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A Facile Synthesis of Diphosphasilacyclopropanes and 1,3-Diphospha-2,4-disilabicyclo[1.1.0]butanes and an *ab Initio* Study of Diphosphadisilabicyclo[1.1.0]butanes and Their Respective 1,3-Diene Isomers

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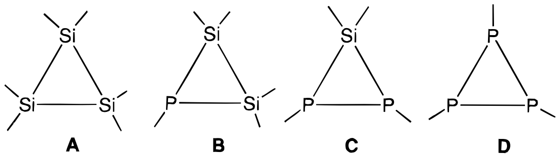
A convenient, stepwise route to diphosphasilacyclopropanes starting from appropriate substituted *P*,*P*′-bis(fluorosilyl)diphosphanes is reported. The reaction of $Is_2Si(F)-PH-PH-Si(F)Is_2$ (Is = 2,4,6-triisopropylphenyl) (**1**), which exists as a 1:2 mixture of stereoisomers (*d*,*l*-racemate and meso form), with 1 equiv of ^nBuLi in THF furnishes the lithium phosphanide $Is_2Si(F)-P[Li(THF)_n]-PH-Si(F)Is_2$ (**5**), which is converted by thermolysis and LiF/THF elimination into the corresponding diphosphasilacyclopropane $Is_2\overline{Si-PH-P}-Si(F)Is_2$ (**2a**). The unusually low s-contribution of the Si−P/P−P bonds and ring strain of the SiP_2 skeleton in **2a** is reflected by its low values of the $^1J(P-H)$ (147 Hz) and $^1J(P,P)$ coupling constants (0 Hz!). Compound **2a** consists of an almost regular SiP_2 triangle as shown by single-crystal X-ray analysis. Lithiation of the P−H function in **2a** in the presence of THF leads to the corresponding $P-Li(THF)_3$ derivative **2b** which has also been characterized by X-ray analysis. The same product is accessible by double lithiation of **1** with 2 equiv of ^nBuLi in THF. The SiP_2 three-membered ring is isosceles, having different Si−P distances (2.252(3) and 2.171(3) Å), and the P atoms are pyramidally coordinated. Heating of **2b** liberates LiF/THF and furnishes the desired P_2Si_2-bicyclo[1.1.0]butane $(Is)_2\overline{Si-\underline{P-P}}\underline{-Si}(Is)_2$ (**3**), which shows a characteristic high-field resonance signal at $\delta = -300.2$ and ^{29}Si satellites ($^1J(P, Si) = 83$ Hz). Ab initio calculations at the MP2/6-31G* level have been performed in order to investigate the stability of the bicyclo[1.1.0]butane-like isomers of $H_4P_2Si_2$ versus their respective buta-1,3-diene-like pendants.

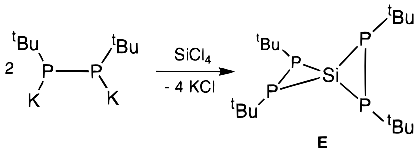
Introduction

Heterocyclopropanes and bicyclo[1.1.0]butanes having a silicon−phosphorus skeleton are remarkable reactive molecules, which are suitable for the systematic investigation of ring strain of small cycles. It seems interesting in that context to learn how the geometric and electronic properties are influenced by the number and positions of the silicon and phosphorus atoms in the skeleton. One remarkable feature of cyclotrisilanes **A**[1] (Chart 1) in particular is that they possess higher ring strain by 10 kcal mol^{-1} compared to cyclopropanes, whereas cyclotriphosphanes **D** are almost unstrained.[2,3] The ring strain in Si_nP_m three-membered rings ($n + m = 3$) **A**−**D**,[4] which drastically drops within the series $Si_3 > Si_2P > SiP_2 > P_3$, may also be reflected by the very different synthetic access and reactivity of these ring systems.[5]

Chart 1



Nowadays, some crystalline derivatives of the type **A**−**D** have been prepared and structurally established due to experimentally improved methods. The synthesis of the first crystalline disilaphosphacyclopropanes **B** was achieved very recently via electrocyclic ring closure reaction of a 1,3-disila-2-phosphaallyl anion.[6] The synthetic strategy of intermolecular cyclocondensation sequences and salt elimination has also been employed in the first synthesis of derivatives of type **C**, in which a 1,2-dipotassium 1,2-diphosphandiide has been reacted with dichlorodiorganosilanes. Worthy of note is also the synthesis of the spirocyclic P_4Si skeleton in **E**, which exists in two diastereomeric forms (see eq 1).

