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Notes

Restricted Rotation about the P−C Bond in the Triorganosilane {4-*t*-Bu-2,6-[P(O)(O-*i*-Pr)$_2$]$_2$C$_6$H$_2$}SiPh$_2$H: Identification of a Novel Rotamer and Its Conversion to the Siliconium Salt {4-*t*-Bu-2,6-[P(O)(O-*i*-Pr)$_2$]$_2$C$_6$H$_2$}SiPh$_2$$^+PF_6$$^-$

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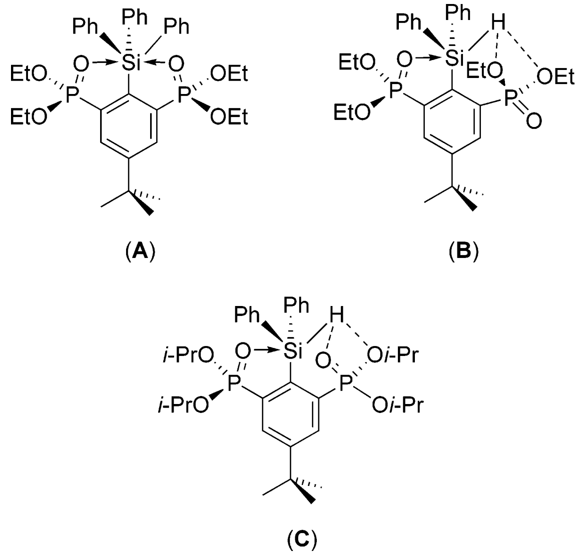
*Summary: The syntheses and structures of the [4 + 1]-coordinated triorganosilane {4-t-Bu-2,6-[P(O)(O-i-Pr)$_2$]$_2$-C$_6$H$_2$}SiPh$_2$H (**5**) and of the intramolecularly coordinated triorganosiliconium hexafluorophosphate {4-t-Bu-2,6-[P(O)(O-i-Pr)$_2$]$_2$C$_6$H$_2$}SiPh$_2$$^+PF_6$$^-$ (**6**) are reported. In the solid state, compound **5** adopts a rotameric form that differs from those found for {4-t-Bu-2,6-[P(O)(OEt)$_2$]$_2$-C$_6$H$_2$}SiPh$_2$R (R = Ph, H).*

Introduction

In recent papers[1−3] we reported the syntheses and structures of the intramolecularly coordinated organosilanes {4-*t*-Bu-2,6-[P(O)(OEt)$_2$]$_2$C$_6$H$_2$}SiPh$_2$R (**1**, R = Ph; **2**, R = H). In the solid state, the silicon atom in the tetraorganosilane **1** is [4 + 2]-coordinated by four carbons and two P═O oxygens, giving rise to an A-type rotamer (Chart 1). For the triorganosilane **2**, however, a B-type rotamer (Chart 1) was identified with one P═O group pointing away from the silicon atom and the silicon-bonded hydrogen atom formally bisecting the (Et)O−P−O(Et) angle. Consequently, the silicon atom in this triorganosilane is [4 + 1]-coordinated. In CD$_2$Cl$_2$ solution at −75 °C, compound **2** shows hindered rotation about the P−C bond, as was evidenced by observation of two equally intense ^{31}P NMR resonances at 19.2 and 19.4 ppm.

