Journal of Organometallic Chemistry 649 (2002) 276–288

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Synthesis of 1,4-disilacyclohexa-2,5-dienes

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Received 27 August 2001; received in revised form 7 December 2001; accepted 7 December 2001

Dedication to Academician M.G. Voronkov on the occasion of this 80th birthday

Abstract

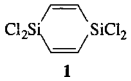
Title compounds of the type 2,3,5,6-tetraphenyl-1,4-di-X-1,4-di-Y-1,4-disilacyclohexa-2,5-diene wherein $X = Y = NMe_2$ (**4**); $X = NMe_2$, $Y = Cl$ (*cis*, *trans*-**5**); $X = NMe_2$, $Y = Me$ [(*trans*)-**6**] and $X = t$-Bu, $Y = Cl$ (*trans*-**8**) were synthesized from $Si_2(NMe_2)_5Cl$, sym-$Si_2(NMe_2)_4Cl_2$, sym-$Si_2(NMe_2)_4Me_2$, and sym-$Si_2Cl_4(t\text{-Bu})_2$, respectively, in the presence of diphenylacetylene at 200 °C. Similarly the analogous title compound from the combination of 1-phenyl-1-propyne and $Si_2(NMe_2)_5Cl$ [$X = Y = NMe_2$ (*cis* and *trans*-**7**) was synthesized. In all cases where *cis*/*trans* diastereomers could arise from two different silicon substituents (**5**, **6**, **8**) the *trans* isomer was the sole or dominant product. Evidence for the intermediacy of the silylene $Si(NMe_2)_2$ in these reactions was gained from a trapping experiment. Compound **4** upon treatment with $SiCl_4$, $SiBr_4$ or PI_3 provided the corresponding 1,1,4,4-tetrahalo derivatives **9a**–**c**, respectively. Treatment of **4** with MeOH or PhOH gave the 1,1,4,4-tetramethoxy and tetraphenoxy analogues **9d** and **9e**, respectively. The tetrachloro derivative **9a** upon LAH reduction led to the corresponding tetrahydro compound **10**, while the reaction of **9a** with H_2O gave the tetrahydroxy derivative **11**. Allowing (*trans*)-**6** to react with $SiCl_4$ provided a ca. 1:1 *cis*/*trans* ratio of the derivative **12** in which $X = Cl$, $Y = Me$, and possible pathways that rationalize this loss of stereochemistry are proposed. Synthesis of *trans*-**13** in which $X = t$-Bu, $Y = H$ was achieved by LAH reduction of **8**. All of the title compounds except **8** experience free phenyl rotation at room temperature. At −30 °C this rotation in **8** is essentially halted. The molecular structures of **4**, **8**, **9c**, **9e**, **10** and **13** were determined by X-ray crystallography. © 2002 Published by Elsevier Science B.V.

Keywords: 1,4-Disilacyclohexadiene synthesis; Disilane reactions; Acetylene reactions

1. Introduction

We reported in a recent communication [1] that disilanes Si_2Cl_6 and $Si_2(OMe)_6$ are good catalysts for cyclo-trimerizing alkynes into the corresponding aromatic products in moderate to excellent yields at ca. 200 °C in a sealed tube. A reaction pathway involving silyl radicals was proposed [1], which was further supported with additional experiments in a more recent publication [2] from these laboratories. We also disclosed that in reactions with alkynes increased substitution of the chloro groups of Si_2Cl_6 with dimethylamino substituents gave generally increasing ratios of 1,4-disilacyclohexa-2,5-dienes to cyclotrimerized products.

Thus, it appeared to us that disilanes with multiple dimethylamino groups could be quite efficient for synthesizing 1,4-disilacyclohexa-2,5-dienes under comparatively mild conditions, in sharp contrast to the original synthesis of **1** which was reported by others to take place at ca. 450 °C where the silylene diradical $SiCl_2$ (generated from Si_2Cl_6 via disproportionation) was proposed as the reactive intermediate [3]. Although gas phase reactions of acetylenes with silylene sources at elevated temperatures were for many years a traditional route to substituted 1,4-disilacyclohexa-2,5-dienes [4], other approaches have since been developed in which transition complexes of metals such as Ni or Pd were utilized as catalysts, allowing reactions to be carried out at lower temperatures more quickly [5–7]. An efficient catalytic process that takes



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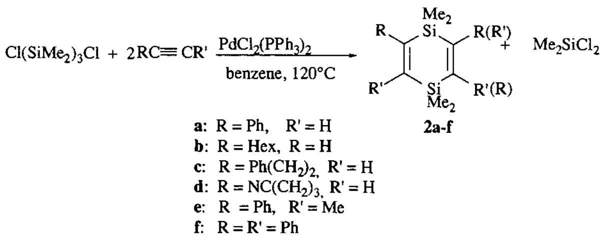
PII: S0022-328X(02)01142-7

place in solution at 120 °C to give **2a**–**f** was more recently described [5], but it uses trisilanes as the source of silylene (reaction 1) which are less accessible than disilanes. Other less common methods include Pt-catalyzed hydrosilylation–dimerization of acetylenes that contain chelating substituents, and the silylation–cyclization of bis(organolithium) derivatives (reaction 2) [6,7]. A few years ago, a new synthetic approach was reported to give bis(1,4-disilacyclohexa-2,5-dienes **3a**–**c** via a bis(cyclodisilabutane)/alkyne reaction catalyzed by $(H_2C{=}CH_2)Pt(PPh_3)_2$ (Scheme 1) [8]. These approaches, however, did not provide us with a practical way to synthesize 1,4-disilacyclohexa-2,5-dienes bearing functional groups that are easily transformed for further elaboration.



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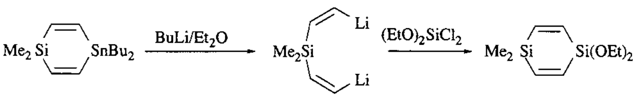

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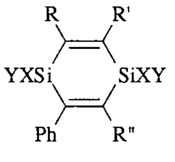
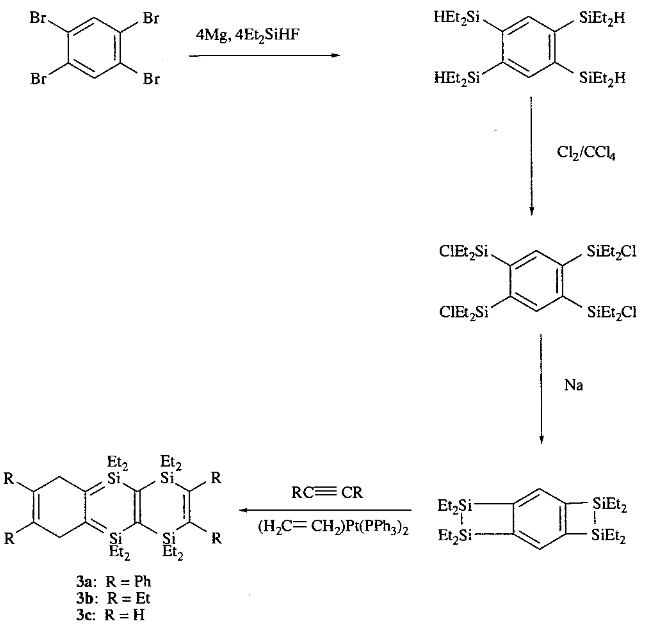


	X	Y	R	R′	R″
4	NMe_2	NMe_2	Ph	Ph	Ph
cis,trans-**5**	NMe_2	Cl	Ph	Ph	Ph
(*trans*)-**6**	NMe_2	Me	Ph	Ph	Ph
trans-**7**	NMe_2	NMe_2	Me	Ph	Me
cis-**7**	NMe_2	NMe_2	Ph	Me	Me
trans-**8**	*t*-Bu	Cl	Ph	Ph	Ph
9a	Cl	Cl	Ph	Ph	Ph
9b	Br	Br	Ph	Ph	Ph
9c	I	I	Ph	Ph	Ph
9d	OMe	OMe	Ph	Ph	Ph
9e	OPh	OPh	Ph	Ph	Ph
10	H	H	Ph	Ph	Ph
11	OH	OH	Ph	Ph	Ph
cis,trans-**12**	Me	Cl	Ph	Ph	Ph
trans-**13**	H	*t*-Bu	Ph	Ph	Ph



Scheme 1.

In this paper we describe syntheses for **4**–**8**, **9a**–**e** and **10**–**13** in good yields under relatively mild reaction conditions. Reaction pathways for the formation of these products are also suggested. The molecular structures of **4**, **8**, **9c**, **9e**, **10** and **13** were obtained by X-ray crystallography.

2. Experimental

NMR spectra were measured on Bruker AX-200 (^{29}Si), Bruker DRX-400 (^1H and ^{13}C), and Bruker MSL-300 (solid MAS ^{29}Si) instruments. High resolution mass spectra (HRMS) and X-ray structure determinations were performed in the Iowa State University's Instrument Services unit and elemental analysis were carried out by Desert Analytics.