 (1)

The compounds **A**−**E** contain sterically congested organic and/or silyl groups for steric protection. As expected, the

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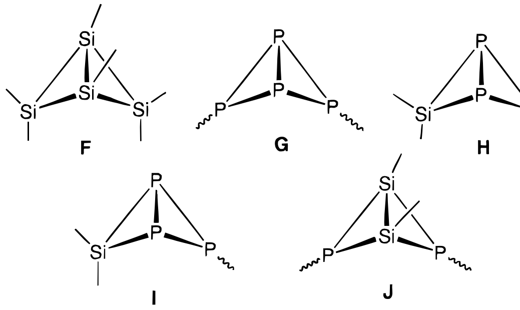
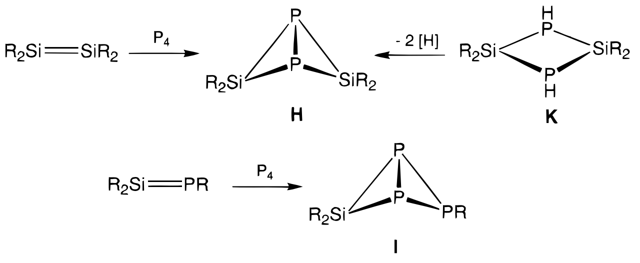
Chart 2



Scheme 1



bicyclic derivatives **F**−**J** (Chart 2) are stronger strained than their corresponding halves, i.e., the respective heterocyclopropane increments. Hence, the bicyclo[1.1.0]tetrasilanes **F** are strained to such an extend that the Si−Si bridgehead bond has merely 25% of the strength of the basal Si−Si bonds, so that H_2O already add across this bond at very mild reaction conditions.[8] The P−P bridgehead bond in **G**,[9] however, possesses partial π-character, whereas this is lost in **H** where the peripheral RP groups are substituted by isoelectronic SiR_2 fragments.[2,10]

Compounds of the type **H** and **I** are formed (Scheme 1) upon degradation reactions of P_4 with silylidenesilanes[10] and -phosphanes.[11] **H** may also be accessible by a stepwise dehydrogenation of 1,3-diphospha-2,4-disilacyclobutanes **K**.[12] The existence of compounds of type **J** is hitherto merely proven by trapping experiments.[13]

We report a new facile synthesis of SiP_2 and Si_2P_2 derivatives **C** and **D**, starting from the 1,2-bis(fluorosilyl)diphosphane **1**, and *ab initio* calculations of valence isomers with the composition $H_4P_2Si_2$, which have been performed in order to establish the relative stability of possible P_2Si_2-bicyclo[1.1.0]butanes versus their P_2Si_2-buta-1,3-diene isomers.

Experimental Results and Discussion

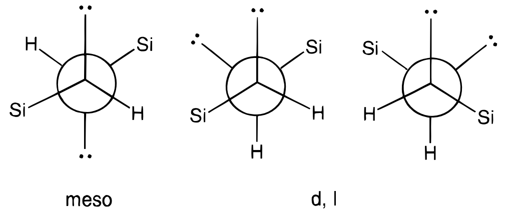
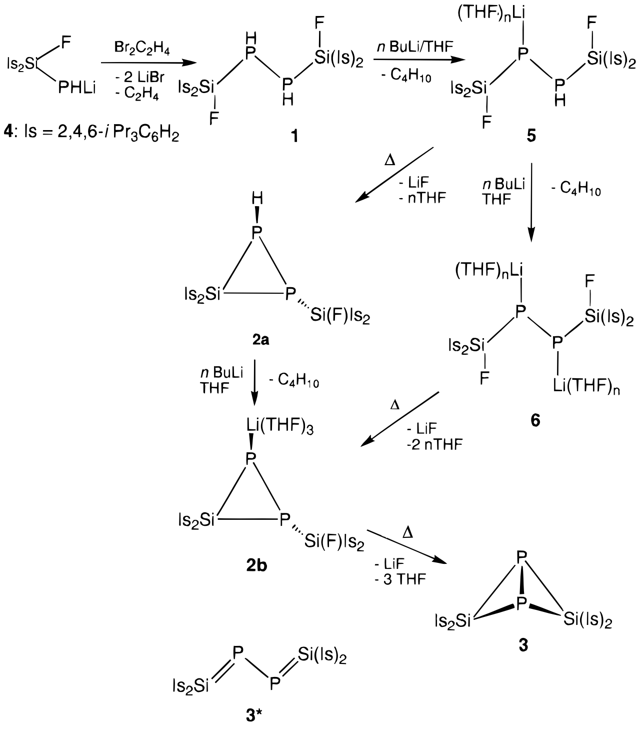


Figure 1. Diastereomers of **1** (meso and *d,l*-forms) shown in a Newman view.

