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Synthesis, Strain, Conformational Analysis, and Molecular and Crystal Structures of 1,1,4,4-Tetraphenyl-1,4-disilacyclohexane and 1,1,4,4-Tetraphenyl-1,4-disilacyclohexa-2,5-diene[†]

Jadwiga E. Laska and Piotr Kaszynski*

Organic Materials Research Group, Department of Chemistry, Vanderbilt University, Nashville, Tennessee 37235

S. Joshua Jacobs[‡]

Sandia National Laboratories, Albuquerque, New Mexico 87185

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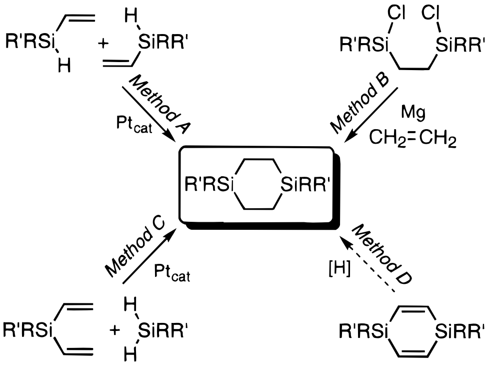
Hydrogenation of 1,1,4,4-tetraphenyl-1,4-disilacyclohexa-2,5-diene (**2**) to 1,1,4,4-tetraphenyl-1,4-disilacyclohexane (**1**) provides an efficient new route to 1,4-disilacyclohexanes with isolated overall yields 10 times higher than previously available syntheses. Molecular and crystal structures of **1** and **2** determined by single-crystal X-ray diffraction show that the saturated compound **1** adopts the ideal chairlike conformation, while the unsaturated analogue **2** has a planar 1,4-disilacyclohexa-2,5-diene ring. Ab initio geometry optimizations and vibrational frequency calculations at the 3-21G*/SCF level of theory confirm that the orientations of the phenyl rings observed in **1** represents the global minimum on the potential-energy surface. Calculations of the transition state for the phenyl ring rotations in **1** reveal a barrier height of $\Delta G^{\ddagger} = 4.09$ kcal/mol. Energy profiles of chairlike and boatlike distortions of 1,4-disilacyclohexa-2,5-diene (**12**) were calculated and compared with the observed deviation from planarity in other derivatives of **12**. Calculation of ring strain energies revealed that diene **12** and its saturated analogue 1,4-disilacyclohexane (**4**) are almost strain free (1.2 and 0.7 kcal/mol, respectively), resembling their carbon analogues.

Introduction

Synthesis of 1,4-disilacyclohexanes by hydrosilylation−dimerization of vinylsilanes (*Method A* and related *Method C*, Scheme 1) is a rather inefficient process usually leading to polymeric materials[1−4] (Scheme 1). The best yields of the cyclic dimers are about 6%,[3] but the isolation of the six-membered ring dimers is further complicated by the formation of various amounts of five-membered ring products.[2,3] The high preference for the formation of five-membered rings, ascribed to the kinetics of the generation of the organoplatinum intermediates,[5,6] and the low yields of the dimerization reactions make the isolation of the desired isomer from the mixture very difficult and the method impractical.

Reductive insertion of ethylene to 1,4-dichloro-1,4-disilabutanes represents another approach to 1,4-disilacyclohexanes (*Method B*, Scheme 1).[7,8] This multistep route gives only a modest yield of the product and requires a radical anion stabilizing substituent on ethylene.

Scheme 1



Reaction of silylenes with acetylenes appears to be a general route to substituted 1,4-disilacyclohexa-2,5-dienes,[9−14] which can, in principle, be hydrogenated to

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[†] Dedicated to Prof. Günter Maier on the occasion of his 65th birthday.

[‡] Present address: Texas Instruments Inc., Dallas, TX 75243.

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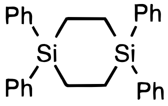
the desired 1,4-disilacyclohexanes (*Method D*, Scheme 1). The silylene is usually generated by pyrolysis of an appropriate disilane, and its reaction with an acetylene takes place in the gas phase. A recently described efficient catalytic process takes place in solution above 100 °C, but it uses much less accessible trisilanes as the source of silylene.[15]

Other methods of generation of 1,4-disilacyclohexa-2,5-dienes are less general, and they include Pt-catalyzed hydrosilylation−dimerization of acetylenes containing chelating substituents[16] and silylation−cyclization of bis(organolithium) derivatives.[17]

In our pursuit of carbosilanes, we focused on 1,1,4,4-tetraphenyl-1,4-disilacyclohexane (**1**) as a precursor for other cyclic and polycyclic organosilanes. Silane **1** was



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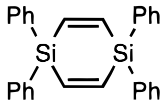

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first reported 40 years ago as a mixture of five- and six-membered ring derivatives melting at 131−134.5 °C.[1] A poorly characterized material melting at 207.5−208.5 °C has been obtained via *Method C* (Scheme 1), but no yield was reported.[18,19]

Here we describe a new and efficient route to 1,1,4,4-tetraphenyl-1,4-disilacyclohexane (**1**, Scheme 1) by hydrogenation of 1,1,4,4-tetraphenyl-1,4-disilacyclohexa-2,5-diene (**2**) (*Method D*). We also provide X-ray structures of the first 1,4-disilacyclohexane and first C-unsubstituted 1,4-disilacyclohexa-2,5-diene and compare them with the results of ab initio calculations with the emphasis on conformational analysis, ring distortions, and ring strain energies.

Results and Discussion

Synthesis. A recent literature report showed that 1,1,4,4-tetramethoxy-1,4-disilacyclohexa-2,5-diene (**3**) can be conveniently prepared on a multigram scale by flow pyrolysis of hexamethoxydisilane in the presence of acetylene.[13] The diene **3** is much easier to handle than the corresponding tetrachloro compound,[10,11] and its methoxy groups also undergo facile nucleophilic displacement with, e.g., a hydride anion.[13]

Silane **3** was prepared in 35−38% yields, and it smoothly reacted with phenylmagnesium bromide to give 1,1,4,4-tetraphenyl-1,4-disilacyclohexa-2,5-diene (**2**) in high yield (Scheme 2). Subsequent hydrogenation of the resulting diene **2** in the presence of Pd/charcoal gave 1,1,4,4-tetraphenyl-1,4-disilacyclohexane (**1**) almost quantitatively. This route, three steps from commercially available materials, results in an isolated, purified yield of 27%—an order of magnitude better than the previously reported synthesis of the impure material.