Diethyl ether, pentane and THF were distilled from sodium–benzophenone; $CHCl_3$ was distilled from CaH_2 under nitrogen; and xylenes were distilled under N_2 from sodium and stored over 4 Å molecular sieves. Hexachlorodisilane, *symmetrical*-dimethyltetrachlorodisilane and hexamethyldislane were purchased from Aldrich Chemical Co., and hexamethoxydisilane was purchased from Gelest, Inc. and were used as received. Benzil, 1-phenyl-1,2-propanedione, anhydrous dimethylamine, *tert*-butylchlorodiphenylsilane, silicon tetrachloride, phosphorus trichloride, phosphorus tribromide, silicon tetrabromide, phosphorus tri-iodide, diphenylacetylene, phenylacetylene, 1-phenyl-1-propyne and sodium–mercury amalgam were purchased from Aldrich Chemical Co. and were also used as received.

2.1. Synthesis of disilane starting materials

Dimethyl-*tetrakis*(dimethylamino)disilane [10], *symmetrical*-di-*tert*-butyltetraphenyldisilane [11], and *symmetrical*-di-butyltetrachlorodisilane [11] were prepared by literature methods. Although the synthesis of *hexakis*(dimethylamino)disilane, *pentakis*(dimethylamino)-chlorodisilane and *tetrakis*(dimethylamino)dichloro-disilane had been reported [9,12], we used a modified method described below that gave higher yields and purities. The following example describes the general procedure for the synthesis of disilanes bearing multiple dimethylamino groups using the improved method.

2.1.1. Synthesis of symmetrical-di-tert-butyldichloro-bis(dimethylamino)disilane

In a 250 ml flask equipped with a magnetic stirrer, Et$_2$O (ca. 100 ml) was added, followed by the addition of *symmetrical*-di-*tert*-butyltetrachlorodisilane (3.12 g, 10.0 mmol). The flask was stoppered with a septum, and its weight was recorded before dimethylamine was introduced. The flask was then cooled with liquid nitrogen, and dimethylamine was introduced from a gas cylinder through a needle, whereupon a white precipitate formed immediately. The flask was weighed frequently and the addition of dimethylamine was stopped when 2.70 g (60.0 mmol, 50% excess) had been introduced. (For the syntheses of sym-Si$_2$Cl$_2$(NMe$_2$)$_4$ and Si$_2$Cl(NMe$_2$)$_5$, however, the weight of HNMe$_2$ was carefully controlled so that only the stoichiometric amount of dimethylamine was added.) The mixture was allowed to warm up slowly and was vigorously stirred for 20 h at room temperature. After the reaction, unreacted HNMe$_2$ was allowed to escape through a needle inserted into the septum. The solid material (presumably [H$_2$NMe$_2$]Cl) was filtered off and washed with 5 × 30 ml of Et$_2$O. The solvent and the volatile materials were removed under reduced pressure giving the product (85% yield) which in the case of sym-Si$_2{}^t$Bu$_2$Cl$_2$(NMe$_2$)$_2$ was analyzed as a mixture of two conformers (in a 1:1 ratio) that possessed satisfactory purity as determined by ^{1}H- and ^{13}C-NMR spectroscopy. ^{1}H-NMR (CDCl$_3$): δ 2.65 (s, 12H), 2.61 (s, 12H), 1.04 (s, 18H), 1.01 (s, 18H); ^{13}C-NMR (CDCl$_3$): δ 39.32, 38.70, 26.90, 26.56, 26.38, 26.22. M.p.: 25 °C. EIHRMS; Calc. for C$_{12}$H$_{30}$N$_2$Cl$_2$Si$_2$: 328.1325; found: 328.1328. Elemental analysis: Calc. for C$_{12}$H$_{30}$N$_2$Cl$_2$Si$_2$: C, 43.90; H, 9.14; Cl, 21.65; N, 8.54; Si, 17.07; Found: C, 43.47; H, 9.09; Cl, 21.38; N, 8.12; Si, 17.98%. The yields of Si$_2$(NMe$_2$)$_6$ and Si$_2$Cl(NMe$_2$)$_5$ were 80 and 85%, respectively.

2.1.2. General method for synthesizing 1,4-disilacyclohexa-2,5-dienes

The disilane and an alkyne (diphenylacetylene or 1-phenyl-1-propyne) were combined in a glass tube. After cleaning the inside wall of the tube with a cotton swab, the tube was flushed with nitrogen and then it was cooled with liquid nitrogen (for liquid reaction mixtures) and flame sealed under vacuum. In these reactions, the height of the reaction mixture was about one fifth of that of the glass tube. The mixture in the glass tube was heated to ca. 200 °C for 2 days in an oil bath. Crystal formation was generally observed after the reaction mixture was allowed to cool to ambient temperature. The tube was quickly opened in a hood, and the liquid portion decanted. The crystalline product was washed several times by the stated amount of pentane, and was dried under vacuum.

*2.1.3. Synthesis of 2,3,5,6-tetraphenyl-1,1,4,4-tetrakis(dimethylamino)-1,4-disila cyclohexa-2,5-diene (**4**)*

Pentakis(dimehthylamino)chlorodislane (3.11 g, 10.0 mmol) was combined under nitrogen with diphenylacetylene (2.05 g, 11.5 mmol) in a tube which was sealed under vacuum and heated to 200 °C for 2 days in an oil bath, during which time the color of the reaction mixture became brown. Upon allowing the tube to cool undisturbed to room temperature, crystal formation was observed. The tube was opened in a hood and the liquid portion was removed by decantation. The crystalline material was washed with a 5 × 10 ml of pentane. Drying the crystals under vacuum afforded 2.64 g of the title product (45% yield). ^{1}H-NMR (CDCl$_3$): δ 6.83–7.03 (m, 20H), 2.34 (s, 24H); ^{13}C-NMR (CDCl$_3$): δ 158.43, 143.69, 128.88, 126.95, 124.76, 38.11; ^{29}Si-NMR (MAS): δ −33.11. M.p.: 260–265 °C. CIMS (NH$_3$, negative); m/z (relative intensity, ion): 588.2 ([M −], 18.83), 544.2 ([M − NMe$_2$], 4.04). Elemental analysis: Calc. for C$_{36}$H$_{44}$N$_4$Si$_2$: C, 73.42; H, 7.53; N 9.51. Found: C, 72.40; H, 7.53; N 9.39%. The liquid product contained a substantial amount of Si(NMe$_2$)$_3$Cl according to ^{1}H, ^{13}C and mass spectroscopies. Crystals of **4** suitable for X-ray analysis were obtained directly from the product of the reaction.

*2.1.4. Synthesis of isomeric-2,3,5,6-tetraphenyl-1,4-bis(dimethylamino)-1,4-dichloro-1,4-disilacyclohexa-2,5-dienes (**5**)*

The conditions for this reaction were similar to those for the synthesis of **4** except that Si$_2$Cl$_2$(NMe$_2$)$_4$ (3.03 g, 10.0 mmol) and diphenylacetylene (2.07 g, 11.5 mmol) were used as starting materials. After the reaction, the product was analyzed by ^{1}H- and ^{13}C-NMR spectroscopies as a mixture of two isomeric 1,4-disila-2,5-dienes (with one major isomer and a trace amount of the other) and a minor amount of hexaphenylbenzene. The by-product [Si(NMe$_2$)$_3$Cl], was separated by decantation and the crystalline material was washed with 5 × 10 ml of pentane. Drying the crystals under vacuum afforded 1.43 g of material which was analyzed by ^{1}H-NMR spectroscopy as 75% of a mixture of isomers of **5** and 25% hexaphenylbenzene. Removal of the hexaphenylbenzene was accomplished by recrystallization from methylene chloride, giving a 10% yield of **5**. Attempts to separate the isomers by column chromatography failed. ^{1}H-NMR ($CDCl_3$): δ 7.00–7.08 (m, 20H), 2.33 (s, 12H); ^{13}C-NMR ($CDCl_3$): δ 157.30, 140.19, 128.76, 127.33, 125.97, 37.23. M.p. (dec.): 250 °C. CIMS (NH_3, positive); *m/z* (relative intensity, ion): 571.1 ([M$^+$], 20.13), 535.1 ($[M-Cl]^+$, 6.07, 525.9 ($[M-NMe_2]^+$, 3.55). EIHRMS; Calc. for $C_{32}H_{32}Cl_2N_2Si_2$: 570.1481; found: 570.1493.

