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A Cyclic Phosphonium Ion with an Asymmetrically Substituted Selenide-Stabilized Silicon Center: Synthesis, Structure, and Substituent Effects

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A new heterocyclic four-membered CPSeSi cation was synthesized in its racemic form by $B(C_6F_5)_3$-mediated ring-closing reaction starting from the hydrosilane precursor. The cation has an asymmetrically substituted silicon center, which is stabilized by a selenium–silicon bond. The phosphonium hydroborate and its precursor were characterized by single-crystal X-ray diffraction analysis and NMR spectroscopy. ^{77}Se, ^{31}P, and ^{29}Si NMR spectroscopic parameters proved to be sensitive probes for determining small electronic changes around the silylium-type center. Density functional theory (DFT) calculations of the ring-opening energy of the selenium-based cation gave insight into the stability of the Se–Si bond and revealed a stronger intramolecular stabilization of the silicon atom compared to a coordinating phosphane sulfide function. For the first time, the influence of a C_6F_5 group at the silicon atom of these type of cations was also investigated, showing a slightly increased stabilization of the Se–Si linkage in the cyclic selenium-based cation.

Introduction

Small inorganic cyclic cations play an important role in exploring new bonding concepts and reactivities.[1] Donor functions containing chalcogen atoms have emerged as promising tools for taming the Lewis acidity of cationic silicon centers.[2] The intramolecular stabilization by formation of silicon–chalcogen interactions also opened up new perspectives for fixing defined stereochemical configurations on asymmetrically substituted, Lewis acidic silicon centers.[3] In recent years, systematic investigations of the chiral memory of stereogenic silylium-type silicon centers have been carried out.[4] In this context, phosphane chalcogenide functions (P$^+$–Ch$^-$; Ch = chalcogen) turned out to be powerful stabilizing moieties because particularly strong Ch–Si bonds can be formed through intramolecular coordination to silylium-type centers.[5] The P$^+$–Ch$^-$ group has been shown to guarantee the configurational integrity of the stereogenic Lewis acidic silicon center during the sequence of ring-closure to a four-membered cyclic cation and subsequent ring-opening.[5a] Since the stereochemical consistency at the stereogenic Lewis acidic silicon center is a mandatory criterion for applications of optically pure chiral cations in asymmetric cation-directed catalysis,[6] knowledge of electronic and steric effects, and the influence of the chalcogen atom on the strength of the intramolecular stabilization of the silicon atom in chalcogen-based cyclic cations is needed.[5c]

Herein, we describe the synthesis and structural characterization of a new selenium-based cation with an asymmetrically substituted silicon center in its racemic form. The influence of a silicon-bound phenyl and perfluorinated aryl substituent on the strength of the intramolecular Ch–Si coordination was quantified by density functional theory (DFT) calculations and discussed in the context of our previous studies on the influence of substituents on the ring stability. NMR spectroscopic parameters determined for the new phosphane selenide-stabilized cation served as a useful diagnostic tool to estimate the electronic structure and the stabilization of the silylium-type center.

Results and Discussion

The synthesis of the selenium-based cyclic phosphonium cation **4** was achieved in three steps following a previously reported synthetic route (Scheme 1).[5c] First, (di-*tert*-butylphosphanyl)methyllithium was reacted with *tert*-butyl-chlorophenylsilane (**1**) to give the phosphorus(III) precursor **2** in