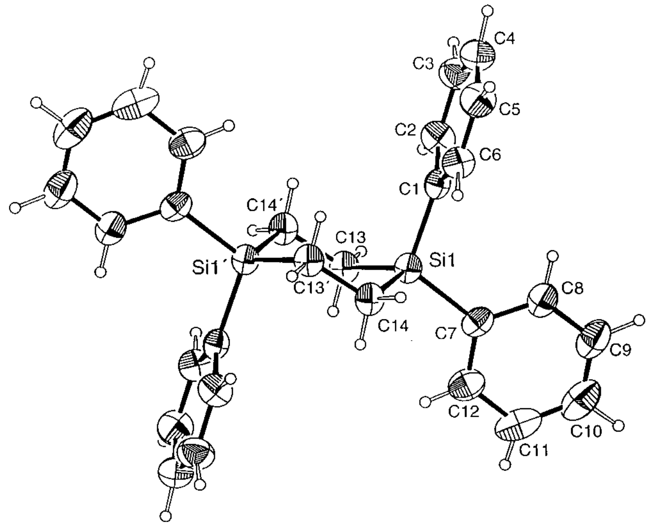
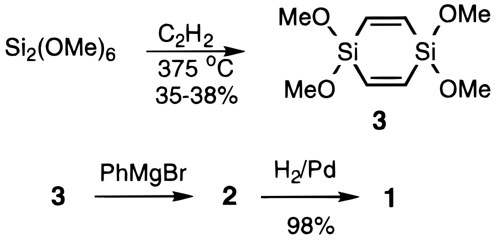


Figure 1. ORTEP representation of **1** with ellipsoids drawn in at 30% probability. For clarity, hydrogen atoms were assigned arbitrary radii.

Scheme 2



Silanes **1** and **2** sublime above 190 and 150 °C, respectively, and they can be conveniently purified by vacuum sublimation. The melting point (208−209 °C) and IR spectrum of **1** are in good agreement with the more recent report,[18] and these data indicate that the product described in the original paper was indeed a mixture of isomers.[1] Repetition of the original experiment[1] of H_2PtCl_6-catalyzed dimerization of diphenylvinylsilane (1% in benzene, 20 h of reflux; *Method A*, Scheme 1) confirms that **1** is formed as a minor component of a complex mixture of products that constitute a small high-boiling fraction (up to 250 °C/0.1 Torr). Capillary gas chromatographic analysis shows that another compound, with $m/z = 420$ and very similar fragmentation pattern (presumably the five-membered isomer), is present along with **1** at a ratio of about 4:1. Upon standing, a small quantity of impure **1** (about 85% by GC) crystallized from the high-boiling fraction.

Crystal and Molecular Structures. X-ray analysis of a monoclinic crystal of **1** revealed an ideal chairlike conformation (Figure 1), while triclinic crystals of its unsaturated analogue **2** show near ideal planarity of the 1,4-disilacyclohexadiene ring, as evident from Figure 2. The experimental details are collected in Table 1, and selected bond lengths and angles for **1** and **2** are shown in Tables 2 and 3, respectively.

1,1,4,4-Tetraphenyl-1,4-disilacyclohexane (1). Molecular Structure. The crystal structure of **1** provides the first experimental data on the geometry of the 1,4-disilacyclohexane ring. The ring adopts a chair form in which the Si atoms are 0.83 Å away from the four

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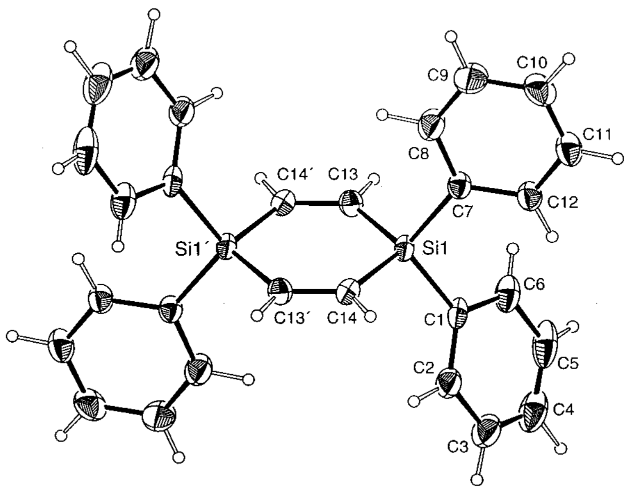

Figure 2. ORTEP representation of **2a** with ellipsoids drawn in at 30% probability. For clarity, hydrogen atoms were assigned arbitrary radii.

Table 1. Crystal Data and Summary of X-ray Data Collection

	1	**2**
formula	$C_{28}H_{28}Si_2$	$C_{28}H_{24}Si_2$
fw	420.72	416.67
color of cryst	colorless	colorless
cryst dimens, mm	0.30 × 0.20 × 0.32	0.25 × 0.25 × 0.65
space group	$P2_1/a$	$P\bar{1}$
a, Å	7.667(2)	10.813(4)
b, Å	19.102(3)	11.63(2)
c, Å	8.440(1)	10.21(2)
α, deg		104.8(1)
β, deg	99.37(2)	95.92(8)
γ, deg		103.47(7)
V, $Å^3$	1219.6(4)	1190(3)
Z	2	2
D(calcd), g/cm^3	1.145	1.163
abs coeff, cm^{-1}	13.88	14.2
transmn factors	0.85−1.00	0.92−1.00
scan speed, deg/min	8.0	8.0
scan width	$1.78 + 0.30 \tan \theta$	$1.63 + 0.30 \tan \theta$
limits of data collcn	$20° \le 2\theta \le 120°$	$20° \le 2\theta \le 120°$
total no. of reflns	2046	3751
no. of unique reflns	1893	3532
no. with $I > 3.0\sigma(I)$	1485	3029
$R(F)$	0.043	0.048
$R_w(F)$	0.059	0.064
goodness-of-fit	2.59	3.01
max Δ/σ in final cycle	0.00	0.06
max/min peak (final diff peak) (e^-/Å3)	0.14, −0.25	0.28, −0.52

Table 2. Selected Values of Bond Distances (Å) and Angles (deg) for 1,1,4,4-Tetraphenyl-1,4-disilacyclohexane (1)

Bond Distances			
Si(1)−C(1)	1.867(3)	Si(1)−C(14)	1.873(3)
Si(1)−C(7)	1.876(3)	C(13)−C(14)	1.542(4)
Si(1)−C(13)	1.871(3)	Phenyl C−C (av)	1.38(2)
Bond Angles			
C(1)−Si(1)−C(7)	110.3(1)	C(7)−Si(1)−C(13)	109.3(1)
C(1)−Si(1)−C(13)	109.1(1)	C(7)−Si(1)−C(14)	110.7(1)
C(1)−Si(1)−C(14)	109.2(1)	C(13)−Si(1)−C(14)	108.1(1)

Table 3. Selected Values of Bond Distances (Å) and Angles (deg) for 1,1,4,4-Tetraphenyl-1,4-disilacyclohexa-2,5-diene (2)

