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Synthesis and Solid State Structures of Sterically Congested Sodium and Cesium Silyl(fluorosilyl)phosphanide Aggregates and Structural Characterization of the Trimeric Sodium Bis(trimethylsilyl)amide

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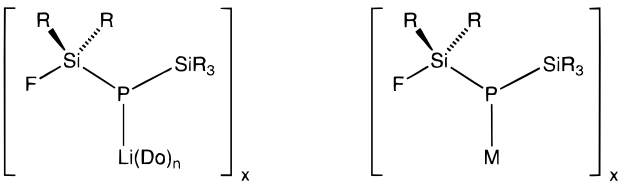
Metalation of the silyl(fluorosilyl)phosphane $\mathrm{Is_2(F)Si{-}PH(SiR_3)}$ (**3a**; Is = 2,4,6-triisopropylphenyl, $\mathrm{R_3Si = Me_2(Pr^{\mathit{i}}Me_2C)Si}$) at phosphorus with $\mathrm{NaN(SiMe_3)_2}$ (**4**) in the molar ratio of 1:1 in toluene leads to the solvent-free sodium derivative **1a** which forms a $\mathrm{Na_2P_2}$-dimer in solution and in the solid state. The coordinatively unsaturated Na centers are each additionally bonded to a fluorine atom, so that a ladder-like, puckered tricyclic $\mathrm{F_2Na_2P_2Si_2}$ skeleton results as the central structural motif. The same conversion of **3a** into **1a** under less polar reaction conditions (hexane) and the complete conversion of the silyl(fluorosilyl)phosphane $\mathrm{Is_2(F)Si{-}PH(SiPr^{\mathit{i}}_3)}$ (**3b**) into its Na derivative **1b** is kinetically hampered and can only be achieved if 2 equiv of sodium amide **4** are employed. Excess **4** may be recovered by fractional crystallization, from which its molecular $\mathrm{Na_3N_3}$-trimer was isolated and structurally characterized for the first time. The unusual molecular polymeric cesium phosphanide $\mathrm{[Is_2(F)Si{-}PCs(SiPr^{\mathit{i}}_3)\cdot 0.5THF]}$ (**2**) was prepared by the metalation of **3a** with elemental cesium in toluene in the presence of little THF. The structure of **2** was determined by X-ray diffraction.

Introduction

Sterically hindered lithium silyl(fluorosilyl)phosphanides **A** are valuable synthetic starting materials in light of transmetalation reactions, i.e., the synthesis of kinetically stable diphosphanyl-substituted stannandiyle, germandiyle, and plumbandiyle derivatives,[1] and for the preparation of kinetically stable compounds having a Si═P bond (silylidenephosphanes, "phosphasilenes"). The latter compounds have been formed by thermolysis and LiF elimination, starting from lithium (fluorosilyl)silylphosphanides.[2] However, their synthetic access is strongly dependent on several factors such as the size of the organic groups at silicon, the polarity of the solvent, and the Lewis acidity of the lithium centers. The parameters which influence the aggregation state in solution are well understood. Whereas solid state structures of the lithium phosphanides **A**, which display a remarkable progression of structures dependent on steric and electronic features, are well established,[3] only little structural information is known concerning the respective heavier alkali metal phosphanides **B**, Chart 1.[4] In this paper we report on the syntheses and molecular structures of the new donor solvent-free/solvent-poor sodium and cesium silyl(fluorosilyl)phosphanide clusters **1** and **2**, respectively. In connection with that, $\mathrm{NaN(SiMe_3)_2}$ (**4**), which has been used for the synthesis of **1**, has been structurally characterized, for the first time, which forms a cyclic trimer, in contrast to a previous study that revealed that **4** exists as polymeric chains of $[\mathbf{4}]_n$ units.[5]

Chart 1



A: R = 2,4,6-Triisopropylphenyl, *t* Bu
Do = Donor Molecule
x = Grade of Assoziation