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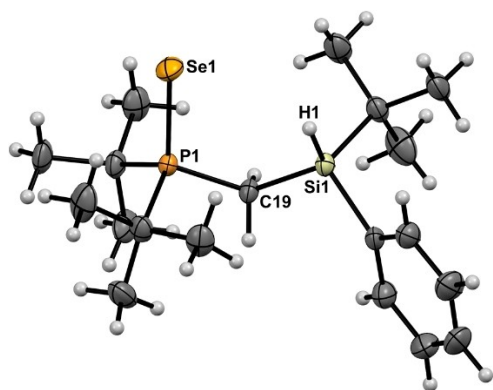E-mail: jonathan.bauer@ur.de
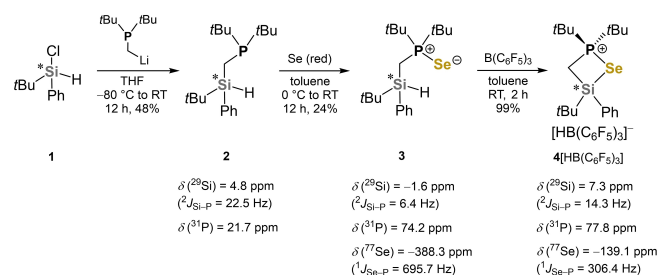
Scheme 1. Synthetic route towards the racemic selenium-based heterocyclic phosphonium hydroborate **4**[HB(C$_6$F$_5$)$_3$].

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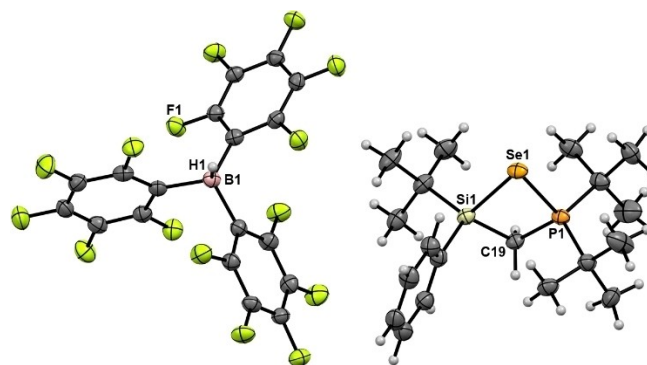**Chemistry Europe**
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a moderate yield of 48%.[7] Oxidation with red selenium afforded phosphane selenide **3** in 24% yield of pure crystalline material. Compound **3** crystallized in the monoclinic crystal system, space group $P2_1/c$ (Figure 1 and Table 1). Cation formation by ring-closing hydride abstraction was accomplished with tris(pentafluorophenyl)borane and smoothly led to the phosphonium hydroborate **4**[HB(C_6F_5)$_3$] in the form of a crystalline material. The molecular structure of **4**[HB(C_6F_5)$_3$] was

determined by single-crystal X-ray diffraction analysis (triclinic crystal system, space group $P\bar{1}$) (Figure 2 and Table 2).

The ^{77}Se NMR spectroscopic parameters are affected in the same way as previously described for all-*tert*-butyl-substituted cyclic CPSeSi cations.[5c] Ring formation upon hydride abstraction led to a significant downfield shift of the ^{77}Se NMR signal from -388.3 ppm in compound **3** to -139.1 ppm in the ion pair **4**[HB(C_6F_5)$_3$] [$\Delta\delta(^{77}$Se$) = 249.2$ ppm]. At the same time, the $^1J_{Se-P}$ coupling constant decreases by 56% from 695.7 Hz to

Figure 1. Molecular structure of compound **3** in the crystal (displacement ellipsoids set at the 50% probability level). Selected bond lengths /Å and angles/° (at 123 K): P(1)-Se(1) 2.1262(6), P(1)-C(19) 1.819(2), Si(1)-C(19) 1.905(2), Se(1)-P(1)-C(19) 112.62(7), P(1)-C(19)-Si(1) 119.1(1).

Figure 2. Molecular structure of ion pair **4**[HB(C_6F_5)$_3$] in the crystal (displacement ellipsoids set at the 50% probability level). Selected bond lengths /Å and angles/° (at 123 K): P(1)-Se(1) 2.2204(5), P(1)-C(19) 1.803(3), Si(1)-C(19) 1.894(3), Si(1)-Se(1) 2.3416(6), P(1)-C(19)-Si(1) 97.2(1), P(1)-Se(1)-Si(1) 74.82(1), C19-Si(1)-Se(1) 90.15(9), C19-P(1)-Se(1) 96.55(9).

