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Synthesis and Unusual Thermal Behavior of (Lithium phosphino/amino) Difluorosilanes†

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The sterically hindered *meta*-terphenyl trifluorosilanes $Tip_2C_6H_3SiF_3$ (**1**), $Mes_2C_6H_3SiF_3$ (**2**) (Tip = 2,4,6-triisopropylphenyl; Mes = 2,4,6-trimethylphenyl), and trifluoro(2,4,6-tri-*tert*-butylphenyl)silane 2,4,6-*tert*-$Bu_3C_6H_2SiF_3$ (**3**) react unconventionally with lithium bis(trimethylsilyl)phosphide $LiP(SiMe_3)_2$ to form corresponding lithium (aryldifluosilanyl)trimethylsilylphosphides $ArSiF_2P(Li)SiMe_3$ (Ar = $Tip_2C_6H_3$, **5**; $Mes_2C_6H_3$, **6**; 2,4,6-*tert*-$Bu_3C_6H_2$, **7**) and fluorotrimethylsilane rather than LiF. The central Si−P bond lengths of **5**−**7** are short and positioned somewhere between typical single and double silicon−phosphorus bonds. The thermolysis of lithium [difluoro(2,4,6-tri-*tert*-butylphenyl)silanyl]trimethylsilylphosphide (**7**) led to 2,4-diorgano-[1,3,2,4]diphosphadisiletane derivatives $R_2Si(PH)_2SiR_2$ (R_2Si = 5,7-di-*tert*-butyl-3,3-dimethyl-2,3-dihydro-1*H*-benzo[*b*]silole) **11** and $R_2Si(PH)(PSiMe_3)SiR_2$ (R_2Si = 5,7-di-*tert*-butyl-3,3-dimethyl-2,3-dihydro-1*H*-benzo[*b*]silole) **12**. The lithium and sodium bis(trimethylsilyl)amides react conventionally with **1**−**3** to form thermally stable bis(trimethylsilyl)aminodifluoroarylsilanes $ArSiF_2N(SiMe_3)_2$ (Ar = $Tip_2C_6H_3$, **18**; $Mes_2C_6H_3$, **19**; 2,4,6-*tert*-$Bu_3C_6H_2$, **20**). The reaction of sodium amide and *meta*-terphenyl trifluorosilanes $Tip_2C_6H_3SiF_3$ (**1**) produced the 2,4-diorgano-[1,3,2,4]diazadisiletane $Tip_2C_6H_3$-$Si(F)(NH)_2(F)SiC_6H_3Tip_2$ (**21**). The transannular nonbonding Si−Si distance in the ring of **21** was found to be 2.4911(13) Å.

Introduction

The search for stable compounds with (p−p) π multiple bonds formed from elements beginning with the second long period of the periodic table is one of the central themes of organometallic chemistry.[1−3] The number of the known stable triply bonded substances is still understandingly low. This field of organometallic chemistry is considered as “a final challenge” in the (p−p) π multiple bonds of heavier elements.[4] The subject of molecules containing phosphorus−silicon and nitrogen−silicon triple bonds has attracted limited efforts so far. For example, the silaphosphacubane, which could be considered as a tetramer of *tert*-butyl phosphasilyne, has been characterized by X-ray analysis.[5] Theoretical studies predicted the relative stability and existence of such triply bonded silicon and phosphorus molecules.[6,7] An attempt to prepare silicon−silicon triply bonded species has been published recently.[8] In this report we describe a synthetic approach for a possible route to a compound with triple bonding between phosphorus and silicon.

Results and Discussion

Steric protection is considered one means to stabilize the (p−p) π multiple bonds of heavier elements. The *meta*-terphenyl groups have been shown to stabilize lead and germanium compounds with interesting bonding patterns.[9,10] A 2,4,6-tri-*tert*-butylphenyl group is utilized widely to isolate double-bonded silicon compounds.[11−13] Both of the above kinds of the protective groups were tested in the current report. The corresponding aryltrifluorosilanes were chosen instead of trichlorosilane derivatives because of the low steric hindrance created by fluoride atoms over chloride atoms as well as NMR activity of the ^{19}F nucleus, giving an extra analytical tool for the characterization of the molecules of interest. The *meta*-terphenyl trifluorosilanes $Tip_2C_6H_3SiF_3$ (**1**) and $Mes_2C_6H_3SiF_3$ (**2**) (Tip = 2,4,6-triisopropylphenyl; Mes = 2,4,6-trimethylphenyl) were prepared by a known

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† DuPont contribution #08408. Dedicated to Professor Adrian G. Brook on the occasion of his 79th birthday.

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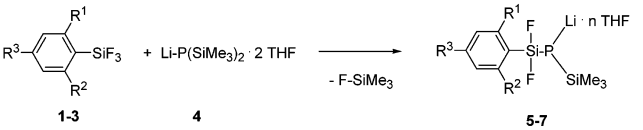
10.1021/om0304412 CCC: $25.00

Scheme 1



1:R^1=R^2=2,4,6-triisopropylphenyl; R^3=H
2:R^1=R^2=2,4,6-trimethylphenyl; R^3=H
3:R^1=R^2=R^3=*tert*-Bu

5:R^1=R^2=2,4,6-triisopropylphenyl; R^3=H; n=2
6:R^1=R^2=2,4,6-trimethylphenyl; R^3=H; n=2
7:R^1=R^2=R^3=*tert*-Bu; n=3

procedure.[8] Authors of the above publication have noticed an unusual ^{19}F NMR shift of compound **1**, which was out of the normal range for aryltrifluorosilanes. We have recorded the ^{19}F NMR shift of compound **1**, which is quite regular for this type of structure: δ (^{19}F) −131.19 ppm versus the published value of −64.6.[8] We did not record substantial differences in chemical shifts of ^{29}Si NMR spectra for compounds **1** and **2**. We determined δ (^{29}Si) for **1** and **2** to be − 71.8 and − 73.1 ppm, respectively. Previously published values for **1** and **2** were δ (^{29}Si) − 72.8 and − 73.6 ppm, respectively. The X-ray analysis of compound **1** revealed the expected bonding pattern. The trifluoro(2,4,6-tri-*tert*-butylphenyl)silane (**3**) was prepared by known procedures.[14,15] The NMR spectral data were close to the reported values.

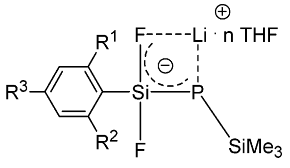
Synthesis of Lithium (Aryldifluorosilanyl)trimethylsilylphosphides. 1,3-Trimethylsilyl migration and 1,2-trimethylsilyl elimination were used to construct the multiple bonds of silicon compounds.[16] Therefore, the silicon−phosphorus precursors with potential 1,2-fluorotrimethylsilane elimination were synthesized by the reaction of trifluorosilanes **1**−**3** and lithium bis(trimethylsilyl)phosphide bis(tetrahydrofuran) (**4**).