2.1.5. Synthesis of 2,3,5,6-tetraphenyl-1,4-dimethyl-1,4-bis(dimethylamino)-1,4-disilacyclohexa-2,5-diene ***(6)***

In a glass tube were placed sym-$Si_2Me_2(NMe_2)_4$ (2.62 g, 10.0 mmol) and then diphenylacetylene (2.07 g, 11.5 mmol). The tube was cooled in liquid nitrogen, flamed sealed under vacuum and heated to 200 °C for 2 days, during which time the reaction mixture was observed to become light brown. After the reaction, the tube was allowed to cool to room temperature upon which crystals were observed to form. The tube was opened in a hood, the liquid portion was removed by decantation and the crystals were washed with 5 × 10 ml of pentane. Drying the crystals under vacuum gave (presumably *trans*) **6** in 75% yield. ^{1}H-NMR ($CDCl_3$): δ 6.82–7.06 (m, 20H), 2.38 (s, 12H), 0.12 (s, 6H); ^{13}C-NMR ($CDCl_3$): δ 157.40, 143.29, 128.34, 127.08, 124.85, 38.41, -3.36. M.p.: 243–245 °C. EIHRMS; Calc. for $C_{34}H_{38}N_2Si_2$: 530.2574; found: 530.2579. Elemental analysis: Calc. for $C_{34}H_{38}N_2Si_2$: C, 76.98; H, 7.17; N, 5.28, Si, 10.57. Found: C, 77.00; H, 7.26; N, 5.28; Si, 10.75%. Although the crystals obtained were suitable for X-ray diffraction, the molecular structure could not be solved (see Section 3).

*2.1.6. Synthesis of 3,6-dimethyl-2,5-diphenyl-1,1,4,4-tetrakis(dimethylamino)-1,4-disilacyclohexa-2,5-diene (trans-**7**) and 3,5-dimethyl-2,6-diphenyl-1,1,4,4-tetrakis(dimethylamino)-1,4-disilacyclohexa-2,5-diene (cis-**7**)*

Pentakis(dimethylamino) chlorodisilane (3.11 g, 10.0 mmol) was combined with 1-phenyl-1-propyne (1.11 g, 10.5 mmol) in a glass tube which was then cooled with liquid nitrogen and flame sealed under vacuum. The tube was heated to 200 °C for 2 days in an oil bath during which time the reaction mixture (a brown solution) was observed to reflux. After the reaction, the tube was allowed to cool to room temperature followed by further cooling to -18 °C in a freezer for 1 day. The tube was then opened in a hood, the liquid portion was removed by decantation and the solid was washed with 3 × 10 ml of pentane precooled in dry ice, followed by drying under vacuum. The product analyzed as a mixture of about 95% of one of the isomers with presumably *trans*-**7** isomer dominating, judging from the single ^{1}H-NMR peak and the single ^{13}C-NMR peak for the NMe_2 group for the dominant species. Yield: 70%. ^{1}H-NMR ($CDCl_3$): δ 6.94–7.29 (m, 10H); ^{13}C-NMR ($CDCl_3$): δ 156.25, 152.28, 144.15, 127.90, 127.69, 125.07, 37.80, 18.59. M.p.: 168–170 °C. EIHRMS; Calc. for C_{26} $H_{40}N_4Si_2$: 464.2792; found: 464.2798. This compound was quite soluble in pentane, in contrast to the other 1,4-disilacyclohexa-2,5-dienes synthesized here. That this product is an isomeric mixture is supported by its reaction with $SiCl_4$ which produced products consisting of 95% of one tetrachloro product. ^{1}H-NMR ($CDCl_3$): δ 7.16–7.44 (m, 10 H), 1.91 (s, 6H); ^{13}C-NMR ($CDCl_3$): δ 153.63, 152.22, 136.72, 128.52, 128.16, 127.59, 17.90.

*2.1.7. Synthesis of trans-2,3,5,6-tetraphenyl-1,4-dichloro-1,4-di-tert-butyl-1,4-disilacyclohexa-2,5-diene (trans-**8**)*

Symmetrical-di-*tert*-butyldichlorobis(dimethylamino)-disilane (3.29 g, 10.0 mmol) was combined with diphenylacetylene (2.13 g, 12.0 mmol) in a glass tube which was then cooled with liquid nitrogen and flame sealed under vacuum. The tube was heated to 210 °C for 3 days, during which time a brown solution formed. The tube was allowed to cool to ambient temperature, and was further cooled at ca. -18 °C in a freezer for 2 days. However, no crystal formation was observed. The tube was opened in a hood, and pentane [precooled in dry ice (20 ml)] was added to precipitate the product. The tube was then stoppered with a septum and stored in a freezer for 5 h, during which time the product precipitated. The solution was removed with a syringe, and the precipitate was washed with 5 × 5 ml of pentane. Drying the precipitate under vacuum afforded the product as a powder. Only one isomer (*trans*-**8**) was observed. Yield: 5%. ^{1}H-NMR ($CDCl_3$): δ 6.52–7.54 (m, br, 20H), 0.51 (s, 18H); ^{13}C-NMR ($CDCl_3$): δ 156.95, 141.79, 130.01, 127.18 (br), 125.99, 26.70, 22.27. M.p.: 285–287 °C. EIHRMS; Calc. for $C_{36}H_{38}Cl_2Si_2$: 596.1889; found: 596.1898. Elemental analysis: Calc. for $C_{36}H_{38}Cl_2Si_2$: C, 72.48; H, 6.29; Cl, 11.91; Si, 9.40; found: C, 72.26; H, 6.33; Cl, 11.94; Si, 9.01%. Crystals suitable for X-ray diffraction spectroscopy were obtained by recrystallization from $CHCl_3$.

2.1.8. General procedure for the synthesis of 2,3,5,6-tetraphenyl-1,1,4,4-tetrahalo-1,4-disilacyclohexa-2,5-dienes ***9a–c***

Compound **4** was halogenated with $SiCl_4$, PCl_3, $SiBr_4$ or PI_3 to obtain the corresponding title products in 95, 95, 95 and 70% yields, respectively. The synthesis of **9a** is given as an example. In a 100 ml flask equipped with a magnetic stirrer, were placed **4** (2.94 g, 5.00 mmol) and then Et_2O (50 ml). $SiCl_4$ (8.50 g, 50.0 mmol) was introduced through a syringe and the mixture was refluxed at 45 °C for 24 h during which time a white precipitate formed. After the reaction, the mixture was filtered under nitrogen and the white precipitate was washed with 5×10 ml of pentane. Drying the precipitate under vacuum afforded the product as a powder. Yield: 95%. ^{1}H-NMR ($CDCl_3$): δ 7.07–7.18 (m, 20H); ^{13}C-NMR ($CDCl_3$): δ 155.96, 136.71, 128.93, 127.17. M.p. (dec.): 287 °C. EIHRMS; Calc. for $C_{28}H_{20}Cl_4Si_2$: 553.9828; found: 553.9832. Elemental analysis: Calc. for $C_{28}H_{20}Cl_4Si_2$: C, 60.64; H, 3.61; Cl, 25.63; Si 10.11; found: C, 60.60; H, 3.54; Cl, 25.47; Si, 10.04%.

*2.1.9. Characterization of 2,3,5,6-tetraphenyl-1,1,4,4-tetrabromo-1,4-disilacyclohexa-2,5-diene **(9b)***

^{1}H-NMR ($CDCl_3$): δ 7.07–7.20 (m, 20H); ^{13}C-NMR ($CDCl_3$): δ 155.13, 136.70, 129.26, 127.51, 127.12. M.p.: 280 °C (decomposition). EIHRMS; Calc. for $C_{28}H_{20}Br_4Si_2$: 729.7827; found: 729.7828.

*2.1.10. Characterization of 2,3,5,6-tetraphenyl-1,1,4,4-tetraiodo-1,4-disilacyclohexa-2,5-diene **(9c)***

^{1}H-NMR ($CDCl_3$): δ 7.07–7.19 (m, 20H); ^{13}C-NMR ($CDCl_3$): δ 152.93, 137.50, 129.96, 127.32, 127.00. M.p. (dec.): 200 °C. CIMS (NH_3); *m/z* (relative intensity, ion): 937.0, 0.67 $[M + NH_3]^+$. Crystals suitable for X-ray diffraction were obtained by recrystallization from methylene chloride.

*2.1.11. Synthesis of 2,3,5,6-tetraphenyl-1,1,4,4-tetramethoxy-1,4-disilacyclohexa-2,5-diene **(9d)***

In an NMR tube were placed **4** (55.4 mg, 0.100 mmol) and 1.2 ml of Et_2O and then $Si_2(OMe)_6$ (48.4 mg, 0.20 mmol) was introduced through a syringe. The mixture was vibrated for 5 h in an ultrasonic bath. During the reaction, a white precipitate formed. The volatile materials were removed under vacuum, and the product was washed with 3×1 ml of pentane and then dried under reduced pressure. Yield: 90%. ^{1}H-NMR ($CDCl_3$): δ 7.00–7.11 (m, 20H), 3.33 (s, 12H); ^{13}C-NMR ($CDCl_3$): δ 156.14, 140.82, 128.82, 127.60, 125.89, 50.96. M.p.: 188–190 °C. EIHRMS; Calc. for $C_{32}H_{32}O_4Si_2$: 536.1839; found: 536.1841.