Table 1. Crystal data and structure refinement of compound **3**.	
Formula	$C_{19}H_{35}PSeSi$
M/g mol^{-1}	401.49
T/K	123(1)
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	10.3720(2)
b/Å	15.5409(3)
c/Å	13.7454(2)
α/°	90
β/°	103.546(2)
γ/°	90
V/Å^3	2153.99(7)
Z	4
Z'	1
ρ/g cm^{-3}	1.238
μ/mm^{-1}	3.543
Crystal size/mm^3	0.33×0.06×0.03
λ/Å	1.54184
Radiation type	Cu K$_\alpha$
θ range/°	4.364–73.483
Reflections, collected	9702
Reflections, independent	4237
Reflections with I > 2(I)	3663
R_{int}	0.0305
Parameters	212
Restraints	0
GooF	1.038
wR_2 (all data)	0.0829
wR_2	0.0787
R_1 (all data)	0.0404
R_1	0.0327
$\Delta\rho_{fin}$ (max/min) /e Å^{-3}	0.608/−0.373

Table 2. Crystal data and structure refinement of compound **4**[HB(C_6F_5)$_3$].	
Formula	$C_{37}H_{35}BF_{15}PSeSi$
M/g mol^{-1}	913.48
T/K	123(1)
Crystal system	Triclinic
Space group	$P\bar{1}$
a/Å	11.4288(4)
b/Å	13.4171(4)
c/Å	14.2558(4)
α/°	98.249(3)
β/°	103.401(3)
γ/°	113.040(3)
V/Å^3	1888.71(11)
Z	2
Z'	1
ρ/g cm^{-3}	1.606
μ/mm^{-1}	2.167
Crystal size/mm^3	0.39×0.11×0.07
λ/Å	1.39222
Radiation type	Cu K$_\beta$
θ range/°	2.981–69.006
Reflections, collected	19206
Reflections, independent	9323
Reflections with I > 2(I)	8156
R_{int}	0.0317
Parameters	537
Restraints	12
GooF	1.025
wR_2 (all data)	0.1020
wR_2	0.0973
R_1 (all data)	0.0454
R_1	0.0388
$\Delta\rho_{fin}$ (max/min) /$e\cdot$Å^{-3}	0.613/−0.567

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306.4 Hz, which is typical for cationic four-membered CPSeSi ring systems.[5c] The somewhat stronger highfield shift of the ^{77}Se NMR signal of the *tert*-butylphenyl-patterned cation **4** compared to the di-*tert*-butyl derivatives[5c] indicates slightly different electronic situations around the silicon atom. ^{29}Si NMR spectroscopy shows a doublet at 7.3 ppm with a $^2J_{Si-P}$ coupling constant of 14.3 Hz. While the change in the Si–P coupling constant $[\Delta(^2J_{Si-P}) = 7.9$ ppm] between precursor **3** and cation **4** follows the expected trend with increasing phenyl group substitution at the silicon center in four-membered CPChSi cations,[5c] the ^{29}Si NMR signal is shifted slightly to higher field compared to the corresponding sulfur-based system that was previously reported.[5a] This is already indicative of a slightly stronger intramolecular stabilization in the selenium-based cation **4**. The influence of the newly formed selenium–silicon bond on the ^{31}P NMR chemical shift is negligible, changing from 74.2 ppm (**3**) to 77.8 ppm (**4**), which reflects the observed deshielding properties of the phosphorus atom in phosphane chalcogenide-based cyclic cations.[5c]

With an angular sum of 358.7°, the four-membered cycle deviates slightly from the ideal planar geometry, which is indeed found in the symmetrically substituted all-*tert*-butyl analogue.[5c] This ring distortion is designed to counteract an unfavorable intramolecular steric repulsion between the two ecliptically arranged *tert*-butyl groups on the silicon and phosphorus atom, thereby reducing the ring strain in the Si(*t*Bu)Ph-structured cation **4** (Figure 2).