Scheme 2



Our previous results on the synthesis of inert Si═P compounds (silylidenephosphanes) and of small ring compounds with a Si,P skeleton, starting from sterically congested fluorosilyl-substituted lithium phosphanides by thermally induced LiF elimination,[14] prompted us to expand this method to build up P_2Si and P_2Si_2 derivatives of the type **2** and **3**, respectively. We therefore synthesized the 1,2-bis(difluorosilyl)-1,2-diphosphane **1** (Scheme 2), which indeed can be converted via the P_2Si-cyclopropanes **2a**,**b** into the desired P_2Si_2 butterfly-like compound **3**. **1** has been prepared by the reaction of the fluorodiarylsilyl-substituted lithium phosphanide **4** with 1,2-dibromoethane in 83% yield.This reaction type of reductive P−P bond formation was invented by Issleib et al.[15]

1 exists as a 1:2 mixture of diastereomers (*d,l*-racemate and meso form; see Figure 1), which has been proven by ^{31}P and ^{19}F NMR spectroscopy (see Table 1). The ^{31}P NMR spectrum shows two doublets of doublets in the ratio of 2:1, whereby the more intense signal at higher field is assigned to the meso isomer, which probably is preferred by steric reasons. Correspondingly, the ^{19}F NMR spectrum reveals two singlets in the ratio 2:1.

The relatively small magnitude of the $^{1}J(P, H)$ coupling constant, compared to that values observed for unhindered diphosphanes,[16] indicates low 3s character of the phosphorus valence orbitals. The drastically different values of the $^{2}J(P,H)$ coupling constants for the two diastereomers reflect the stere-

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Table 1. $\delta(^{31}P)$ and $\delta(^{19}F)$ NMR Data for **1**, **2a**, **2b**, and **5** (J in Hz)

compd	$\delta(^{31}P)$	$\delta(^{19}F)$	$^1J(P,H)$	$^2J(P,H)$	$^1J(P,P)$
1 (*d*, *l*)	−190.6 (d, d)	−136.7 (s)	153	44	
1 (meso)	−195.8 (d, d)	−136.2 (s)	129	70	
2a	−273.9 (d, PSiF)[a]	−132.9 (d)[a]		0	0
	−267.1 (d, PH)		147	0	0
2b	−250.2 (dd, PSiF)[b]	−147.7 (d)[b]			46
	−303.3 (d, PLi)				46
5	−244.5 (d, PLi)	−136.7 (s)		0	212
	−164.7 (dd, PH)	−136.9 (s)	176	0	212

[a] $^2J(P,F) = 38$ Hz. [b] $^2J(P,F) = 16$ Hz.

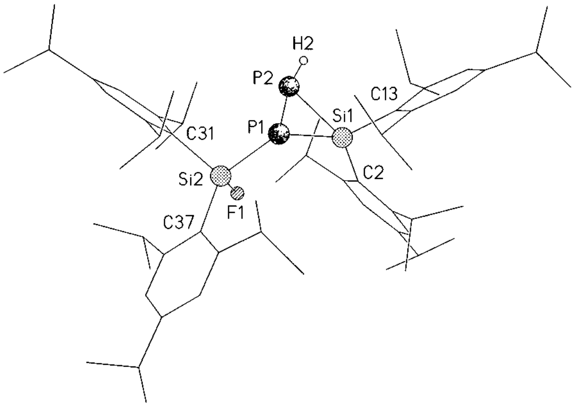

Figure 2. Molecular structure of **2a**. H atoms (except for P2) are omitted for clarity.

ochemical site of the P−H hydrogen atoms with respect to the phosphorus lone pairs: hence, the syn conformation in the meso form reveals a much larger value than that observed for the *d,l* form.[17]

The constitution of **1** has been confirmed by a single-crystal X-ray diffraction analysis.[18] Unfortunately, the compound is disordered in solid state and, therefore, a discussion of structural parameters is not reasonable.

1 reacts with 1 equiv of ^{n}BuLi in THF, affording the monolithium derivative **5**, which is slightly soluble in etheric and aromatic solvents. Its structure was elaborated by ^{31}P NMR spectroscopy (see Table 1). Heating of **5** as a slurry in THF and toluene at 80 °C furnishes the P_2Si-cyclopropane **2a** in quantitative yield. **2a** was isolated in the form of colorless crystals in 90% yield. Worthy of note are its ^{31}P NMR spectroscopic data and the fact that the scalar $^1J(P,P)$ coupling constant is zero (see Table 1). The ^{31}P nuclei appear strongly shielded. Other compounds of the type **C** and **E** exhibit even stronger deshielded ^{31}P nuclei ($\delta = -110$ to -152) than **2a**.[5] The small $^1J(P,H)$ coupling constant, which usually is 170−200 Hz for acyclic P−H-containing phosphanes, and the unprecedented $^1J(P,P)$ coupling constant of zero reflect the unusually low s-character of the phosphorus valence orbitals.[17]