The synthetic route shown in Scheme 1 involves the elimination of fluorotrimethylsilane rather than lithium fluoride. This unusual mode of preferential elimination of Me$_3$SiF over conventional LiF has been encountered in the syntheses of lithium salts of boryl phosphides.[17,18] The authors cited the relatively weak P−Si bond, energetically favorable Si−F bonds, and the greater degree of solvation of the Li$^+$ cation as an explanation of Me$_3$SiF elimination in its reaction. It can be an explanation in our case too, plus additional delocalization of electron density from the phosphorus atom onto the difluorosilicon moiety of the molecules **5**−**7**. The silicon in **5**−**7** is substituted by two very electronegative fluorines, which remove electron density from the silicon and effectively contract its radius. Also, the presence of two electropositive substituents at phosphorus (trimethylsilyl and lithium) means that σ-character in the phosphorus σ-bonding increases. This tends to shorten the σ-bonds to phosphorus somewhat so that a shorter P−SiF$_2$Ar bond is the result. As can be seen from Table 1, the central Si−P bond lengths of **5**−**7** are indeed shorter than a normal P−Si single-bond distance of 2.25 Å.[19] However, they are longer than the isolated (p−p) π P=Si double-bond lengths found for phosphasilenes, for example, 2.094(3), 2.053(2), and 2.062(1) Å.[20] The central Si−P bond lengths of **5**−**7** are positioned somewhere in the middle between single and double silicon−phosphorus bonds. The earlier research on isoelectronic lithium salts of boryl phosphides[17,18] has established a higher degree of multiple bonding between boron and phosphorus. Taking in account well-known examples of lithium silicon−heteroallyl structures,[20,21] the two-dimensional mesomeric form of **8** can be drawn as an explanation for the short Si−P bond representing compounds **5**−**7** in the solution. The comparison of (F)-Si−P bond lengths of compounds **5**−**7** with corresponding numbers of monofluorosubstituted silylphosphides, for example 2.169(2), 2.172(2),[22] 2.200(1),[23] 2.171(2),[24] and 2.161 (4) Å,[25] reveals that difluorosubstituted derivatives **5**−**7** appear to have shorter (F)P−Si bonds.

Table 1. Selected Bond Lengths (Å) and Angles (deg) of 5−7

bond, angle	5	6	7
(F)Si−P	2.151(2)	2.146(3)	2.1592(10)
P−Si	2.240(2)	2.232(3)	2.2060(10)
P−Li	2.633(9)	2.558(19)	2.542(5)
Si−F(1) to Li	1.634(3)	1.588(4)	1.6158(15)
Si−F(2)	1.612(2)	1.604(5)	1.6138(17)
Li−F	2.644(10)		
(F)Si−P−Si	98.12(7)	98.45(12)	98.48(4)
(F)Si−P−Li	82.6(2)	94.7(4)	120.55(11)
F−Si−P	110.25(12)	113.6(2)	111.79(7)
F−Si−F	99.17(14)	99.5(3)	97.72(8)

Scheme 2



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The type of solvation of the Li$^+$ cation in **5**−**7** controls the structure of aryl fragments of the compounds. The *meta*-terphenyl derivatives **5** and **6** have the lithium cation coordinated with two molecules of THF and additional coordination with a fluorine atom in **5**, and coordination with *meta*-mesityl rings in **6** in the solid state. Figure 1 shows the interaction of the lithium cation with fluorine and phosphorus atoms as well as with two oxygen atoms of THF molecules retaining a four-coordination state.

The lithium cation of compound **6** as shown in Figure 2 coordinates with two oxygen atoms of THF molecules, but does not coordinate with fluorine atoms. Instead, it

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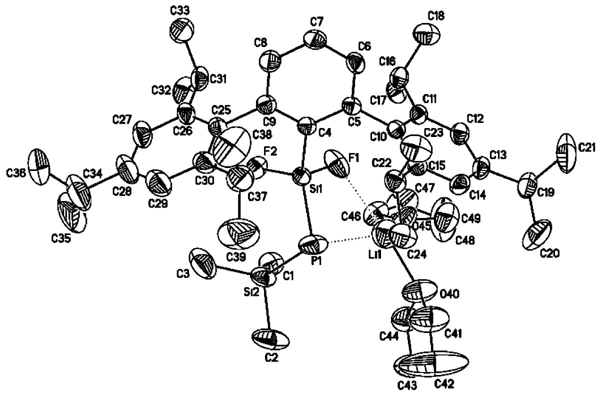

Figure 1. ORTEP drawing of bis(tetrahydrofuran)lithium [difluoro(2,6-bis(2,4,6-triisopropylphenyl)phenyl)silanyl]-trimethylsilylphosphide (**5**). Thermal ellipsoids are drawn at the 50% probability level.

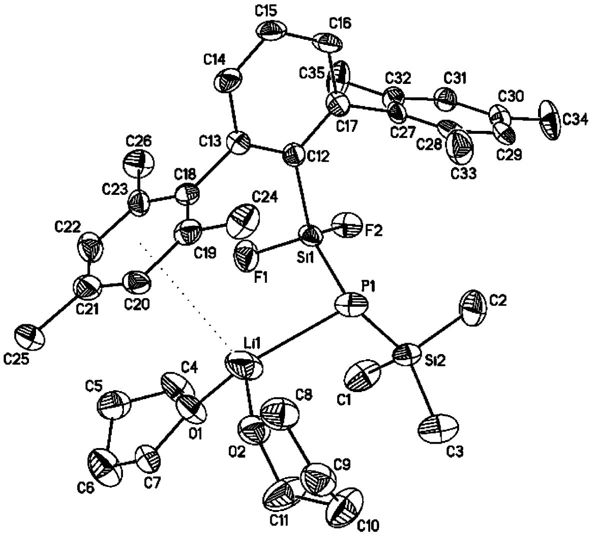

Figure 2. ORTEP drawing of bis(tetrahydrofuran)lithium [difluoro(2,6-bis(2,4,6-trimethylphenyl)phenyl)silanyl]-trimethylsilylphosphide (**6**). Thermal ellipsoids are drawn at the 50% probability level.

interacts with a *meta*-mesityl ring. The distances between Li1 and C18−C23 carbon atoms are in the range 3.06−4.10 Å, resulting in a Li−centroid distance of 3.35 Å. The sum of the van der Waals radii of the lithium atom (1.80 Å) and the carbon atom (1.70 Å) is 3.50 Å and is thus 0.44 Å larger than the shortest values found here. Examples of the Menshutkin interactions in the *meta*-terphenyl series of heavier dipnictenes have been published.[26,27]

The lithium cation in compound **7** coordinates with three oxygen atoms of three molecules of THF and with the phosphorus atom. The ORTEP drawing of substance **7** is presented in Figure 3.

The *meta*-terphenyl groups allow additional room in close vicinity of the difluorosilicon moiety for F−Li or *meta*-aryl−Li interactions in **5** and **6**. The 2,4,6-tri-*tert*-butylphenyl group does not provide steric leeway between the *tert*-butyl groups, difluorosilicon moiety, and lithium cation to establish additional weak interactions.

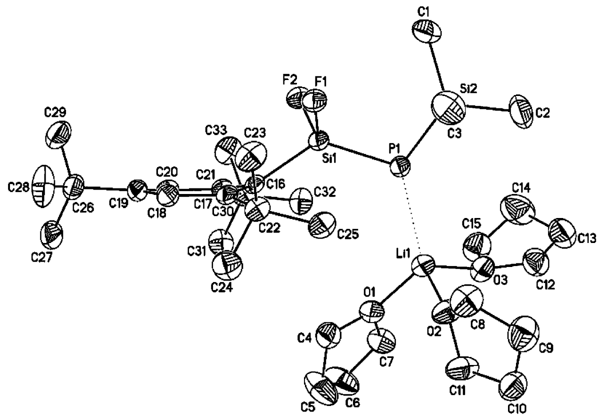

Figure 3. ORTEP drawing of tris(tetrahydrofuran)lithium [difluoro(2,4,6-tri-*tert*-butylphenyl)silanyl]trimethylsilylphosphide (**7**). Thermal ellipsoids are drawn at the 50% probability level.

Table 2. ^{7}Li, ^{19}F, ^{29}Si, and ^{31}P NMR Data of 5−7

δ/J	5	6	7
δ ^{7}Li [ppm]	7.15	7.21	7.53
δ ^{19}F [ppm]	−99.7	−104.3	−95.3
$^1J_{SiF}$ [Hz]	346	344	343
δ ^{29}Si [ppm]: Si(F)	−4.5	−5.7	−8.4
SiMe$_3$	3.5	3.9	6.72
δ ^{31}P [ppm]	−309.5	−305.0	−279.8
$^2J_{PF}$ [Hz]	53	52	48

According to NMR data from Table 2, the fluorine atoms of **5**−**7** in the solution appear to be equivalent. The lithium signals in **5**−**7** do not show any coupling with phosphorus or fluorine atoms, but the signals are somewhat broad, which indicate possible Li exchange between phosphorus and both fluorine atoms. The upfield chemical shifts in ^{31}P NMR spectra of **5**−**7** reflect the shielding effect of the negative charge on the phosphorus atoms.