*2.1.12. Synthesis of 2,3,5,6-tetraphenyl-1,1,4,4-tetraphenoxy-1,4-disilacyclohexa-2,5-diene **(9e)***

This synthesis is analogous to that of **9a**–**d**, except that $P(OPh)_3$ was used as the derivatizing agent. The product was washed with 3×1 ml pentane and dried under reduced pressure. Yield: 95%. ^{1}H-NMR ($CDCl_3$): δ 6.68–7.12; ^{13}C-NMR ($CDCl_3$): δ 157.24, 153.43, 139.16, 129.21, 128.76, 126.26, 122.07, 119.79. EIMS; *m/z* (relative intensity, ion): 784.3 ($[M^+]$, 5.26). EIHRMS; Calc. for $C_{52}H_{40}O_4Si_2$: 784.2465; found: 784.2475. Elemental analysis: Calc. for $C_{52}H_{40}O_4Si_2$: C, 79.59; H, 5.10. Found: C, 79.10; H, 5.19%. Crystals suitable for X-ray diffraction spectroscopy were obtained by recrystallization from $CHCl_3$.

*2.1.13. Synthesis of 2,3,5,6-tetraphenyl-1,4-disilacyclohexa-2,5-diene **(10)***

In a 50 ml flask equipped with a magnetic stirrer were placed **9a** (2.77 g, 5.00 mmol) and then THF (25 ml and $LiAlH_4$ (0.76 g, 20 mmol). The mixture was refluxed at 75 °C for 24 h. After the reaction, $LiAlH_4$ was destroyed with 20 ml of MeOH. The mixture was filtered, and volatiles were removed under reduced pressure. The product was purified by column chromatography using $CHCl_3$ as the eluent. Yield: 70%. ^{1}H-NMR ($CDCl_3$): δ 7.01–7.16 (m, 20H), 4.58 (s, 4H); ^{13}C-NMR ($CDCl_3$): δ 152.01, 141.67, 128.14, 128.06, 126.34. M.p.: 240–242 °C. EIHRMS; Calc. for $C_{28}H_{24}Si_2$: 416.1417; found: 416.1422. Elemental analysis: Calc. for $C_{28}H_{24}Si_2$: C, 80.77; H, 5.77; Si, 13.46; found: C, 80.55; H, 5.49; Si, 13.15%. Subliming the compound under vacuum at 200 °C gave crystals suitable for X-ray diffraction.

*2.1.14. Synthesis of 2,3,5,6-tetraphenyl-1,1,4,4-tetrahydroxy-1,4-disilacyclohexa-2,5-diene **11***

In a 50 ml flask equipped with a magnetic stirrer were placed **9a** (1.38 g, 2.50 mmol) and then acetone (25 ml). After **9a** had dissolved, distilled water (0.90 g, 50.0 mmol) was added dropwise through a syringe with stirring whereupon a white precipitate was formed. The reaction mixture was stirred at room temperature for 2 h and then filtered. The precipitate was washed with 3×5 ml of Et_2O followed by 3×5 ml of pentane and then the product was dried under reduced pressure. Yield: 98%. ^{1}H-NMR (THF-d_8): δ 6.88–7.09 (m, 20H), 5.51 (s, 4H); ^{13}C-NMR (THF-d_8): δ 157.21, 143.25, 130.20, 127.62, 125.51. M.p.: >300 °C. EIMS; *m/z* (relative intensity, ion): 480.1 ($[M^+]$, 0.70); CIMS (NH_3, negative) 479.9 ($[M-]$, 52.80). EIHRMS; Calc. for $C_{28}H_{24}O_2Si_2$: 480.1213; found: 480.1221. Elemental analysis: Calc. for $C_{28}H_{24}O_2Si_2$: C, 70.00; H, 5.00; Si, 11.67. Found: C, 70.57; H, 5.08; Si, 11.74%.

*2.1.15. Synthesis of 1,4-dichloro-1,4-dimethyl-2,3,5,6-tetraphenyl-1,4-disilacyclohexa-2,5-diene **(12)***

The preparation of this compound was analogous to that of **9a**–**c**, except that **6** and $SiCl_4$ were used as starting materials. Although only one isomer of **6** (presumably the *trans*) was used in the reaction, a mixture of diastereomers in a ca. 1:1 ratio was obtained. Attempts to separate these two isomers by fractional sublimation or column chromatography failed. ^{1}H-NMR ($CDCl_3$): δ 6.98–7.13 (m, 20H), 0.37 (s, 3H), 0.30 (s, 3H); ^{13}C-NMR ($CDCl_3$): δ 156.47, 156.44, 128.51, 128.38, 127.66, 127.60, 126.23, 0.40, 0.25. M.p.:

> 300 °C. EIHRMS; Calc. for $C_{30}H_{26}Cl_2Si_2$: 512.095015; found: 512.0959674.

2.1.16. Synthesis of trans-2,3,5,6-tetraphenyl-1,4-dihydro-1,4-di-tert-butyl-1,4-disilacyclohexa-2,5-diene (13)

The preparation of this compound is analogous to that of **10** except that **8** and $LiAlH_4$ were employed as starting materials. The yield of 75%, includes about 10% of a minor (presumably *cis*) isomer. ^{1}H-NMR ($CDCl_3$): δ 6.82–7.07 (m, 24 H), 4.97 (s, 2 H, *trans*), 4.50 (s, 0.32 H, *cis*), 0.84 (s, 3.14 H, *cis*), 0.41 (s, 18 H, *trans*); ^{13}C-NMR ($CDCl_3$) (*trans*): δ 154.43, 143.59, 129.71, 127.49, 125.59, 28.34, 19.90; ^{13}C-NMR ($CDCl_3$) (*cis*): δ 156.69, 140.28, 129.34, 127.02, 125.43, 29.49, 20.00. M.p.: 238–240 °C. Crystals suitable for X-ray diffraction spectroscopy were obtained by recrystallization from methylene chloride.

2.1.17. Variable temperature NMR studies of 8

The ^{1}H- and ^{13}C-NMR spectra of **8** were measured at different temperatures to investigate restrictions on the free rotation of the four phenyl groups. ^{1}H-NMR at − 30 °C ($CDCl_3$): δ 7.52–7.54 (d, 2H), 7.21 (t, 2H), 6.97 (t, 2H), 6.85 (t, 2H), 6.50–6.52 (d, 2H); ^{13}C-NMR ($CDCl_3$): δ 156.52, 141.55, 129.83, 129.64, 127.34, 126.90, 125.87, 26.47, 22.26. ^{1}H-NMR at 25 °C ($CDCl_3$): δ 6.52–7.54 (m, br, 20H), 0.51 (s, 18H); ^{13}C-NMR ($CDCl_3$): δ 156.95, 141.79, 130.01, 127.18 (br), 125.99, 26.70, 22.27. ^{1}H-NMR at 50 °C ($CDCl_3$): δ 6.52–7.54 (br, 20H), 0.46 (s, 18H); ^{13}C–NMR ($CDCl_3$): δ 157.16, 141.92, 130.14, 127.20, 126.04, 26.80, 22.29. At temperatures below 0 °C, five different protons were observed. At − 30 °C, the ^{1}H-NMR spectrum also showed five well-separated peaks. Moreover, six distinct ^{13}C signals were observed at that temperature. From room temperature to 50 °C, two pairs of ^{13}C peaks associated with the phenyl groups began to coalesce. Small changes in the chemical shifts of the *tert*-butyl groups also occurred with temperature.

2.1.18. X-ray crystallographic determinations

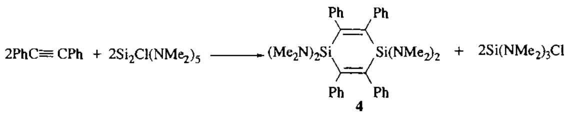
A crystal of compound **4** was mounted on a glass fiber on an Enraf–Nonius CAD4 for data collection at 293(2) ± 1 K. The cell constants for the data collection were determined from reflections found from a 360° rotation photograph. Lorentz and polarization corrections were applied. A nonlinear correction based on the decay in the standard reflections was also applied to the data. A series of azimuthal reflections was collected for the crystal and a semi-empirical absorption correction was applied to the data.

For compounds **8**, **9c**, **9e**, **10** and **13**, a crystal was selected from oil under ambient conditions and was attached to the tip of a glass capillary. The crystal was mounted in a stream of cold nitrogen at 173(2) K and centered in the X-ray beam using a video camera. Crystal evaluation and data collection were performed on a Bruker CCD-1000 diffractometer with a diffractometer-to-crystal distance of 5.08 cm. The initial cell constants were obtained from three series of ω scans at different starting angles. Each series consisted of 20 frames at intervals of 0.3° in a 6° range about ω with an exposure time of 10 s per frame. The reflections were successfully indexed by an automated indexing routine built into the SMART program. The data were collected using the hemisphere data collection routine. The reciprocal space was surveyed to the extent of 1.2 hemispheres to a resolution of 0.80 Å. The highly redundant data sets were corrected for Lorentz and polarization effects. The absorption correction was based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements. A summary of crystallographic data including unit cells and refinement data for each of the structure analyses appears in Table 1.