Both compounds **1** and **2** are easily converted by reaction with triphenylcarbonium hexafluorophosphate to give the intramolecularly coordinated triorganosiliconium hexafluorophosphate {4-*t*-Bu-2,6-[P(O)(OEt)$_2$]$_2$-C$_6$H$_2$}SiPh$_2$$^+PF_6$$^-$ (**3**), which, however, was only characterized in situ by ^{29}Si and ^{31}P NMR spectroscopy. Attempts at isolating single crystals of **3** suitable for X-ray diffraction analysis failed. On the other hand, the corresponding triorganotin hexafluorophosphate {4-*t*-Bu-2,6-[P(O)(O-*i*-Pr)$_2$]$_2$C$_6$H$_2$}SnPh$_2$$^+PF_6$$^-$ (**4**) containing isopropoxy instead of ethoxy groups could be completely characterized. Bearing in mind the ongoing interest in triorganosiliconium ions in general[4−8] and the role of the {4-*t*-Bu-2,6-[P(O)(OEt)$_2$]$_2$C$_6$H$_2$}SiPh$_2$$^+$ cation as an intermediate in the synthesis of intramolecularly coordinated benzoxaphosphasiloles[3] in particular, it appeared to be worthwhile to synthesize the isopropoxy-substituted analogue {4-*t*-Bu-2,6-[P(O)(O-*i*-Pr)$_2$]$_2$C$_6$H$_2$}-SiPh$_2$$^+PF_6$$^-$ (**6**) and to investigate its structure in more detail. This goal was achieved, and in addition, in the course of our studies we learned that the molecular

Chart 1


(**A**) (**B**)

(**C**)

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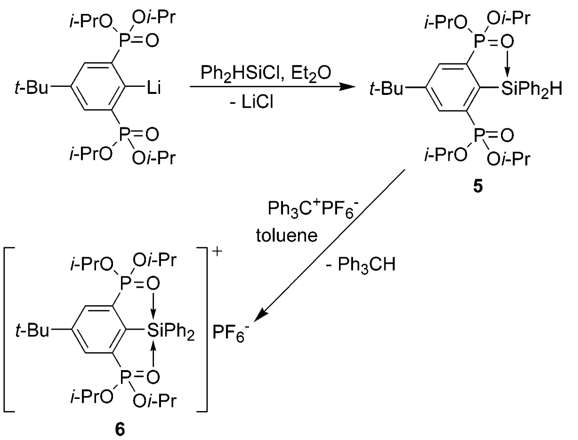
10.1021/om0492247 CCC: $30.25

Scheme 1



structure of the corresponding triorganosilane {4-*t*-Bu-2,6-[P(O)(O-*i*-Pr)$_2$]$_2$C$_6$H$_2$}SiPh$_2$H (**5**), the precursor for compound **6**, is different from that of its ethoxy-substituted analogue **2**.

Results and Discussion

The reaction of the in situ generated organolithium compound {4-*t*-Bu-2,6-[P(O)(O-*i*-Pr)$_2$]$_2$C$_6$H$_2$}Li with diphenylchlorosilane afforded in poor yield the triorganosilane {4-*t*-Bu-2,6-[P(O)(O-*i*-Pr)$_2$]$_2$C$_6$H$_2$}SiPh$_2$H (**5**), as colorless, low-melting crystals (Scheme 1).

Compound **5** was characterized by NMR and IR spectroscopy, with the data being comparable with those of its ethoxy-substituted analogue **2** (see the Experimental Section).

The molecular structure of compound **5** is shown in Figure 1, and selected geometric parameters are collected in Table 1.

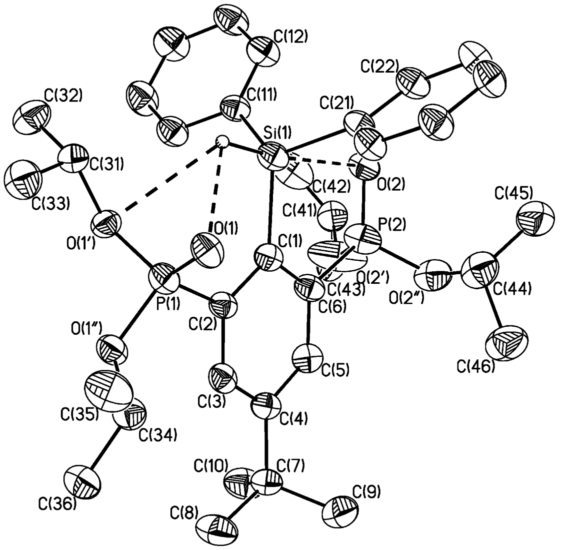


Figure 1. General view (SHELXTL) of a molecule of **5** showing 30% probability displacement ellipsoids and the atom numbering.