Thermochemical calculations on the M062X/6-311+G(d,p) level of theory[8] allowed to quantify the influence of the chalcogen atom and the nature of the aryl substituent at the silicon atom (Figure 3). The ring-opening energy for the selenide-stabilized cation **4** was calculated to be $+44.0$ kcal mol^{-1}. This is a noticeable increase in energy compared to the previously reported sulfur-based Si(*t*Bu)Ph-patterned cation,[5a] which would require an energy of $+42.3$ kcal mol^{-1} for a hypothetical ring opening (Figure 3).
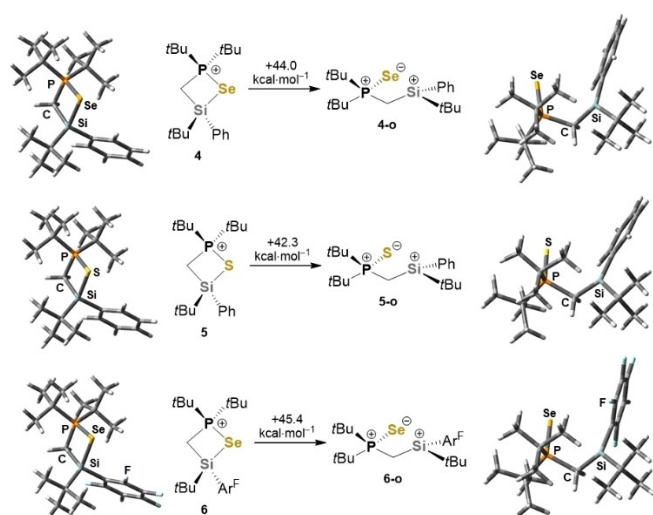
The advantage of the described ring-closing reaction is the efficient anchimeric assistance of the P$^+$–Ch$^-$ group and the resulting strong Ch–Si bond, while B(C$_6$F$_5$)$_3$ simultaneously abstracts the hydride ion from the silicon center. This hydride abstraction should also accept the presence of strongly electron-withdrawing groups on the silicon atom, since "free" silylium ions are never formed during this process. Therefore, we investigated for the first time the influence of a silicon-bound perfluorinated aryl group on the stability of the four-membered cyclic cation using DFT calculations in order to pave the way towards particularly stable chiral cations that still exhibit Lewis acidic sites for cation-directed activation. The calculation of the hypothetic ring-opening reaction of cyclic cation **6** to the open form **6-o** shows that a C$_6$F$_5$ group indeed increases the ring-opening energy (Figure 3). However, this increase in energy is lower than expected by only 1.4 kcal mol^{-1} with respect to the phenyl-substituted cation **4**.

Conclusions

This work complements previous studies on silicon-chiral phosphonium ions[5a] and on structural influences in four-membered CPChSi cations.[5c] The new cyclic selenium-based phosphonium hydrobrate **4**[HB(C$_6$F$_5$)$_3$] with an asymmetrically substituted silicon center was synthesized in its racemic form and fully characterized by X-ray crystallography and multinuclear NMR spectroscopy. This cation represents a promising candidate for providing further stereochemically pure Lewis acids. The selenium atom serves as additional useful NMR sensitive probe that is directly attached to the silylium-type center to determine the electronic nature of the small cyclic cations. In general, the calculations show that changing the chalcogenide or the electronic structure of the aryl ring results in only minor changes in the ring-opening energy. As one result of the investigation, the selenide-stabilized silicon center leads to an increased stabilization of the four-membered ring compared to the sulfur-based analogue. This is of significance in terms of preserving the stereochemical integrity of Lewis acidic silicon centers in small ring systems. In addition, the influence of a perfluorinated aryl ring on the thermochemical properties of the cyclic cation was studied, showing that a C$_6$F$_5$ group leads to an additional increase in the stabilization energy of the Se–Si linkage, albeit smaller than expected.

Figure 3. Gibbs energies (ΔG) for the ring-opening as a measure of the stabilization provided by the intramolecular coordination of the phosphane chalcogenide function to the silylium center, calculated on the M062X/6-311+G(d,p) level of theory.[8] Ar^F = C$_6$F$_5$.