B: M = Na, K, Rb, Cs
x = Grade of Assoziation

Results and Discussion

4 is an excellent sodation reagent toward secondary phosphanes which even deprotonates the phosphorus atom in relatively nonpolar solvents, leading to donor

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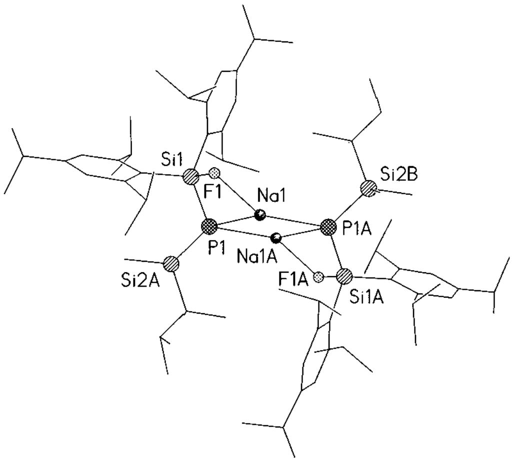
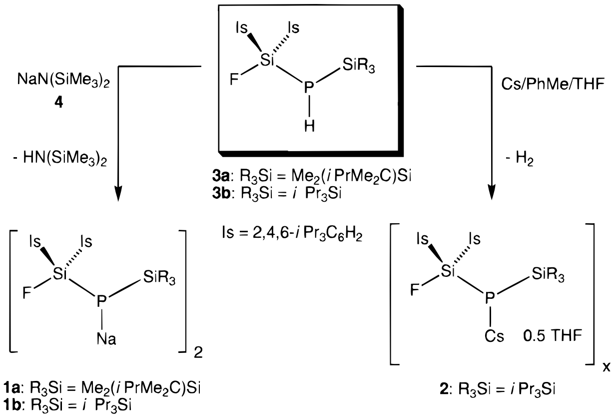


Figure 1. Molecular structure of **1a**. H atoms are omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 1a

Na1−P1	2.960 (4)	P1−Si1	2.175 (3)
Na1A−P1	2.831 (4)	P1−Si2A	2.104 (4)
Na1−F1	2.262 (5)	Si1−F1	1.673 (3)
P1−Na1−P1A	105.45 (11)	Na1−P1−Na1A	74.55 (11)
F1−Na1−P1A	141.78 (13)	Si1−P1−Na1A	125.03 (10)
F1−Na1−P1	69.11 (12)	Si1−P1−Si2A	117.20 (14)
Na1−F1−Si1	110.1 (2)	F1−Si1−P1	102.5 (2)

solvent-free sodium phosphanides. Thus, if **3a** is allowed to react with **4** in the molar ratio of 1:1 in toluene at room temperature, eq 1, the reaction progress can be easily monitored by means of ^{31}P and ^{19}F NMR spectroscopy. After 12 h, the NMR spectra reveal that **3a** ($\delta(^{31}P) = -213.7$ (d, $^{1}J(P, H) = 190$ Hz); $\delta(^{19}F) = -127.1$ (s)) has been completely converted into the desired sodium phosphanide **1a** ($\delta(^{31}P) = -269.8$ (s, $h_{1/2} = 140$ Hz); $\delta(^{19}F) = -112.1$ (s, $h_{1/2} = 212$ Hz). **1a** is aggregated in solution which is supported by the considerable line width of the ^{31}P and ^{19}F resonance signals. Consistently, cryoscopic measurements in benzene (concentration range c = 0.01−0.09 M) prove that the degree of association amounts to $n \approx 2$. This aggregation is retained in the solid state, which has been elaborated by a single-crystal structure determination. Its molecular model is shown in Figure 1, and selected geometrical parameters are summarized in Table 1.