Table 1. Selected Bond Lengths (Å), Bond Angles (deg), and Torsion Angles (deg) for 5 and 6

	5	**6**
P(1)−O(1)	1.4727(14)	1.5123(13)
P(1)−O(1′)	1.5826(18)	1.5451(15)
P(1)−O(1″)	1.5852(16)	1.5535(14)
P(2)−O(2)	1.4692(17)	1.5120(15)
P(2)−O(2′)	1.563(2)	1.5511(14)
P(2)−O(2″)	1.580 (2)	1.5537(15)
P(3)−F(3)		1.5551(17)
P(3)−F(4)		1.5795(17)
P(3)−F(2)		1.5945(19)
P(3)−F(1)		1.5949(17)
P(3)−F(5)		1.5967(16)
P(3)−F(6)		1.5969(16)
Si(1)−C(21)	1.872(2)	1.869(2)
Si(1)−C(11)	1.867(3)	1.882(2)
Si(1)−C(1)	1.922(3)	1.891(2)
Si(1)−O(1)		1.9225(14)
Si(1)−O(2)	2.7378(18)	1.9312(14)
Si(1)−H(1)	1.419(15)	
O(1)−H(1)	2.722(14)	
O(1′)−H(1)	2.587(14)	
O(1)−P(1)−O(1′)	116.99(10)	114.50(8)
O(1)−P(1)−O(1″)	114.32(9)	113.85(8)
O(1′)−P(1)−O(1″)	100.57(9)	103.88(8)
O(1)−P(1)−C(2)	112.65(10)	102.66(8)
O(1′)−P(1)−C(2)	105.24(11)	109.67(9)
O(1″)−P(1)−C(2)	105.72(12)	112.53(9)
O(2)−P(2)−O(2′)	116.59(14)	114.67(8)
O(2)−P(2)−O(2″)	115.67(11)	112.08(8)
O(2′)−P(2)−O(2″)	99.48(17)	104.72(8)
O(2)−P(2)−C(6)	112.28(13)	102.88(9)
O(2′)−P(2)−C(6)	104.54(15)	107.56(8)
O(2″)−P(2)−C(6)	106.88(13)	115.19(9)
C(21)−Si(1)−C(11)	121.15(13)	119.65(9)
C(21)−Si(1)−C(1)	113.79(12)	122.73(9)
C(11)−Si(1)−C(1)	111.68(11)	117.55(9)
C(21)−Si(1)−O(1)		91.68(8)
C(11)−Si(1)−O(1)		95.42(8)
C(1)−Si(1)−O(1)		85.58(7)
C(21)−Si(1)−O(2)	78.29(9)	89.55(8)
C(11)−Si(1)−O(2)	73.47(9)	92.93(8)
C(1)−Si(1)−O(2)	81.63(10)	85.08(8)
O(1)−Si(1)−O(2)		169.61(7)
P(1)−O(1)−Si(1)		119.92(8)
P(2)−O(1)−Si(1)		120.48(8)
H(1)−Si(1)−C(11)	102.7(6)	
H(1)−Si(1)−C(21)	99.7(5)	
H(1)−Si(1)−C(1)	104.8(6)	
H(1)−Si(1)−O(2)	173.5(6)	
P(1)−O(1)−H(1)	76.6(3)	
P(1)−O(1′)−H(1)	79.6(3)	
P(1)−C(2)−C(3)−C(4)		−177.11(16)
Si(1)−C(1)−C(2)−C(3)		175.88(15)