3. Results and discussion

3.1. Synthesis of 1,4-disilacyclohexa-2,5-dienes

In the reaction of diphenylacetylene with $Si_2Cl(NMe_2)_5$ (carried out in a sealed tube at 200 °C) crystalline **4** was obtained in 45% yield, together with the liquid by-product $Si(NMe_2)_3Cl$ (reaction 3). The constitution of the latter product was confirmed by ^{1}H-NMR, ^{13}C-NMR and MS spectroscopies. When sym-$Si_2Cl_2(NMe_2)_4$was used in this reaction, however, the isomeric products **5a** and **5b** were obtained in about 20% yield, accompanied by the formation of *ca* 5% of the trimerization product hexaphenylbenzene. In this case, one isomer, presumably *trans*-**5**, was the dominant product, with a trace amount *cis*-**5**. The by-product, as expected, was again $Si(NMe_2)_3Cl$ (reaction 4).



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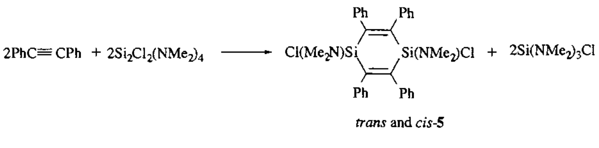

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A silylene pathway similar to that proposed in the literature [13] is suggested here as is illustrated in Scheme 2 for the synthesis of **4**. Amino groups (including the dimethylamino group) are known to stabilize silylenes [14], including an example (**14**) that is stable at

Table 1
Crystallographic data for structure refinement parameters for **4**, **8**, **9c**, **9e**, **10**, and **13**

	4	**8**	**9c**	**9e**	**10**	**13**
Empirical formula	$C_{36}H_{44}N_4Si_2$	$C_{38}H_{38}Cl_2Si_2$	$C_{29}H_{21}Cl_3I_4Si_2$	$C_{52}H_{40}O_4Si_2$	$C_{28}H_{24}Si_2$	$C_{36}H_{40}Si_2$
Formula weight	588.93	597.74	1039.59	785.02	416.65	528.86
Temperature (K)	293(2)	173(2)	173(2)	173(2)	173(2)	173(2)
Wavelength (λ, Å) (Mo–K_α) 5025	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Tetragonal	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/n$	$P2_1/c$	$P4(2)nm$	$P2_1/n$	$P2_1/c$	$P1$
Unit cell dimensions						
a (Å)	8.963(2)	9.7708(8)	11.7536(5)	9.1542(5)	7.8373(4)	12.0270(5)
b (Å)	15.510(3)	9.3984(8)	11.7536(5)	17.1747(6)	11.9759(7)	69.5348(10)
c (Å)	12.473(2)	17.8150(14)	12.2191(6)	15.6315(7)	12.3495(7)	12.1135(5)
α (°)	90	90	90	90	90	69.5348(10)
β (°)	98.15(3)	103.939(1)	90	97.649(1)	99.120(1)	77.0789(10)
γ (°)	90	90	90	90	90	63.6759(10)
V (Å^3)	1716.4(6)	1587.8(2)	1688.03(13)	2010.26(17)	1144.46(11)	1577.52(11)
Z	2	2	2	2	2	2
D_{calc} (Mg m^{-3})	1.140	1.250	2.045	1.297	1.209	1.113
Absorption coefficient (mm^{-1})	0.133	0.304	4.019	0.137	0.167	0.134
F(000)	632	632	972	824	440	568
Crystal size (mm)	0.4 × 0.4 × 0.3	0.46 × 0.40 × 0.10	0.35 × 0.35 × 0.30	0.45 × 0.45 × 0.40	0.45 × 0.40 × 0.35	0.50 × 0.40 × 0.40
Theta range for data collection (°)	2.11–27.47	2.36–26.37	2.40–28.30	1.95–26.37	2.38–27.37	1.69–26.37
Index ranges	$-1 \leq h \leq 11$, $-1 \leq k \leq 20$, $-16 \leq l \leq 16$	$-12 \leq h \leq 1$, $10 \leq k \leq 11$, $0 \leq l \leq 22$	$-15 \leq h \leq 15$, $-15 \leq k \leq 15$, $-16 \leq l \leq 15$	$-11 \leq h \leq 11$, $0 \leq k \leq 17$, $0 \leq l \leq 19$	$-9 \leq h \leq 9$, $0 \leq k \leq 14$, $0 \leq 1 \leq 15$	$-14 \leq h \leq 15$, $-13 \leq k \leq 15$, $0 \leq 1 \leq 16$
Reflections collected	5025	9799	14 104	17 677	8638	13 896
Independent reflections	3937 [$R_{int} = 0.0340$]	3241 [$R_{int} = 0.0274$]	2183 [$R_{int} = 0.0334$]	4086 [$R_{int} = 0.0334$]	2331 [$R_{int} = 0.0197$]	6397 [$R_{int} = 0.0172$]
Completeness to theta = 26.37° (%)	NA	99.8	99.0	99.5	99.8	99.2
Absorption correction	Semi-empirical	Semi-empirical	Empirical with SADABS	Empirical with SADABS	Empirical with SADABS	Empirical with SADABS
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	NA	32 41/0/184	2183/3/10	0.9474 and 0.9411	2331/0/144	6397/0/357
Final R indices [$I > 2\sigma(I)$] [a]	$R_1 = 0.0689$, $wR_2 = 0.1623$	$R_1 = 0.0333$, $wR_2 = 0.0782$	$R_1 = 0.0275$, $wR_2 = 0.0775$	$R_1 = 0.0338$, $wR_2 = 0.0854$	$R_1 = 0.0314$, $wR_2 = 0.0841$	$R_1 = 0.0442$, $wR_2 = 0.1092$
R Indices (all data) [a]	$R_1 = 0.1611$, $wR_2 = 0.2070$	$R_1 = 0.0530$, $wR_2 = 0.0835$	$R_1 = 0.0286$, $wR_2 = 0.0782$	$R_1 = 0.0451$, $wR_2 = 0.0907$	$R_1 = 0.0385$, $wR_2 = 0.0879$	$R_1 = 0.0494$, $wR_2 = 0.1092$
Goodness-of-fit on F^2 [b,c]	1.147, 1.035	1.031	1.052	1.035	1.048	1.038
Largest difference peak and hole (e Å^{-3})	0.306 and −2.58	0.328 and −2.07	1.920 and −0.744	0.325 and −0.300	0.326 and −0.200	0.367 and −0.292

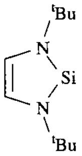
[a] $R_1 = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$, $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{0.5}$, where $w = 1/[\sigma^2(F_o)^2) + aP)^2 + bP + d + e \sin\theta]$.

[b] $\mathrm{GooF} = [\Sigma[w(F_o^2 - F_c^2)^2]/(n-p)]^{0.5}$.

[c] Twin component contributions were 0.52(3) and 0.48(3).

room temperature [15]. In an attempt to substantiate a silylene pathway for the formation of **4** and **5a**,**b**, we carried out their syntheses in the presence of quinones such as benzil, and dienes such as 1,3-butadiene which are well known traps for R_2Si: [16]. However, we discovered that disilanes with electron-withdrawing groups such as halogen and alkoxy reacted smoothly with 1,2-quinones and 1,4-quinones to give doubly silylated products [17]. We therefore attempted to react Si$_2$(NMe$_2$)$_5$Cl or Si$_2$(NMe$_2$)$_4$Cl$_2$ with benzil in CHCl$_3$ either at room temperature or at 75 °C. Because no reaction was observed at either temperature, there was a possibility that such a mixture at 180 °C (which is in the temperature range where our reactions are carried out) might give rise to silylene adducts that could be trapped. When benzil and Si$_2$(NMe$_2$)$_5$Cl were heated to 180 °C in a sealed tube, a brown insoluble material was formed. Washing the reaction mixture with pentane gave a gray precipitate, which appeared to be an oligomeric material by ^{1}H- and ^{13}C-NMR spectroscopies.

Moreover, mass spectroscopy did not reveal the presence of a silylene adduct. When *trans*,*trans*-1,4-diphenyl-1,3-butadiene was used as a trap, however, an HRMS of the reaction mixture gave a major peak for **15** (calc. for C$_{20}$H$_{26}$NSi: 322.18653; found: 322.186597) thus supporting a silylene pathway for our reactions.



