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Structure-Directing Properties of Lithium Chloride in Supramolecular {4-*t*-Bu-2,6-[P(O)(OEt)$_2$]$_2$C$_6$H$_2$}SiH$_2$Ph·LiCl·2H$_2$O. Intermolecular P═O→Li versus Intramolecular P═O→(H)Si Coordination[†]

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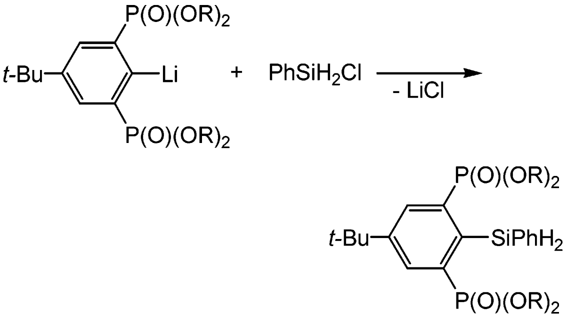
The synthesis of the novel diorganosilanes {4-*t*-Bu-2,6-[P(O)(OR)$_2$]$_2$C$_6$H$_2$}Si(H)$_2$Ph (**5**, R = Et; **6**, R = *i*-Pr) is reported. Compound **5** reacts with lithium chloride in the presence of air moisture to give the complex **5**·LiCl·2H$_2$O (**5a**). The crystal and molecular structures of the diorganosilane **6** and complex **5a** were determined by single-crystal X-ray diffraction analysis. The latter compound shows unprecedented (**5**·Li$^+$)$_6$ hexamers which are further linked by water to give a two-dimensional coordination polymer. The reaction of compound **6** with [Ph$_3$C]$^+$PF$_6^-$ provided in situ a mixture of the triorganosiliconium salts {4-*t*-Bu-2,6-[P(O)(O-*i*-Pr)$_2$]$_2$C$_6$H$_2$}Si(X)Ph$^+$PF$_6^-$ (**7**, X = H; **8**, X = F), whereas reaction with CCl$_4$ gave a mixture of the benzoxasilaphospholes [1(*P*),3(*Si*)-P(O)(O-*i*-Pr)OSi(X)Ph-6-*t*-Bu-4-P(O)(O-*i*-Pr)$_2$]-C$_6$H$_2$ (**9**, X = H; **10**, X = Cl).

Introduction

Recently, we reported the syntheses and molecular structures of the [4 + 2]-coordinated[1a] tetraorganosilanes {4-*t*-Bu-2,6-[P(O)(OR)$_2$]$_2$C$_6$H$_2$}SiPh$_3$ (**1**, R = Et; **2**, R = *i*-Pr).[1b,2] In both cases in the solid state the silicon atom is intramolecularly coordinated by four carbon and two P═O oxygen atoms. In contrast, in each of the triorganosilanes {4-*t*-Bu-2,6-[P(O)(OR)$_2$]$_2$C$_6$H$_2$}SiPh$_2$H (**3**, R = Et; **4**, R = *i*-Pr) one P═O group points away from the silicon atom, with the consequence that the latter adopts a [4 + 1] coordination.[3,4] Moreover, compounds **3** and **4** show different rotamers.[4] Given these observations, it was a logical consequence to prepare {4-*t*-Bu-2,6-[P(O)(OR)$_2$]$_2$C$_6$H$_2$}SiPhH$_2$ (R = Et, *i*-Pr), in which a further phenyl group at silicon is replaced by hydrogen, and to look at the impact this reduction of steric crowding would have on the P═O→Si coordination. In course of our studies we noticed the ability of the diorganosilane {4-*t*-Bu-2,6-[P(O)(OEt)$_2$]$_2$C$_6$H$_2$}SiPhH$_2$ to complex lithium cation and, by including water and chloride ion, to form a two-dimensional sheetlike coordination polymer.

Results and Discussion

The ethoxy- and isopropoxy-substituted diorganosilanes **5** and **6**, respectively, were obtained by reaction of the in situ generated organolithium compound {4-*t*-Bu-2,6-[P(O)(OR)$_2$]$_2$C$_6$H$_2$}Li with phenylchlorosilane, PhSiH$_2$Cl (eq 1). Compound **5** is an oil at room temperature, whereas the diorganosilane **6** is a crystalline solid. Both compounds are quite soluble in common organic solvents.



(1)

5, R = Et
6, R = *i*-Pr

The identity in solution of the diorganosilanes was confirmed by NMR spectroscopy (see Experimental Section). The ^{1}H-coupled ^{29}Si spectra show triplet-of-triplet resonances at δ −41.0 ($^1J(^1\text{H}-^{29}\text{Si})$ = 207 Hz, $J(^{29}\text{Si}-^{31}\text{P})$ = 5 Hz, **5**) and −42.2 ($^1J(^{29}\text{Si}-^1\text{H})$ = 206 Hz, $^3J(^{29}\text{Si}-^{31}\text{P})$ = 5.9 Hz, **6**). These resonances are low-frequency-shifted with respect to that of Ph$_2$SiH$_2$ ($\delta(^{29}\text{Si})$ −33.6) and hint at [4 + 1]-coordinated silicon atoms in compounds **5** and **6**. The $^1J(^1\text{H}-^{29}\text{Si})$ coupling constants differ only slightly from those in Ph$_2$SiH$_2$ (200 Hz)[5] and the triorganosilane **3** (196 Hz),[3] indicating only small differences in the s-character of the corresponding Si−H bonds.

[†] Dedicated to Professor Martin Dräger on the occasion of his retirement. This work contains part of the Ph.D. thesis of K.P. and of the planned Ph.D. thesis of K.D. Parts of this work were first presented at the 2nd European Organosilicon Days, Munich, Sept 11−12, 2003, Book of Abstracts P148, and the 11th International Conference on the Coordination and Organometallic Chemistry of Germanium, Tin, and Lead, Santa Fe, NM, June 27−July 2, 2004, Book of Abstracts O54.

(1) (a) It has been known for a long time that silicon is able to expand its coordination number beyond 4. Recently, it has been demonstrated that the nature of the bonds in such highly coordinated silicon compounds is predominantly ionic rather than covalent. See: Kocher, N.; Henn, J.; Gostevskii, B.; Kost, D.; Kalikhman, I.; Engels, B.; Stalke, D. *J. Am. Chem. Soc.* **2004**, *126*, 5563−5568. (b) Mehring, M.; Jurkschat, K.; Schürmann, M. *Main Group Met. Chem.* **1998**, *21*, 635−641.

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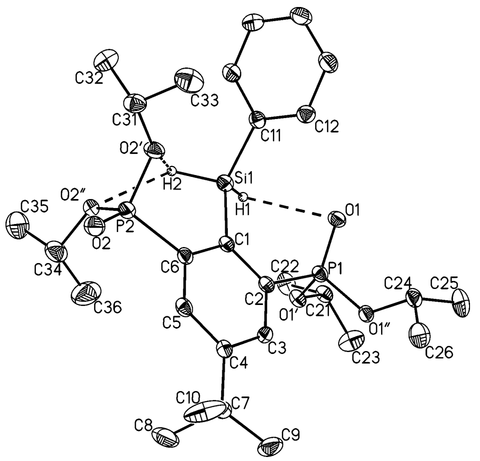

Figure 1. General view (SHELXTL) of a molecule of **6** showing the atom numbering. Symmetry transformations used to generate equivalent atoms: (a) $y + {}^{2}/_{3}, -x + y + {}^{1}/_{3}, -z + {}^{1}/_{3}$; (b) $x - y - {}^{1}/_{3}, x - {}^{2}/_{3}, -z + {}^{1}/_{3}$.