The structure of **2a**, as depicted in Figure 2, was unequivocally determined by an X-ray diffraction analysis. Its selected geometry parameters are presented in Table 2. **2a** consists of an almost regular P_2Si triangle with endocyclic Si−P distances of 2.241(3), 2.246(3) and a P−P distance of 2.246(3) Å, respectively. The exocyclic Si−P distance amounts to 2.262(3) Å and is marginally longer than the endocyclic one. The P2−H hydrogen atom was localized in the Fourier map and refined. Both phosphorus atoms are strongly pyramidal coordinate, with the sum of bond angles at P1 and P2 of 273.3(1) and 251(5)°, respectively. Hence, the geometric parameters are identical with those observed for other P_2Si derivatives **C**.[5,7]

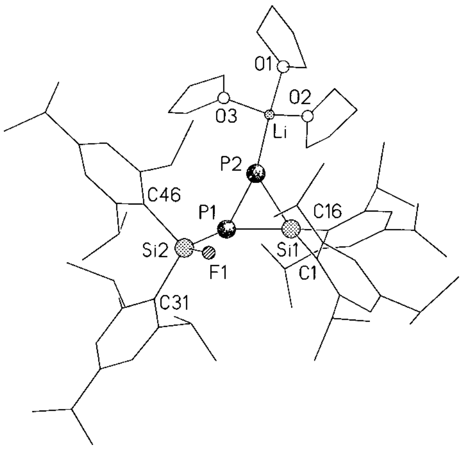

Figure 3. Molecular structure of **2b**. H atoms are omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **2a**

P1−Si1	2.243(3)	P1−Si2	2.264(3)
P2−Si1	2.251(3)	Si2−F1	1.609(4)
P1−P2	2.251(3)		
Si1−P1−P2	60.12(9)	C1−Si1−C16	110.3(3)
P2−P1−Si2	99.58(10)	C16−Si1−P1	113.7(2)
Si1−P1−Si2	113.58(10)	C1−Si1−P1	129.2(2)
P1−P2−Si1	59.76(8)	C1−Si1−P2	122.9(2)
P1−Si1−P2	60.11(9)		

Table 3. Selected Bond Lengths (Å) and Angles (deg) for **2b**

P1−Si1	2.255(3)	P2−Li	2.568(13)
P2−Si1	2.171(3)	Li−O3	1.927(13)
P1−P2	2.256(3)	Li−O2	1.938(13)
P1−Si2	2.252(3)	Li−O1	1.993(13)
Si2−F1	1.613(4)		
Si1−P1−P2	57.53(8)	C1−Si1−P1	128.8(2)
P2−P1−Si2	100.41(10)	C1−Si1−P2	125.3(2)
Si1−P1−Si2	109.05(10)	P2−Li−O1	106.0(5)
P1−P2−Si1	61.22(8)	P2−Li-O2	124.0(6)
P1−P2−Li	120.2(3)	P2−Li−O3	113.3(6)
P1−Si1−P2	61.25(8)	O2−Li−O3	102.6(6)
C1−Si1−C16	105.5(3)	O3−Li−O1	102.8(6)
C16−Si1−P1	114.6(2)	O2−Li−O1	106.1(6)

2a can be lithiated at the P2 atom by its reaction with ^{n}BuLi, affording yellow crystals of **2b**. The latter compound is also accessible by the dilithiation of **1** with 2 equiv of ^{n}BuLi in THF at −78 °C, leading to the intermediate **6**. The latter subsequently undergoes ring closure reaction at 0 °C and LiF elimination. The intact P_2Si three-membered ring structure in **2b** is proven by its characteristic multinuclei NMR spectroscopic data (see Table 1). The geometrical parameters of **2b** (see Table 3), which have been established by an X-ray diffraction analysis, reveal that the lithiation of the P2 center in **2a** has a strong influence on the electronic structure of the P_2Si skeleton. (Figure 3).

The P_2Si three-membered ring in **2b** is isosceles, with practically unchanged Si1−P1 (2.255(3) Å) and P1−P2 distances (2.256(3) Å) compared to **2a**. The Si1−P2 distance, however, is 2.171(3) Å, significantly shorter (ca. 0.08 Å) than the Si1−P1 distance and the respective values in **2a**. This shortening is probably due to the stronger Si1−P2 bond polarity.

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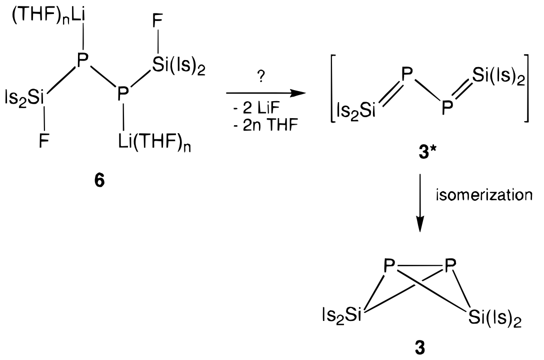
(18) **1** crystallizes in tetragonal space group $P4/nnc$, with $a = b = 19.31(1)$ Å, $c = 18.83(1)$ Å, $V = 6817$ Å^3, and $Z = 8$.