Bond Distances			
Si(1)−C(1)	1.867(3)	Si(2)−C(27)	1.858(3)
Si(1)−C(7)	1.866(4)	Si(2)−C(28)	1.861(4)
Si(1)−C(13)	1.856(4)	C(13)−C(14)	1.334(4)
Si(1)−C(14)	1.858(4)	C(27)−C(28)	1.333(4)
Si(2)−C(15)	1.869(4)	Phenyl C−C (av)	1.38(3)
Si(2)−C(21)	1.876(4)		
Bond Angles			
C(1)−Si(1)−C(7)	110.0(2)	C(15)−Si(2)−C(21)	108.7(1)
C(1)−Si(1)−C(13)	109.0(2)	C(15)−Si(2)−C(27)	109.8(2)
C(1)−Si(1)−C(14)	109.2(2)	C(15)−Si(2)−C(28)	108.3(2)
C(7)−Si(1)−C(13)	109.7(2)	C(21)−Si(2)−C(27)	111.1(2)
C(7)−Si(1)−C(14)	110.2(2)	C(21)−Si(2)−C(28)	109.2(2)
C(13)−Si(1)−C(14)	108.6(2)	C(27)−Si(2)−C(28)	109.7(2)

Table 4. Selected Experimental and Calculated Bond Lengths (Å) and Angles (deg) for 1, 1,4-Disilacyclohexane (4), and Cyclohexane (5)

	1 (exp)	**1** (calcd)[a]	**4** (calcd)[a]	cyclohexane (**5**)[b]
Si−C	1.871(3), 1.873(3)	1.889	1.890 (1.897)	na
C−C	1.542(4)	1.570	1.573 (1.550)	1.528(6)[c]
Si···Si	3.416(2)	3.476	3.438 (3.454)	2.940[c,d]
$H\cdots C_{Ph}$[e]	2.83(3)	2.803	na	na
H···H[e]	2.42(4), 2.54(4)	2.431	na	na
C−Si−C	108.1(1)	107.2	108.7 (108.5)	111.3(5)[c,f]
C−C−Si	112.3(2), 113.2(2)	112.7	112.2 (113.0)	na
t[g]	0.83	0.85	0.84 (0.82)	0.66[c]
Θ[h]	131.2	130.6	130.4 (132.2)	130.2[c]

[a] Gas-phase calculation (HF/3-21G*) at C_{2h} symmtery. Values in parentheses were obtained using the HF/6-31G* method. [b] Phase II in Kahn, R.; Fourme, R.; Andre, D.; Renaud, M. *Acta Crystallogr.* **1973**, *29B*, 131. [c] Mean value. [d] $C_1\cdots C_4$ intraring separation. [e] Closest nonbonding distance. [f] C−C−C angle. [g] Silicon-atom distance from the four-carbon plane. [h] Deviation of the Si atoms from the four-carbon plane. Ring puckering angle α = 180° − Θ.

carbon plane, forming a ring puckering angle α of 48.8° or a distortion from planarity Θ = 131.2° (Θ = 180 − α). The ring internal angles centered on the carbon atoms are somewhat bigger (112.3(2)° and 113.2(2)°) than those centered on silicon atoms (108.1(1)°), and they slightly deviate from the angles found in cyclohexane[20,21] (111.55(15)°) and 2-silapropane[22] (111.98(17)°). The observed small opening of the C-centered angles and the contraction of the Si-centered angles observed in **1** is crystallographically significant (>5*σ*) and consistent with the results of ab initio calculations (Table 4). The similarity in computational results for **1** and the parent **4** suggests that the role of the phenyl substituents and the crystal packing forces in the angle change is minimal.

Computationally, 1,4-disilacyclohexane (**4**) and cyclohexane[21] (**5**) have similar values of intraring and ring puckering angles (Table 4);[23] however, cyclohexane is more compact than **4**, whose calculated geometry is shown in Figure 3a. The Si···Si intraring separation is about 0.5 Å longer and the Si atoms are 0.17 Å further away from the ring plane of **4** than the corresponding carbon atoms in **5**. This is largely a result of the difference in Si−C and C−C bond lengths.

Analysis of the experimental data of **1** shows that the four phenyl groups are arranged in two orthogonal sets (axial and equatorial) of mutually parallel rings, resulting in almost ideal C_{2h} symmetry (Figure 1). The axial

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(23) The results obtained for cyclohexane phase II at 115 K (ref 21) are in excellent agreement with those obtained from gas-phase electron diffraction (ref 20). Atomic coordinates listed in ref 21 allowed us to build a model of **5** for further examination.

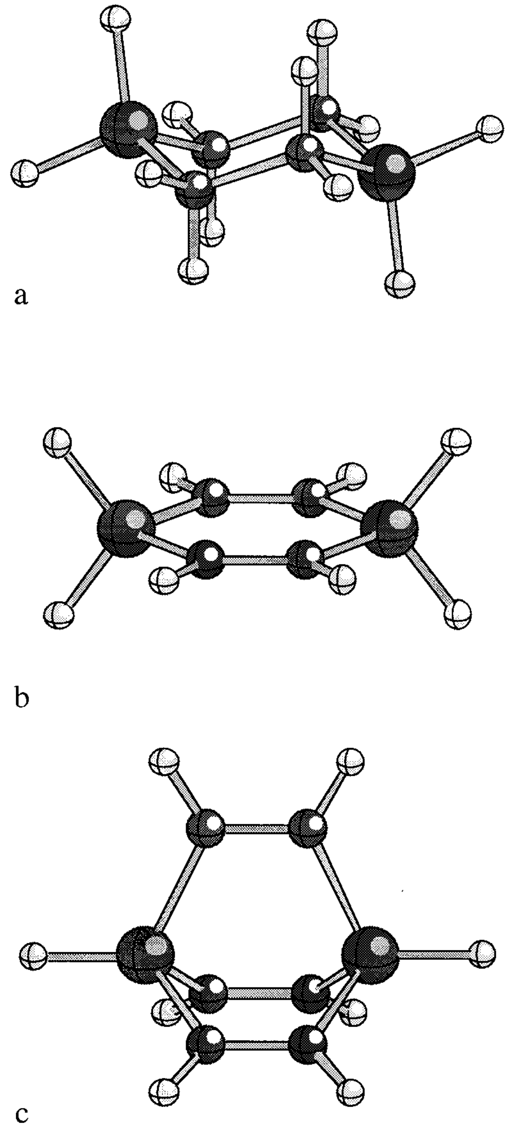


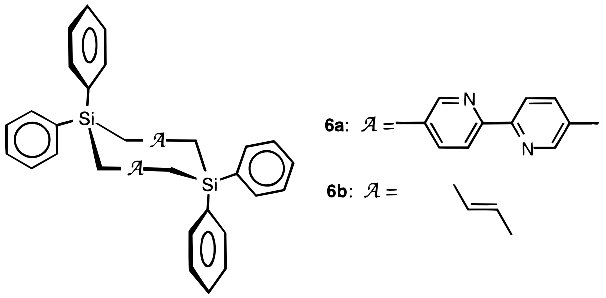
Figure 3. HF/6-31G*-optimized structure of (a) 1,4-disilacyclohexane (**4**) with C_{2h} symmetry, (b) 1,4-disilacyclohexa-2,5-diene (**12**) with D_{2h} symmetry, and (c) 1,4-disilabicyclo[2.2.2]octa-2,5,7-triene (**13**) with D_{3h} symmetry.