1a is an ionic compound which possesses $P\bar{1}$-symmetry, so that a rhomboidally distorted planar Na_2P_2 ring is imposed. The coordinatively unsaturated Na centers are, however, each additionally bonded to F atoms, so that a ladder-like, puckered tricyclic $F_2Na_2P_2Si_2$ skeleton results as the central structural motif. Furthermore, the Na centers possess close contacts with H atoms of nearby methyl groups. The structure of **1a** essentially resembles the structural features of the related THF-solvated phosphanides [$Bu^t_2Si(F)-P(Mes)M(THF)_2$] (M = Na, K; Mes = 2,4,6-trimethylphenyl) which have been reported previously.[4] However, the latter are dimers having a $F_2M_2P_2Si_2$ eight-membered ring. Apparently, the presence of two THF molecules precludes the formation of two Na−P bonds in [$Bu^t_2Si(F)-P(Mes)Na(THF)_2]_2$, that is, a ladder-like tricyclic $F_2Na_2P_2Si_2$ skeleton as in **1a** is unfavorable. The two distinctly different Na−P distances of 2.831(4) and 2.960(4) Å indicate that a regular coordination of the Na centers is hampered by steric reasons. The Na−P distances are practically identical with those values observed for other sodium phosphanides.[4,6] The Na−F distance of 2.262(5) Å is significantly shorter than that value in [$Bu^t_2Si(F)-P(Mes)Na(THF)_2]_2$ (2.383(2) Å)[4] but, as expected, shorter than that in solid NaF (2.307 Å) and longer than that for NaF vapor (1.926 Å).[7] The coordination of the sodium atoms to fluorine implies a Si−F bonding activation. This is supported by the relatively long Si−F distance of 1.673(3) Å, which is 0.06 Å longer than those observed for similar phosphanides without intra- and/or intermolecular metal−fluorine bonds.[8] Interestingly, the stronger polarity of the Si−P bond in **1a** also results in a relatively short Si−P distance of 2.175(3) Å, which is about 0.1 Å shorter than those in nonmetalated derivatives[9] but slightly longer than in [$Bu^t_2Si(F)-P(Mes)Na(THF)_2]_2$ (2.163(1) Å).[4] The Na1−Na1′ distance is 3.509(5) Å, that is no attractive interaction occurs between these centers. Despite the fact that the Na centers are already coordinated to F atoms, the NaF elimination tendency of **1a** is surprisingly low. The latter occurs only above 130 °C, so that the corresponding silylidenephosphane cannot be isolated under such drastic reaction conditions.[2] The thermal stability of **1a** is probably due to the high Lewis acidity of the coordinatively unsaturated Na center, which prevents the separation and agglomeration of NaF. Addition of only small amounts of THF to a solution of **1a** in toluene drastically accelerates the rate of NaF elimination, so that elimination already occurs at 70 °C and the respective silylidenephosphane can be isolated (^{31}P and ^{29}Si NMR spectroscopy).[10]

The metalation of phosphanes is a relative complex matter. It is by necessity accompanied by association equilibrium reactions of the base with the phosphane and is strongly dependent on solvent polarity. The

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(10) The NMR spectroscopic data of the Si═P compounds are identical with those previously reported in ref 2a.

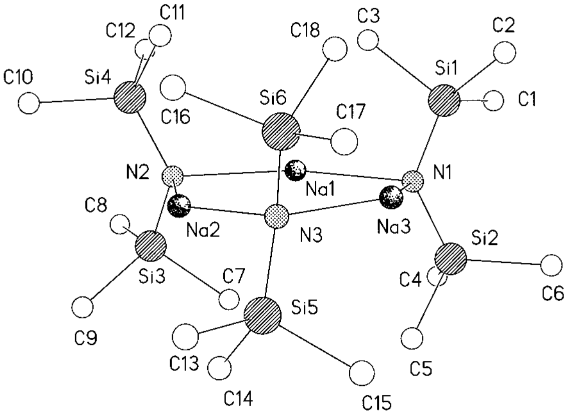

Figure 2. Solid state structure of trimeric **4**. H atoms are omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 4