Thermal Behavior of Lithium (Aryldifluorosilanyl)trimethylsilylphosphides 5−7. The chelate interaction between the lithium cation and fluorine atoms in **5**−**7** makes them interesting candidates for Li−F elimination experiments to form structures with (p−p) π P=Si double bonds. The substances **5**−**7** are thermally stable up to 100 °C in the hydrocarbon solutions, but undergo unusual rearrangements at higher temperatures. The mode of these rearrangements depends on the aryl groups at the silicon atom. The thermolysis of the 2,4,6-triisopropylphenyl derivative **5** in the toluene solution at 110 °C for 24 h resulted in the Norrish type 1 cleavage[28,29] of the central Si−P bond to yield the silane **9** formed by hydrogen abstraction of the parent silicon radical. The selectivity in the formation of difluoro(2,6-bis(2,4,6-triisopropylphenyl)phenyl)-silane (**9**) in the above thermolysis was 74% according to ^{19}F and ^{29}Si NMR spectral data. The product **9** has typical chemical shifts at δ (^{29}Si) − 12.47 and (^{19}F) −124.90 ppm with $^1J_{SiF}$ equal to 293.6 Hz for monocarbo-substituted difluorosilanes.[30,31] The selectivity of

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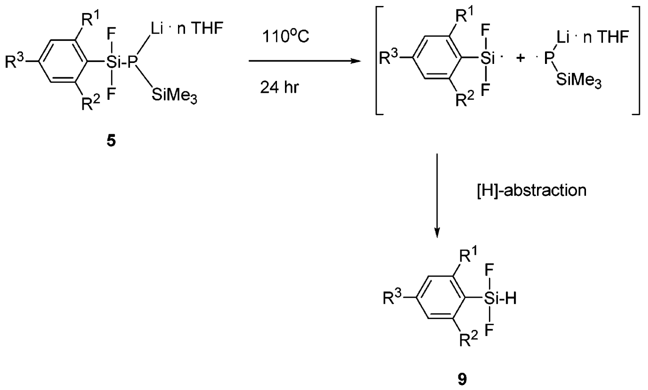
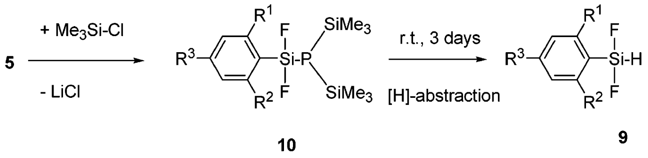
Scheme 3



Scheme 4



the thermolysis of **9** according to ^{31}P NMR spectral data was very poor. Over 50 phosphorus-containing products were recorded. A few are standouts by their intensities: Two products are downfield at δ (^{31}P) 173.40 (d, 60.7 Hz) and δ (^{31}P) 170.02 (d, 62.0 Hz), and one compound is upfield at δ (^{31}P) −252.11 (t, 40.0 Hz). The values of the chemicals shifts of the downfield products are in agreement with known values for phosphorus−silicon double bonds,[20] and possible coupling with fluorine or another phosphorus atom could account for doublets with slightly increased values due to the multiplicity of phosphorus−silicon bonding. The attempts to isolate these products were unsuccessful. It is difficult to draw conclusions on their actual structure due to the complexity of possible alternatives. The structure of the compound with an upfield signal was assigned after the reaction of chlorotrimethylsilane with lithium salt **5**. Compound **10** has the same values in the ^{31}P NMR spectra. Perhaps due to steric hindrance, the derivative **10** was not stable and decomposed in 3 days to form difluoro(2,6-bis(2,4,6-triisopropylphenyl)phenyl)silane (**9**) according to X-ray analysis.

Thermolysis of substance **6** in the toluene solution at 110 °C for 6 h was an even less selective process than that for **5** according to ^{19}F and ^{29}Si ^{31}P NMR spectra. For example, over 70 phosphorus-containing products were recorded with about the same signal intensities. They vary from an analogous downfield signal at δ (^{31}P) 165.73 (d, 64.8 Hz) to the cluster of the signals upfield at δ (^{31}P) −251.00 ppm, which are usual values of chemical shifts for polysilylphosphine derivatives.

The thermolysis of the lithium salts **5**−**7** with *meta*-terphenyl groups at the silicon atom requires higher temperatures than di-*tert*-butylsilyl analogues (0 or 80 °C).[22−25] The loss of the selectivity in the experiments with **5** and **6** may be associated with an increased amount of side reactions at higher temperatures. The thermolysis experiments in the solutions of *ortho*-dichlorobenzene at 170 °C or without solvents in a vacuum or under argon produced basically the same results.

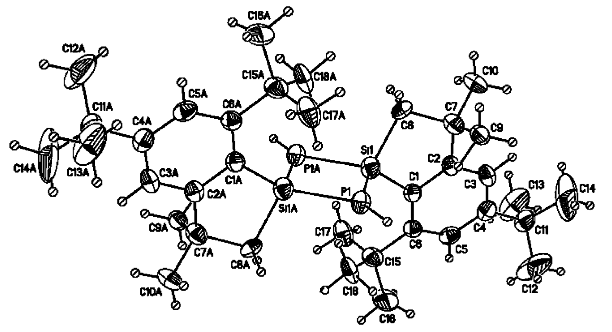
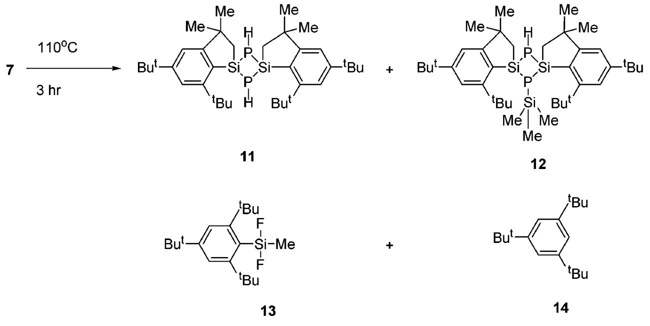


Figure 4. ORTEP drawing of 2,4-diorgano-[1,3,2,4]diphosphadisiletane (**11**). Thermal ellipsoids are drawn at the 50% probability level.

Scheme 5



Heating the lithium salt **7** in toluene solution at 110 °C for 3 h led to a more selective process than that for compounds **5** and **6**, with the formation of four major compounds. The 2,4-diorgano-[1,3,2,4]diphosphadisiletane (**11**) has a typical,[32−41] for organometallic cyclobutane structures, upfield signal in the ^{31}P NMR spectrum at δ (^{31}P) −158.48 (d, 169.5 Hz). There is a minor (about 10%) isomer of **11** in the solution, δ (^{31}P) −142.81 (d, d, 170.0 and 36.0 Hz), −150.02 (d, d 174.0 and 36.0 Hz), which have could resulted from PH-*cis*/PH-*trans* (phosphorus inversion) or *cis*-/*trans*-isomerism of 5,7-di-*tert*-butyl-3,3-dimethyl-2,3-dihydro-1*H*-benzo[*b*]silole moiety of compound **11**. Both kinds of the phenomena were reported in the family of [1,3,2,4]diphosphadisiletane.[32] The ORTEP drawing of **11** is shown in Figure 4, confirming the structure.

The ^{31}P NMR spectrum of product **12** has two signals for phosphorus atoms at δ (^{31}P) −158.54 (d, d 164.0 Hz, 34.0 Hz (P−H)) and δ (^{31}P) −176.69 (d 34.0 Hz (P−Si)). The X-ray analysis was instrumental in assignment of the structure for **12**. The ORTEP drawing of **12** is presented in Figure 5.