Si−C_{Ph} distance in **1** (1.867(3) Å) appears to be somewhat shorter than the corresponding equatorial bond length (1.876(3) Å). Both compare well to the mean Si−C_{Ph} bond length (1.875 (average) Å) in other cyclic[24,25] and acyclic[26,27] derivatives of diphenylsilane. The C_{Ph}−Si−C_{Ph} angle in **1** is 110.3(1)° (exp) or 110.2° (theory) and falls in the range of 106.5° and 112.1° observed in other diphenylsilane derivatives.

The equatorial rings, Ph_{eq}, in **1** are almost coplanar with the C_{Ph}−Si−Si plane (3.5° dihedral angle), while the Ph_{ax} rings are orthogonal (90° dihedral angle) to the same plane. In this orientation of the phenyl rings, the shortest H···H contact is observed between the ortho hydrogens, H_{ortho}, of the Ph_{ax} group and the equatorial hydrogens of the C_2 atom of the disilacyclohexane ring, H_{eq} (2.42(4) and 2.54(4) Å) while one closest H···C contact (2.83(3) Å) is found for the Ph_{eq} ortho hydrogens and the Ph_{ax} ring (Table 4). These interatomic distances are close to the sums of van der Waals radii, which are 2.4 Å for the H−H and 2.9 Å for the H−C_{Ph} interactions.[28]

Intramolecular nonbonding H···H close contacts in the previously reported cyclic[24,25] diphenylsilane derivatives are typically outside the van der Waals distance, with the exception for those in a recently reported macrocycle **6a**.[24]

Silanes **6a**[24] and **6b**[25] are close analogues of **1**, showing the arrangement of the phenyl groups very similar to that in **1**. The axial phenyl rings, Ph_{ax}, in **6a** and **6b** are orthogonal to the C_{Ph}−Si−Si plane (dihedral angles of 89° and 85°, respectively), while the equatorial rings in **6a**, Ph_{eq}, are close to coplanar with the same plane (dihedral angle of 6°). This results in short H_{ortho}···C_{Ph} and H_{ortho}···H_{eq} distances in **6a** (2.69 and 2.41 Å, respectively), making the former distance slightly shorter than that in **1**. The positions of the hydrogen atoms in **6b** were not reported.



Conformational Analysis. Since **1** and the other two silanes **6a** and **6b** show similar arrangements of the phenyl rings, it is very likely that this preference is related to the thermodynamic stability of the observed conformers rather than to the crystal packing forces. To confirm this hypothesis, the relative energies of **1A** and the two other conformers **1B** and **1C** with C_{2h} symmetry (Figure 4) were calculated at the HF/3-21G* level of theory. Geometries of all three conformers were optimized under a C_{2h} symmetry constraint, and the frequencies at the optimized geometries were calculated using the same basis set.

Normal-mode analysis of conformers **1A**, **1B**, and **1C** indicates that **1B** represents a first-order transition state while **1C** is a hilltop on the potential-energy surface (second-order transition state). Lowering the C_{2h} symmetry in **1B** to C_2 removes a single imaginary vibrational frequency ($-11\ \mathrm{cm}^{-1}$, A_u) and relaxes the transition structure to **1A**, indicating that **1B** is a transition state between two degenerate minima represented by **1A**. The calculated free-energy difference $\Delta G°$ between the ground and transition states yields the activation energy of the interconversion $\Delta G^{\ddagger} = 4.09$ kcal/mol (Table 5).

The calculated thermodynamic stability can be related to unfavorable steric interactions in each conformer. For instance, **1A** shows two H_{ortho}···C_{Ph} (2.80 Å) contacts, **1B** reveals four H_{ortho}···H_{ax} (2.32 Å) and two H_{ortho}···C_{Ph} (2.72 Å) contacts, while in **1C** there are two C_{Ph}···C_{Ph}

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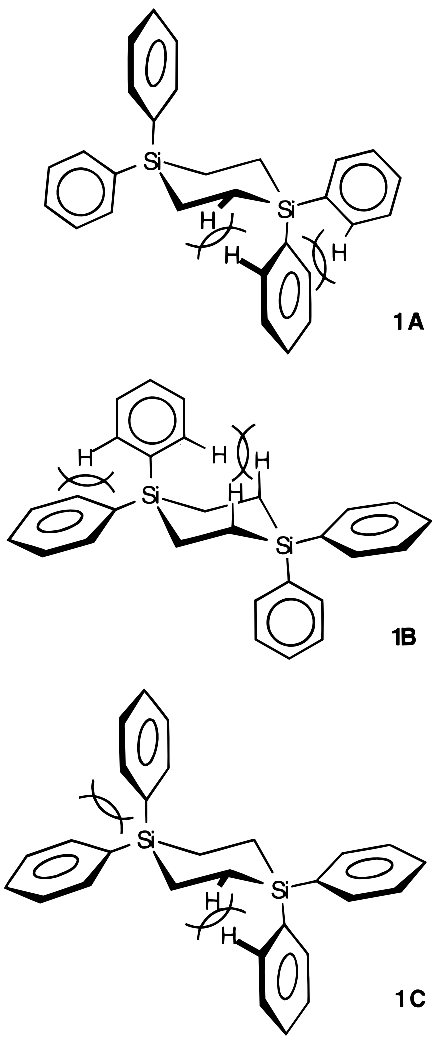

Figure 4. Three C_{2h} conformers of **1** with indicated orientations of the Ph rings relative to the C_{Ph}–Si–Si plane: (a) **1A**, $Ph_{ax} = 90°$, $Ph_{eq} = 0°$, (b) **1B**, $Ph_{ax} = 0°$, $Ph_{eq} = 90°$, and (c) **1C**, $Ph_{ax} = 90°$, $Ph_{eq} = 90°$. Important H···H and H···C_{Ph} steric interactions are also shown.

Table 5. Relative Energies (kcal/mol) of Three Conformers of 1[a]

	1A	1B[b]	1C[c]
ΔSCF	0[d]	+3.79	+3.37
ZPE[e]	304.12	304.38	304.00
$\Delta H°_{298}$	0	+3.50	(+2.16)
$\Delta G°_{298}$	0	+4.09	(+5.60)

[a] HF/3-21G* level of theory. [b] Transition state. [c] Second-order transition state. [d] SCF energy −1645.735724 Hartree. [e] Zero-point vibrational energy correction.

close contacts (3.10 Å) that corresponds to 91% of the van der Waals C–C separation. This clearly indicates the greater steric congestion in conformers **1B** and **1C** as compared with **1A** and contributes to their lower thermodynamic stability.

Additional support for the thermodynamic stability of **1A** is provided by experimental and theoretical analysis of phenylcyclohexane,[29] in which the equatorial conformer is preferred to the axial one by about 3 kcal/mol. The general trend of conformational stability in phenylcyclohexane, Ph_{eq} (0°) > Ph_{eq} (90°) > Ph_{ax} (90°) > Ph_{ax} (0°), is in good agreement with that observed in **1**.