Table 1. Selected Bond Lengths (Å) and Bond Angles (deg) for 6

Si(1)−C(1)	1.906(2)	P(2)−O(2′)	1.5686(14)
Si(1)−C(11)	1.873(2)	P(2)−O(2″)	1.5779(15)
Si(1)−H(1)	1.348(15)	Si(1)−O(1)	3.0204(15)
Si(1)−H(2)	1.421(15)	Si(1)−O(2′)	3.1086(15)
P(1)−O(1)	1.4662(14)	Si(1)−O(2″)	3.5848(16)
P(1)−O(1′)	1.5681(14)	O(1)−H(1)	2.658(14)
P(1)−O(1″)	1.5875(14)	O(2′)−H(2)	2.793(15)
P(2)−O(2)	1.4649(15)	O(2″)−H(2)	2.624(16)
H(1)−Si(1)−H(2)	104.1(9)	C(1)−C(2)−P(1)	121.55(15)
H(1)−Si(1)−C(1)	109.4(6)	C(1)−C(6)−P(2)	125.23(16)
H(1)−Si(1)−C(11)	111.0(6)	C(2)−C(1)−Si(1)	121.08(15)
H(2)−Si(1)−C(1)	107.2(6)	C(6)−C(1)−Si(1)	123.20(15)
H(2)−Si(1)−C(11)	106.5(6)	C(11)−Si(1)−C(1)	117.68(9)
H(2)−Si(1)−O(1)	165.5(6)		

Notably, in contrast to both the ethoxy- and isopropoxy-substituted triorganosilanes **3**[3] and **4**[4] no hindered rotation about the P−C bond was observed for the diorganosilane **6** in solution on the ^{31}P NMR time scale down to 203 K.

The molecular structure of the diorganosilane **6** is shown in Figure 1, and selected bond distances and bond angles are given in Table 1.

The configuration of the silicon atom is best described as that of a tetrahedron (mean angle 109.31°, variation between 117.7(1) and 104.1(9)°). The O(1) atom is approaching the Si(1) atom via the tetrahedral face defined by H(1), C(1), and C(11), giving rise to intramolecular O(1)⋯Si(1) and O(1)⋯H(1) distances of 3.0204(14) and 2.66(1) Å, respectively. These distances are shorter than the sum of the van der Waals radii[6,7] of silicon (2.10 Å) and oxygen (1.50 Å) and of oxygen and hydrogen (1.20−1.45 Å), respectively. The Si(1)⋯O(1) distance is longer than the corresponding Si(1)⋯O(2) distances in {4-*t*-Bu-2,6-[P(O)(O*i*-Pr)$_2$]$_2$C$_6$H$_2$}SiPh$_2$H (**4**; 2.7378(18) Å[4]) and {4-*t*-Bu-2,6-[P(O)(OEt)$_2$]$_2$C$_6$H$_2$}SiPh$_2$H (**3**; 2.918(2) Å[3]). Compound **6** exhibits a rotamer similar to that for the ethoxy-substituted triorganosilane **3**:[3] that is, one P═O oxygen points toward the silicon atom, whereas the other one is turned away, giving rise to O(2′)⋯H(2) and O(2″)⋯H(2) distances of 2.793(15) and 2.624(16) Å, respectively. In compound **3**[3] the corresponding distances O(1′)⋯H(1) (2.47(2) Å) and O(1″)⋯H(1) (2.51(2) Å) are shorter. The Si(1)−H(1) and Si(1)−H(2) distances differ by 0.073 Å and exhibit different coordination sides. This is reflected in the IR spectrum of compound **6** (KBr pellet) showing two $\tilde{\nu}$(Si−H) bands at 2176 and 2164 cm^{-1}. Two Si−H distances (1.389 and 1.404 Å) were also reported for [2,4,6-(OMe)$_3$C$_6$H$_2$]2SiH$_2$[8] and were associated with two IR absorptions (KBr pellet) at $\tilde{\nu}$(Si−H) 2190 and 2155 cm^{-1}. However, given the low accuracy of the Si−H distance determination by X-ray crystallography, tracing the IR data back to such small differences of the Si−H distances remains questionable. This view is supported by the findings on compound **5a** (see below). The $\tilde{\nu}$(Si−H) values in compound **6** suggest larger force constants for the Si−H bonds than in Ph$_2$SiH$_2$ ($\tilde{\nu}$(Si−H) 2135 cm^{-1}; Nujol)[9] and intramolecularly coordinated diorganosilanes such as 1,4-{[2,6-(CH$_2$NMe$_2$)$_2$-C$_6$H$_3$]SiH$_2$}$_2$C$_6$H$_4$ ($\tilde{\nu}$(Si−H) 2114, 2157 cm^{-1}; KBr),[10] [2,6-(CH$_2$NMe$_2$)$_2$C$_6$H$_3$]$_2$SiH$_2$ (2174 cm^{-1}; CHCl$_3$),[11] and [2,6-(CH$_2$NMe$_2$)$_2$C$_6$H$_3$]Si(H)$_2$Ph (2111 cm^{-1}; CCl$_4$).[12]

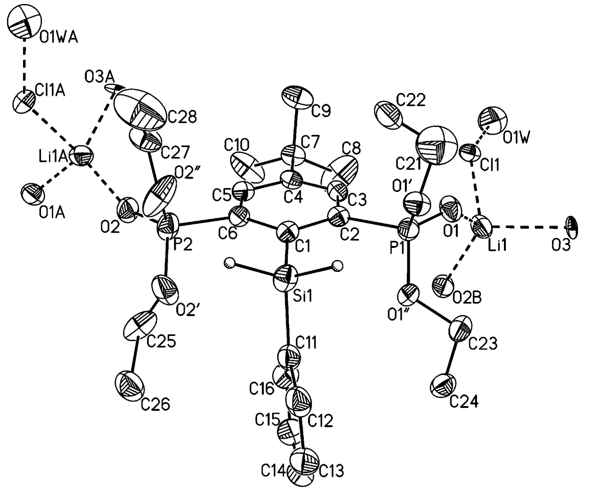

Figure 2. Section of the structure of complex **5a** showing the coordination at the lithium cation and at silicon (SHELXTL), with 30% probability displacement ellipsoids and the atom numbering shown. Symmetry transformations used to generate equivalent atoms: (a) $y + {}^{2}/_{3}, -x + y + {}^{1}/_{3}, -z + {}^{1}/_{3}$; (b) $x - y - {}^{1}/_{3}, x - {}^{2}/_{3}, -z + {}^{1}/_{3}$.

In a first attempt to prepare the ethoxy-substituted compound **5**, we had chosen a nonaqueous workup procedure and noticed formation of a solid material, the elemental analysis of which roughly fit the formula **5**·LiCl. We then treated compound **5** with a stoichiometric amount of lithium chloride and, after recrystallization from THF in the presence of air moisture, obtained analytically pure **5**·LiCl·2H$_2$O, hereafter referred to as **5a**, as a single-crystalline material.