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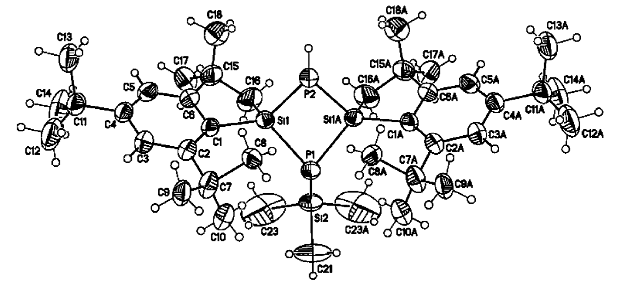
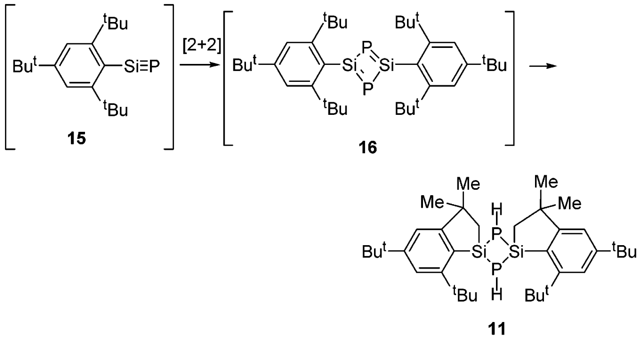


Figure 5. ORTEP drawing of 2,4-diorgano-[1,3,2,4]diphosphadisiletane (**12**). Thermal ellipsoids are drawn at the 50% probability level.

Scheme 6



Scheme 7

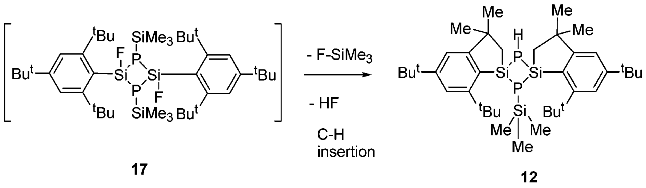
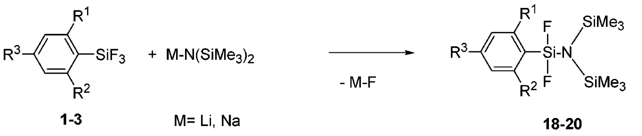


Table 3. Interplanar Angles of (2,4,6-Tri-*tert*-butylphenyl)silane Derivatives 3, 7, and 11−13

compound	dihedral angle of θ (deg)	dihedral angle of θ^1 (deg)
3	12.0	20.3
7	14.1	20.6
11	1.6	1.8 (disordered average)
12	0.9	3.2 (disordered average)
13	10.3	12.0

Scheme 8



1:R^1=R^2=2,4,6-triisopropylphenyl; R^3=H
2:R^1=R^2=2,4,6-trimethylphenyl; R^3=H
3:R^1=R^2=R^3=*tert*-Bu

18:R^1=R^2=2,4,6-triisopropylphenyl; R^3=H;
19:R^1=R^2=2,4,6-trimethylphenyl; R^3=H;
20:R^1=R^2=R^3=*tert*-Bu; n=3

Difluoromethyl(2,4,6-tri-*tert*-butylphenyl)silane (**13**) was isolated from the reaction mixture by recrystallizing from pentane at -30 °C. The ^{29}Si NMR spectrum of **13** contains the chemical shift at δ (^{29}Si) -13.48 ppm, which is close to the published value of -13.39 ppm.[15] 1,3,5-Tri-*tert*-butylbenzene (**14**) was crystallized last from the pentane solution of the reaction mixture and additionally purified by sublimation. ^{1}H spectral data and the melting point of **14** were close to known values.[42]

The mechanism of the formation **11** and **12** includes the 1,2-elimination of lithium fluoride and/or fluorotrimethylsilane. Those steps can generate the highly reactive species with multiple phosphorus silicon bonds capable of inserting into a C−H bond of *tert*-butyl groups and gradually building the structures **11** and **12** through σ-bond formation only. One possible intermediate would be phosphasilyne **15**, which can undergo [2+2] cycloaddition in self-trapping mode to form an intermediate, **16**.

The same pattern of dimerization of a compound with a triple bond between the carbon and phosphorus to form the four-membered cyclic 1,3-diphospha-1,3-diene intermediate analogous to **16** is known.[43] The example of intramolecular C−H insertion into a silicon carbon double bond was published.[44] Alternative pathways to **12** without involvement of phosphasyline **15**, for example, may be explained by elimination of fluorotrimethylsilane and hydrogen fluoride from the dimer **17**, to yield **12**, as in Scheme 7.

We did not isolate the intermediate **15** or **17**. Both alternatives are speculative, but they would explain the formation of the isolated compounds **11** and **12**. The mechanism of the formation of compound **13** is perhaps analogous to the formation of the silane **9**, but instead of hydrogen abstraction, the methyl migration from the trimethylsilyl group took place. The migration of the methyl group from the trimethylsilyl group in polysilanes in the style of the retro-Brook rearrangement is known.[45] 1,3,5-Tri-*tert*-butylbenzene (**14*)*** was likely a product of hydrogen abstraction of an intermediate 2,4,6-tri-*tert*-butylphenyl radical in the above thermolysis process.

As has been noticed in the literature,[11,46−51] (2,4,6-tri-*tert*-butylphenyl)silane derivatives possess a unique feature: the six-membered ring of 2,4,6-tri-*tert*-butylphenyl group is bent out of the plain drastically with an additional bending of the silicon atom. Two interplanar angles (θ and θ^1) can quantify this effect (Marshall effect).

The values of interplanar angles of θ and θ^1 for compounds **3**, **7**, and **11**−**13** are compiled in Table 3.

The deviations for the phosphorus compounds **11** and **12** are far less distorted.

Synthesis and Thermal Behavior of Sterically Hindered Aminoaryldifluorosilanes 18−20. The silicon−nitrogen substrates **18**−**20** with potential 1,2-fluorotrimethylsilane elimination were prepared by the reaction of trifluorosilanes **1**−**3** and lithium or sodium bis(trimethylsilyl)amides. Despite the reaction shown

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[42] Ditto, S. R.; Card, R. J.; Davis, P. D.; Neckers, D. C. *J. Org. Chem.* **1979**, *44*, 894.

[43] Ito, S.; Sugiyama, H.; Yoshifuji, M. *Chem. Commun.* **2002**, 1744.

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[50] Miracle, G. E.; Ball, J. L.; Powell, D. R.; West, R. *J. Am. Chem. Soc.* **1993**, *115*, 11598.

[51] Klingebiel, U.; Noltemeyer, M. *Eur. J. Inorg. Chem.* **2001**, 1889.

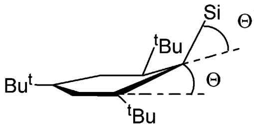


Figure 6. Outstanding features of (2,4,6-tri-*tert*-butylphenyl)silane derivatives **3**, **7**, and **11**−**13**.

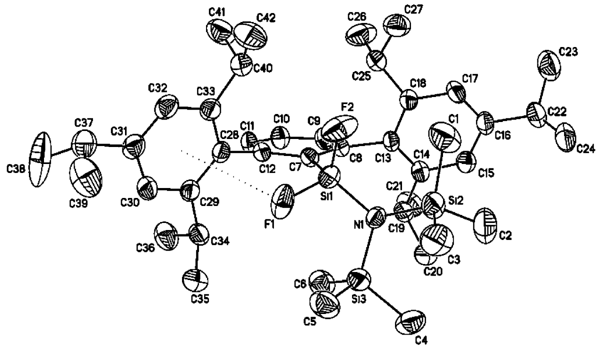


Figure 7. ORTEP drawing of bis(trimethylsilyl)aminodifluoro(2,6-bis(2,4,6-triisopropylphenyl)phenyl)silane (**18**). Thermal ellipsoids are drawn at the 50% probability level.