1,1,4,4-Tetraphenyl-1,4-disilacyclohexa-2,5-diene (2). Molecular Structure. Unlike the previously studied 1,4-disilacyclohexa-2,5-dienes **7**–**10** (Table 6), diene **2** is unsubstituted at the vinylic positions and its silicon atoms have four identical substituents. Apparently, this preserves the planar D_{2h} structure of the diene ring in the solid state (Figure 2). Selected bond angles and distances for **2** and **7**–**10** are included in Table 6.

In contrast to derivative **2**, the symmetrical diene **7**[30] with phenyl substituents at the vinylic positions shows a significant chairlike distortion, presumably due to the intramolecular interactions of the phenyl groups. Smaller methyl vinylic substituents in **9-trans**[31] allow for a planar diene ring, which adopts a twisted-boat conformation in the cis isomer, **9-cis**,[31] due to transannular interactions of the bulky TMS substituents. The boat conformation is even more pronounced in the unsymmetrical diene **10** with bulky TMS and phenyl substituents.[32] The largest deviation from planarity is observed in 1,4-disilabicyclo[2.2.2]octa-2,5,7-triene **11**,[33] in which the geometrically constrained 1,4-disilacyclohexa-2,5-diene ring is puckered by 47° (Table 6).

Two crystallographically independent molecules, **2a** and **2b**, are found in the unit cell. The Si–C and the C=C bond lengths in both forms of **2** appear shortest in the series of dienes **7**–**10**. The silicon-centered ring interior angles are smaller (109.1° (average)) than those centered on the carbon atoms (125.4° (average)). The former represent the lower value, while the latter are the higher values in the series. The sum of the intraring angles is 719.8(2)° in both molecules **2a** and **2b**, which is indistinguishable from the 720° required for a planar hexagon. The molecular dimensions of the diene ring in **2**–**11** are in a good agreement with the calculated values for the parent diene **12** and the triene **13** shown in Figure 3.

The four phenyl rings in **2** are arranged in two sets related by a center of inversion. The C_{Ph}–Si mean distance in **2** is 1.870(4) Å, which compares well with 1.872(3) Å for the same distance in **8**.[34] The phenyl rings form 110.0(2)° and 108.7(1)° C_{Ph}–Si–C_{Ph} angles in molecule **2a** and **2b**, respectively. In molecule **2a**, the rings are twisted from the C_{Ph}–Si–Si plane by 11° and 54° and their planes form a 62° angle with each other, while the same numbers for molecule **2b** are 42°, 63°, and 83°, respectively. There are no significant close contacts, and the shortest such distances are 2.87(3) and 3.07(3) Å for H_{ortho}···C_{Ph} in molecule **2a** and **2b**, respectively.

Crystal Structure. Molecules **2a** occupy the faces, while the rings of molecules **2b** are positioned at the corners of the unit cell. The crystal packing diagram of six molecules (two **2a** and four **2b**) is shown in Figure

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(29) Schaefer, T.; Beaulieu, C.; Sebastian, R. *Can. J. Chem.* **1991**, *69*, 503.

(30) Bokiy, N. K.; Struchkov, Y. T. *Zh. Strukt. Khim.* **1965**, *6*, 571.

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(33) Sekiguchi, A.; Gillette, G. R.; West, R. *Organometallics* **1988**, *7*, 1226.

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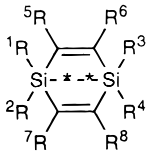
Table 6. Comparison of Molecular Dimensions of 2 with other 1,4-Disilacyclohexa-2,5-dienes



	distances (Å)				angles (deg)		
	Si–C	C=C	Si···Si	t^a	C–Si–C	Si–C–C	θ^b
2; $R^1 = R^2 = R^3 = R^4 = Ph$, $R^5 = R^6 = R^7 = R^8 = H$							
a (mol 1)	1.856(4), 1.858(4)	1.334(4)	3.499(5)	0.028	108.6(2)	125.3(2), 126.1(2)	178.5 chair
b (mol 2)	1.858(3), 1.861(4)	1.333(4)	3.474(3)	0.024	109.7(2)	124.9(2), 125.4(2)	178.7 chair
7;[c] $R^1 = R^2 = R^3 = R^4 = Me$, $R^5 = R^6 = R^7 = R^8 = Ph$							
	1.87, 1.92	1.30	3.46	0.20	108.5	124.0, 126.0	169.6 chair
8;[d] $R^1 = R^3 = R^5 = R^8 = Ph$, $R^2 = R^4 = Me$, $R^6 = R^7 = SiMe_3$							
	1.893(3), 1.878(3)	1.355(4)	3.416	0.054	113.7(1)	127.3(2), 118.9(2)	177.0 chair
9-cis;[e] $R^1 = R^3 = R^5 = R^6 = R^7 = R^8 = Me$, $R^2 = R^4 = SiMe_3$ (cis)							
	1.871(2), 1.873(2) 1.868(2), 1.875(2)	1.350(3) 1.348(3)	3.405	0.15, 0.20	112.23(10), 112.11(10)	122.9–123.5	171.7, 169.0 boat[f]
9-trans;[e] $R^1 = R^3 = R^5 = R^6 = R^7 = R^8 = Me$, $R^2 = R^4 = SiMe_3$ (trans)							
	1.871(1)	1.347(2)	3.423	0.072	112.52(6)	123.46(10)	176.0 boat
10;[g] $R^1 = R^3 = R^4 = Me$, $R^2 = R^6 = R^7 = SiMe_3$, $R^5 = R^8 = Ph$							
	1.882(7), 1.884(7) 1.896(8), 1.895(6)	1.344(9) 1.347(10)	3.343	0.37, 0.30	112.5(3) 111.7(3)	117.7(5), 119.2(5) 124.4(6), 126.5(6)	159.0, 163.3 boat[h]
11;[i] $R^1R^3 = PhC{=}CPh$, $R^2 = R^4 = Me$, $R^5 = R^6 = R^7 = R^8 = Ph$							
	1.886–1.904 1.894 avg	1.334–1.367 1.351 avg	2.93	0.86 avg	101.4–107.4 103.7 avg	113.6–123.1 116.0 avg	129.0–136.6 132.7 avg
12;[j] $R^1 = R^2 = R^3 = R^4 = R^5 = R^6 = R^7 = R^8 = H$							
a	1.879	1.333	3.486	0.0	110.1	125.0	180.0
b	1.871	1.328	3.470	0.0	110.2	124.9	180.0
13;[j] $R^1R^3 = CH{=}CH$, $R^2 = R^4 = R^5 = R^6 = R^7 = R^8 = H$							
a	1.900	1.332	2.948	0.86	103.3	115.2	133.2
b	1.895	1.327	2.933	0.86	103.3	115.1	133.1

[a] Silicon-atom distance from the four-carbon plane obtained from molecular models. [b] Same as in Table 4 but for clarity defined here as the Si–∗–∗ angle in which asterisks are the midpoints between the two carbon atoms as shown in the formula. Values obtained from molecular model. [c] Bokiy, N. K.; Struchkov, Y. T. *Zh. Strukt. Khim.* **1965**, *6*, 571. [d] Ishikawa, M.; Sugisawa, H.; Kumada, M.; Higuchi, T.; Matsui, K.; Hirotsu, K. *Organometallics* **1982**, *1*, 1473. [e] Rich, J. D.; Shafiee, F.; Haller, K. J.; Harsy, S. G.; West, R. *J. Organomet. Chem.* **1984**, *264*, 61. [f] Twisted boat with the four-carbon dihedral angle of 6.2°. [g] Ishikawa, M.; Matsuzawa, S.; Higuchi, T.; Kamitori, S.; Hirotsu, K. *Organometallics* **1985**, *4*, 2040. [h] Twisted boat with the four-carbon dihedral angle of 1.6°. [i] Sekiguchi, A.; Gillette, G. R.; West, R. *Organometallics* **1988**, *7*, 1226. [j] Optimized molecular geometry: (a) HF/6-31G*; (b) HF/6-311G(2df,2p).