As for compound **2**, the silicon atom in **5** adopts a monocapped-tetrahedral configuration, with the O(2) atom being the capping atom at the opposite face from the hydrogen atom. This configuration can be seen as a real structure along the path tetrahedron → trigonal bipyramid (geometrical goodness[9−11] $\Delta\Sigma(\theta) = 39.4°$). The silicon atom is displaced in the direction of H(1) by 0.403(2) Å from the plane defined by C(1), C(11), C(21). The most remarkable differences between the structures of the ethoxy-substituted derivative **2** and the isopropoxy-substituted derivative **5** are (i) the Si(1)−O(2) distances (2.918(2) Å for **2**, 2.738(2) Å for **5**) and, associated with this, the P(2)−O(2) distances (1.460(2) Å for **2**, 1.469(2) Å for **5**), (ii) the C(11)−Si(1)−C(21) angles (114.7(1)° for **2**, 121.2(1)° for **5**), and (iii) that in **5** the second P=O oxygen (O1) points to H(1) in such a way that H(1) is formally bisecting the O=P−O(*i*-Pr) angle. Thus, compound **5** represents a rotamer of type **C** (Chart 1).

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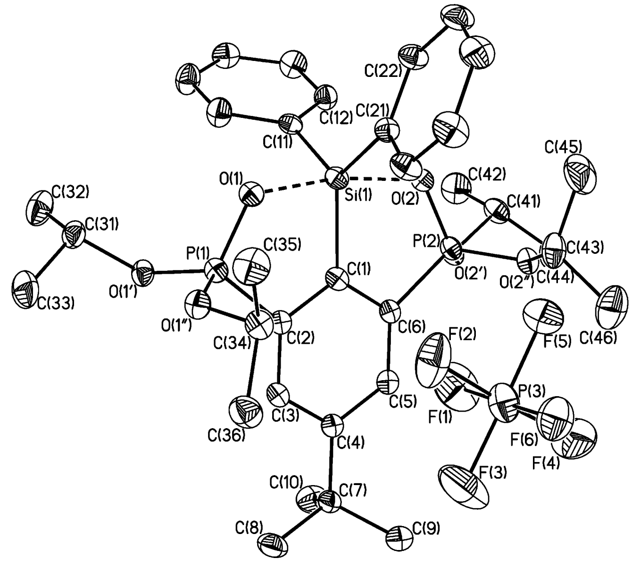

Figure 2. General view (SHELXTL) of a molecule of **6** showing 30% probability displacement ellipsoids and the atom-numbering scheme.

The variable-temperature ^{1}H and ^{31}P NMR spectra of compound **5** indicate hindered rotation about the P−C bond. Thus, the ^{31}P NMR spectrum (see the Supporting Information) at room temperature shows a sharp singlet resonance at 17.6 ppm ($\nu_{1/2}$ 2 Hz) which decoalesces at 223 K into two equally intense resonances at δ 17.8 and 18.2, indicating that rotation becomes slow on the ^{31}P NMR time scale. At 213 K each signal additionally shows a $^{4}J(^{31}P-^{31}P)$ coupling of 10 Hz. The ^{1}H NMR spectrum (see the Supporting Information) at room temperature exhibits two doublet resonances for the methyl protons of the isopropoxy groups, a singlet resonance for the *tert*-butyl protons, a singlet resonance for the Si−H proton, and a broad singlet for the OCH protons. The aromatic H3/5 protons show a broad doublet at δ 8.17. At 213 K, the signal for the methyl protons of the isopropoxy groups splits into four equally intense resonances, and the OCH− as well as the H3/5 signals each decoalesce into two equally intense resonances. No decoalescence is observed for the *tert*-butyl and the Si−H signals.

Compound **5** reacts with triphenylcarbonium hexafluorophosphate, $Ph_3C^+PF_6^-$, to give the intramolecularly coordinated triorganosiliconium hexafluorophosphate $\{4\text{-}t\text{-Bu-}2,6\text{-}[P(O)(O\text{-}i\text{-}Pr)_2]_2C_6H_2\}SiPh_2^+PF_6^-$ (**6**) as colorless crystals (Scheme 1). The molecular structure of compound **6** is shown in Figure 2, and selected geometrical data are given in Table 1.