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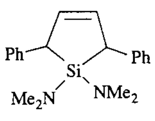

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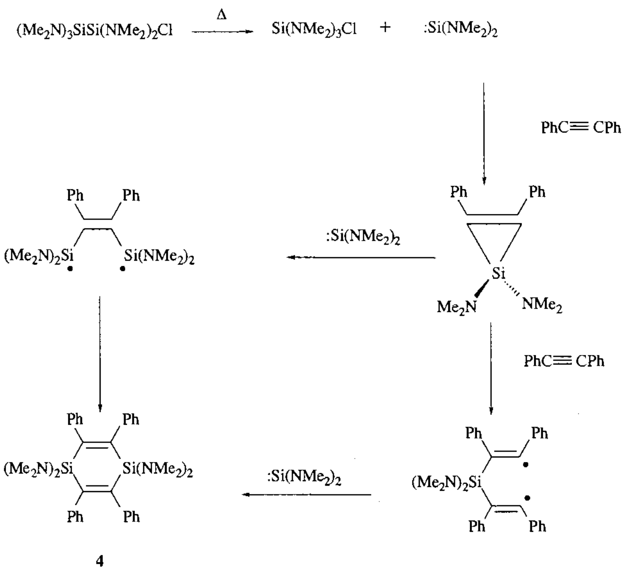
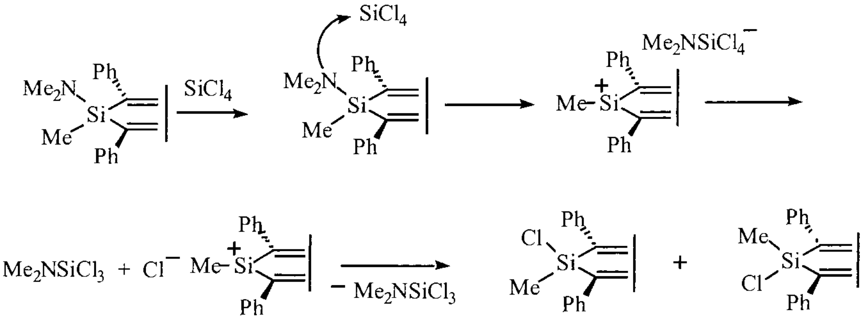
When Si$_2$(NMe$_2$)$_6$was allowed to react with diphenylacetylene, not surprisingly, **4** was obtained. However, the yield of this reaction dropped to ca. 20%, which is less than half of that obtained from the Si$_2$Cl(NMe$_2$)$_5$/PhC≡CPh reaction. This result may be rationalized on the basis of the relative strengths of the Si–Si linkages in the two disilanes, since a chloro substituent is expected to be more electron-withdrawing than a dimethylamino group, thereby weakening the Si–Si bond. Moreover, Si$_2$Cl(NMe$_2$)$_5$ is a less sterically hindered disilane, the generation of the silylene Si(NMe$_2$)$_2$ species via disproportionation of the disilane may be more facile, owing to the less sterically hindered by-product Si(NMe$_2$)$_3$Cl that is formed compared with that formed in the Si$_2$(NMe$_2$)$_6$/PhC≡CPh, namely Si(NMe$_2$)$_4$.



Scheme 2.

When the non-symmetric alkyne 1-phenyl-1-propyne was allowed to react with Si$_2$Cl(NMe$_2$)$_5$, the isomeric products **7** were isolated (in ca. 10:1 ratio) in good yield. Here *trans*-**7** dominates according to ^{1}H- and ^{13}C-NMR spectroscopies (see Section 2). Similarly, when sym-Si$_2$Me$_2$(NMe$_2$)$_4$ was allowed to react with diphenylacetylene in a sealed tube, the corresponding *trans* product **6** was obtained in 75% yield. Interestingly, only a trace amount of *cis*-**6** was detected. When more bulky groups were introduced, much lower product yields were obtained, even though higher temperatures and prolonged reaction times were employed. Thus in the reaction of sym-Si$_2^t$BuCl$_2$(NMe$_2$)$_2$ with diphenylacetylene, the corresponding *trans* product **8** was obtained exclusively in less than 5% yield at 210 °C over a period of 3 days. In this reaction the silylene SiCl^{t}Bu is expected to be the reactive species.

The varying yields obtained from diphenylacetylene with the various dimethylamino disilanes can be attributed to a combination of electronic effects on the Si–Si bond strength and steric effects of the substituents. Thus the least sterically hindered disilane Si$_2$Me$_2$(NMe$_2$)$_4$ gave product **6a** (*trans*) in 75% yield, whereas the highly bulky Si$_2^t$Bu$_2$Cl$_2$(NMe$_2$)$_2$ reacted incompletely with diphenyl acetylene. It is apparent that the presence of multiple dimethylamino groups on disilanes favors disilane disproportionation reactions, perhaps because the weakness of the Si–N bond (compared with the Si–Cl linkage [18]) facilitates the thermal cleavage of this bond, leading to the formation of reactive silylene species that are electronically stabilized by one or more NMe$_2$ groups. As reported by us earlier [2], when diphenylacetylene was allowed to react with disilanes with zero, two, three, four, five and six dimethylamino groups at 200 °C for 40 h, we found that the ratio of disilacyclohexadiene to hexaphenylbenzene generally rose from zero in the case of the Si$_2$Cl$_6$/PhC≡CPh reaction (i.e. hexaphenylbenzene as the only detectable product) to infinity (i.e., **9a** as the sole detectable product) in the Si$_2$(NMe$_2$)$_5$Cl/PhC≡CPh and Si$_2$(NMe$_2$)$_6$/PhC≡CPh reactions. Because the Cl atom is more electron-withdrawing than the NMe$_2$ group [19], the Si–Si link in Si$_2$(NMe$_2$)$_5$Cl is weakened and the Si–N bond is weaker than Si–Cl bond, thus facilitating disproportionation to give Si(NMe$_2$)$_2$ species. However, as more NMe$_2$ groups are substituted by Cl atoms, silyl radical generation via homolytic Si–Si cleavage will be increasingly favored over silylene production. Although the mono-substituted disilane Si$_2$(NMe$_2$)Cl$_5$ was not obtained in pure form, the impure material led to



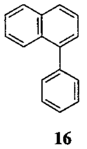
Scheme 3.

hexaphenylbenzene as the only detectable product as was the case with Si_2Cl_6.

Interestingly, silanes bearing dimethylamino groups, such as $Si(NMe_2)_3Cl$ and $Si(NMe_2)_4$ are unreactive toward diphenylacetylene at 210 °C for 3 days. Products **4** and **5** might have been expected if silylene formation had occurred. This observation further supports the idea that the presence of a Si–Si bond in disilanes bearing dimethylamino groups favors the disproportionation process involved in silylene generation.

Pyrolysis of either $Si_2(NMe_2)_5Cl$ or $Si_2(NMe_2)_4Cl_2$ at 200 °C in a sealed tube gave oligomeric products, together with $Si(NMe_2)_3Cl$, as was confirmed by ^1H- and ^{13}C-NMR, and mass spectroscopies. This is consistent with our suggestion that in these disproportionation reactions $Si(NMe_2)_2$ [or $Si(NMe_2)Cl$] together with $Si(NMe_2)_3Cl$ [or $Si(NMe_2)_2Cl_2$] are formed. These highly reactive silylenes could then lead to oligomeric products. However, efforts to trap silylene species in these experiments failed.

Interestingly, when phenylacetylene was allowed to react with either $Si_2Cl(NMe_2)_5$ or sym-$Si_2Cl_2(NMe_2)_4$, no product analogous to **4** or **5** was detected. Instead, the cyclodimerization product **16** was obtained as the dominant product (85% conversion) together with the two isomeric trimers 1,3,5-triphenylbenzene and 1,2,4-triphenylbenzene (15% conversion) as shown by ^1H- and ^{13}C-NMR, and GC-mass spectroscopies. This result is consistent with our earlier observations on the tendency of terminally conjugated alkynes to undergo thermal dimerization



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[2]. As expected, oligomeric material and $Si(NMe_2)_3Cl$ were also formed from the pyrolysis of these disilanes. It should be noted that the triphenylbenzenes are also formed in the absence of a disilane [2].

*3.2. Reactions of 1,4-disilacyclohexa-2,5-dienes **4**, **6**, **7**, **8**, **9a***

3.2.1. Halide substitution

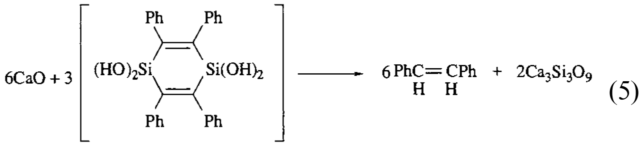
It was found that the dimethylamino groups on **4**, **6** and **7** are quite labile. When **4** was treated with excess $SiCl_4$ at 45 °C in Et_2O for 3–4 h, **9a** was obtained in 95% yield. Analogous treatment of **4** with PCl_3 also afforded **9a**, and **9b** was obtained analogously in the reaction of PBr_3 (or $SiBr_4$) with **4**. The reaction of **4** with PI_3 gave product **9c** in 70% yield.

Although *trans*-**6** is formed in the $Si_2Me_2(NMe_2)_4$/$PhC{\equiv}CPh$ reaction, treatment of this product with $SiCl_4$, gave both *cis*-**12** and *trans*-**12** in a ca. 1:1 ratio. It is suggested that halogen substitution can occur via an ionic pathway facilitated by the formation of a five-coordinate silicon intermediate as shown in Scheme 3. A covalent pathway would seem to be more attractive, however, since the reaction occurs in a rather nonpolar solvent (ether). The first two paths in Scheme 4 are expected to lead to stereoretention of each silicon configuration in the substrate molecule, while the third path in this scheme would result in the formation of the opposite configuration at silicon. Apical departure of the dimethylamino group in this path could be facilitated by a second $SiCl_4$ molecule.