5. Inspection of the packing diagram revealed intermolecular interactions as close as 2.60 Å between H_{meta} and a phenyl ring in two molecules **2b**. The shortest H···H contacts are observed between the vinylic hydrogens of **2a** and H_{ortho} of **2b** (2.55(6) Å).

Ring Distortions. Significant deviations from planarity seen in some of the dienes (e.g., **7** and **10**) suggest that the 1,4-disilacyclohexa-2,5-diene (**12**) is flexible and can easily accommodate both boat- and chairlike distortions. Earlier MNDO studies of **12** and other 1,4-diheteracyclohexa-2,5-dienes showed that the potential-energy curves for their boatlike bending are rather flat, with **12** and 1,4-cyclohexadiene (**14**) being the least flexible.[32] However, the quality of these calculations makes the quantitative assesment of the energies unreliable.

The original calculations[32] were reproduced using the HF/6-31G* method, yielding the parabolic potential-energy profile of the chairlike (C_{2h}) and boatlike (C_{2v}) distortions of **12** from planarity by a puckering angle $\alpha = 180 - \Theta$ (Figure 6). Energy and frequency calculations confirmed that a planar structure of 1,4-disilacyclohexa-2,5-diene (**12**) with D_{2h} symmetry is the global minimum on the conformational-energy surface (Figure 3b). This agrees with the previous theoretical[35,36] and experimental studies of 1,4-cyclohexadiene (**14**) and its dihetera derivatives.[31,32,37]

In the boatlike structure with the angle α of 50°, the axial 1,4-hydrogen atoms are within van der Waals contact (d = 2.282 Å), which leads to an additional increase in energy. The difference of 4.4 kcal/mol between the extrapolated energy (17.9 kcal/mol) and the calculated value (22.3 kcal/mol) can be considered a measure of the H···H interaction at this distance.

The chairlike distortion energy profile is more steep than the boat bending of **12**. Without correcting for the twisting seen in **9-cis** and **10**, the two types of distortions are equally exemplified in Table 6. However, the largest chairlike distortion reaches value of $\alpha = 10.4°$ (diene **7**), while the boat bending can be as large as 21° (compound **10**). These distortions correspond to an energy difference of 1.5 and 2.2 kcal/mol, respectively, according to the plot in Figure 6.

Ring Strain Energies. Cyclohexane (**5**) and cyclohexene (**15**) are virtually unstrained hydrocarbons, and

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(35) Lipkowitz, K. B.; Rabideau, P. W.; Raber, D. J.; Hardee, L. E.; Schleyer, P. v. R.; Kos, A. J.; Kahn, R. A. *J. Org. Chem.* **1982**, *47*, 1002.

(36) Lipkowitz, K.; Burkett, A.; Landwer, J. *Heterocycles* **1986**, *24*, 2757.

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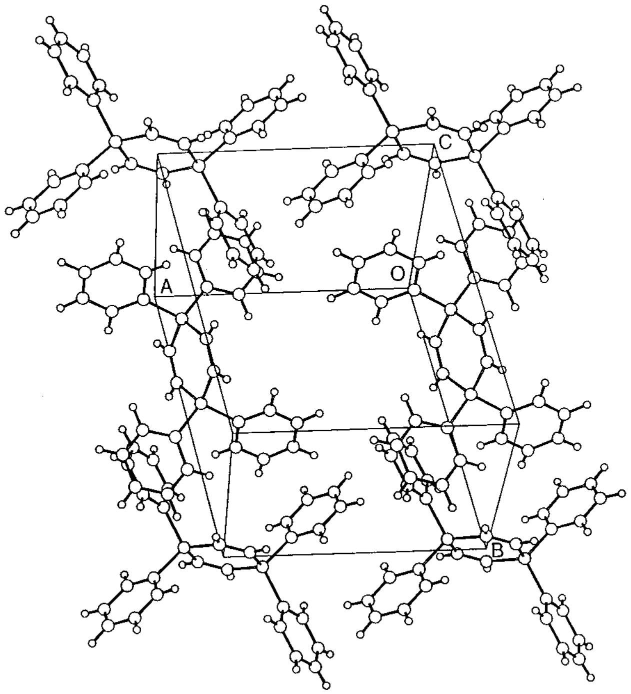

Figure 5. Packing diagram of **2** (hydrogen atoms omitted). Molecules **2a** occupy the faces, and molecules **2b** are positioned at the corners of the unit cell.

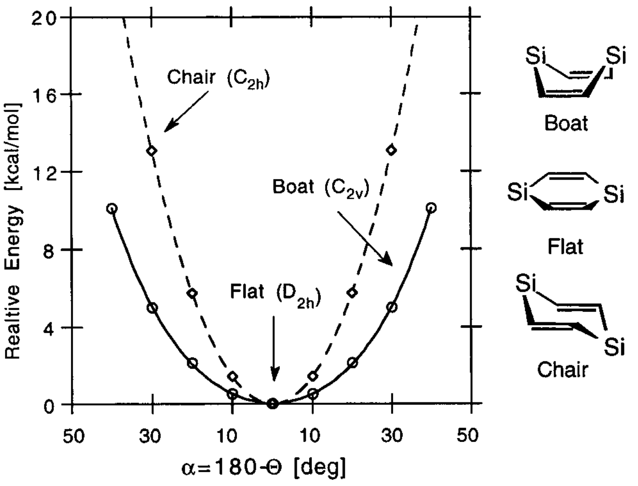

Figure 6. Calculated (HF/6-31G*) energy profile as a function of the puckering angle α (corrected for ZPE) for boat (—) and chair (- - -) distortions of 1,4-disilacyclohexa-2,5-diene (**12**). Best fit functions for the solid line and dashed line parabola are $E°_{\rm rel} = (1.057 \times 10^{-6})\alpha^4 + (4.535 \times 10^{-3})\alpha^2$ and $E°_{\rm rel} = (0.283 \times 10^{-6})\alpha^4 + (14.109 \times 10^{-3})\alpha^2$, respectively.

their strain energies (SEs) have been calculated to be slightly negative, −0.7 and −0.2 kcal/mol, respectively.[38] The introduction of two relatively large electropositive silicon atoms into cyclohexane to form **4** certainly alters the geometry and electronic symmetry of the ring, as evident from changes of intraring distances and valence angles (Table 4). To quantify the strain effect of the silicon atoms in six-membered rings and to predict the energetic outcome of hydrogenation of **2** to **1**, we calculated enthalpy changes in the homodesmotic reactions[39] shown in Scheme 3. The results collected in Table 7 predict a small relief of SE (0.5 kcal) upon hydrogenation of **12** to **4** and a small increase of SE (0.8 kcal) for the hydrocarbon analogues.