Experimental Section

General Remarks. All experiments were performed in an inert atmosphere of purified nitrogen by using standard Schlenk techniques or an MBraun Unilab 1200/780 glovebox. Glassware was heated at 140 °C prior to use. Dichloromethane, pentane, tetrahydrofuran (THF), and toluene were dried and degassed with an MBraun SP800 solvent purification system. *tert*-Butylchlorophenylsilane (**1**),[5b] (di-*tert*-butylphosphanyl)methyllithium,[5b,9] and tris-(pentafluorophenyl)borane[10] were synthesized according to reported literature procedures. Red selenium was kindly provided by the Scheer group. CD$_2$Cl$_2$ ($\geq$99.8%, Fluorochem) used for NMR

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spectroscopy was dried over CaH_2. NMR spectra were either recorded on a Bruker Avance 400 (400.13 MHz) or on a Bruker Avance III HD 400 (400.13 MHz) at 25 °C. Chemical shifts (δ) are reported in parts per million (ppm). ^{1}H and ^{13}C{^{1}H} NMR spectra are referenced to tetramethylsilane (SiMe$_4$, $\delta = 0.0$ ppm) as external standard, with the deuterium signal of the solvent serving as internal lock and the residual solvent signal as an additional reference. ^{11}B{^{1}H}, ^{19}F{^{1}H}, ^{31}P{^{1}H}, ^{77}Se{^{1}H}, and ^{29}Si{^{1}H} NMR spectra are referenced to BF$_3$·OEt$_2$, CFCl$_3$, 85 % H$_3$PO$_4$, SeMe$_2$, and SiMe$_4$, respectively. Hydrogen, carbon, and fluorine atoms of aromatic rings are denoted as H_{Ph}, C_{Ph}, C_{Ar} or specified with the subscripts ipso, ortho, meta, and para. For the assignment of the multiplicities, the following abbreviations are used: s = singlet, bs = broad singlet, d = doublet, bd = broad doublet, bq = broad quartet, m = multiplet. High-resolution mass spectrometry was carried out on a Jeol AccuTOF GCX and an Agilent Q-TOF 6540 UHD spectrometer. Elemental analyses were performed on a Vario MICRO cube apparatus. The original NMR spectra can be found in the Supporting Information.

Single-Crystal X-Ray Diffraction Analysis. The crystals of compounds **3** and **4**[HB(C$_6$F$_5$)$_3$] were selected and measured on a GV50 diffractometer equipped with a TitanS2 detector. The crystals were kept at $T = 123(1)$ K during data collection. Data collection and reduction were performed with CrysAlisPro, Version 1.171.39.46 (**3**) and Version 1.171.41.89a {**4**[HB(C$_6$F$_5$)$_3$]}.[11] For all compounds, a numerical absorption correction based on Gaussian integration over a multifaceted crystal model and an empirical absorption correction using spherical harmonics as implemented in SCALE3 ABSPACK scaling algorithm were applied. Using Olex2,[12] the structures were solved with ShelXT[13] and a least-square refinement on F^2 was carried out with ShelXL.[14] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms at the carbon atoms were located in idealized positions and refined isotropically according to the riding model. Figures 1 and 2 were created using Mercury 4.1.0.[15]

Compound **3**: The asymmetric unit contains one molecule. The hydrogen atom at the silicon atom was located from the difference Fourier map and refined without restraints.

Compound **4**[HB(C$_6$F$_5$)$_3$]: The asymmetric unit contains one ion pair. The CH$_2$ group and the selenium atom of the four-membered cycle are disordered over two positions and superimpose each other in the ratio 95:5. The restraints SIMU, SADI, and DFIX were applied to model this disorder. The hydrogen atom at the boron atom was located in an idealized position.