The molecular structure of compound **5a** is shown in Figure 2, and selected geometrical data are given in Table 2. Relevant crystallographic parameters are listed in Table 3.

In contrast to the triorganosilanes **3** and **4** and the isopropoxy-substituted diorganosilane **6** both P═O oxygen atoms point away

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Table 2. Selected Bond Lengths (Å), Bond Angles (deg), and Torsion Angles (deg) for 5a[a]

Si(1)−C(1)	1.920(4)	P(2)−O(2)	1.466(3)
Si(1)−C(11)	1.864(4)	P(2)−O(2′)	1.551(4)
Si(1)−O(1′)	3.427(3)	P(2)−O(2″)	1.529(4)
Si(1)−O(1″)	3.190(3)	O(1′)−H(1)	2.52(3)
Si(1)−O(2′)	3.091(4)	O(1″)−H(1)	2.93(3)
Si(1)−O(2″)	3.427(3)	O(2′)−H(2)	2.49(3)
Si(1)−H(1)	1.52(3)	O(2″)−H(2)	2.38(3)
Si(1)−H(2)	1.41(3)	O(2)−Li(1a)	1.925(6)
P(1)−O(1)	1.463(3)	Li(1)−O(1)	1.911(7)
P(1)−O(1′)	1.558(3)	Li(1)−O(2b)	1.925(6)
P(1)−O(1″)	1.560(3)	Li(1)−O(3)	2.383(8)
Cl(1)−O(1W)	2.391(12)	Li(1)−Cl(1)	2.424(10)

C(11)−Si(1)−C(1)	112.0(2)	C(1)−C(6)−P(2)	123.4(3)
C(1)−Si(1)−H(1)	113(1)	C(1)−C(2)−P(1)	125.1(3)
C(1)−Si(1)−H(2)	103(1)	C(6)−C(1)−Si(1)	122.6(3)
C(11)−Si(1)−H(1)	106(1)	C(2)−C(1)−Si(1)	121.6(3)
C(11)−Si(1)−H(2)	111(1)	C(2)−C(1)−C(6)	115.7(3)
H(1)−Si(1)−H(2)	111(2)	C(3)−C(4)−C(5)	115.4(3)
C(2)−P(1)−O(1)	113.1(2)	C(1)−C(2)−C(3)	120.8(3)
C(2)−P(1)−O(1′)	109.7(2)	C(2)−C(3)−C(4)	123.5(3)
C(2)−P(1)−O(1″)	102.5(2)	P(1)−O(1)−Li(1)	141.3(2)
O(1)−P(1)−O(1′)	112.1(2)	O(3)−Li(1)−Cl(1)	99.6(5)
O(1)−P(1)−O(1″)	115.3(2)	O(1)−Li(1)−O(2b)	105.9(3)
O(1′)−P(1)−O(1″)	103.4(2)	O(1w)−Cl(1)−Li(1)	144.3(4)

O(1)−P(1)−C(2)−C(3)	1.1(3)
Si(1)−C(1)−C(2)−P(1)	−5.3(4)
Si(1)−C(1)−C(6)−P(2)	9.0(4)
O(2)−P(2)−C(6)−C(5)	5.1(3)
Si(1)−C(1)−C(2)−C(3)	172.2(2)
H(1)−Si(1)−C(1)−C(2)	34(1)
H(2)−Si(1)−C(1)−C(2)	154(1)

[a] Symmetry transformations used to generate equivalent atoms: (a) $y + {}^2/_3$, $x - {}^2/_3$, $-z + {}^1/_3$; (b) $x - y - {}^1/_3$, $x - {}^2/_3$, $-z + {}^1/_3$.

Table 3. Crystallographic Data for 5a and 6

	5a	6
formula	$C_{144}H_{228}Cl_6Li_6O_{36}P_{12}Si_6\cdot 12H_2O$	$C_{28}H_{46}O_6P_2Si$
fw	3545,98	568.68
cryst syst	trigonal	triclinic
cryst size, mm	0.25 × 0.25 × 0.23	0.13 × 0.10 × 0.10
space group	$R\bar{3}$	$P\bar{1}$
a, Å	22.9449(5)	9.9842(14)
b, Å	22.9449(5)	12.0381(14)
c, Å	30.6051(5)	14.063(2)
α, deg	90	95.873(7)
β, deg	90	108.262(5)
γ, deg	120	96.767(6)
V, Å^3	13953.9(5)	1576.5(4)
Z	3	2
ρ_{calcd}, Mg/m^3	1.266	1.198
μ, mm^{-1}	0.306	0.213
F(000)	5652	612
θ range, deg	3.36−27.45	2.98−25.36
index ranges	$-29 \le h \le 29$, $-25 \le k \le 25$, $-39 \le l \le 39$	$-12 \le h \le 12$, $-14 \le k \le 14$, $-16 \le l \le 15$
no. of rflns collcd	31 915	22 426
completeness to θ_{max}, %	99.6	99.6
no. of indep rflns/R_{int}	7095/0.031	5752/0.032
no. of rflns obsd with $I > 2\sigma(I)$	2730	3233
no. of refined params	418	369
GOF(F^2)	0.859	0.833
R1(F) ($I > 2\sigma(I)$)	0.0625	0.0369
wR2(F^2) (all data)	0.1768	0.0793
$(\Delta/\sigma)_{max}$	0.001	0.001
largest diff peak/hole, e/Å^3	0.758/−0.444	0.414/−0.295

from the silicon atom, leaving the latter in a distorted-tetrahedral configuration (mean angle 109.33°, variation between 103 and 113°) by coordination of two carbon and two hydrogen atoms. In addition, the tetrahedral faces are capped with the ethoxy oxygen atoms O(1′), O(1″), O(2′), and O(2″) at Si−O distances ranging between 3.091(3) and 3.427(3) Å, which are shorter than the sum of the van der Waals radii of silicon and oxygen.[6,7]

As for the isopropoxy-substituted lithium chloride free compound **6**, the Si(1)−H(1) (1.52(3) Å) and Si(1)−H(2) (1.41(3) Å) distances are different, but both hydrogen atoms show the same coordination environment. Apparently, the latter is the dominating feature, as the different distances are not reflected in the IR spectrum of **5a** (KBr pellet), showing only one absorption at $\tilde{\nu}$(Si−H) 2205 cm^{-1}. The P═O oxygen atoms coordinate to the lithium cation with Li(1)−O(1) and Li(1)−O(2B) distances of 1.911(7) and 1.925(6) Å, respectively, giving rise to formation of a ring structure composed of six diorganosilane molecules **5** and six lithium cations (Figure 3).

The Li−O distances are in the same range as those in the complexes $\{Li\cdot 2H_2O\cdot[O{=}P(NMe_2)_3]\}_2{}^{2+}\cdot 2Cl^-$ (1.936(4)−2.013(3) Å),[13] $([(NMe_2)_3P{=}O\cdot LiCl]_4$ (1.86(1)−1.88(1) Å),[14] $\{CH_2[P(O)(O\text{-}i\text{-}Pr)_2]_2\cdot LiCl\}_2$ (1.928(3)−2.056(3) Å),[10] and $[LiCl\cdot 2THF]_2$ (1.937(3)−1.956(3) Å).[15] The tetrahedral coordination sphere at each lithium cation is completed by one chloride anion (Li(1)···Cl(1) = 2.424(10) Å) and one water oxygen (Li(1)−O(3) = 2.241(11) Å). Within the large $(\mathbf{5}\cdot Li^+)_6$ ring the $SiPhH_2$ moieties point to the center of the latter and lie alternating above and beneath the ring plane. The silicon-bound phenyl groups are orthogonal to the ring plane. One water molecule links three $(\mathbf{5}\cdot Li^+)_6$ rings via hydrogen bridges (O(1W)···Cl(1) = 2.391(12) Å) to give a two-dimensional network with local propeller-type structures (Figure 3).