Table 4. ^{19}F and ^{29}Si NMR Data of 18−21

δ/J	18	19	20	21
δ ^{19}F [ppm]	−108.20	−112. 77	−107.69	−108.79
$^1J_{SiF}$ [Hz]	275.9	275.8	269.0	314.0
δ ^{29}Si [ppm]: Si(F)	−47.72	−47.91	−48.65	−39.7
SiMe$_3$	6.99	5.75	5.95	

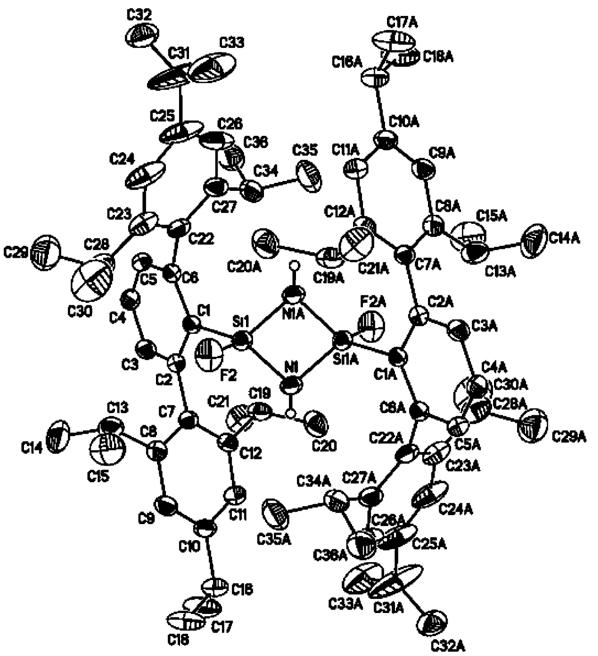
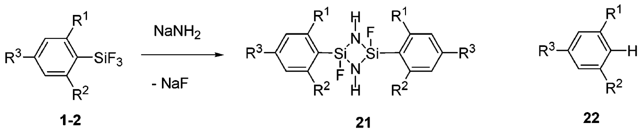


Figure 8. ORTEP drawing of 2,4-diorgano-[1,3,2,4]diazadisiletane (**21**). Thermal ellipsoids are drawn at the 50% probability level.

Scheme 9



1:R^1=R^2=2,4,6-triisopropylphenyl; R^3=H
2:R^1=R^2=2,4,6-trimethylphenyl; R^3=H

21:only for R^1=R^2=2,4,6-triisopropylphenyl; R^3=H;
22:only for R^1=R^2=2,4,6-trimethylphenyl; R^3=H;

in Scheme 1, the conventional elimination of Li/NaF took place. It appears that phosphorus in compounds **5**−**7** can accumulate the negative charge more efficiently due to its vacant d-orbitals, which are lacking in nitrogen derivatives **18**−**20**, to form the energy favorable ionic structures **5**−**7**. These can be considered as examples of Bronsted silicon heteroacids with the following fragments: (Si−N−Li);[47,51,52] (Si−P−Li) stabilized by steric bulk and/or a difluorosilane moiety. It looks like the silicon phosphides **5**−**7** are stronger Bronsted heteroacids than silicon amides **18**−**20**.

The ^{19}F and ^{29}Si NMR data of **18**−**20** shown in Table 4 are in agreement with published values for this type of compound.[47,51,52] The ORTEP drawing of **18** can be viewed in Figure 7.

The fluorine atoms in **18** and **19** exhibit a Menshutkin interaction with the *meta*-phenyl ring. For **18** the distances between the F1 and the C28−C33 carbon atoms are in the range 2.76−4.28 Å, resulting in a F−centroid distance of 3.32 Å. For **19** the distances between the F2 and the C22−C27 atoms are in the range 2.83−4.07 Å, resulting in a F−centroid distance of 3.22 Å. The sum of the van der Waals radii of the fluorine atom (1.50 Å) and the carbon atom (1.70 Å) is 3.20 Å and thus is 0.44 Å larger than the shortest distances found here.

The thermolysis experiments with **18**−**20** failed to produce any new compounds. Heating the samples of **18**−**20** in the solution of *ortho*-dichlorobenzene for 2 weeks at 170 °C did not cause any change according to ^{19}F and ^{29}Si NMR data. The compounds **18**−**20** sublimate readily in a vacuum (0.1 mm) at a temperature above 150 °C without any sign of fluorotrimethylsilane elimination.

To avoid steric overcrowding of difluorosilanes **18**−**20**, reactions of sodium amide with trifluorosilanes **1** and **2** were carried out.

As can be seen from Scheme 9, the reaction depends on the nature of the *meta*-terphenyl protective group; the sterically more hindered (2,6-bis(2,4,6-triisopropylphenyl)phenyl) derivative **1** formed compound **21** with the 1,3-diaza-2,4-disilacyclobutane fragment selectively. The reaction with the less sterically protected (2,6-bis(2,4,6-trimethylphenyl)phenyl) derivative **2** led to desilanization with the formation of 2,6-bis(2,4,6-trimethylphenyl)benzene (**22**). The ORTEP drawing of **21** is depicted in Figure 8.

The transannular nonbonding silicon−silicon distance in the ring of **21** was found to be 2.4911(13) Å, which is a typical value for such small four-membered rings containing two opposite silicon atoms. This phenomenon has been investigated by various theoretical methods.[51] The existence of a transannular σ-bond has been excluded, but the "unsupported π-bond", which lies in the plane of the ring, was used for the explanation.

The structures of products of the reaction in Scheme 9 suggest the formation of highly reactive intermediates, even though we do not have any direct evidence of those intermediates. One possible route described in Scheme 10 is as follows: the sterically more protected 2,4,6-

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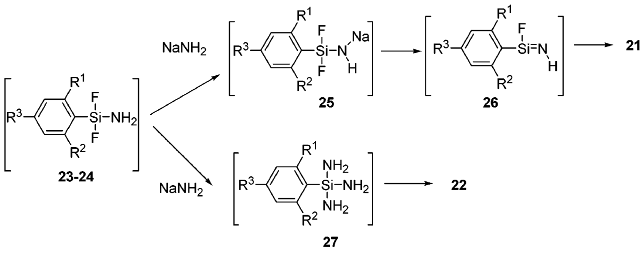
Table 5. Summary of Crystal Data, Data Collection, and Structure Refinement Parameters of 5−7 and 11

	5	**6**	**7**	**11**
empirical formula	$C_{47}H_{74}F_2LiO_2PSi_2$	$C_{70}H_{100}F_4Li_2O_4P_2Si_4$	$C_{33}H_{62}F_2LiO_3PSi_2$	$C_{18}H_{29}PSi$
fw	803.15	1269.68	638.92	304.47
cryst color, form	colorless oval	colorless plate	colorless plate	colorless plate
cryst syst	monoclinic	orthorhombic	triclinic	triclinic
space group	$I2/a$	$Pca21$	$P\bar{1}$	$P\bar{1}$
a (Å)	35.59(3)	20.973(4)	9.0800(11)	9.2635(10)
b (Å)	11.096(10)	12.496(3)	10.2208(13)	9.8504(11)
c (Å)	25.75(2)	27.890(6)	23.750(3)	11.6103(13)
α (deg)			79.227(2)	75.059(3)
β (deg)	96.492(17)		86.878(2)	78.959(3)
γ (deg)			63.756	65.244(2)
V (Å^3)	10104(15)	7309(3)	1941.0(4)	925.32(18)
Z	8	4	2	2
density (g/cm^3)	1.056	1.154	1.093	1.093
abs μ (mm^{-1})	0.14	0.18	0.17	0.20
F(000)	3488	2720	696	332
cryst size (mm)	0.30 × 0.14 × 0.13	0.50 × 0.48 × 0.08	0.25 × 0.22 × 0.05	0.06 × 0.02 × 0.01
scan mode	ω	ω	ω	ω
detector	BrukerCCD	BrukerCCD	BrukerCCD	BrukerCCD
θ_{max} (deg)	26.35	28.31	28.32	28.22
no. unique reflns	10 318	16 397	8727	3276
no. obsd reflns	507	7927	5085	1469
no. params	507	791	391	267
S^a	1.09	1.12	0.976	0.866
R indices [$I > 2\sigma(I)$]^b	R1 = 0.073 wR2 = 0.168	R1 = 0.092 wR2 = 0.202	R1 = 0.054 wR2 = 0.123	R1 = 0.065 wR2 = 0.136
R indices (all data)^b	R1 = 0.156 wR2 = 0.217	R1 = 0.199 wR2 = 0.257	R1 = 0.113 wR2 = 0.156	R1 = 0.158 wR2 = 0.169
max diff peak, hole (e/Å^3)	0.524,−0.408	2.149,−0.443	0.667,−0.469	0.391,−0.246

[a] GooF = $S = \{\sum[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$, where n is the number of reflections, and p is the total number of refined parameters. [b] R1 = $\sum||F_o| - |F_c||/\sum|F_o|$, wR2 = $\{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$ (sometimes denoted as R_w2).