Hyperconjugation between the P2 center and the Si1−C16 σ* orbital can be excluded since the Si1−C1 and the Si1−C16 distances are identical. The Li center is pyramidally coordinated; that is, it is bound to the P2 atom and the oxygen atoms of the three THF molecules. The Li−P2 distance of 2.568(13) Å is inconspicous. Both P atoms are strongly pyramidal, with the sum of bonding angles of 267.0 (P1) and 303.4° (P2), respectively.

Heating of a slurry of **2b** in toluene at 80 °C leads solely to **3**, showing a characteristic high-field resonance signal at $\delta = -300.2$ with ^{29}Si satellites (^1J(P,Si) = 83 Hz). Its composition is proven by mass spectrometry and elemental analysis. The ^{1}H- and ^{31}P-NMR spectroscopical data of **3** are identical with those already reported in the literature.[12] The synthesis of **3** here described is much more convenient than the previously reported method via P−Hg-substituted 1,3-diphospha-2,4-disilacyclobutanes[12] and is readily variable for the synthesis of other derivatives. The P$_2$Si$_2$ butterfly-like compounds of the type **3** have a relatively long P−P-bridgehead bond (ca. 2.38 Å versus 2.24 Å for the P−P bond in **2a**) and also tend to undergo a ring inversion via an unusual silanediyl fragmentation in the transition state.[10] The weak P−P bond is mostly due to Baeyer ring strain and repulsion between the two negatively charged P atoms (σ-effect of the Si$^+$—P$^-$ polarized bonds). This electronic situation prompted us to search for a synthesis of the corresponding heterobuta-1,3-diene **3***, its constitutional isomer. Since we have shown that even crystalline doubly-bonded silicon−phosphorus compounds (silylidenephosphanes and 1,3-disila-2-phosphaallyl systems)[6,14] can be prepared if the steric congestion at the low-coordinate silicon atom is sufficient, it seems promising to find a rearrangement reaction from **3** to **3***. However, neither the thermally induced one-pot conversion of **1** via **6**, according to eq 2, nor irradiation of **3** gave any spectroscopic indication for **3*** as possible transient species. This suggests that the desired isomer **3*** is probably less stable than **3**. In order to get insight into the relative stability of the P$_2$-Si$_2$-bicyclic compounds versus their low-coordinated butadiene isomers, we have performed ab initio calculations of the respective parent compounds **7a**−**g** (Chart 3).



(2)

Ab Initio Calculations

Ab initio calculations of stationary points on the H$_4$P$_2$Si$_2$ energy surface were investigated by employing the program package GAUSSIAN 94.[19] Geometry optimization of minima and transition structures as well as the corresponding frequency calculations were performed at the MP2/6-31G* level of theory. The quadratic synchronous transit approach (QST2) was applied for locating transition structures.

Chart 3

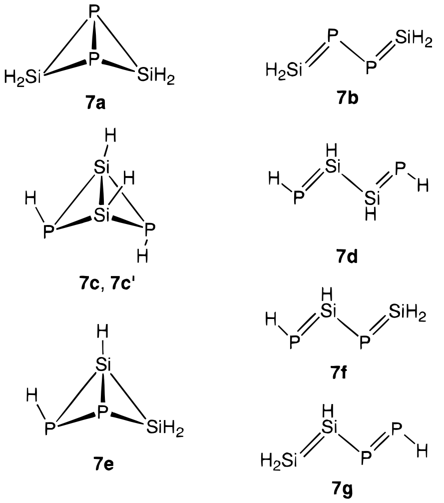


Table 4. MP2/6-31G* Calculated Minimum Energy Geometries (Å, deg) of H$_4$P$_2$Si$_2$ Isomers with Geometry Parameters of only the P$_2$Si$_2$ Skeletons Mentioned

7a	C_{2v}	P−P 2.405, P−Si 2.217, P−Si−P 65.7, Si−P−P−Si 101.6[c]
7b	C_{2h}	P−Si 2.086, P−P 2.210, Si−P−P 96.5
7c	C_s	Si−Si 2.580, Si−P 2.254,[a] Si−P−Si 69.8,[a] H−Si−Si 90.7, P−Si−Si−P 132.8[c]
7c′	C_s	Si−Si 2.187, Si−P 2.278,[a] Si−P−Si 57.4,[a] H−Si−Si 150.4, P−Si−Si−P 116.5[c]
7d	C_{2h}	P−Si 2.095, Si−Si 2.295, P−Si−Si 120.6
7e	C_1	Si−Si 2.263, P−P 2.255, Si−P 2.323,[b] Si−P 2.236,[a] P−P−Si−Si 112.7[c]
7f	C_s	P−Si(H$_2$) 2.079, P(H)−Si 2.086, P−Si(H) 2.217, Si(H$_2$)PSi 95.6, P−Si−P(H) 120.0
7g	C_1	Si−Si 2.171, Si−P 2.218, P−P 2.063, Si−Si−P 116.0, Si−P−P 98.9, P−P−Si−Si 162.1

[a] Average values. [b] Bridge bond. [c] Folding angle.