Scheme 3

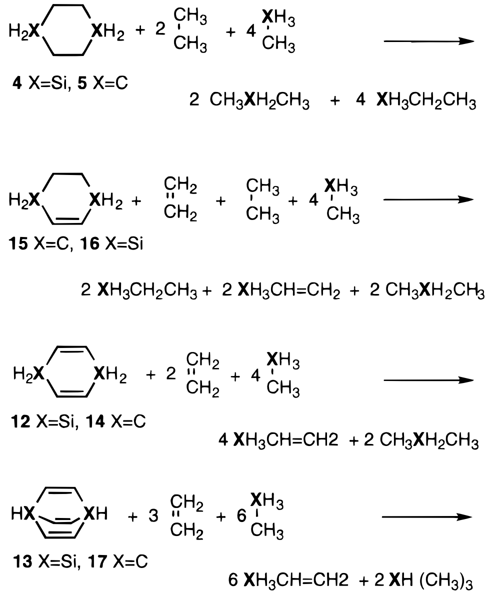

Table 7. Homodesmotic Strain Energies of Silanes and Hydrocarbons[a]

C_{2h}[b]		C_2[b]		D_{2h}[b]		D_{3h}[b]	
4[c]	**5**[d]	**16**[c]	**15**[d]	**12**[c]	**14**[d]	**13**[c]	**17**[d]
0.7	0.3	1.0	0.4	1.2	−0.5	25.3	28.0

[a] Strain energies in kcal/mol were calculated (HF/6-31G*) from the sum of the electronic and thermal energies at 298 K scaled by the 0.9135 factor. [b] Symmetry imposed in the calculations. [c] X = Si. [d] X = C.

The calculated SEs for the silicon derivatives are higher than those obtained for their carbon analogues by about 0.5−1.5 kcal/mol. These differences can be rationalized in terms of significant intramolecular polarization and electrostatic interactions in silanes **4** and **12** as compared with the carbon analogues **5** and **14**.

An estimate of the magnitude of such interactions comes from conformational analysis of butane and 1,4-disilabutane, whose gauche conformations represent a part of the cyclohexane and 1,4-disilacyclohexane ring, respectively. Our calculations at the HF/6-31G* level of theory confirm the earlier experimental[40] and computational[41] findings and show that gauche 1,4-disilabutane is 1.50 kcal/mol higher in free energy than the anti form. This difference, in turn, is 0.48 kcal/mol higher than the corresponding free energy difference between gauche and anti butane. Since the Si−H···H−Si distance is large (2.97 Å), this significant increase in the steric energy in 1,4-disilabutane has been attributed to repulsive electrostatic interactions between the positively charged silicon centers (+0.68 or +0.24 for SiH_3).[41] This notable bond polarization results in a dipole moment of 1.0 D in gauche 1,4-disilabutane, while the dipole moment for gauche butane is calculated (HF/6-

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(38) Wiberg, K. B.; Nakaji, D. Y.; Morgan, K. M. *J. Am. Chem. Soc.* **1993**, *115*, 3527.

(39) George, P.; Trachtman, M.; Bock, C. W.; Brett, A. M. *Tetrahedron* **1976**, *32*, 317.

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31G*) to be 0.08 D with a C−H···H−C separation of 2.40 Å.

The strong local Si−C dipole moments cancel in **4** and **12** due to molecular symmetry but manifest themselves in quadrupole tensor values which are larger by about 50% as compared with the hydrocarbon analogues.

For completeness of this analysis, the SE of the two trienes, **13** and **17**, were also compared. The trienes, which can be viewed as severely distorted dienes **12** and **14**, show significant strain energies arising from contractions of the ring internal bond angles and transannular interactions of the bridgehead atoms. For instance, the Si−C−C and the C−Si−C angles in **13** are smaller than those in **12** by 7° and 10°, respectively (Table 6), and the calculated nonbonding interbridgehead distance in **13** is 69% of the van der Waals separation (4.2 Å).[28] In bicyclo[2.2.2]octa-2,5,7-triene (**17**), the change in the valence bond angles is identical to that in **13** and the bridgehead-to-bridgehead separation is 26% inside the van der Waals separation (3.4 Å). Despite the relatively closer Si···Si distance, triene **13** has a lower SE than the corresponding carbon analogue **17** by about 3 kcal/mol. This may result from a much smaller sensitivity to the change of the valence angles of a Si atom as compared to a C center, which becomes the dominant contribution to the SE in the trienes.

Conclusions

Hydrogenation of 1,1,4,4-tetrasubstituted 1,4-disilacyclohexa-2,5-dienes provides the first practical multigram synthesis of pure C-unsubstituted 1,4-disilacyclohexanes. X-ray analysis of **1** demonstrated an almost ideal chair conformation of the 1,4-disilacyclohexane ring. The geometry of the ring and the orientation of the phenyl groups in the crystal structure of **1** are in excellent agreement with ab initio calculations, which also predict a 4.1 kcal/mol barrier to the internal rotation of the phenyl groups.

Ring deformations observed in derivatives of diene **12** are within 2.2 kcal/mol, and the ring can accommodate large substituents through boatlike distortions that are less energetic than chairlike ones.

1,4-Disilacyclohexane (**4**), 1,4-disilacyclohexa-2,5-diene (**12**), and 1,4-disila-2-cyclohexene (**16**) are relatively strain-free ring systems with SEs slightly higher than those for the corresponding hydrocarbons. The higher SE for the silanes than for the hydrocarbons can be attributed in part to the electrostatic interactions of highly polarized C−Si bonds. Hydrogenation of diene **2** to the saturated silane **1** proceeds with a small relief of strain of about 0.5 kcal/mol.

Computational Methods

Ab initio calculations were carried out using the Gaussian94 package[42] on an SGI R8000 workstation. Geometry optimizations and frequency calculations were undertaken at the Hartree−Fock (HF) level using 3-21G*, 6-31G*, or 6-311-(2df,2p) basis sets. The calculated ZPVE and thermal vibrational energies were scaled down by 0.9409 (HF/3-21G* calculations) or 0.9135 (HF/6-31G* calculations).[43] Molecular models of all molecules were built and analyzed in a Cerius2 graphic interface using literature crystallographic coordinates or Gaussian 94 output files.

General Procedures for X-ray Crystallography. All measurements were performed on a Rigaku AFC6S diffractometer with graphite-monochromated Cu Kα ($\lambda = 1.541\ 78$ Å) radiation. Relevant crystal and data collection parameters for the present study are given in Table 1.