Na1−N1	2.377 (2)	N1−Si1	1.702 (2)
Na1−N2	2.386 (2)	N1−Si2	1.696 (2)
Na2−N2	2.404 (2)	N2−Si3	1.698 (2)
Na2−N3	2.364 (2)	N2−Si4	1.697 (2)
Na3−N3	2.371 (2)	N3−Si5	1.700 (2)
Na3−N1	2.385 (2)	N3−Si6	1.699 (2)
Na1−N1−Na3	100.01 (7)	N1−Na1−N2	142.77 (7)
Na1−N2−Na2	97.39 (7)	N2−Na2−N3	139.48 (7)
Na2−N3−Na3	102.81 (7)	N3−Na3−N1	136.85 (7)

Table 3. Selected Close Na−C and Na−H Distances (Å) in 4

Na1−C3	2.86	Na1−H3c	2.52
Na1−C7	2.94	Na1−H7c	2.51
Na2−C14	2.96	Na2−H14a	2.56
Na2−C11	3.21	Na2−H11c	2.64
Na3−C5	3.19	Na3−H5c	2.67
Na3−C18	2.99	N3−H18a	2.63

Table 4. Comparison of Selected Distances (Å) and Angles (deg) for the Trimeric and Polymeric Forms of 4

	[**4**]$_3$	[**4**]$_\infty$
Na−N	2.381	2.350
N−Si	1.699	1.690
Si−C	1.882	1.870
N−Na−N	139.7	150.2
Na−N−Na	100.1	102.0
Si−N−Si	125.3	125.6

latter is impressively demonstrated by the reaction of **3a** with **4** in hexane: in this medium, **3a** can only be completly converted to **1a** at room temperature if 2 molar equiv of $NaN(SiMe_3)_2$ (**4**) have been employed. We believe that this is due to the relatively small dissociation rates and lower basisity of **4** in hexane and, thus, the higher kinetic stability of heteroaggregate intermediates which are formed during the reaction, although the phosphane shape also seems to have a considerable influence on the metalation rate. Thus, **3b** ($\delta(^{31}P) = -235.1$ (d, $^1J(P,H) = 198$ Hz); $\delta(^{19}F) = -123.9$ (s)) reacts with **4** in toluene in the molar ratio of 1:1 at room temperature after 2 days with only 50% conversion to the desired phosphanide **1b** ($\delta(^{31}P) = -294.3$ (s, $h_{1/2} =$ 167 Hz); $\delta(^{19}F) = -114.6$ (s, $h_{1/2} = 222$ Hz)). The complete conversion of **3b** into **1b** has been achieved with 2 molar equiv of **4**. The 1 mol excess of **4**, however, may be recovered after the reaction (see below). This ratio implies that aggregation processes occur with incorporation of two molecules **4**. The initial aggregation of **3b** with two molecules of **4** seems likely since **4** is dimeric in solution.[5] However, no structural information on such possible intermediates could be deduced from the temperature-dependent ^{31}P and ^{19}F NMR spectra of mixtures. The temperature dependence of the NMR spectra is probably due to exchange processes and line-broadening by ^{23}Na ions ($I = {}^3/_2$). As already mentioned, the 1 mol excess of **4** can be recovered by fractional crystallization in toluene. A single-crystal X-ray diffraction analysis revealed that **4** forms a trimer. Until now it has been believed that **4** consists of polymeric chains in the solid state.[5] The present result shows that **4** may exist in another modification comparable with the trimeric structure of the lithium homologue.[11] The trimer consists of an almost planar Na_3N_3 six-membered ring with maximal deviations of 0.08 Å from the best plane, as shown in Figure 2. Selected geometrical parameters are given in Table 2.

The average N−Na−N, Na−N−Na, and Si−N−Si angles are 139.7°, 100.1°, and 125.3°, respectively. The Na−N distances are slightly different (2.364−2.404(2) Å, average 2.381(2) Å), whereas the Si−N distances are equal (average value 1.698 Å). Each Na center shows C−H coordination to two methyl groups nearby which, however, originate from different $N(SiMe_3)_2$ groups. The respective Na−C and Na−H distances are presented in Table 3. Additionally, the trimeric units are associated via two comparatively short intermolecular Na−H distances of around 2.61 Å per molecule.