Scheme 10



23, 25, 26:$R^1=R^2$=2,4,6-triisopropylphenyl; R^3=H
24,27:$R^1=R^2$=2,4,6-trimethylphenyl; R^3=H

trisopropylphenyl intermediate **23** with a monoamino difluorosilane function undergoes metalation with sodium amide to generate sodium salt **25**, which gives the imino(fluoro)silane **26** after the elimination of sodium fluoride. The dimerization of intermediate **26** in [2+2] cycloaddition in self-trapping mode leads to compound **21**.

The sterically less crowded intermediate **24** with mesityl substituents in the *meta*-terphenyl group can form triaminosilane **27**, which relieves the steric bulk by elimination of 2,4,6,2′′,4′′,6′′-hexamethyl-1,1′:3′,1′′-terphenyl **22**. Again, we have no unambiguous evidence for the identity of intermediates **23**−**27**; however they would explain the formation of isolated compounds **21** and **22**. Intramolecular condensation of lithium amide and trifluoro(2,4,6-tri-*tert*-butylphenyl)silane (**3**) has been found to form acyclic structures only.[47] The CCDC contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk). The deposition numbers are CCDC 215435−215447.

Experimental Section

The *meta*-terphenyl trifluorosilanes $Tip_2C_6H_3SiF_3$ (**1**) and $Mes_2C_6H_3SiF_3$ (**2**) (Tip = 2,4,6-triisopropylphenyl; Mes = 2,4,6-trimethylphenyl) were prepared by a known procedure.[8] The trifluoro(2,4,6-tri-*tert*-butylphenyl)silane (**3**) was synthesized accordingly to the literature.[14,15]

Bis(tetrahydrofuran)lithium [Difluoro(2,6-bis(2,4,6-triisopropylphenyl)phenyl)silanyl]trimethylsilylphosphide (5). *meta*-Terphenyl trifluorosilanes $Tip_2C_6H_3SiF_3$ (**1**, 2.0 g, 0.00353 mol), 1.27 g (0.00387 mol) of lithium bis(trimethylsilyl)phosphide bis(tetrahydrofuran) (**4**), and 40 mL of diethyl ether were stirred at room temperature for 5 days. The solvent was removed in a vacuum, and the residue was recrystallized from 20 mL of pentane at −30 °C. The yield of bis(tetrahydrofuran)lithium [difluoro(2,6-bis(2,4,6-triisopropylphenyl)phenyl)silanyl]trimethylsilylphosphide (**5**) was 2.44 g (86%) as colorless crystals with mp 121.36 °C. Anal. Calcd for $C_{47}H_{74}F_2LiO_2PSi_2$ (MW 803.17): C, 70.28; H, 9.29. Found: C, 69.92; H, 9.07. ^{1}H NMR (C_6D_6): δ 0.25 (s, 9 H, Me_3Si), 1.19 (d, $^3J_{H,H}$ = 6.7 Hz, 12 H, Me), 1.30 (d, $^3J_{H,H}$ = 6.7 Hz, 12 H, Me), 1.35 (s, br, 8 H, CH_2), 1.51 (d, $^3J_{H,H}$ = 6.7 Hz, 12 H, Me), 2.71 (m, 4 H, CH), 3.15 (m, 2 H, CH), 3.42 (s, br, 8 H, CH_2), 7.01−7.25 (m, 7 H, arom. H). ^{7}Li NMR (C_6D_6): δ 7.15 (s, br). ^{19}F NMR (C_6D_6): δ −99.7 (d, $^2J_{PF}$ = 53 Hz, $^1J_{SiF}$ = 346 Hz). ^{29}Si NMR (C_6D_6): δ −4.5 (s, br), 3.5 (s, br). ^{31}P NMR (C_6D_6): δ −309.5 (t, $^2J_{PF}$ = 53 Hz).

Bis(tetrahydrofuran)lithium[difluoro(2,6-bis(2,4,6-trimethylphenyl)phenyl)silanyl]trimethylsilylphosphide (6). *meta*-Terphenyl trifluorosilanes $Mes_2C_6H_3SiF_3$ (**2**, 2.0 g, 0.00502 mol), 1.81 g (0.00551 mol) of lithium bis(trimethylsilyl)phosphide bis(tetrahydrofuran) (**4**), and 20 mL of THF were stirred at room temperature for 4 days. The solvent was removed in a vacuum, and the residue was recrystallized from 20 mL of pentane at −30 °C. The yield of bis(tetrahydrofuran)lithium [difluoro(2,6-bis(2,4,6-trimethylphenyl)phenyl)silanyl]-

Table 6. Summary of Crystal Data, Data Collection, and Structure Refinement Parameters of 12, 18, and 21

	12	18	21
empirical formula	$C_{39}H_{65}P_2Si_3$	$C_{42}H_{67}F_2NSi_3$	$C_{42}H_{55}FNSi$
fw	680.12	708.24	620.96
cryst color, form	colorless prism	colorless block	colorless block
cryst system	orthorhombic	orthorhombic	monoclinic
space group	*Pnma*	*P*212121	*P*21/*c*
a (Å)	9.7121(14)	15.9934(9)	13.9095(17)
b (Å)	28.021(4)	23.5445(12)	15.979(2)
c (Å)	15.778(2)	11.4333(6)	17.970(2)
α (deg)			
β (deg)			109.335(2)
γ (deg)			
V ($Å^3$)	4294.0(11)	4305.3(4)	3768.8(8)
Z	4	4	4
density (g/cm3)	1.052	1.093	1.094
abs *μ* (mm^{-1})	0.21	0.15	0.09
F(000)	1484	1544	1348
cryst size (mm)	0.30 × 0.05 × 0.05	0.26 × 0.18 × 0.14	0.38 × 0.38 × 0.32
scan mode	*ω*	*ω*	*ω*
detector	BrukerCCD	Raxis II-IP	BrukerCCD
θ_{max} (deg)	28.28	24.11	28.34
no. unique reflns	5303	6620	8859
no. obsd reflns	2499	5242	5180
no. params	280	452	423
S^a	1.29	0.93	1.00
R indices [$I > 2\sigma(I)$]^b	R1 = 0.091 wR2 = 0.239	R1 = 0.042 wR2 = 0.087	R1 = 0.059 wR2 = 0.138
R indices (all data)^b	R1 = 0.191 wR2 = 0.290	R1 = 0.059 wR2 = 0.092	R1 = 0.118 wR2 = 0.171
max diff peak, hole (e/$Å^3$)	0.465,−0.390	0.228,−0.167	0.615,−0.457

[a] GooF = $S = \{\sum[w(F_o^2 - F_c^2)^2]/(n-p)\}^{1/2}$, where *n* is the number of reflections, and *p* is the total number of refined parameters. [b] R1 = $\sum||F_o| - |F_c||/\sum|F_o|$, wR2 = $\{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$ (sometimes denoted as R_w^2).

trimethylsilylphosphide (**6**) was 2.45 g (77%) as colorless crystals with mp 101.56 °C. Anal. Calcd for $C_{35}H_{50}F_2LiO_2PSi_2$ (MW 634.85): C, 66.22; H, 7.94. Found: C, 66.16; H, 7.92. ^{1}H NMR (C_6D_6): δ 0.30 (s, 9 H, Me_3Si), 1.20 (s, 6 H, Me), 1.48 (s, br, 8 H, CH_2), 1.57 (s, 12 H, Me), 3.53 (s, br, 8 H, CH_2), 7.18−7.50 (m, 7 H, arom. H). ^{7}Li NMR (C_6D_6): δ 7.21 (s, br). ^{19}F NMR (C_6D_6): δ −104.3 (d, $^2J_{PF}$ = 52 Hz, $^1J_{SiF}$ = 344 Hz). ^{29}Si NMR (C_6D_6): δ −5.7 (s, br), 3.9 (s, br). ^{31}P NMR (C_6D_6): δ −305. 0 (t, $^2J_{PF}$ = 52 Hz).