Cell constants and orientation matrixes for data collection were obtained from systematic searches of limited hemispheres of reciprocal space; sets of diffraction maxima were located whose setting angles were refined by least squares. The space group was determined from consideration of unit cell parameters, statistical analysis of intensity distribution, and, where appropriate, systematic absences. Subsequent solution and refinement of this structure confirmed the choice.

Data collection was performed using continuous $\omega-2\theta$ scans with a stationary background (peak/bkgd counting time = 2:1). Data were reduced to a unique set of intensities and associated σ values in the usual manner. The structure was solved by direct methods (SHELXS-86, DIRDIF) and Fourier techniques. All non-hydrogen atoms were refined anisotropically. Final difference maps were featureless.

X-ray Crystallography of 1,1,4,4-Tetraphenyl-1,4-disilacyclohexane (1). The space group was identified as monoclinic $P2_1/a$ (alternate setting of No. 14) by consideration of unit cell parameters, systematic absences, and statistical analysis of intensity distribution and probable crystal packing. The choice of the unit cell was confirmed by subsequent solution and refinement of the structure. All of the hydrogens were located in the difference maps and successfully refined. Selected bond distances and angles are listed in Table 2, and an ORTEP[44] diagram is shown in Figure 1.

X-ray Crystallography of 1,1,4,4-Tetraphenyl-1,4-disilacyclohexa-2,5-diene (2). The space group was identified as the triclinic $P\bar{1}$ (No. 2) by consideration of unit cell parameters and statistical analysis of intensity distribution and probable crystal packing. The choice of the unit cell was confirmed by subsequent solution and refinement of the structure. All of the hydrogens were located in the difference maps and successfully refined. Selected bond distances and angles are listed in Table 3, and an ORTEP[44] diagram is shown in Figure 2.

Experimental Section

Hexamethoxydisilane was purchased form Gelest, Inc., and was used without further purification. Mass spectrometry was performed using a Hewlett-Packard 5890 GCMS instrument. Elemental analyses were provided by Atlantic Microlab, Norcross, GA. FTIR spectra were recorded on a Nicolet Magna 500 instrument in KBr pellets. NMR spectra were obtained using a Bruker 300 MHz instrument in $CDCl_3$ and referenced to the residual $CHCl_3$ (^1H NMR) or $CDCl_3$ (^{13}C NMR). ^{29}Si NMR spectra were recorded on a Bruker 400 MHz instrument in $CDCl_3$ and referenced to TMS. Melting points were obtained on Boetius PHMK 05 hot stage.

1,1,4,4-Tetraphenyl-1,4-disilacyclohexane (1). Hydrogen (195.5 mL) was slowly absorbed by a solution of

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[42] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*, revision E.1; Gaussian, Inc.: Pittsburgh, PA, 1995.

[43] Foresman, J. B.; Frisch, A. *Exploring Chemistry with Electronic Structure Methods,* 2nd ed.; Gaussian, Inc.: Pittsburgh, PA, 1996.

[44] Johnson, C. K. *ORTEP I I*; Report ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.

diene **2** (1.75 g, 4.2 mmol) in ethyl acetate (330 mL) containing palladium on charcoal (325 mg) at room temperature. The catalyst was filtered off, and the solution was evaporated leaving 1.75 g (99% yield) of a practically pure white solid of silane **1**. An analytical sample was obtained by sublimation (180 °C/0.06 Torr) followed by recrystallization from heptane: mp 208−209 °C, >195 °C subl. (lit.[18] 207.5−208.5 °C); ^{1}H NMR δ 1.47 (s, 8H), 7.30−7.37 (m, 12H), 7.47−7.51 (m, 8H); ^{13}C NMR δ 6.11, 127.95, 129.25, 134.42, 136.07; ^{29}Si NMR δ −9.3; IR 532, 701, 758, 1107, 1116, 1410, 1426, 2876, 2899, 3000, 3012, 3061 cm^{-1}; EIMS *m*/*e* 420 (19, M$^+$), 391 (36), 364 (30), 342 (23), 314 (66), 286 (78), 259 (84), 209 (23), 181 (100), 105 (82). Anal. Calcd for $C_{28}H_{28}Si_2$: C, 79.94; H, 6.71. Found: C, 79.87; H, 6.77.

1,1,4,4-Tetraphenyl-1,4-disilacyclohexa-2,5-diene (2). A solution of 1 M phenylmagnesium bromide in THF (75 mL, 75 mmol) was slowly added to a cooled (−78 °C) solution of **3** (4.18 g, 18 mmol) in THF. The reaction mixture was stirred at room temperature overnight and then quenched with diluted hydrochloric acid, and the product was extracted with CH_2Cl_2. Combined organic extracts were washed several times with water and dried ($MgSO_4$). The solvent was evaporated, leaving 7.2 g of a pale-yellow solid, which was sublimed (150 °C/0.06 Torr; earlier oily fractions were discarded) and recrystallized from heptane or isopropyl ether, giving 5.70 g (76% yield based on impure **3**) of the diene **2**: mp 158−159 °C; >150 °C subl.; ^{1}H NMR δ 7.35−7.38 (m, 12H), 7.48 (s, 4H), 7.57−7.60 (m, 8H); ^{13}C NMR δ 128.06, 129.64, 134.82, 135.20, 148.47; ^{29}Si NMR δ −37.4; IR 575, 665, 687, 708, 718, 1109, 1337, 1426, 2931, 2996, 3019, 3038, 3050, 3064 cm^{-1}; EIMS *m*/*e* 416 (0.7, M$^+$), 338 (100), 259 (38), 207 (40), 181 (38), 105 (63). Anal. Calcd for $C_{28}H_{24}Si_2$: C, 80.71; H, 5.81. Found: C, 80.66; H, 5.81.

1,1,4,4-Tetramethoxy-1,4-disilacyclohexa-2,5-diene (3). The diene was prepared according to the literature procedure[13] by flow pyrolysis of hexamethoxydisilane (20 drops per min) in the presence of a large excess of acetylene at 360 °C. Pyrolysis was carried out in a quartz tube (60 cm × 2.5 cm) position at a 30° angle to the level.[45]

WARNING! The apparatus must be well flushed with dry nitrogen before starting vigorous passing of acetylene to avoid uncontrolled combustion or explosion.

A short path distillation (Kugel rohr, 75 °C/1 Torr; lit.[13] 70 °C/0.3 Torr) yielded 35−38% of about 85% pure (by GCMS) diene **3** as a colorless liquid, which was used in the subsequent transformations without further purification.

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Supporting Information Available: Tables of anisotropic thermal parameters, H atom parameters, and bond distances and angles for **1** and **2**, packing diagram for **1**, ORTEP diagram of **2b**, and Gaussian input files and summary of calculations for conformers **1A**, **1B**, and **1C** (37 pages). Ordering information is given on any current masthead page.

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[45] We are grateful to Prof. Gunter Maier for his helpful comments and suggestions concerning the pyrolysis and preparation of **3**.