The silicon atom shows a distorted-trigonal-bipyramidal configuration (geometrical goodness[9−11] $\Delta\Sigma(\theta) = 87.3°$) with C(1), C(11), and C(21) in equatorial and O(1) and O(2) in axial positions. The intramolecular Si(1)−O(1) and Si(1)−O(2) distances amount to 1.922(1) and 1.931(1) Å, respectively, reflecting Pauling-type bond orders[12−15] of 0.91 and 0.85. These distances are notably shorter than the corresponding distances in the [4 + 1]-coordinated triorganosilanes **2**[2] (2.918(2) Å) and **5** (2.738(2) Å). These short distances are also reflected by the α and α' angles[16] C(1)−C(2)−P(1) (110.27(15)°) and C(1)−C(6)−P(2) (109.58(14)°), being 16.3 and 11.7°, respectively, smaller than the corresponding angles in the triorganosilane **2**.[2]

In comparison with the O(1)−Sn(1)−O(2) angle in the corresponding triorganotin hexafluorophosphate $\{4\text{-}t\text{-Bu-}2,6\text{-}[P(O)(O\text{-}i\text{-}Pr)_2]_2C_6H_2\}SnPh_2^+PF_6^-$ (**4**)[3] the O(1)−Si(1)−O(2) angle in compound **6** is increased from 159.01(9) to 169.61(7)°.

The torsion angles P(1)−C(2)−C(3)−C(4) and Si(1)−C(1)−C(2)−C(3) of −177.11(16) and 175.88(15)° reveal opposite displacements of the silicon atom and the $P(O)(O\text{-}i\text{-}Pr)_2$ groups from the aromatic ring plane.

The ^{29}Si NMR spectrum of compound **6** shows a low-frequency resonance at δ −66.9. Comparable compounds are $[C_6H_3(CH_2NMe_2)_2\text{-}2,6]SiHPh^+$ (δ −29.7)[17] and $[C_6H_4(CH_2OMe)\text{-}2]_2SiH^+$ (δ −47.2).[8] The high-frequency ^{31}P NMR chemical shift of **6** at δ 28.0 is comparable with those of the related ethoxy-substituted organosilicon cation **3** (δ 29.6) and the corresponding organotin cation $\{4\text{-}t\text{-Bu-}2,6\text{-}[P(O)(O\text{-}i\text{-}Pr)_2]_2C_6H_2\}SnPh_2^+PF_6^-$ (**2**; δ 26.1).[3]

Experimental Section

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

IR spectra (cm^{-1}) were recorded on a Bruker IFS 28 spectrometer. Varian Mercury 200, Bruker DPX-300, and DRX-400 spectrometers were used to obtain ^{1}H, ^{13}C, ^{29}Si and ^{31}P NMR spectra. ^{1}H, ^{13}C, ^{29}Si, and ^{31}P NMR chemical shifts δ are given in ppm and were referenced to Me_4Si and H_3PO_4 (85%, ^{31}P). NMR spectra were recorded at room temperature unless otherwise stated. The atom numberings for compounds **5** and **6** are those given in Figures 1 and 2, respectively. Elemental analyses were performed on a LECO-CHNS-932 analyzer.

Crystallography. Intensity data for the colorless crystals of compounds **5** and **6** were collected on a Nonius KappaCCD diffractometer with graphite-monochromated Mo Kα radiation at 173 K. The data collections covered almost the whole sphere of reciprocal space with four sets at different κ angles and 509 (**5**) and 814 frames (**6**) via ω rotation ($\Delta/\omega = 1°$, **5**; $\Delta/\omega = 0.5°$, **6**) at two times 60 (**5**) and 60 s (**6**) for **1** per frame. The crystal-to-detector distances were 4.4 (**5**) and 3.4 cm (**6**). Crystal decay was monitored by repeating the initial frames at the end of data collection. On analysis of the duplicate reflections, there was no indication for any decay. The structure was solved by direct methods (SHELXS97[18]) and successive difference Fourier syntheses. Refinement applied full-matrix least-squares methods (SHELXL97).[19] The H atoms were placed in geometrically calculated positions using a riding model with U_{iso} constrained at 1.2 for non-methyl and 1.5 for methyl groups times the U_{eq} value of the carrier C atom, whereas the H atom (H(1)) (**5**) bonded to Si(1) was located in the difference Fourier map and refined isotropically. One isopropoxy group in **5** is disordered over two positions with occupancies of 0.4 (C(41′), C(43′)) and 0.6 (C(41), C(43)). Atomic scattering factors for neutral atoms and real and imaginary dispersion terms were taken from ref 20. The figures were created by SHELXTL.[21]