Tris(tetrahydrofuran)lithium [Difluoro(2,4,6-tri-*tert*-butylphenyl)silanyl]trimethylsilylphosphide (7). Trifluoro(2,4,6-tri-*tert*-butylphenyl)silane (**3**, 2.0 g, 0.00605 mol), 1.98 g (0.00603 mol) of lithium bis(trimethylsilyl)phosphide bis(tetrahydrofuran) (**4**), and 30 mL of THF were stirred at room temperature for 5 days. The solvent was removed in a vacuum, and the residue was recrystallized from 20 mL of pentane at −30 °C. The yield of tris(tetrahydrofuran)lithium [difluoro(2,4,6-tri-*tert*-butylphenyl)silanyl]trimethylsilylphosphide (**7**) was 2.75 g (71%) as colorless crystals with mp 118.69 °C. Anal. Calcd for $C_{33}H_{62}F_2LiO_3PSi_2$ (MW 638.93): C, 62.03; H, 9.78. Found: C, 61.89; H, 9.54. ^{1}H NMR (C_6D_6): δ 0.26 (s, 9 H, Me_3Si), 1.15 (s, 18 H, Me), 1.48 (s, br, 12 H, CH_2), 1.73 (s, 9 H, Me), 3.40 (s, br, 12 H, CH_2), 7.01 (s, 2 H, arom. H). ^{7}Li NMR (C_6D_6): δ 7.53 (s, br). ^{19}F NMR (C_6D_6): δ −95.3 (d, $^2J_{PF}$ = 30 Hz, $^1J_{SiF}$ = 343 Hz). ^{29}Si NMR (C_6D_6): δ −8.4 (s, br), 6.72 (s, br). ^{31}P NMR (C_6D_6): δ −279.8 (t, $^2J_{PF}$ = 30 Hz).

Thermolysis of 5. Formation of Difluoro(2,6-bis(2,4,6-triisopropylphenyl)phenyl)silane (9). A 0.2 g (0.000249 mol) sample of bis(tetrahydrofuran)lithium [difluoro(2,6-bis-(2,4,6-triisopropylphenyl)phenyl)silanyl]trimethylsilylphosphide (**5**) and 0.4 g of toluene-*d*$_8$ were placed into a 5 mm NMR tube and heated in an oil bath at 110 °C under nitrogen for 24 h. The formed crystals were filtered and recrystallized from toluene again to yield 0.10 g (74%) of difluoro(2,6-bis(2,4,6-triisopropylphenyl)phenyl)silane (**9**) as colorless crystals with mp 239.77 °C. Anal. Calcd for $C_{36}H_{50}F_2Si$ (MW 548.86): C, 78.78; H, 9.18. Found: C, 78.60; H, 9.17. ^{1}H NMR (C_6D_6): δ 1.08 (d, $^3J_{H,H}$ = 6.9 Hz, 6 H, Me), 1.17 (d, $^3J_{H,H}$ = 6.9 Hz, 6 H, Me), 1.27 (d, $^3J_{H,H}$ = 6.9 Hz, 12 H, Me), 1.35 (d, $^3J_{H,H}$ = 6.9 Hz, 6 H, Me), 1.45 (d, $^3J_{H,H}$ = 6.9 Hz, 6 H, Me), 2.75−3.15 (m, 6 H, CH), 7.05−7.15 (m, 7 H, arom. H). ^{19}F NMR (C_6D_6): δ −124.90 (d, $^1J_{SiF}$ = 293.6 Hz). ^{29}Si NMR (C_6D_6): δ −12.47 (t, $^1J_{SiF}$ = 293.6 Hz).

Thermolysis of 7. Formation of 2,4-Diorgano-[1,3,2,4]-diphosphadisiletane (11), 2,4-Diorgano-[1,3,2,4]diphosphadisiletane (12), Difluoromethyl(2,4,6-tri-*tert*-butylphenyl)silane (13), and 1,3,5-Tri-*tert*-butylbenzene (14). A 0.2 g (0.000313 mol) sample of tris(tetrahydrofuran)lithium [di-fluoro-(2,4,6-tri-*tert*-butylphenyl)silanyl]trimethylsilylphosphide (**7**) and 0.4 g of toluene-*d*$_8$ were placed into a 5 mm NMR tube and heated in an oil bath at 110 °C under nitrogen for 3 h. The thermolysis has been carried out two times to obtain sufficient quantities of the reaction products for complete characterization. The crystals of **12** were precipitated upon cooling the thermolysis mixture to ambient temperature. The yield of 2,4-diorgano-[1,3,2,4]diphosphadisiletane (**11**) was 0.018 g (19%) as a few colorless crystals with mp 295.08 °C. Anal. Calcd for $C_{36}H_{58}P_2Si_2$ (MW 608.96): C, 71.00; H, 9.60; P, 10.17. Found: C, 70.93; H, 9.62; P, 10.09. ^{1}H NMR (C_6D_6): δ 0.89 (m, br, 4 H, CH_2−Si), 1.30 (s, br, 36 H, Me), 1.39 (s, br, 18 H, Me), 7.05−7.15 (m, 4 H, arom. H). ^{31}P NMR (C_6D_6): δ −158.48 (d, $^1J_{PH}$ = 169.5 Hz). The X-ray analysis was carried out. An ORTEP drawing of **11** is shown in Figure 4. The solvent from the above crystallization mixture was removed in a vacuum. The residue was redissolved in 40 mL of pentane. The 2,4-diorgano-[1,3,2,4]diphosphadisiletane (**12**) was precipitated from this solution at room temperature. The yield of 2,4-diorgano-[1,3,2,4]diphosphadisiletane (**12**) was 0.012 g (11%) as a few colorless crystals with mp 147.98 °C. Anal. Calcd for $C_{39}H_{66}P_2Si_3$ (MW 681.15): C, 68.77; H, 9.77; P, 9.09. Found: C, 68.65; H, 9.71; P, 8.87. ^{1}H NMR (C_6D_6): δ 0.10 (s, 9 H, Me_3Si), 0.80 (m, br, 4 H, CH_2−Si), 1.15 (s, br, 36 H, Me), 1.60 (s, br, 18 H, Me), 6.95−7.35 (m, 4 H, arom. H). ^{31}P NMR (C_6D_6): δ −158.54 (d,d $^1J_{PH}$ = 164.0 Hz, $^2J_{PP}$ = 34.0 Hz), −176.69 (d, $^2J_{PP}$ = 34.0 Hz). The X-ray analysis was carried out. An ORTEP drawing of **12** is shown in Figure 5. Difluoromethyl(2,4,6-tri-*tert*-butylphenyl)silane (**13**) was crystallized from the above pentane solution at −30 °C. The yield of **13** was 0.0072 g (7%) as a few colorless crystals with mp 134.03 °C. Anal. Calcd for $C_{19}H_{32}F_2Si$ (MW 326.54): C, 69.89; H, 9.88. Found: C, 69.70; H, 9.87. ^1H NMR (C_6D_6): δ 0.40 (t, $^3J_{F,H}$ = 4.2 Hz, 3 H, MeSi), 1.46 (s, 27 H, Me), 7.35 (s, 2 H, arom. H). ^{29}Si NMR (C_6D_6): δ −13.48 (t, $^1J_{SiF}$ 283.4 Hz). The X-ray analysis was carried out. Further concentration of the mother liquor from the previous steps produced 1,3,5-tri-*tert*-butylbenzene (**14**). Compound **14** was purified additionally by sublimation at 100 °C and 1 mm vacuum. The yield of **14** was 0.00463 g (6%) as white crystals with mp 71.08 °C. ^1H NMR (C_6D_6): δ 1.40 (s, 27 H, Me), 7.34 (s, 2 H, arom. H).