The geometrical parameters of the trimeric and polymeric form, as shown in Table 4, are in agreement with the exception of the endocyclic angles N−Na−N (139.7° vs 150.2°) and the Na−N distances (2.381 vs 2.355 Å). Apparently, the geometrical changes at the sodium center are, in comparison with the strong distorted tetrahedral coordination at nitrogen, energetically favored.

In order to learn about the influence of cesium on the molecular structure and the metal−fluoride elimination rate of silyl(fluorosilyl)phosphanides, we synthesized the cesium salt **2**, starting from **3b** and elemental cesium. However, elemental cesium only reacts with **3b** in toluene at room temperature if a small amount of THF is present. Apparently, the metalation seems to be kinetically inhibited without THF and leads to P−Si bond cleavage at elevated reaction temperatures ($T >$ 40 °C) in toluene solution. The metalation has been monitored by means of ^{31}P NMR spectroscopy. After 14 h, the reaction mixture shows only one high-field signal at $\delta = -325$. The Cs salt **2** has been isolated in the form of pale-yellow crystals which are very soluble even in aliphatic hydrocarbons. Its ^1H NMR spectrum shows that the compound is a THF-solvated phosphanide with the ratio of THF to disilylphosphanide units of 1:2. Yellow plates, which were suitable for a single-crystal X-ray diffraction analysis, have been grown from concentrated hexane solutions. The molecular architecture of this unusual coordination polymer is shown in Figure 3, and selected geometrical parameters are given in Table 5.

The Si_2P−phosphanide units compose a chain polymer which incorporates two differently coordinated Cs

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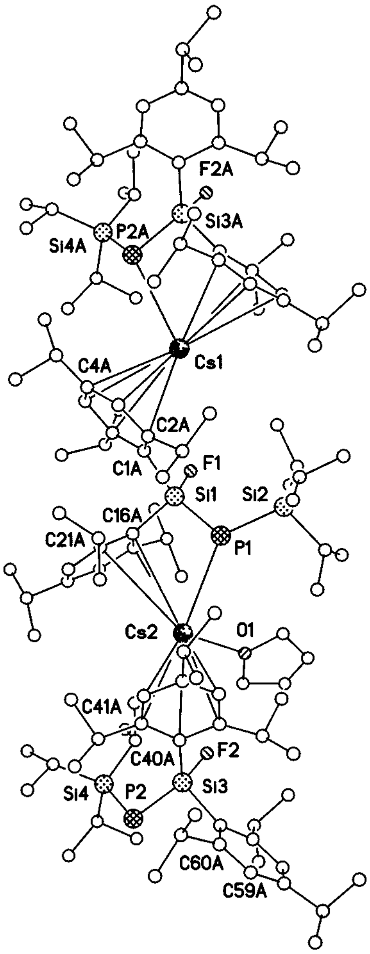

Figure 3. Molecular unit of polymeric **2** in the solid state. H atoms are omitted for clarity.

Table 5. Selected Bond Lengths (Å) and Angles (deg) for 2

Cs1−P2A	3.517 (6)	Cs1−C1A	3.51 (2)
Cs2−P1	3.536 (7)	Cs1−C2A	3.48 (2)
Cs2−O1	3.288 (14)	Cs1−C4A	3.52 (2)
Cs2−C16A	3.66 (2)	Cs1−C59B	3.893 (14)
Cs2−C21A	3.89 (2)	Cs1−C60B	3.59 (2)
Cs2−C43A	3.76 (2)	Cs2−C40A	3.66 (2)
P1−Si1	2.136 (7)	P2A−Si3A	2.149 (7)
P1−Si2	2.227 (8)	P2A−Si4A	2.222 (7)
Si1−F1	1.624 (9)	Si3A−F2A	1.647 (9)
Si1−P1−Si2	111.6 (3)	Si1−P1−Cs2	100.4 (2)
P1−Si1−F1	114.0 (4)	Si2−P1−Cs2	132.1 (2)
Si3A−P2A−Si4A	110.3 (3)	Si3A−P2A−Cs1	97.3 (2)
P2A−Si3A−F2A	115.3 (4)	Si4A−P2A−Cs1	136.2(2)

