5 (Me$_2$Si), 1.6 (Me$_3$Si), 125.3, 126.3, 126.8, 127.4, 127.5, 127.8, 146.2, 146.5, 146.9 (phenyl ring carbons), 142.6, 163.5, 166.9, 181.2 (olefinic carbons). Anal. Calcd for $C_{29}H_{36}Si_3$: C, 74.29; H, 7.74. Found: C, 74.49; H, 7.83. All spectral data obtained for 21 were identical with those of an authentic sample.[10]

Reaction of 20 with Hydrogen Chloride. In a 25-mL two-necked flask fitted with a condenser and an inlet tube for hydrogen chloride was placed a solution of 64.0 mg (0.14 mmol) of 20 and 17.7 mg (0.078 mmol) of cetane in 8 mL of dry benzene. Hydrogen chloride gas was passed into the solution for 15 min at room temperature. The solvent was evaporated under reduced pressure, and then 2 mL of methyllithium (4 mmol) was added to the residue. The mixture was stirred for 2 h at room temperature

and hydrolyzed with water. The mixture was analyzed by VPC as being 1,1-diphenylethene[22] (74%) and phenyltris(trimethylsilyl)ethene[15] (49%). All spectral data obtained for both products were identical with those of authentic samples.

Reaction of 13 with a Catalytic Amount of $NiCl_2(PEt_3)_2$. A mixture of 98.0 mg (0.42 mmol) of 13, 3.2 mg (9×10^{-3} mmol) of $NiCl_2(PEt_3)_2$, and 45.8 mg (0.28 mmol) of tridecane was placed in a glass tube. The tube was sealed under reduced pressure and heated for 15 h at 135 °C. VPC analysis of the mixture showed the presence of dimer 11 in 45% yield. Recrystallization of the mixture from ethanol gave 26.6 mg of 11, mp 182–183 °C. All spectral data for 11 were identical with those of an authentic sample.[20]

Supplementary Material Available: A table of observed and calculated structure factors (2 pages). Ordering information is given on any current masthead page.

(22) An authentic sample was obtained from Aldrich Chemical Co., Inc.

A Rationalized Synthesis and X-ray Crystal Structure of Cp₃Co₂MoFe(CO)₅CCO₂-*i*-Pr: A Heterometallic M₄C Closo Cluster

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A series of synthetic manipulations carried out on the cluster system Co₃(CO)₉CR, where R = CO₂-*i*-Pr, yields a variety of mixed-metal clusters. Treatment with Cp₂Ni, [CpNi(CO)]₂, or [CpMo(CO)₃]₂ leads to replacement or modification of one, two, or all three of the original Co(CO)₃ vertices. Upon treatment with Fe₂(CO)₉, these tetrahedral M₃CR molecules can be expanded to the analogous M₃Fe(CO)₃CR square-based pyramidal systems. However, CpMo(CO)₂(CpCo)₂(μ-CO)CR yields the closo trigonal bipyramidal molecule Cp₃Co₂MoFe(CO)₅CR which has been fully characterized by single-crystal X-ray diffraction. It crystallizes in the monoclinic space group $P2_1/c$ with a = 12.309 (5) Å, b = 14.731 (6) Å, c = 17.298 (7) Å, β = 124.63 (6)°, and Z = 4. The structure has been solved by direct and Fourier methods and refined by full-matrix least squares to R_1 and R_2 values of 0.0522 and 0.0571 for 3133 observed reflections. The cluster adopts a butterfly arrangement of metal atoms with the CpCo moieties at the wingtips. The concept of isolobality is used to compare this latter molecule, which is one of the few examples of a heterometallic closo trigonal-bipyramidal M₄CR cluster, with previously known homometallic Fe₄CR clusters.

Introduction

Early organotransition-metal cluster syntheses were, to some extent, serendipitous,[1] but recent publications from several laboratories[2] have laid a solid basis for devising logical routes to selected systems. Typically, Stone and his co-workers[3] have pioneered the use of the metal–carbyne synthon (L$_n$M≡CR) as a method for obtaining a plethora of clusters (Scheme I). In contrast, Vahrenkamp

has noted that it is possible to treat the RCCo₃(CO)₉ system with radicals ML$_n$ so as to displace a Co(CO)₃ unit

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