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Table 2. Crystallographic Data for 5 and 6

	5	6
formula	$C_{34}H_{50}O_6P_2Si$	$[C_{34}H_{49}O_6P_2Si]^+[PF_6]^-$
fw	644.77	788.73
cryst syst	monoclinic	monoclinic
cryst size, mm	0.24 × 0.24 × 0.22	0.14 × 0.12 × 0.12
space group	$P2_1/c$	$P2_1/c$
a, Å	9.630(2)	11.7014(8)
b, Å	12.454(4)	15.5567(10)
c, Å	30.096(7)	21.8031(14)
β, deg	92.830(16)	97.183(4)
V, Å^3	3605.1(16)	3937.8(4)
Z	4	4
ρ_{calcd}, Mg/m^3	1.188	1.330
μ, mm^{-1}	0.194	0.250
F(000)	1384	1656
θ range, deg	2.95−25.00	3.03−27.51
index ranges	$-11 \le h \le 11$, $-14 \le k \le 14$, $-35 \le l \le 35$	$-15 \le h \le 15$, $-20 \le k \le 20$, $-28 \le l \le 28$
no. of rflns collcd	21 013	50 518
completeness to θ_{max}	84.8	99.7
no. of indep rflns/R_{int}	5396/0.041	9036/0.042
no. of obsd rflns with $I > 2\sigma(I)$	2376	5126
no. of refined params	410	451
GOF (F^2)	0.826	0.906
R1(F) ($I > 2\sigma(I)$)	0.0393	0.0437
wR2(F^2) (all data)	0.0681	0.1119
$(\Delta/\sigma)_{max}$	0.001	<0.001
largest diff peak/hole, e/Å^3	0.200/−0.282	0.579/−0.355

Crystallographic data are given in Table 2 and selected bond distances and angles in Table 1.