Reactivity of 6 toward Trityl Hexafluorophosphate, $[Ph_3C]^+PF_6^-$, and Tetrachloromethane, Respectively. The ^{29}Si NMR spectrum of a C_6D_6 solution of the diorganosilane **6** to which had been added 1 molar equiv of $[Ph_3C]^+PF_6^-$ and which had been kept at room temperature for 24 h displayed a singlet at δ −77.7 (signal A) and a doublet-of-triplets resonance at δ −88.6 ($^1J(^{29}Si{-}^{19}F) = 255$ Hz, $J(^{29}Si{-}^{31}P) = 13$ Hz; signal B). Signal A is assigned to the intramolecularly coordinated siliconium salt {4-*t*-Bu-2,6-[P(O)(O-*i*-Pr)$_2$]$_2$C$_6$H$_2$}Si(H)Ph$^+$PF$_6^-$ (**7**) (Scheme 1).

This assignment gets support from the ^{1}H-coupled ^{29}Si spectrum, showing a doublet with $^1J(^{29}Si{-}^1H) = 305$ Hz. The latter value is larger than that of the diorganosiliconium salt $[2\text{-}(CH_2PMe_2)C_6H_4]_2SiH^+OSO_2CF_3^-$ ($^1J(^1H{-}^{29}Si) = 251$ Hz)[16] but is comparable with the value of 302 Hz reported for $([8\text{-}(OMe)_2C_{10}H_6]_2SiH^+OSO_2CF_3^-)$.[17] Signal B is assigned to the fluorine-substituted siliconium ion {4-*t*-Bu-2,6-[P(O)(O-*i*-Pr)$_2$]$_2$C$_6$H$_2$}Si(F)Ph$^+$ (**8**) (Scheme 1). This assignment is supported by (i) the ^{31}P NMR spectrum showing a doublet resonance at δ 25.6 ($J(^{31}P{-}^{19}F) = 11$ Hz) and (ii) the ^{19}F NMR spectrum showing a triplet resonance at δ −151.5 ($J(^{19}F{-}^{31}P) = 11$ Hz, $^1J(^{19}F{-}^{29}Si) = 254$ Hz). Furthermore, the electrospray mass spectrum of the reaction mixture shows two mass clusters of similar intensities (65% and 75%) centered at m/z 585.3 and 543.2, respectively. These clusters are assigned to the fluorine-substituted siliconium cation {4-*t*-Bu-2,6-[P(O)(O-*i*-Pr)$_2$]$_2$C$_6$H$_2$}-Si(F)Ph$^+$ (**8**) and to the protonated fluorine-substituted benzox-

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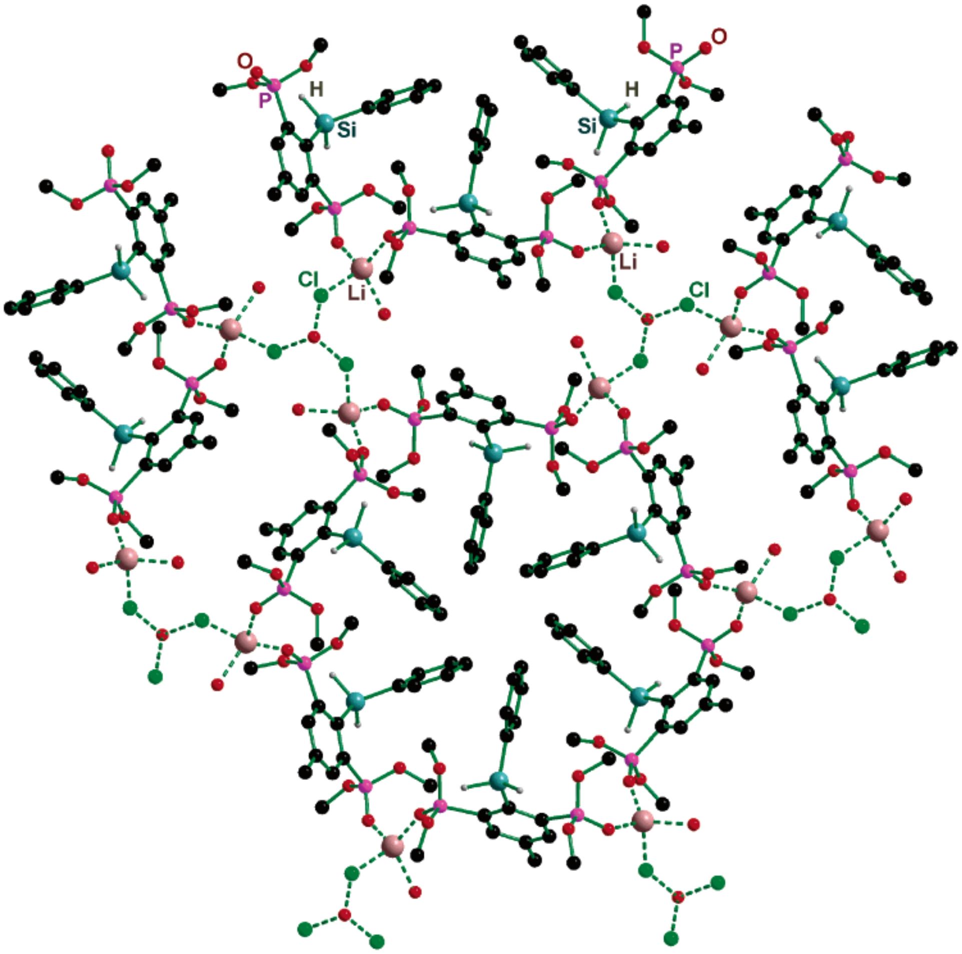
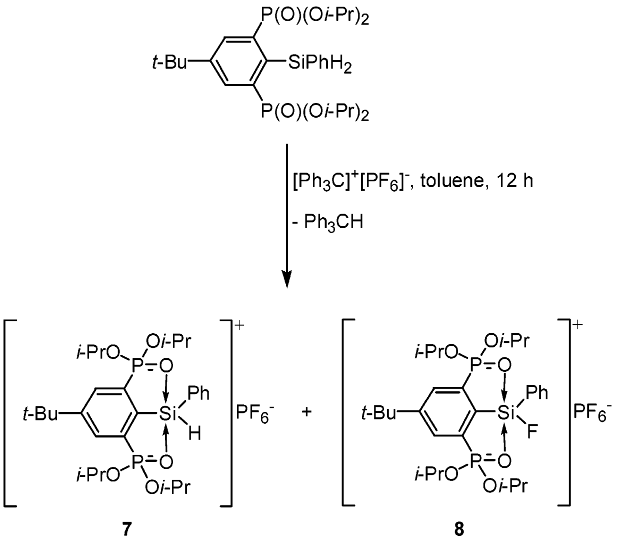


Figure 3. View of the two-dimensional structure of **5a** composed of ($\mathbf{5}\cdot Li^+$) hexamers, chloride anions, and water molecules. Methyl groups are omitted for clarity.