centers (Cs1 and Cs2). Each Cs center is connected to one P atom and bonded by two aryl groups of different Is$_2$Si(F) functions. The Cs2 center is further coordinated by one THF molecule. It appears that the Cs1 center is doubly η^6-coordinated to its two aryl ligands, whereby the aryl groups originate from two different Si$_2$P−phosphanide units. On the other side, the Cs2 center shows two different coordination modes (η^3 and η^6) toward its aryl ligands. The centroid distances between the aryl rings and the respective η^6-coordinated Cs ions are 3.19 (C1−C6) and 3.41 Å (C55−C60) for Cs1 and 3.40 Å (C40−C45) for Cs2, that is, they resemble those values observed for other π-arene solvates.[12] However, if the arene ring is part of a π-carbanion, the centroid distance between the η^6-coordinated Cs ion and the arene ligand can be slightly smaller.[13] Apparently, the coordination of THF at the Cs2 center results in much weaker Cs2−C(aryl) interactions which are reflected by longer Cs−C distances, as summarized in Table 5. The Cs−P distances are identical with those values observed for related Cs phosphides.[14] The reluctance of the Cs cations and F centers to form a Cs−F bond is apparently imposed by steric restrictions and their different hardness. Interestingly, the relatively low Cs−F affinity drastically enhances the thermal stability of both salts. Hence, **2** does not eliminate CsF even at 130 °C in toluene, nor does addition of THF initiate CsF elimination. This underlines that Si−F activation and a relatively high M−F lattice energy are prerequisites for M−F elimination and successful synthesis of Si═P compounds from silyl(fluorosilyl)phosphanides.

Experimental Section

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 sodium amide **4** was purcheased from Aldrich. The starting compounds Is$_2$Si(F)PH(SiR$_3$) (**3a**) and (**3b**) were prepared as previously described.[2]

Physical Measurements. ^{1}H NMR (200 MHz), ^{31}P NMR (81 MHz), and ^{19}F NMR (89 MHz) measurements were recorded on a Jeol-FX90Q and/or a Bruker AC200 spectrometer. Chemical shifts (δ) are given relative to external standards (^{1}H to SiMe$_4$; ^{31}P to 85% H$_3$PO$_4$ (aq); ^{19}F to CFCl$_3$). All isolated compounds gave C, H analyses consistent with their formulas.

General Procedures. Synthesis of *P*-Sodium (Fluorobis(2,4,6-triisopropylphenyl)silyl)(thexyldimethylsilyl)phosphanide (1a). A solution of 4.15 g (6.6 mmol) of **3a** in 50 mL of toluene was treated with 1.21 g (6.6 mmol) of **4** at −70 °C. After 1 h of stirring, the solution was allowed to warm to room temperature and was stirred for 6 h. The solvent was evaporated in vacuum (10^{-2} Torr), and the residue was dissolved in 20 mL of hexane. The cloudy solution was filtered through a GIV frit, and the clear filtrate was concentrated to 5 mL and stored at 4 °C, affording the desired product in the form of pale yellow crystals. Yield: 4.03 g (6.2 mmol, 94%). Mp 149−152 °C (dec). ^{1}H NMR (C$_6$D$_6$, 300 K): δ 0.62 (br, 6 H, Si*Me*$_2$), 0.90 (d, ^3J(H,H) = 6.8 Hz, 6 H, SiCCH*Me*$_2$), 0.99 (br, 6 H, SiC*Me*$_2$), 1.21 (br, 24 H, *o*-CH*Me*$_2$), 1.83 (sept, ^3J(H,H) = 6.8 Hz, 1 H, SiCC*H*Me$_2$), 2.78 (br. m, 2 H, *p*-C*H*Me$_2$), 4.01 (br, 4 H, *o*-C*H*Me$_2$), 7.12 (s, 4 H, aromatic H). ^{31}P NMR (C$_6$D$_6$, 300 K): δ −269.8 (s, $h_{1/2}$ = 140 Hz). ^{19}F NMR (C$_6$D$_6$, 300 K): δ −112.1 (s, $h_{1/2}$ = 212 Hz). Anal. Calcd for $C_{38}H_{65}FNaPSi_2$: C, 70.10; H, 10.06. Found: C, 69.48; H, 10.00.