Eight minimum geometries out of three types of valence isomers of H$_4$P$_2$Si$_2$ were optimized. These are I (**7a**,**b**), II (**7c**,**c′**,**d**), and III (**7e**−**g**) according to the different distribution of H atoms. The geometry parameters of the P$_2$Si$_2$ skeletons are presented in Table 4. As a result of strain relief long bridgehead bond length can be observed throughout. These are d(P−P) = 2.405 Å (**7a**), d(Si−Si) = 2.580 Å (**7c**), and d(Si−P) = 2.323 Å (**7e**). A remarkable phenomenon is bond-stretch isomerism which results in two minima **7c** and **7c′** which differ mainly by two different Si−Si bridge bond lengths and, consequently, two different folding angles for the three-membered ring moieties.

Inspection of the relative energies of H$_4$P$_2$Si$_2$ isomers in Table 5 leads to the result that the bicyclo[1.1.0]butane-like structures are more stable throughout than the corresponding buta-1,3-diene-like isomers. The structure **7a** represents the global minimum. The most stable buta-1,3-diene-like isomer is **7f**, where the number of heteronuclear bonds (P−Si) is maximal. This yet unknown structure turned out to be kinetically labile due to the relatively low activation barrier of 14.6 kcal mol^{-1} to the bicyclic isomer **7e**.

Bond-stretch isomerism has been considered in the past in carbon ring systems.[20] However, no example of isomers which differ principally in the bridge bond length has been found experimentally. Bond-stretch isomerism in bicyclo[1.1.0]-

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Table 5. MP2/6-31G* Calculated Relative Energies d (E+ZPE) (kcal mol^{-1}) of Stationary Points on the $H_4P_2Si_2$ Hypersurface[a]

7a	**7b**		
0.0	42.0		
7c	TS(**c**-**c'**)	**7c'**	**7d**
21.7	36.3	35.7	40.6
7e	TS(**e**-**f**)	**7f**	**7g**
17.4	50.3	35.7	49.4

[a] The compounds **7a**−**7g** are minima out of the three types of valence isomers; TS (**c**, **c′**) and TS (**e**, **f**) are transition structures for the interconversion of bond-stretch isomers **7c**, **7c′** and **7e**, **7f**, respectively.

tetrasilane[21] turned out to be an artifact of insufficient theories.[22] The pair of $H_4P_2Si_2$ compounds **7c**,**c′** represents a new type of bond-stretch isomers. However, the calculated energy barrier separating **7c′** from **7c** is quite small, 0.6 kcal mol^{-1}. Hence, **7c′** is not likely to be a viable isomer.

Experimental Details

All work was performed under anaerobic and anhydrous conditions by using Schlenk techniques. Solvents were distilled from Na/K alloy and saturated with dry argon. The starting compound $Is_2Si(F)PHLi$ was prepared as previously described.[23] NMR spectroscopic measurements: ^{1}H NMR (200 MHz), ^{31}P NMR (81 MHz), ^{19}F NMR (89 MHz), and ^{7}Li NMR (77.8 MHz) measurements were recorded on a Jeol-FX90Q and/or Bruker AC200 spectrometer. Chemical shifts (δ) are given relative to external standards (^{1}H to $SiMe_4$; ^{31}P to 85% aqueous H_3PO_4; ^{19}F to $CFCl_3$; ^{7}Li to aqueous LiBr). All isolated compounds gave C, H analyses consistent with their formulas. The composition of **2b** was confirmed indirectly by its protolysis and formation of **2a**.