Bis(trimethylsilyl)aminodifluoro(2,6-bis(2,4,6-triisopropylphenyl)phenyl)silane (18). A 2.0 g (0.00353 mol) sample of *meta*-terphenyl trifluorosilane $Tip_2C_6H_3SiF_3$ (**1***)*, 0.71 g (0.00387 mol) of sodium bis(trimethylsilyl)amide, and 40 mL of benzene were stirred at room temperature for 5 days. The solvent was removed in a vacuum, and the residue was recrystallized from 20 mL of pentane at −30 °C. The yield of bis(trimethylsilyl)aminodifluoro(2,6-bis(2,4,6-triisopropylphenyl)phenyl)silane (**18**) was 2.20 g (88%) as colorless crystals with mp 204.67 °C. Anal. Calcd for $C_{42}H_{67}F_2NSi_3$ (MW 708.24): C, 71.23; H, 9.54. Found: C, 71.20; H, 9.53. ^1H NMR (C_6D_6): δ 0.05 (s, 18 H, Me_3Si), 1.19 (d, $^3J_{H,H}$ = 6.7 Hz, 12 H, Me), 1.30 (d, $^3J_{H,H}$ = 6.7 Hz, 12 H, Me), 1.51 (d, $^3J_{H,H}$ = 6.7 Hz, 12 H, Me), 2.71 (m, 4 H, CH), 3.15 (m, 2 H, CH), 6.60−7.40 (m, 7 H, arom. H). ^{19}F NMR (C_6D_6): δ −108.20 ($^1J_{SiF}$ = 275.9 Hz). ^{29}Si NMR (C_6D_6): δ −47.72 (s, br), 6.99 (s, br).

Bis(trimethylsilyl)aminodifluoro(2,6-bis(2,4,6-trimethylphenyl)phenyl)silane (19). A 1.0 g (0.00251 mol) sample of *meta*-terphenyl trifluorosilane $Mes_2C_6H_3SiF_3$ (**2**), 0.55 g (0.00329 mol) of lithium bis(trimethylsilyl)amide, and 20 mL of benzene were stirred at room temperature for 5 days. The solvent was removed in a vacuum, and the residue was recrystallized from 20 mL of pentane at −30 °C. The yield of bis(trimethylsilyl)aminodifluoro(2,6-bis(2,4,6-trimethylphenyl)phenyl)silane (**19**) was 0.99 g (73%) as colorless crystals with mp 134.34 °C. Anal. Calcd for $C_{30}H_{43}F_2NSi_3$ (MW 539.92): C, 66.74; H, 8.03. Found: C, 66.54; H, 8.02. ^1H NMR (C_6D_6): δ 0.23 (s, br, 18 H, Me_3Si), 2.33 (s, br, 18 H, Me), 6.95−7.41 (m, 7 H, arom. H). ^{19}F NMR (C_6D_6): δ −112.77 ($^1J_{SiF}$ 274.8 Hz). ^{29}Si NMR (C_6D_6): δ −47.91 (s, br), 5.75 (s, br).

Bis(trimethylsilyl)aminodifluoro(2,4,6-tri-*tert*-butylphenyl)silane (20). A 2.0 g (0.00605 mol) sample of trifluoro-(2,4,6-tri-*tert*-butylphenyl)silane (**3**), 1.21 g (0.00726 mol) of lithium bis(trimethylsilyl)amide, and 20 mL of THF were stirred at room temperature for 3 days. The solvent was removed in a vacuum, and the residue was recrystallized from 20 mL of pentane at −30 °C. The yield of bis(trimethylsilyl)aminodifluoro(2,4,6-tri-*tert*-butylphenyl)silane (**20**) was 2.23 g (78%) as colorless crystals with mp 94.47 °C. Anal. Calcd for $C_{24}H_{47}F_2NSi_3$ (MW 471.89): C, 61.09; H, 10.04. Found: C, 61.04; H, 10.04. ^1H NMR (C_6D_6): δ 0.10 (s, br, 18 H, Me_3Si), 1.30 (s, br, 9 H, Me), 1.45 (s, br, 18 H, Me), 7.44 (s, 2 H, arom. H). ^{19}F NMR (C_6D_6): δ −107.69 ($^1J_{SiF}$ 269.0 Hz). ^{29}Si NMR (C_6D_6): δ −48.65 (s, br), 5.95 (s, br).

2,4-Diorgano-[1,3,2,4]diazadisiletane (21). A 0.5 g (0.00088 mol) sample of *meta*-terphenyl trifluorosilane $Tip_2C_6H_3SiF_3$ (**1**), 0.11 g (0.00282 mol) of sodium amide, and 10 mL of benzene were stirred at room temperature for 7 days. The solvent was removed in a vacuum, and the residue was recrystallized from 20 mL of pentane at −30 °C. The yield of 2,4-diorgano-[1,3,2,4]-diazadisiletane (**21**) was 0.30 g (63%) as colorless crystals with mp 261.89 °C. Anal. Calcd for $C_{72}H_{100}F_2N_2Si_2$ (MW 1087.75): C, 79.50; H, 9.27; N, 2.58. Found: C, 79.15; H, 9.55; N, 2.64. ^1H NMR (C_6D_6): δ 0.95 (d, $^3J_{H,H}$ = 6.7 Hz, 12 H, Me), 1.25 (d, $^3J_{H,H}$ = 6.7 Hz, 12 H, Me), 1.43 (d, $^3J_{H,H}$ = 6.7 Hz, 12 H, Me), 2.85 (m, 4 H, CH), 3.10 (m, 2 H, CH), 6.90 −7.20 (m, 7 H, arom. H). ^{19}F NMR (C_6D_6): δ −108.79 ($^1J_{SiF}$ 314.09 Hz). ^{29}Si NMR (C_6D_6): δ −39.7 (s, br).

2,4,6,2″,4″,6″-Hexamethyl-1,1′:3′,1″-terphenyl (22). A 1.0 g (0.00251 mol) sample of *meta*-terphenyl trifluorosilane $Mes_2C_6H_3SiF_3$ (**2**), 0.33 g (0.00846 mol) of sodium amide, and 20 mL of benzene were stirred at room temperature for 7 days. The solvent was removed in a vacuum, and the residue was recrystallized from 20 mL of pentane at −30 °C. The yield of 2,4,6,2″,4″,6″-hexamethyl-1,1′:3′,1″-terphenyl (**22**) was 0.57 g (72%) as colorless crystals with mp 226.09 °C. Anal. Calcd for $C_{24}H_{46}$ (MW 314.46): C, 91.67; H, 8.33. Found: C, 91.30; H, 8.34. ^1H NMR (C_6D_6): δ 2.02 (s, 12 H, Me), 2.11 (s, 6 H, Me), 6.76 (s, 1 H, arom. H), 6.84 (s, 4 H, arom. H), 7.00 (d, $^3J_{H,H}$ = 7.8 Hz, 2 H, arom. H), 7.25 (t, $^3J_{H,H}$ = 7.8 Hz, 1 H, arom. H).

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Supporting Information Available: Structure refinement statistics and tables of atomic coordinates, bond lengths, bond angles, and anisotropic displacement parameters of compounds **5**−**9**, **11**−**14**, and **18**−**22**. This material is available free of charge via the Internet at http://pubs.acs.org.

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