Reaction of 3a with 2 Equiv of Sodium amide (4) in Hexane; Isolation of the Trimeric Form of 4. In a similar procedure as that for the synthesis of **1a**, 3.81 g (6.0 mmol) of **3a** was treated with 2 molar equiv of **4** (2.2 g, 12.0 mmol) in 40 mL of hexane at room temperature. After complete conversion of **3a** into **1a** (16 h, ^{31}P NMR), the cloudy solution was filtered and the filtrate was concentrated to 10 mL. Fractional crystallization at 4 °C afforded almost 1 mol excess of **4** as a trimeric modification (0.89 g, 5.3 mmol) in the form

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Table 6. Crystal Data and Structure Refinement for 1a, 2, and 4

	1a	**2**	**4**
formula	$C_{38}H_{65}FNaPSi_2$	$C_{82}H_{142}Cs_2F_2OP_2Si_4$	$C_{18}H_{54}N_3Na_3Si_6$
fw	651.04	1622.08	550.15
temperature (K)	203(2)	203(2)	203(2)
cryst syst	triclinic	monoclinic	triclinic
space group	$P\bar{1}$	$C2/c$	$P\bar{1}$
cell dimens			
a (Å)	10.607(9)	39.18(5)	8.819(4)
b (Å)	14.56(2)	18.35(3)	12.544(7)
c (Å)	14.786(14)	25.00(4)	16.901(9)
α (deg)	115.77(7)	90	102.07(4)
β (deg)	90.34(7)	97.02(8)	94.65(4)
γ (deg)	101.51(8)	90	105.79(4)
volume ($Å^3$)	2004(3)	17839(47)	1740(2)
Z	2	8	12
calcd density ($g\ cm^{-3}$)	1.079	1.208	1.050
F(000)	712	6848	600
cryst size (mm)	0.6 × 0.25 × 0.15	0.6 × 0.5 × 0.3	0.5 × 0.4 × 0.2
θ_{max} (deg)	25.12	20.00	29.00
hkl-range	−12/12, −17/15, 0/17	−37/37, 0/17, 0/24	−12/11, −17/16, 0/23
no. of reflns colld	7091	8327	9231
no. of indep reflns	7091	8327	9231
abs coeff (mm^{-1})	0.167	0.950	0.288
parameters	460	510	291
goodness-of-fit on F^2	1.022	1.011	1.052
R1 [$I > 2\sigma(I)$]	0.077	0.075	0.040
wR2 (all data)	0.251	0.194	0.108
resid electron density (e $Å^{-3}$)	0.766/−0.634	0.551/−0.634	0.299/−0.192

of colorless large cubes, and further crystallization finally yielded pale yellow **1a**.

Synthesis of *P*-Sodium (fluoro*bis*(-2,4,6-triisoropyl-phenyl)silyl)(triisopropylsilyl)phosphanide (1b). A solution of 7.06 g (11.0 mmol) of **3b** in 50 mL of toluene was treated with 4.03 g (22.0 mmol) of **4** at −70 °C. After 1 h of stirring, the solution was allowed to warm to room temperature and stirred for 16 h. The solvent was evaporated in vacuum (10^{-2} Torr), and the residue dissolved in 20 mL of hexane. The cloudy solution was filtered through a GIV frit, and the orange filtrate was concentrated to 10 mL and stored at 4 °C, affording firstly the one molar excess of **4** (trimeric!) in the form of colorless cubes and finally the desired product in the form of a yellow powder. Yield: 7.21 g (10.48 mmol, 95%). Mp 131−138 °C (dec). ^1H NMR (C_6D_6, 300 K): δ 1.24 (br, 12 H, *p*-CH*Me*$_2$), 1.33 (d, *J*(H,H) = 7.0 Hz, 18 H, SiCH*Me*$_2$), 1.36 (d, *J*(H,H) = 6.8 Hz, 24 H, *o*-CH*Me*$_2$), 2.41 (br. m, 2 H, *p*-*CH*Me$_2$), 4.16 (br sept, 4 H, *o*-*CH*Me$_2$), 7.05 (s, 4 H, aromatic H). ^{31}P NMR (C_6D_6, 300 K): δ −294.3 (s, $h_{1/2}$ = 167 Hz). ^{19}F NMR (C_6D_6, 300 K): δ −114.6 (s, $h_{1/2}$ = 222 Hz). Anal. Calcd for $C_{39}H_{67}FNaPSi_2$: C, 70.44; H, 10.16. Found: C, 69.58; H, 10.10.