[{2,6-Bis(diisopropoxyphosphonyl)-4-*tert*-butyl}phenyl]hydridodiphenylsilane (5). To a solution of 1,3-bis(diisopropoxyphosphonyl)-5-*tert*-butylbenzene (13.55 g, 29.30 mmol) in diethyl ether/*n*-hexane (250 mL, 1:1) was added dropwise, at −78 °C, LiN-*i*-Pr$_2$ in *n*-hexane/tetrahydrofuran (100 mL, 3:1, 0.34 M). The reaction mixture was stirred for 4 h at −40 °C. To the stirred solution of {[2,6-bis(diisopropoxyphosphonyl)-4-*tert*-butyl}phenyl]lithium was added dropwise a solution of chlorodiphenylsilane (6.53 g, 29.85 mmol) in diethyl ether/*n*-hexane (40 mL, 1:1) at −40 °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 this mixture extracted with diethyl ether (2 × 80 cm^3). The organic layers were combined, washed with water (3 × 150 cm^3), dried (Na$_2$SO$_4$), and concentrated under reduced pressure. Column chromatography (SiO$_2$/EtOAc) of the residue and crystallization from hexane afforded 2.13 g (12%) of **5** as a colorless solid; mp 75−77 °C. ^{1}H NMR (400.13 MHz, CD$_2$Cl$_2$): $T = 293$ K, δ 1.01 (d, $^3J(^1H-^1H) = 6.0$ Hz, 12H) and 1.17 (d, $^3J(^1H$-$^1H) = 6.0$ Hz, 12H) (C(CH$_3$)(CH$_3$)′), 1.40 (s, 9H; CH$_3$), 4.37 (unresolved, 4H; OCH (P)), 6.01 (s, $^1J(^1H-^{29}Si) = 194$ Hz, 1H; Si−H), 7.29 (m, 6H; H$_{m/p}$), 7.66 (m, 4H; H$_o$), 8.17 (d, $^3J(^1H-^{31}P) = 13.6$ Hz, 2H; H$_{3,5}$); $T = 213$ K, δ 0.74 (d, $^4J(^1H-^{31}P) = 5.0$ Hz, 6H), 1.01 (d, $^4J(^1H-^{31}P) = 5.0$ Hz, 6H), 1.11 (d, $^4J(^1H-^{31}P) = 3.0$ Hz, 6H), and 1.18 (d, $^4J(^1H-^{31}P) = 3.0$ Hz, 6H) (C(CH$_3$)(CH$_3$)′), 1.32 (s, 9H; CH$_3$), 3.76 (d, $^3J(^1H-^{31}P) = 5.0$ Hz, 2H) and 4.72 (d, $^3J(^1H-^{31}P) = 5.0$ Hz, 2H) (OCH (P)), 5.87 (s, $^1J(^1H-^{29}Si) = 192$ Hz, 1H; Si−H), 7.29 (m, 6H; H$_{m/p}$), 7.53 (m, 4H; H$_o$), 7.84 (d, $^3J(^1H-^{31}P) = 14.3$ Hz, 1H) and 8.28 (d, $^3J(^1H-^{31}P) = 14.3$ Hz, 1H) (H$_{3,5}$). ^{13}C{^{1}H} NMR (100.63 MHz, CDCl$_3$): δ 23.48 (d, $^3J(^{13}C-^{31}P) = 2.0$ Hz, 2C) and 23.50 (d, $^3J(^{13}C-^{31}P) = 2.0$ Hz, 2C) (C(*C*H$_3$)(*C*H$_3$)′), 23.74 (d, $^3J(^{13}C-^{31}P) = 2.0$ Hz, 2C) and 23.76 (d, $^3J(^{13}C-^{31}P) = 2.0$ Hz, 2C) (C(*C*H$_3$)(*C*H$_3$)′), 30.8 (s, 3C; C(*C*H$_3$)$_3$), 34.8 (s, 1C; *C*(CH$_3$)$_3$), 70.63 (d, $^2J(^{13}C-^{31}P) = 2.5$ Hz, 2C) and 70.66 (d, $^2J(^{13}C-^{31}P) = 2.5$ Hz, 2C) (O*C*H), 127.0 (s, 4C; C$_m$), 128.2 (s, 2C; C$_p$), 133.9 (unresolved, 2C; *C*$_{3,5}$), 135.8 (s, 6C; C$_o$), 136.1 (s, 2C; C$_i$), 139.2 (dd, $^1J(^{13}C-^{31}P) = 189$ Hz, $^3J(^{13}C-^{31}P) = 18$ Hz, 2C; C$_{2,6}$), 140.6 (t, $^2J(^{13}C-^{31}P) = 20$ Hz, 1C; C$_1$), 151.4 (t, $^3J(^{13}C-^{31}P) = 13$ Hz, 1C; C$_4$). ^{31}P{^{1}H} NMR (161.98 MHz, CD$_2$Cl$_2$): $T = 293$ K, δ 17.6; $T = 213$ K, δ 17.8 (d, $^4J(^{31}P-^{31}P) = 10$ Hz), 18.2 (d, $^4J(^{31}P-^{31}P) = 10$ Hz). ^{29}Si NMR (79.49 MHz, CDCl$_3$): δ −26.9 (dt, $^1J(^{29}Si-^1H) = 195$ Hz, $J(^{29}Si-^{31}P) = 5$ Hz). IR (KBr): $\tilde{\nu}$(Si−H) 2190, $\tilde{\nu}$(P=O) 1251 cm^{-1}. Anal. Calcd for $C_{34}H_{50}O_6P_2Si$: C, 63.3; H, 7.8. Found: C, 63.5; H, 8.1.