Synthesis of *P,P′*-Bis[fluorobis(2,4,6-triisopropylphenyl)silyl]-diphosphane, 1. A solution of 22.7 mmol of $Is_2Si(F)PHLi$ in 30 mL of THF was quenched at −50 °C with 2.13 g (11.35 mmol) of 1,2-dibromoethane (C_2H_4 evolution) in 5 mL of hexane, and the mixture was stirred for 8 h and allowed to warm to room temperature. The solvent was evaporated, and the pale-red residue was extracted with warm hexane and filtered through a GIII frit to remove LiBr. The product crystallizes in hexane at 4 °C in the form of colorless cubes, yielding 18.2 g (18.8 mmol, 83%). Mp: 175 °C. **1** is a 2:1 mixture of *d,l*- and meso-diastereomers. ^{1}H NMR (C_6D_6, 300 K): δ 0.58 (d, 1H, PH, ^1J(H,P) = 128 Hz), 0.91−1.24 (br m, 72 H, *o,p*-CHMe$_2$), 1.75 (d, 1H, PH, ^1J(H,P) = 152 Hz), 2.74 (sept, 4 H, *p*-CHMe$_2$, J(H,H) = 6.5 Hz), 3.71 (sept, 8 H, *o*-CHMe$_2$, J(H,H) = 6.6 Hz), 7.07 (s, 8 H, arom H). ^{19}F NMR (C_6D_6, 300 K): δ −136.7 (s), 136.2 (s) in the ratio 2:1. ^{31}P NMR (C_6D_6, 300 K): δ −195.8 (dd, ^1J(P,H) = 129 Hz, ^2J(P,H) = 70 Hz), −190.6 (dd, ^1J(P,H) = 153 Hz, ^2J(P,H) = 44 Hz). MS (EI), *m/z* (%): 485 [(M/2)$^+$, 10], 453 [Is_2SiF^+, 100). Anal. Calcd for $C_{60}H_{94}F_2P_2Si_2$ (M_r = 971.52): C, 74.18; H, 9.75. Found: C, 74.11; H, 9.64.

Synthesis of 1-(Fluorobis(2,4,6-triisoropylphenyl)silyl)-2*H*-3,3-bis-(2,4,6-triisopropylphenyl)-1,2-diphospha-2-silacyclopropane, 2a. A solution of 3.6 g (3.71 mmol) of **1** in 30 mL of THF was treated with 1.5 mL of ^{n}BuLi (2.5 M in hexane, 3.71 mmol) at −78 °C to furnish a light-red solution. Stirring of the solution at room temperature for 4 h leads to the pale-yellow monolithium salt **5**, which is only slightly soluble in THF and, therefore, precipitates from the reaction mixture. Heating of the slurry at 80 °C finally furnishes a colorless solution from which the desired product **2a** was isolated in the form of colorless crystals at 4 °C. Yield: 3.20 g (3.34 mmol, 90%). Mp: 126 °C. ^{1}H NMR (C_6D_6, 300 K): δ 0.58 (d, 1H, PH, ^1J(H,P) = 147 Hz), 1.1−1.6 (br m, 72 H, *o,p*-CHMe$_2$), 2.76 (sept, 4 H, p-CHMe$_2$, J(H,H) = 6.6 Hz), 3.3−4.0 (br m, 8 H, *o*-CHMe$_2$), 7.1 (s, 8 H, arom H). ^{19}F NMR (C_6D_6, 300 K): δ −132.9 (d, ^2J(F,P) = 38 Hz). ^{31}P NMR (C_6D_6, 300 K): δ −273.9 (d, PSiF, ^2J(P,F) = 38 Hz), −267.1(d, ^1J(P,H) = 147 Hz). MS (EI), *m/z* (%): 950 [M$^+$, 7], 907 [(M − Pr)$^+$, 5], 746 [(M − IsH)$^+$, 6], 453 [Is_2SiF^+, 100), 249 [(Is_2SiF − 1H)$^+$, 95]. Anal. Calcd for $C_{60}H_{93}FP_2Si_2$ (M_r = 950.63): C, 75.74; H, 9.85. Found: C, 76.38; H, 10.32.

Table 6. Crystal and Structure Refinement for **2a** and **2b**

	2a	**2b**
formula	$C_{60}H_{93}FP_2Si_2$	$C_{72}H_{123}FLiO_3P_2Si_2$
fw	951.52	1180.82
temp (°C)	20(3)	−70(2)
cryst system	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$
cell dimens (Å, deg)		
a	14.847(3)	14.845(11)
b	22.559(5)	24.59(2)
c	21.071(3)	21.13(2)
α	90	90
β	77.74(1)	93.88(6)
γ	90	90
V (Å^3)	6896(2)	7698(10)
Z	4	4
calcd density (g cm^{-3})	0.974	1.071
F(000)	2200	2716
cryst size (mm)	0.3 × 0.3 × 0.3	0.7 × 0.7 × 0.3
θ_{max} (deg)	23.51	23.0
hkl-range	−7/16, −23/25, −23/23	−16/16, 0/23, 0/23
reflcns collcd	10 649	10 145
indepdt reflcns	10 199	10 145
abs coeff (cm^{-1})	1.33	1.33
params	654	803
goodness-of-fit on F^2	1.035	1.022
R1 [$I > 2\sigma(I)$][a]	0.086	0.077
wR2 (all data)[b]	0.270	0.208
resid electn dens. (e Å^{-3})	0.38/−0.28	0.53/−0.25

[a] R1 = $\sum\{|F_o| - |F_c|/\sum|F_o|\}$ based on $I > 2\sigma(I)$. [b] wR2 = $\{[\sum w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)^2\}^{0.5}$, where w = weighting factor.