3.2.2. Alkoxide and hydroxide substitution

When **4** was heated at 100 °C with excess $Si_2(OMe)_6$ in the absence of a solvent for 5–6 h, colorless crystals of **9d** formed in 80% yield. Compound **9e** was obtained as colorless crystals in 95% yield from the reaction of $P(OPh)_3$ and **4** at 140 °C for 15 h.

When water was added to a solution of **9a** in acetone, **11** formed as a white precipitate in 95% yield. This product is very stable towards air and moisture, and no decomposition was observed at 200 °C for 3 days. When **11** was treated with CaO at 250 °C under vacuum in an attempt to dehydrate **11**, the formation of *cis*- and *trans*-stilbenes was detected by ^1H- and ^{13}C-NMR spectroscopies. According to reaction 5, in which the formation of a cyclic metasilicate such as $Si_3O_9^{6-}$ is suggested, the formation of stable volatile stilbene must constitute a substantial driving force for the cleavage of the robust Si–O bond. However, a highly thermally stable cross-linked polymer was obtained when the dehydration reaction was carried out in refluxing acetic anhydride.



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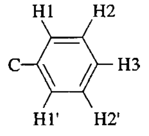
3.2.3. Reduction of 9a with $LiAlH_4$

When **9a** was treated with $LiAlH_4$ in refluxing THF, the corresponding reduction product **10** was obtained in 80% yield. Compound **10** was stable to purification by column chromatography.

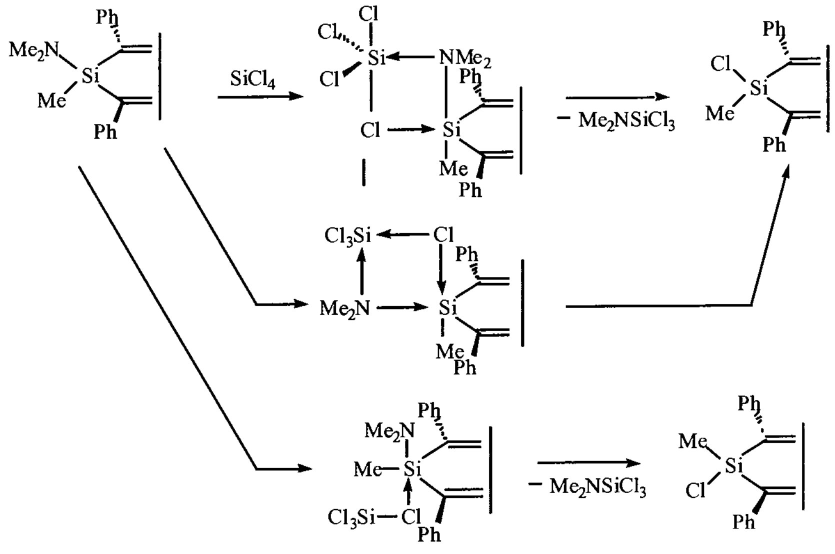
3.3. ^1H- and ^{13}C-NMR spectroscopic study

For compounds **4**, **5**, **6**, **7**, **9a**–**c**, **10** and **11**, the aromatic ^1H-NMR peaks all appeared below 7.24 ppm, the chemical shift for $CHCl_3$ in the NMR solvent $CDCl_3$. For compound **8** (which has the *trans* configuration), however, aromatic chemical shifts as high as 7.54 ppm were also evident. In fact, four equally spaced broad singlets (δ 7.54, 7.18, 6.85, 6.52 ppm) accompanied by a triplet at 6.96 ppm were observed. Similarly, the ^{13}C-NMR spectrum displayed four singlets (δ 156.95, 141.79, 130.01, 125.99, the latter two somewhat broadened) and a broad peak at 127.18 ppm. Because the *tert*-butyl group in **8** is the most sterically hindered group in this series of compounds, this observation could be attributed to restricted rotation of the four phenyl groups owing to the steric encumbrance of the *tert*-butyl groups. Such restricted rotation would be expected to differentiate the five protons and the carbons to which they are bonded in each phenyl substituent.

Variable temperature ^1H- and ^{13}C-NMR spectral studies at 50 °C, ambient temperature and -30 °C revealed changes consistent with restricted rotation of the phenyl groups. Structure **17** represents a phenyl group of **8** which is locked into an orientation wherein its plane is perpendicular to that of the disilacyclohexadiene ring. The chemical environments of H1 and H1′ are different and the same is true of H2 and H2′, owing to the *trans* orientations of the *t*-Bu and chloro groups across the plane of the disilacyclohexadiene ring (see Section 3.4). The VT ^1H-NMR spectrum in Fig. 1a reveals five chemical shifts (two doublets and three ‘triplets’) for the phenyl region of **8**, plus a $CHCl_3$ proton peak stemming from the $CDCl_3$ solvent used. We assign the two doublets to H1 and H1′ since proton couplings in phenyl rings generally decrease significantly from *ortho* to *meta* to *para* oriented pairs of hydrogens. Further support for these assignments comes from the expectation that the difference in the environments of these protons is maximized ($\Delta\delta \cong 1$ ppm) by their proximity to the disilacyclohexadiene ring. This reasoning suggests that the H2 and H2′ resonances should be overlapping doublets of doublets with a smaller separation of their chemical shifts. Thus we assign the resonances at 6.85 and 7.2 ppm to these protons. H3 suffers no change in environment upon rotation. Thus its multiplet resonance does not broaden as significantly, and it persists even at room temperature (Fig. 1c).



17



Scheme 4.

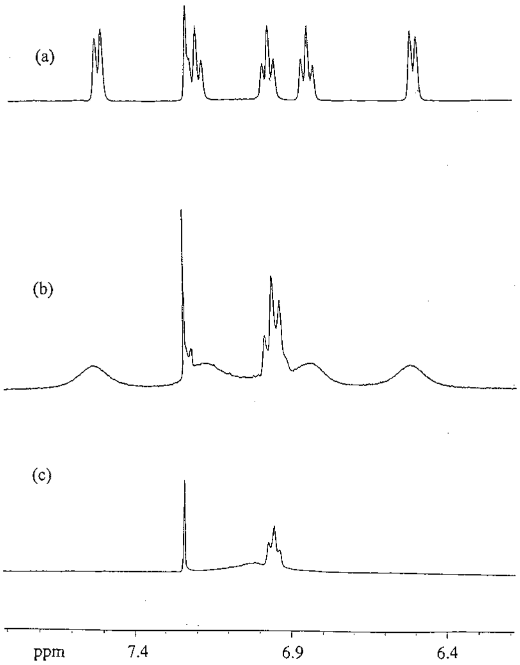


Fig. 1. ^{1}H-NMR spectra for **8** at: (a) −30; (b) 20; and (c) 50 °C.

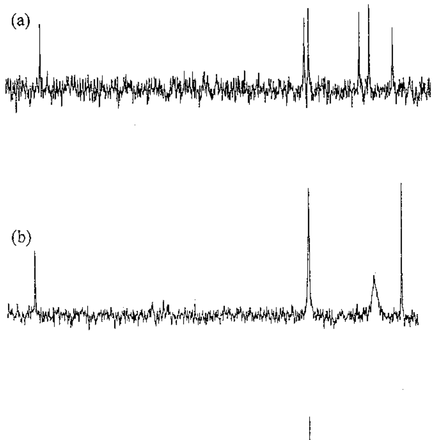


Fig. 2. ^{13}C-NMR spectra for **8** at: (a) −30; (b) 20; and (c) 50 °C.

The VT ^{13}C-NMR spectra (Fig. 2) show the *ipso*-carbon at ca. 141 ppm as expected, and the *para*-carbon at about 126 ppm. Also as expected, the *ortho*- and *meta*-carbon pairs coalesce upon warming. It is tempting to assign chemical shifts to these pairs which are centered at ca. 127 ppm for C1, C1′ and at about 130 ppm for C2, C2′ based on their relative separation (as was done for H1, H1′ and H2, H2′). However, the 2D COSY spectrum does not bear this out and the reverse assignment is unequivocally indicated for reasons that are not clear.

3.4. Structural considerations

Molecular structure determinations by X-ray crystallography were carried out on **4**, **8**, **9c**, **9e**, **10** and **13**. All these compounds featured a planar 1,4-disilacyclohexa-2,5-diene six-membered ring, with four phenyl groups oriented nearly perpendicular to the central ring. Because all of these structures possess an inversion center in the middle of the central ring, these compounds possess C_2 symmetry when all four silicon substituents are identical, except in **4** and **9e** wherein the silicon and ring carbon phenyls are not crystallographically equivalent. Although **10** could possibly have higher symmetry, close inspection indicates that there are also two sets of crystallographically distinguishable phenyl groups in this compound, therefore lowering the expected D_{2h} symmetry.