[{2,6-Bis(diisopropoxyphosphonyl)-4-*tert*-butyl}phenyl]diphenylsilyl Hexafluorophosphate (6). To a solution of [{2,6-bis(diisopropoxyphosphonyl)-4-*tert*-butyl}phenyl]hydridodiphenylsilane (**2**; 0.53 g, 0.86 mmol) in toluene (15 mL) was added, at 0 °C, triphenylcarbonium hexafluorophosphate (0.34 g, 0.87 mmol). After the reaction mixture was stirred for 3 days at room temperature, the precipitate was filtered and half of the solvent was evaporated. Crystallization from toluene at 0 °C afforded 0.39 g (57%) of **6** as colorless crystals, mp 135 °C. ^{1}H NMR (200.13 MHz, C$_6$D$_6$): δ 0.73 (d, $^3J(^1H-^1H) = 6.2$ Hz, 12H) and 0.82 (d, $^3J(^1H-^1H) = 6.2$ Hz, 12H) (C(CH$_3$)(CH$_3$)′), 1.08 (s, 9H; CH$_3$), 4.32 (septet, $^3J(^1H-^1H) = 6.2$ Hz, $^3J_{POCH}(^1H-^{31}P) = 6.2$ Hz, 2H) and 4.36 (septet, $^3J(^1H-^1H) = 6.2$ Hz, $^3J_{POCH}(^1H-^{31}P) = 6.2$ Hz, 2H) (OCH), 6.89 (m, 6H; H$_{m/p}$), 7.66 (m, 4H; H$_o$), 8.12 (d, $^3J(^1H-^{31}P) = 14$ Hz, 2H; H$_{3,5}$). ^{13}C{^{1}H} NMR (100.63 MHz, C$_6$D$_6$): δ 23.34 (d, $^3J(^{13}C-^{31}P) = 2.2$ Hz, 2C), 23.36 (d, $^3J(^{13}C-^{31}P) = 2.2$ Hz, 2C), 23.47 (d, $^3J(^{13}C-^{31}P) = 2.2$ Hz, 2C), and 23.49 (d, $^3J(^{13}C-^{31}P) = 2.2$ Hz, 2C) (C(*C*H$_3$)(*C*H$_3$)′), 31.0 (s, 3C; C(*C*H$_3$)$_3$), 35.9 (unresolved, 1C; *C*(CH$_3$)$_3$), 77.99 (d, $^2J(^{13}C-^{31}P) = 3$ Hz, 1C), 78.02 (d, $^2J(^{13}C-^{31}P) = 3$ Hz, 1C), 78.06 (d, $^2J(^{13}C-^{31}P) = 3$ Hz, 1C), and 78.09 (d, $^2J(^{13}C-^{31}P) = 3$ Hz, 1C) (O*C*H), 129.4 (s, 4C; C$_m$), 129.8 (s, 2C; C$_p$), 132.1 (dd, $^1J(^{13}C-^{31}P) = 183$ Hz, $^3J(^{13}C-^{31}P) = 18$ Hz, 2C; C$_{2,6}$), 132.4 (unresolved, 2C; C$_{3,5}$), 135.0 (s, 4C; C$_o$), 135.5 (t, $J(^{13}C-^{31}P) = 5$ Hz, 2C; C$_i$), 153.1 (t, $^2J(^{13}C-^{31}P) = 22$ Hz, 1C; C$_1$), 159.6 (t, $^3J(^{13}C-^{31}P) = 13$ Hz, 1C; C$_4$). ^{31}P{^{1}H} NMR (81.01 MHz, C$_6$D$_6$): δ 27.97, −142.54 (septet, PF$_6^-$). ^{29}Si NMR (59.63 MHz, toluene/D$_2$O-capillary): δ −66.9. Anal. Calcd for $C_{34}F_6H_{49}O_6P_3Si$: C, 51.4; H, 6.2. Found: C, 51.8; H, 6.1.

Supporting Information Available: Tables giving X-ray crystallographic data for **5** and **6** and figures giving variable-temperature ^{31}P and ^{1}H NMR spectra for **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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