Deposition Numbers 2253440 (for **3**) and 2253441 {for **4**[HB(C$_6$F$_5$)$_3$]} contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

DFT Calculations. Optimization in the gas phase and additional harmonic vibrational frequency analyses were performed with the software package Gaussian 09 (Revision E.01) on the M062X/6-311+G(d,p) level of theory without symmetry restrictions.[8] The GJF input files and the figures of the optimized structures were created with the program GaussView version 5.0.9.[16] For the ground state structures, the vibrational frequency analysis showed no imaginary frequency in the harmonical approximation. Ring-opening energies (ΔG) are given based on the sum of electronic and thermal free energies (Gibbs energies) at 298.15 K in kcal mol^{-1}. The total electronic energies (SCF), the sum of electronic and zero-point energies (ZPE), the sum of electronic and thermal free energies (Gibbs energies) at 298.15 K, and the Cartesian coordinates of the calculated systems can be found in the Supporting Information. The Hartree units were converted as follows:[17] 1 hartree = 2625.4995 kJ mol^{-1}, 1 cal = 4.184 J.

Syntheses. *Di-tert-butyl[(tert-butylphenylsilyl)methyl]phosphane* (**2**). *tert*-Butylchlorophenylsilane (**1**) (1.21 g, 6.1 mmol, 1.0 equiv.) was added to a freshly prepared solution of (di-*tert*-butylphosphanyl)methyllithium (1.01 g, 6.1 mmol, 1.0 equiv.) in THF (10 mL) at −80 °C via syringe. The reaction mixture was allowed to stir at room temperature for 12 h. Then, all volatiles were removed in vacuo and the residue dissolved in pentane. The resulting suspension was filtered and the solids washed with pentane (3× 5 mL). All volatiles of the filtrate were removed in vacuo and the resulting oil was purified via Kugelrohr distillation (85 °C oven temperature, $1.0 \cdot 10^{-3}$ mbar). Di-*tert*-butyl[(*tert*-butylphenylsilyl)methyl]phosphane (**2**) was obtained as a colorless oil. Yield: 935 mg (2.90 mmol, 48 %). ^{1}H NMR (400.30 MHz, CD$_2$Cl$_2$, 298 K): δ 0.97 [s, 9H, SiC(CH$_3$)$_3$], 1.02 [d, $^3J_{P-H}$ = 10.7 Hz, 9H, PC(CH$_3$)$_3$], 1.14 [d, $^3J_{P-H}$ = 10.7 Hz, 9H, PC(CH$_3$)$_3$], 4.22 (m, 1H, SiH), 7.32–7.40 (m, 3H, H_{Ph}), 7.55–7.57 (m, 2H, H_{Ph}). ^{13}C{^{1}H} NMR (100.66 MHz, CD$_2$Cl$_2$, 298 K): δ −0.8 (d, $^1J_{C-P}$ = 42.9 Hz, SiCH$_2$P), 18.1 [d, $^3J_{C-P}$ = 6 Hz, SiC(CH$_3$)$_3$], 27.4 [s, SiC(CH$_3$)$_3$], 29.6 [d, $^2J_{C-P}$ = 14.1 Hz, PC(CH$_3$)$_3$], 29.8 [d, $^2J_{C-P}$ = 13.9 Hz, PC(CH$_3$)$_3$], 32.0 [d, $^1J_{C-P}$ = 25.3 Hz, PC(CH$_3$)$_3$], 32.3 [d, $^1J_{C-P}$ = 24.5 Hz, PC(CH$_3$)$_3$], 127.93 (s, CH$_{meta}$), 129.61 (s, CH$_{para}$), 135.2 (d, $^3J_{C-P}$ = 2.7 Hz, C$_{ipso}$), 136.0 (s, CH$_{ortho}$). ^{29}Si{^{1}H} NMR (79.49 MHz, CD$_2$Cl$_2$, 298 K): δ 4.8 (d, $^2J_{Si-P}$ = 22.5 Hz). ^{31}P{^{1}H} NMR (162.04 MHz, CD$_2$Cl$_2$, 298 K): δ 21.7 (s). HR(ESI+)-MS: Calcd m/z for C$_{19}$H$_{36}$PSi [M+H]$^+$: 323.23. Found: 323.2308. CHN Analysis: Calcd for C$_{19}$H$_{35}$PSi: C, 69.09; H, 10.55. Found for C$_{19}$H$_{35}$PSi(CH$_2$Cl$_2$)$_{0.125}$: C, 70.75; H, 10.94.