Synthesis of 1-(Fluorobis(2,4,6-triisopropylphenyl)silyl)-2-(tris-(tetrahydrofurano)lithio)-3,3-bis(2,4,6-triisopropylphenyl)-1,2-diphospha-2-silacyclopropane, 2b. A solution of 2.26 g (2.33 mmol) of **1** in 30 mL of THF was treated with 1.9 mL (2.5 M solution in hexane, 4.66 mmol) of ^{n}BuLi at −78 °C. The clear light-red solution was allowed to warm to 0 °C within 6 h and stored at 4 °C to furnish crystalline **2b** which was isolated in the form of yellow cubes. The crystals are very air-sensitive and partially undergo protonation reaction to form **2a** if dissolved in toluene/THF (^{31}P NMR). Yield: 2.3 g (1.96 mmol, 84%) of **2b**. ^{19}F NMR ([D$_8$]-THF, 300 K): δ −147.7 (d, ^2J(F,P) = 16 Hz). ^{7}Li NMR ([D$_8$]-THF, 300 K): δ −2.4 (br). ^{31}P NMR ([D$_8$]-THF, 300 K): δ −303.3 (d, PLi, ^1J(P,P) = 46 Hz), −250.2 (dd, PSiF, ^1J(P,P) = 46 Hz, ^2J(P,F) = 16 Hz).

Synthesis of 2,2,4,4-Tetrakis(2,4,6-triisopropylphenyl)-1,3-diphospha-2,4-disilabicyclo[1.1.0]butane, 3. To a stirred solution of 1.64 g (1.69 mmol) of **1** in 50 mL of toluene at −78 °C was added 1.4 mL (2.5 M solution in hexane, 3.38 mmol) of ^{n}BuLi, and the yellowish solution was allowed to warm to room temperature over 6 h. The resulting slurry was subsequently heated at 80 °C to furnish a clear pale yellow solution. The solvent was evaporated to dryness in vacuum (10^{-2} Torr), and the residue was dissolved in a small amount of hexane from which **3** crystallizes in the form of pale yellow plates. Yield: 1.3 g (1.37 mmol, 81%). Mp: 301−302 °C. ^{1}H NMR (C_6D_6, 300 K): δ 0.78 (d, 12 H, *p*-CHMe$_2$, J(H,H) = 6.8 Hz), 0.91 (d, 12 H, *p*-CHMe$_2$, J(H,H) = 6.8 Hz), 1.0−1.29 (m, 48 H, *o*-CHMe$_2$), 2.63 (sept, 4 H, *p*-CHMe$_2$, J(H,H) = 6.8 Hz), 3.75 (sept, 4 H, *o*-CHMe$_2$), 4.01

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(sept, 4 H, *o*-CHMe$_2$, J(H,H) = 4.8 Hz), 6.89 (s, 4 H, arom H), 7.11 (s, 4 H, arom H). ^{31}P NMR (C$_6$D$_6$, 300 K): δ −300.2 (s). MS (EI), *m/z* (%): 930 [M$^+$, 31], 727 [(M − Is)$^+$, 15], 453 [IsSiH$_2$$^+$, 100]. Anal. Calcd for $C_{60}H_{92}P_2Si_2$ (M_r = 931.51): C, 77.35; H, 9.95. Found: C, 77.12; H, 9.81.

Crystal Structure Determinations. Crystal data and details of the structure analyses of **2a**,**b** are given in Table 6. Data Collection: Data were collected in the ω-scan mode, for **2a** with a Syntex R3 Diffractometer (Mo Kα radiation (λ = 0.7107 Å), at room temperature) and for **2b** with a Siemens-Stoe AED2 (Mo Kα radiation, at −70 °C). Solution and refinement: The structures were solved by direct methods (SHELXS-86)[24] and refined by the least-squares method based on F^2 with all measured reflections (SHELXL-93)[25] using anisotropic temperature factors for all non-hydrogen atoms. Hydrogen atoms were included in calculated positions or as part of a rigid group (methyl). Only the hydrogen atom attached to P2 in **2a** was refined. Otherwise common isotropic temperature factors for equivalent hydrogen atoms were refined. In both structures some of the isopropyl groups (especially in the para-position) and some of the THF molecules in **2b** are disordered.

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Supporting Information Available: X-ray crystallographic files, in CIF format, for compounds **2a** and **2b** are available on the Internet only. Access information is given on any current masthead page.

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