Scheme 1



asilaphosphole {[1(*P*),3(*Si*)-P(O)(O-*i*-Pr)OSi(F)Ph-6-*t*-Bu-4-P(O)(O-*i*-Pr)$_2$]C$_6$H$_2$}·H$^+$.

The mechanism that accounts for the formation of the fluorine-substituted siliconium ion is not clear to us, and it was not our intention to investigate this in more detail. One possibility is the generation of hydrogen fluoride by partial hydrolysis of hexafluorophosphate anion, PF_6^-,[18] with trace amounts of water present in the solvent. The hydrogen fluoride reacts with the Si−H function of compound **7** to give compound **8** and hydrogen. The observation of gas bubbles in course of the reaction supports this idea. That organosilanes do indeed react with hydrogen fluorides has been known for a long time,[19] and in the case of compound **7** this is even more favored, as siliconium ions are known to have a rather high affinity toward fluoride ion.[20]

Attempts at separating and isolating compounds **7** and **8** failed. Notably, other intramolecularly coordinated Si−H-containing siliconium salts such as $[2,6\text{-}(CH_2NMe_2)_2C_6H_3]_2SiH^+\text{-}BF_4^-$ ($\delta(^{29}Si)$ −29.0),[11] $[2\text{-}(CH_2NMe_2)C_6H_4]Si(H)Ph^+OSO_2\text{-}CF_3^-$ ($\delta(^{29}Si)$ −56.2),[21] $[8\text{-}(OMe)_2C_{10}H_6]_2SiH^+OSO_2CF_3^-$ ($\delta(^{29}Si)$ −30.0),[17] $[2\text{-}(CH_2OMe)C_6H_4]Si(H)Ph^+OSO_2CF_3^-$ ($\delta(^{29}Si)$ −48.7),[22] $[2\text{-}(CH_2SMe)C_6H_4]Si(H)Ph^+OSO_2CF_3^-$ ($\delta(^{29}Si)$ −42.8),[23] $[2\text{-}(CH_2SMe)C_6H_4]_2SiH^+OSO_2CF_3^-$ ($\delta(^{29}Si)$ −47),[16] $[2\text{-}(CH_2PMe_2)C_6H_4]Si(H)Ph^+OSO_2CF_3^-$ ($\delta(^{29}Si)$ −32.4),[23] and $[2\text{-}(CH_2PMe_2)C_6H_4]_2SiH^+$ $OSO_2CF_3^-$ ($\delta(^{29}Si)$ −104.3)[16] have been reported, whereas triorganosiliconium ions containing Si−F bonds were identified by photoionization mass spectrometry only.[20]

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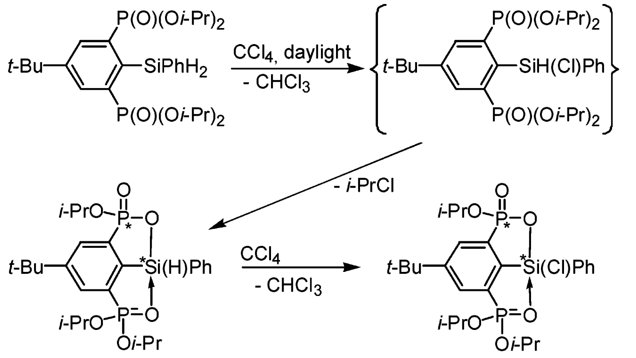
Scheme 2



9 (mixture of two epimers) **10** (mixture of two epimers)

The ^{31}P NMR spectrum of a solution of the diorganosilane **6** in CCl_4 which had been kept in the daylight for 20 days showed a singlet at δ 18.1 (integral 33, unreacted **6**) and two pairs of doublets (ratio between the two pairs approximately 3:2, total integral 57) at δ 19.2 ($J(^{31}P-^{31}P) = 3.9$ Hz)/δ 22.7 ($J(^{31}P-^{31}P) = 3.9$ Hz) and δ 19.3 ($J(^{31}P-^{31}P) = 3.9$ Hz)/δ 22.7-($J(^{31}P-^{31}P) = 3.9$ Hz). These pairs of doublets are assigned to the two epimers of the benzoxasilaphosphole [1(*P*),3(*Si*)-P(O)-(O-*i*-Pr)OSi(H)Ph-6-*t*-Bu-4-P(O)(O-*i*-Pr)$_2$]C_6H_2 (**9**) (Scheme 2).

This assignment is supported by the ^{1}H NMR spectrum, showing for the Si−H protons two doublet-of-doublet resonances, with again a ratio of 3:2, at δ 5.65 ($J(^1H-^{31}P) = 6.7$ and 5.1 Hz) and 5.63 ($J(^1H-^{31}P) = 7.0$ and 3.6 Hz).

In addition, there are another two pairs of doublets (ratio between the two pairs approximately 2:1, total integral 9) at δ 15.7 ($J(^{31}P-^{31}P) = 7.5$ Hz)/δ 18.2 ($J(^{31}P-^{31}P) = 7.5$ Hz) and δ 15.8 ($J(^{31}P-^{31}P) = 7.5$ Hz)/δ 18.0($J(^{31}P-^{31}P) = 7.5$ Hz) which are tentatively assigned to the two epimers of the chloro-substituted benzoxasilaphosphole [1(*P*),3(*Si*)-P(O)(O-*i*-Pr)OSi-(Cl)Ph-6-*t*-Bu-4-P(O)(O-*i*-Pr)$_2$]C_6H_2 (**10**) (Scheme 2). The latter is formed by reaction of compound **9** with CCl_4.

The electrospray mass spectrum (positive mode) of the reaction mixture shows high-intensity, and almost equally intense, mass clusters centered at *m*/*z* 567.5, 525.3, 483.3, 441.3, and 399.3, which are assigned to {4-*t*-Bu-2,6-[P(O)(O-*i*-Pr)$_2$]$_2$-C_6H_2}Si(H)Ph$^+$ (generated from {4-*t*-Bu-2,6-[P(O)(O-*i*-Pr)$_2$]$_2$-C_6H_2}SiH(Cl)Ph by loss of chloride ion; see Scheme 2), the protonated benzoxasilaphosphole [**9**·H]$^+$, and the corresponding species generated by subsequent loss of three 2-methylethene molecules, respectively. In addition, there is a another set of low-intensity, but almost equally intense, mass clusters centered at *m*/*z* 583.5, 541.3, 499.3, 457.2, and 415.2. These mass clusters are assigned to {4-*t*-Bu-2,6-[P(O)(O-*i*-Pr)$_2$]$_2$$C_6H_2$}Si(OH)Ph$^+$ and the corresponding species generated by subsequent loss of four 2-methylethene molecules.