The structures for these compounds are shown in Figs. 3–8 with selected bond distances and angles for each. Compounds **8** and **10** represent the two extremes of this series of 1,4-disilacyclohexa-2,5-dienes in terms of relative steric encumbrance. However, the bond distances and bond angles of the central ring of these two structures are within three times their ESD values. For example, the average Si–C bond distance in **8** is 1.8798(17) Å the C=C bond distance is 1.362(2) Å. These distances are 1.8709(13) Å and 1.3550(18) Å, respectively, in **10**. The bond angles on the central ring of **8** and **10** are C–Si–C′ 111.67(7), Si–C′–C″, 125.25(12) and C–Si–C′ 113.38(6), Si–C′–C″ 124.02(10), respectively. The differences between other corresponding angles are even smaller.

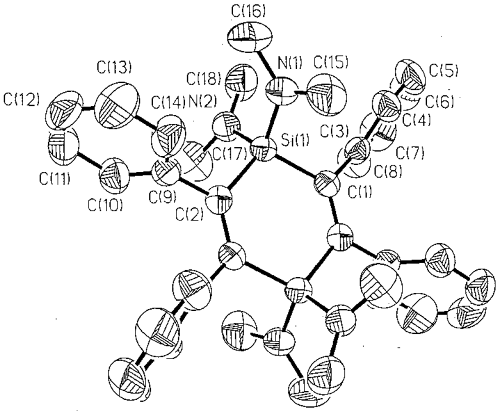


Fig. 3. Computer drawing of the molecular structure of **4**. Selected bond distances (Å) and bond angles (°): C(1)–Si(1): 1.878(3), C(2)–Si(1): 1.881(3), Si(1)–N(1): 1.703(3), Si(1)–N(2): 1.707(3), C(1)A1–C(2)–Si(1): 125.3(2), C(1)A1–C(2)–C(9): 122.1(3), N(1)–Si(1)–N(2): 108.4(2), C(1)–Si(1)–C(2): 110.35.

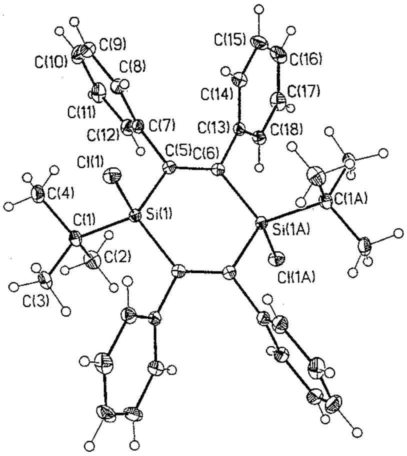


Fig. 4. Computer drawing of the molecular structure of **8**. Selected bond distances (Å) and bond angles (°): C(5)–Si(1): 1.8824(17), C(5)–C(6): 1.362(2), C(1)–Si(1): 1.8971(17), C(5)–C(7): 1.505(2), Si(1)–Cl(1): 2.0853(6), C(5)–Si(1)–C(6A): 111.67(7), Si(1)–C(5)–C(6): 125.25(12), Cl(1)–Si(1)–C(1): 107.07(5), C(5)–C(6)–Si(1A) 123.06.

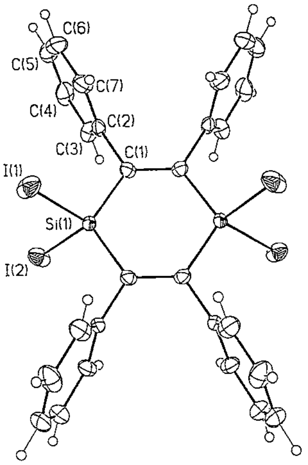


Fig. 5. Computer drawing of the molecular structure of **9c**. Selected bond distances (Å) and bond angles (°): Si(1)–C(1): 1.862(3), Si(1)–C(1A): 1.862(3), Si(1)–I(1) 2.4339(19), Si(1)–I(2): 2.4382(18), C(1)–C(1A): 1.362(6), C(1)–Si(1)–C(1A): 115.3(2), Si(1)–C(1)–C(1A): 122.33(10), I(1)–Si(1)–I(1A): 108.61(5).

In compound **9e** there are eight phenyl groups rendering the molecular quite bulky. Although the central part is essentially the same as in other compounds in this series, the behavior of the two phenoxy groups is interesting. A side view of the structure indicates that there are two sets of phenoxy groups, with two phenyl groups in each set. One set is almost in parallel to the central 1,4-disilacyclohexa-2,5-diene ring while the other is close to being perpendicular to it. This is caused either by the steric hindrance of the phenoxy groups, or electronic repulsion effects from the ring aromatic pi systems.

Attempts to solve the molecular structure of **12** were not completely successful owing to disorder of the methyl and chloro substituents. Thus although the configuration of the rings could be ascertained, the present isomer could not. Crystals of **6** suffered from severe disorder problems. As a result, no meaningful information regarding the isomer present could be obtained. It is likely on steric grounds, however, that the Me_2N groups are *trans* to each other.

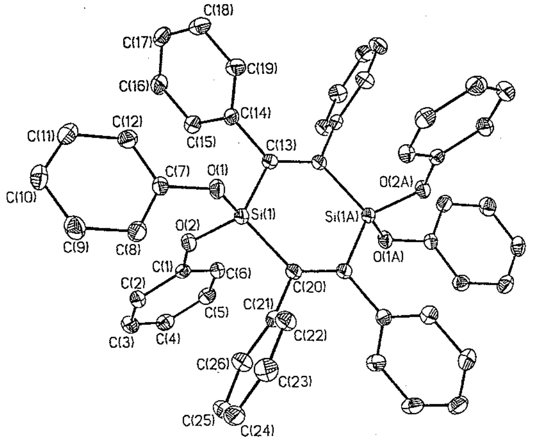


Fig. 6. Computer drawing of the molecular structure of **9e**. Selected bond distances (Å) and bond angles (°): Si(1)–C(13): 1.8661(14), Si(1)–O(1): 1.6287(10), Si(1)–O(2) 1.6334(10), Si(1)–C(20): 1.8569(14), C(13)–C(20A): 1.350(2), C(13)–Si(1)–C(20): 113.41(6), Si(1)–C(13)–C(20A): 123.36(11), C(13A)–C(20)–Si(1): 123.16(11), O(1)–Si(1)–O(2): 103.88(5).

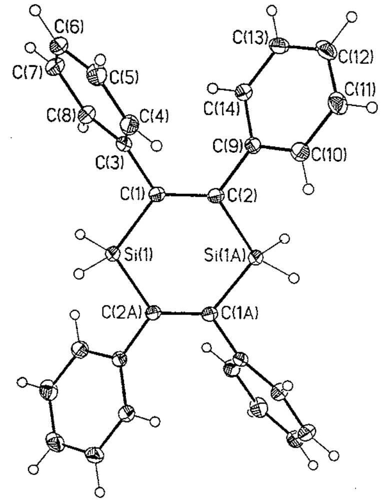


Fig. 7. Computer drawing of the molecular structure of **10**. Selected bond distances (Å) and bond angles (°): C(1)–Si(1): 1.8695(13), Si(1)–C(2A): 1.8723(13), C(1)–C(2): 1.3550(18), C(1)–C(3): 1.4978(17), C(1)–Si(1)–C(2A): 113.38(6), Si(1)–C(1)–C(2): 124.02(10), C(1)–C(2)–Si(1A): 122.58(10).

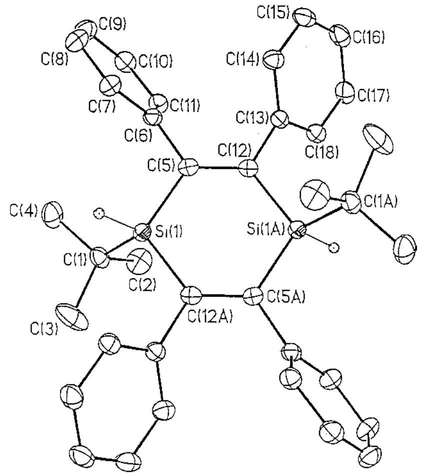


Fig. 8. Computer drawing of the molecular structure of **13**. Selected bond distances (Å) and bond angles (°): C(5)–Si(1): 1.8822(16), Si(1)–C(12A): 1.8842(16), C(5)–C(12): 1.356(2), C(5)–C(6): 1.500(2), C(5)–Si(1)–C(12A): 111.70(7), Si(1)–C(5)–C(12): 123.74(12), C(5)–C(12)–Si(1A): 123.90(12).

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 1755311, 175304, 175306, 175307, 175305, 75303 and 175308 for compounds **4**, **8**, **9c**, **9e**, **10**, **12** and **13**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

The authors thank the National Science Foundation for grant support, Dr Philip Kisanga for helpful suggestions and Professors Andrzej Wroblewski and Robson Matos for assistance.

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