Synthesis of *P*-Cesium (fluorobis(2,4,6-triisopropyl-phenyl)silyl)(triisoropylsilyl)phosphanide·0.5THF (2). A sample of 1.45 g (2.25 mmol) of **3b** in 15 mL of toluene was allowed to react with elemental cesium (0.3 g, 2.25 mmol) at room temperature. The reaction is initiated by addition of 1 drop of THF to the blue-colored mixture. After the metal was completely consumed, the yellow cloudy solution was filtered through a GIV frit and the solvent was evaporated in vacuum (10^{-2} Torr). The solid residue was dissolved in 1 mL of hexane, and the desired product was isolated by fractional crystallization at −15 °C, affording yellow plates. It appears that the product is present in two different modifications: the first fraction gives **2** and the second **2*** (hexane solvate of **2**). Yield: 0.94 g (0.58 mmol, 51.6%) of **2** (mp 114−118 °C (dec)) and 0.13 g of **2*** (mp 86−92 °C (dec)). NMR data for **2**: ^1H NMR (C_6D_6, 300 K) δ 1.18 (br, 12 H, *p*-CH*Me*$_2$), 1.28 (d, *J*(H,H) = 7.0 Hz, 18 H, SiCH*Me*$_2$), 1.31−1.38 (m, 26 H, 2 H of THF, and *o*-CH*Me*$_2$), 2.33 (br. m, 2 H, *p*-*CH*Me$_2$), 3.21 (m, 2 H, THF), 3.89 (br sept., 4 H, *o*-*CH*Me$_2$), 7.05 (s, 4 H, aromatic H); ^{31}P NMR (C_6D_6, 300 K) δ −296.9 (s); ^{19}F NMR (C_6D_6, 300 K) δ −113.8 (s). Anal. Calcd for $C_{82}H_{142}Cs_2F_2OP_2Si_4$: C, 60.72; H, 8.82. Found: C, 61.31; H, 8.90.

Crystal Structure Determinations. Crystal data of **1a**, **2**, and **4** are represented in Table 6. Selected bond distances and angles are given in Tables 1, 2, and 5. Data were collected in the ω-scan mode on a Siemens-Stoe AED2 diffractometer (Mo Kα radiation, λ = 0.7107 Å). Intensities were corrected for absorption effects (ψ-scans). The structures were solved by direct methods (SHELXS-86) and refined by least-squares methods based on F^2 with all measured reflections (SHELXL-93).[15] For **1a** and **4**, all non-hydrogen atoms, for **2** only Cs, P, Si, and F atoms, were refined using anisotropic temperature factors. Hydrogen atoms were inserted in calculated positions or refined as part of a rigid group (methyl). In **2a** a triisopropylsilyl group is rotationally disordered, and in **1a** the silyl group is split over two positions.

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Supporting Information Available: Tables of atomic coordinates, *U* values, and bonding parameters and ORTEP diagrams of **1a**, **2**, and **4** (21 pages). Ordering information is given on any current masthead page.

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[15] Sheldrick, G. M. *SHELXS 86 and SHELXL-93*; Universität Göttingen: Göttingen, Germany, 1986 and 1993.