The mechanism that accounts for the formation of the benzoxasilaphosphole derivatives involves participation of siliconium ions and was discussed in some of our previous works.[24] The ability of siliconium ions to cleave N−C and O−C bonds was also reported by other authors.[25−27]

Conclusion

A systematic investigation, including the results reported in refs 3 and 4, on the organosilanes {4-*t*-Bu-2,6-[P(O)(OR)$_2$]$_2$-C_6H_2}Si(H)$_n$Ph$_{3-n}$ (R = Et, *i*-Pr; *n* = 1, 2)),containing a potentially intramolecularly coordinating pincer-type ligand, reveals that the extent of P═O→Si coordination and the type of rotamer actually observed in the solid state depend on the substituent pattern at silicon as well as on the identity of the substituent R. In the diorganosilane **5** there is no substantial intramolecular P═O→Si interaction but a short, structure-determining Si−H···O distance of 2.66(1) Å is found. In complex **5a**, the Lewis acidic Li$^+$ cation competes with the silicon-bound hydrogen atom for the P═O Lewis base and, by assistance of chloride anion and water, generates an unprecedented supramolecular framework. This suggests that the nonmetalated arylphosphonic ester 5-*t*-Bu-1,3-[P(O)(OR)$_2$]$_2$$C_6H_3$ also should hold potential as ligand in supramolecular chemistry.

Experimental Section

General Considerations. All solvents were dried and purified by standard procedures. All reactions were carried out under an inert atmosphere (argon or nitrogen) using Schlenk techniques.

IR spectra (cm^{-1}) were recorded on a Bruker IFS 28 spectrometer. Bruker DPX-300 and DRX-400 and Varian Mercury 200 spectrometers were used to obtain ^{1}H, ^{13}C, ^{19}F, ^{31}P, and ^{29}Si NMR spectra. ^{1}H, ^{13}C, ^{19}F, ^{31}P, and ^{29}Si NMR chemical shifts δ are given in ppm and were referenced to Me_4Si, CCl_3F, and H_3PO_4 (85%), respectively. NMR spectra were recorded at room temperature unless otherwise stated. Elemental analyses were performed on a LECO CHNS-932 analyzer.

Electrospray mass spectra were recorded in the positive and negative mode on a Thermoquest-Finnigan instrument using CH_3CN as the mobile phase. The compounds **7** and **8**, respectively, were dissolved in acetonitrile and then diluted with the mobile phase to give a solution of approximate concentration 10^{-6} mol L^{-1}. The sample was introduced via a syringe pump operating at 30 μL min^{-1}. The capillary voltage was 2.5 kV, while the capillary temperature was set to 200 °C. Identification of all major ions was assisted by comparison of experimental and calculated isotope distribution patterns. The *m*/*z* values reported correspond to those of the most intense peaks in the corresponding isotope pattern.

Crystallography. Intensity data for the colorless crystals were collected on a Nonius KappaCCD diffractometer with graphite-monochromated Mo Kα (0.710 73 Å) radiation at 173(1) K. The data collection covered almost the whole sphere of reciprocal space with 2 (**5a**) and 5 (**6**) sets at different *k* angles with 218 (**5a**) and 251 (**6**) frames via ω rotation ($\Delta/\omega = 1°$) at 2 × 150 s (**5a**) and 2 × 70 s (**6**) per frame. The crystal-to-detector distances were 3.4 cm. Crystal decays were monitored by repeating the initial frames at the end of data collection. The data were not corrected for absorption effects. On analysis of the duplicate reflections, there were no indications for any decay. The structure was solved by direct methods (SHELXS97[28]) and successive difference Fourier syntheses. Refinement was applied by full-matrix least-squares methods in SHELXL97.

The H atoms (H(1), H(2)) bonded to Si(1) in **5a** were located in the difference Fourier map and refined isotropically. The other H atoms were placed in geometrically calculated positions using a riding model with isotropic temperature factors constrained at 1.2 for nonmethyl and at 1.5 for methyl groups times the U_{eq} value of the carrier C atom.

In **5a** three OEt groups are disordered over two positions with occupancies of 0.33 (C(27′)), 0.5 (C(21), C(22), C(25), C(21′),

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C(22′), C(25′)), and 0.66 (C(27)). The chloride anion as well as the water molecule bonded to the lithium cation are also disordered over three positions (sof values: Cl(1), 0.3; Cl(1′), 0.5; Cl(1″), 0.2; O(3), 0.4; O(3′), 0.25; O(3″), 0.35). The water molecule O(1W) was anisotropically refined with an occupancy of 0.166, and O(2W) was isotropically refined over three positions (sof values: O(2W), 0.166; O(2W′), 0.33; O(2W″), 0.33). In **6** the *tert*-butyl group is disordered over two positions (C(8) > C(10′)) with occupancies of 0.5.

Atomic scattering factors for neutral atoms and real and imaginary dispersion terms were taken from ref 29. The figures were created by SHELXTL.[30] Crystallographic data are given in Table 3 and selected bond distances and angles in Tables 1 (**5a**) and 2 (**6**).

[{2,6-Bis(diethoxyphosphonyl)-4-*tert*-butyl}phenyl]dihydridophenylsilane (5). Chlorophenylsilane (1.78 g, 12.44 mmol) was added dropwise, at −78 °C, to a solution of [{2,6-bis(diethoxyphosphonyl)-4-*tert*-butyl}phenyl]lithium (**1**; 23.59 g, 8.70 mmol) in diethyl ether (100 mL). The reaction mixture was stirred for 16 h (−78 °C to room temperature), and then the solvent was evaporated. The residue was suspended in THF (50 mL) and filtrated with a diatomaceous earth filter. After extraction of the diatomaceous earth filter with THF (2 × 25 mL) the solvent was evaporated. The oily residue was extracted with diethyl ether (4 × 50 mL) to remove 5-*t*-Bu-1,3-[P(O)(OEt)$_2$]$_2$C$_6$H$_3$, resulting in 2.98 g of (62%) **5**·LiCl as a hygroscopic colorless solid. Subsequently, water (25 mL) was added to this solid and the resulting solution was extracted with Et$_2$O (25 mL). The organic part was dried over Na$_2$SO$_4$ followed by filtration of the latter. Evaporation of the diethyl ether in vacuo afforded 1.72 g (61%) of **5** as a colorless oil. ^{1}H NMR (400.13 MHz, C$_6$D$_6$): δ 0.99 (t, $^{3}J(^{1}\mathrm{H}-^{1}\mathrm{H}) = 7$ Hz, 12H; CH$_3$), 1.23 (s, 9H; CH$_3$), 3.87 (complex pattern, 4H; CH$_2$), 4.00 (complex pattern, 4H; CH$_2$), 5.68 (s, $^{1}J(^{1}\mathrm{H}-^{29}\mathrm{Si}) = 206$ Hz, 1H; Si−H), 7.19 (unresolved, 3H; H$_{m/p}$), 7.90 (unresolved, 2H; H$_o$), 8.56 (unresolved, 2H; H$_{3,5}$). ^{13}C{^{1}H} NMR (100.61 MHz, C$_6$D$_6$): δ 16.2 (complex pattern, $^{3}J(^{13}\mathrm{C}-^{31}\mathrm{P}) = 3$ Hz, 4C; CH$_3$), 30.8 (s, 3C; CH$_3$), 34.9 (s, 1C; C), 62.1 (complex pattern, $^{2}J(^{13}\mathrm{C}-^{31}\mathrm{P}) = 3$ Hz, 4C; CH$_2$), 127.5 (s, 2C; C$_m$), 129.1 (s, 2C; C$_p$), 134.1 (complex pattern, 2C; C$_{3,5}$), 136.5 (s, 1C; C$_m$), 138.0 (s, 1C; C$_i$), 138.4 (t, $^{2}J(^{13}\mathrm{C}-^{31}\mathrm{P}) = 19$ Hz, 1C; C$_1$), 139.4 (dd, $^{1}J(^{13}\mathrm{C}-^{31}\mathrm{P}) = 187$ Hz, $^{3}J(^{13}\mathrm{C}-^{31}\mathrm{P}) = 18$ Hz, 2C; C$_{2,6}$), 152.2 (t, $^{3}J(^{13}\mathrm{C}-^{31}\mathrm{P}) = 13$ Hz, 1C; C$_4$). ^{29}Si NMR (79.49 MHz, C$_6$D$_6$) δ −41.0 (tt, $J(^{29}\mathrm{Si}-^{31}\mathrm{P}) = 5$ Hz, $^{1}J(^{1}\mathrm{H}-^{29}\mathrm{Si}) = 207$ Hz). ^{31}P{^{1}H} NMR (161.98 MHz, C$_6$D$_6$): δ 19.6. IR (Nujol): $\tilde{\nu}$(P=O) 1251 cm^{-1}, $\tilde{\nu}$(Si−H) 2185 cm^{-1}. MS: *m/z* (%) 512 (33, M), 511 (100, M − H), 435 (29, M − Ph), 434 (29, M − Ph − H), 391 (24, M − Ph − OEt + H), 361 (30, M − Ph − OEt − Et). Anal. Calcd for C$_{24}$H$_{38}$O$_6$P$_2$Si: C, 56.2; H, 7.5. Found: C, 55.6; H, 7.9.

[{2,6-Bis(diethoxyphosphonyl)-4-*tert*-butyl}phenyl]dihydridophenylsilane·LiCl·2H$_2$O (5a). Lithium chloride (0.043 g, 1.00 mmol) was added to a solution of [{2,6-bis(diethoxyphosphonyl)-4-*tert*-butyl}phenyl]dihydridophenylsilane (**5**; 0.51 g, 0, 99 mmol) in THF (35 mL) and stirred under atmospheric moisture at 20 °C to give a colorless solution. Crystallization at −6 °C afforded 0.32 g (55%) of **5a** as colorless crystals, mp 161 °C. ^{1}H NMR (400.13 MHz, THF-*d*$_8$): δ 1.11 (t, $^{3}J(^{1}\mathrm{H}-^{1}\mathrm{H}) = 7$ Hz, 12H; CH$_3$), 1.37 (s, 9H; CH$_3$), 3.87−3.94 (complex pattern, 4H; CH$_2$), 3.97−4.06 (complex pattern, 4H; CH$_2$), 5.22 (s, $^{1}J(^{1}\mathrm{H}-^{29}\mathrm{Si}) = 206$ Hz, 1H; Si−H), 7.23 (complex pattern, 3H; H$_{m/p}$), 7.68 (complex pattern, 2H; H$_o$), 8.30 (complex pattern, 2H; H$_{3,5}$). ^{1}H NMR (400.13 MHz, THF-*d*$_8$, −70 °C): δ 1.05 ($\nu_{1/2} = 30$ Hz, 12H; CH$_3$), 1.40 (s, 9H; CH$_3$), 3.91 ($\nu_{1/2} = 45$ Hz, 4H; CH$_2$), 4.06 ($\nu_{1/2} = 44$ Hz, 4H; CH$_2$), 5.16 (s, $^{1}J(^{1}\mathrm{H}-^{29}\mathrm{Si}) = 205$ Hz, 1H; Si−H), 7.30 (complex pattern, 3H; H$_{m/p}$), 7.65 (complex pattern, 2H; H$_o$), 8.37 (complex pattern, 2H; H$_{3,5}$). ^{13}C{^{1}H} NMR (100.63 MHz, THF-*d*$_8$): δ 17.5 (complex pattern, $^{3}J(^{13}\mathrm{C}-^{31}\mathrm{P}) = 3$ Hz, 4C; CH$_3$), 32.2 (s, 3C; CH$_3$), 36.6 (s, 1C; C), 63.5 (complex pattern, $^{2}J(^{13}\mathrm{C}-^{31}\mathrm{P}) = 3$ Hz, 4C; CH$_2$), 128.7 (s, 2C; C$_m$), 130.0 (s, 2C; C$_o$), 130.4 (s, 1C; C$_p$), 135.3 (complex pattern, 2C; C$_{3,5}$), 138.1 (s, 1C; C$_i$), 139.9 (t, $^{2}J(^{13}\mathrm{C}-^{31}\mathrm{P}) = 20$ Hz, 1C; C$_1$), 140.7 (dd, $^{1}J(^{13}\mathrm{C}-^{31}\mathrm{P}) = 188$ Hz, $^{3}J(^{13}\mathrm{C}-^{31}\mathrm{P}) = 19$ Hz, 2C; C$_{2,6}$), 153.6 (t, $^{3}J(^{13}\mathrm{C}-^{31}\mathrm{P}) = 13$ Hz, 1C; C$_4$). ^{29}Si NMR (59.63 MHz, THF-*d*$_8$): δ −41.3 (tt, $J(^{29}\mathrm{Si}-^{31}\mathrm{P}) = 5$ Hz, $^{1}J(^{1}\mathrm{H}-^{29}\mathrm{Si}) = 207$ Hz). ^{31}P{^{1}H} NMR (161.98 MHz, C$_6$D$_6$): δ 19.9. IR (KBr): $\tilde{\nu}$(P=O) 1250 cm^{-1}, $\tilde{\nu}$(Si−H) 2205 cm^{-1}. Anal. Calcd for C$_{24}$H$_{42}$ClLiO$_8$P$_2$Si: C, 48.8; H, 7.2. Found: C, 48.3; H, 7.6.

[{2,6-Bis(diisopropoxyphosphonyl)-4-*tert*-butyl}phenyl]dihydridophenylsilane (6). To a solution of 1,3-bis(diisopropoxyphosphonyl)-5-*tert*-butylbenzene (8.00 g, 17.30 mmol) in diethyl ether (200 mL) was added, dropwise at −70 °C, LiN-*i*-Pr$_2$ in diethyl ether/*n*-hexane (31 mL, 2:1, 0.59 M). The reaction mixture was stirred for 8 h at −30 °C. To the stirred solution of [{2,6-bis(diisopropoxyphosphonyl)-4-*tert*-butyl}phenyl]lithium was added dropwise a solution of chlorophenylsilane (2.59 g, 18.17 mmol) in diethyl ether (20 mL) at −35 °C. The reaction mixture was stirred for 12 h (−70 °C to room temperature), and then the solvent was evaporated. The residue was poured into water, and the resulting mixture was extracted with diethyl ether (2 × 80 mL). The organic layers were combined, washed with water (1 × 150 cm^3), dried over Na$_2$SO$_4$, and filtered. The diethyl ether was removed in vacuo to give an oily residue. Column chromatography (SiO$_2$/EtOAc) of this residue afforded 2.46 g (25%) of **6** as a colorless solid, mp 71 °C. ^{1}H NMR (400.13 MHz, CD$_2$Cl$_2$): δ 1.13 (d, $^{3}J(^{1}\mathrm{H}-^{1}\mathrm{H}) = 6.2$ Hz, 12H) and 1.26 (d, $^{3}J(^{1}\mathrm{H}-^{1}\mathrm{H}) = 6.2$ Hz, 12H) (C(CH_3)(CH_3)′(P)), 1.38 (s, 9H; CH_3), 4.62 (unresolved, 4H; OCH), 5.26 (s, $^{1}J(^{1}\mathrm{H}-^{29}\mathrm{Si}) = 205$ Hz, 2H; SiH), 7.28 (m, 3H; $H_{m/p}$), 7.62 (m, 2H; H_o), 8.17 (unresolved, 2H; $H_{3,5}$). ^{13}C{^{1}H} NMR (100.61 MHz, CD$_2$Cl$_2$): δ 23.5 (d, $^{3}J(^{13}\mathrm{C}-^{31}\mathrm{P}) = 2.0$ Hz, 8C; C(CH$_3$)$_2$), 30.8 (s, 3C; C(CH$_3$)$_3$), 35.0 (s, 1C; C(CH$_3$)$_3$), 71.08 (d, $^{2}J(^{13}\mathrm{C}-^{31}\mathrm{P}) = 2.9$ Hz, 2C) and 71.11 (d, $^{2}J(^{13}\mathrm{C}-^{31}\mathrm{P}) = 2.9$ Hz, 2C) (OCH), 127.1 (s, 2C; C_m), 128.7 (s, 1C; C_p), 133.3 (unresolved, 2C; $C_{3,5}$), 134.2 (s, 1C; C_i), 136.0 (s, 2C; C_o), 137.7 (t, $^{2}J(^{13}\mathrm{C}-^{31}\mathrm{P}) = 2.0$ Hz, 1C; C_1), 139.6 (dd, $^{1}J(^{13}\mathrm{C}-^{31}\mathrm{P}) = 188$ Hz, $^{3}J(^{13}\mathrm{C}-^{31}\mathrm{P}) = 19$ Hz, 2C; C$_{2,6}$), 151.9 (t, $^{3}J(^{13}\mathrm{C}-^{31}\mathrm{P}) = 13$ Hz, 1C; C$_4$). ^{31}P{^{1}H} NMR (121.49 MHz, CH$_2$Cl$_2$/D$_2$O capillary): δ 17.71. ^{29}Si NMR (59.63 MHz, CH$_2$Cl$_2$/D$_2$O capillary): δ −42.2 (tt, $^{1}J(^{29}\mathrm{Si}-^{1}\mathrm{H}) = 206$ Hz, $^{3}J(^{29}\mathrm{Si}-^{31}\mathrm{P}) = 5.9$ Hz). IR (KBr): $\tilde{\nu}$(Si−H) 2176, 2164 cm^{-1}; $\tilde{\nu}$(P=O) 1244 cm^{-1}. Anal. Calcd for C$_{28}$H$_{46}$O$_6$P$_2$Si: C, 59.1; H, 8.2. Found: C, 58.8; H, 8.3.

Reaction of [{2,6-Bis(diisopropoxyphosphonyl)-4-*tert*-butyl}phenyl]dihydridophenylsilane (6) with Triphenylcarbonium Hexafluorophosphate. To a suspension of triphenylcarbonium hexafluorophosphate (0.41 g, 1.06 mmol) in toluene (20 mL) was added at 0 °C a solution of [{2,6-bis(diisopropoxyphosphonyl)-4-*tert*-butyl}phenyl]dihydridophenylsilane (0.60 g, 1.06 mmol) in toluene (20 mL). After the reaction mixture had been stirred for 12 h (0 °C to room temperature), the solvent was evaporated and the yellow residue was dissolved in C$_6$D$_6$ and characterized by NMR spectroscopy. ^{19}F{^{1}H} NMR (188.29 MHz): δ −151.5 (t, $J(^{19}\mathrm{F}-^{31}\mathrm{P}) = 11$ Hz, $^{1}J(^{19}\mathrm{F}-^{29}\mathrm{Si}) = 254$ Hz, **8**), −72.2 (d, $^{1}J(^{19}\mathrm{F}-^{31}\mathrm{P}) = 711$ Hz; PF$_6^-$). ^{29}Si{^{1}H} NMR (59.63 MHz): δ −88.6 (dt, $^{1}J(^{29}\mathrm{Si}-^{19}\mathrm{F}) = 255$ Hz, $J(^{29}\mathrm{Si}-^{31}\mathrm{P}) = 13$ Hz, **8**), −77.7 (**7**). ^{29}Si NMR (59.63 MHz): δ −88.7 (doublet of multiplets, $^{1}J(^{29}\mathrm{Si}-^{19}\mathrm{F}) = 257$ Hz), −77.8 (doublet of multiplets, $^{1}J(^{29}\mathrm{Si}-^{1}\mathrm{H}) = 305$ Hz). ^{31}P{^{1}H} NMR (121.49 MHz): δ 28.6 (**7**), 25.6 (d, $J(^{31}\mathrm{P}-^{19}\mathrm{F}) = 11$ Hz, **8**), −142.25 (septet, $^{1}J(^{31}\mathrm{P}-^{19}\mathrm{F}) = 711$ Hz; PF$_6^-$).

Reaction of [{2,6-Bis(diisopropoxyphosphonyl)-4-*tert*-butyl}phenyl]dihydridophenylsilane (6) with CCl$_4$. At room temperature, a sealed NMR tube containing a solution of [{2,6-bis(di-

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isopropoxyphosphonyl)-4-*tert*-butyl}phenyl]dihydridophenylsilane (0.049 g, 0.09 mmol) in tetrachloromethane (0.6 mL) and C_6D_6 (0.004 mL) was exposed to daylight for 20 days. $^{31}P\{^1H\}$ NMR (121.49 MHz): δ 18.1 (s, **6**), 19.2 (d, $J(^{31}P-^{31}P) = 3.9$ Hz)/22.7 (d, $J(^{31}P-^{31}P) = 3.9$ Hz)) and 19.3 (d, $J(^{31}P-^{31}P) = 3.9$ Hz)/22.7 (d, $J(^{31}P-^{31}P) = 3.9$ Hz), belonging to the two epimers of **9**; 15.7 ($J(^{31}P-^{31}P) = 7.5$ Hz)/18.2 ($J(^{31}P-^{31}P) = 7.5$ Hz) and 15.8 ($J(^{31}P-^{31}P) = 7.5$ Hz)/18.0 ($J(^{31}P-^{31}P)$ 7.5 Hz), belonging to the two epimers of **10**. $^{29}Si\{^1H\}$ NMR (59.63 MHz): δ -42.1 (t, $^3J(^{29}Si-^{31}P) = 5$ Hz) (**6**), -40.9 (d, $J(^{29}Si-^{31}P) = 13$ Hz) and -39.7 (d; $J(^{29}Si-^{31}P) = 12$ Hz) (**10**), -40.8 (d; $J(^{29}Si-^{31}P) = 13$ Hz) and -39.6 (d; $J(^{29}Si-^{31}P) = 12$ Hz) (**10**), -38.1 (unresolved), -36.7 (unresolved, $J(^{29}Si-^{31}P) = 6$ Hz) (**9**). ^{29}Si NMR (59.63 MHz): δ -45.6 (unresolved, $^3J(^{29}Si-^{31}P) = 5$ Hz) (**6**), -40.6 (unresolved) and -39.3 (unresolved) (**10**), -39.2 (unresolved) and -38.6 (unresolved), -35.1 (unresolved, $^1J(^{29}Si-^1H) = 79$ Hz) (**9**).

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Supporting Information Available: Tables giving X-ray crystallographic data for **5a** and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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