*Di-tert-butyl[(tert-butylphenylsilyl)methyl]phosphane selenide (**3**)*. Di-*tert*-butyl[(*tert*-butylphenylsilyl)methyl]phosphane (**2**) (359 mg, 1.1 mmol, 1.0 equiv.) was added to a solution of red selenium (90 mg, 1.1 mmol, 1.0 equiv.) in toluene (5 mL) at 0 °C via syringe. The reaction mixture was allowed to stir at room temperature for 12 h. Then, all volatiles were removed in vacuo and the residue was extracted with pentane (3×5 mL). Colorless crystals of compound **3** suitable for single-crystal X-ray diffraction analysis were obtained by recrystallization from pentane at 0 °C. Yield: 108 mg (0.27 mmol, 24 %). ^{1}H NMR (400.30 MHz, CD$_2$Cl$_2$, 298 K): δ 0.96 [s, 9H, SiC(CH$_3$)$_3$], 1.21 [d, $^3J_{P-H}$ = 15.4 Hz, 9H, PC(CH$_3$)$_3$], 1.39 [d, $^3J_{P-H}$ = 15.1 Hz, 9H, PC(CH$_3$)$_3$], 1.68 [ddd (ABX), J_1 = 4.4 Hz, J_2 = 14.2 Hz, J_3 = 54.1 Hz, 2H, SiCH$_2$P], 4.56 (m with satellites, $^3J_{H-P}$ = 3.9 Hz, $^4J_{H-Se}$ = 104.5 Hz, 1H, SiH), 7.33–7.42 (m, 3H, H_{Ph}), 7.56–7.58 (m, 2H, H_{Ph}). ^{13}C{^{1}H} NMR (100.66 MHz, CD$_2$Cl$_2$, 298 K): δ 4.2 (d, $^1J_{C-P}$ = 26.3 Hz, SiCH$_2$P), 17.8 [d, $^3J_{C-P}$ = 4.5 Hz, SiC(CH$_3$)$_3$], 27.4 [s, SiC(CH$_3$)$_3$], 28.0 [dd, $^2J_{C-P}$ = 1.8 Hz, $^2J_{C-P}$ = 5.8 Hz, PC(CH$_3$)$_3$], 37.8 [d, $^1J_{C-P}$ = 34.1 Hz, PC(CH$_3$)$_3$], 38.5 [d, $^3J_{C-P}$ = 34.1 Hz, PC(CH$_3$)$_3$], 128.1 (s, C$_{Ph}$), 129.8 (s, C$_{Ph}$), 134.8 (s, C$_{Ph}$), 135.8 (d, C$_{Ph}$). ^{29}Si{^{1}H} NMR (79.49 MHz, CD$_2$Cl$_2$, 298 K): δ −1.6 (d, $^2J_{Si-P}$ = 6.4 Hz). ^{31}P{^{1}H} NMR (162.04 MHz, CD$_2$Cl$_2$, 298 K): δ 74.2 (s, $^1J_{P-Se}$ = 693.5 Hz). ^{77}Se{^{1}H} NMR (76.31 MHz, CD$_2$Cl$_2$, 298 K): δ −388.3 (d, $^1J_{Se-P}$ = 695.7 Hz). HR(ESI+)-MS: Calcd m/z for C$_{19}$H$_{36}$PSeSi [M+H]$^+$: 403.1489. Found: 403.1492. CHN Analysis: Calcd for C$_{19}$H$_{35}$PSeSi: C, 56.84; H, 8.79. Found: C, 56.39; H, 8.35.

*Compound **4**[HB(C$_6$F$_5$)$_3$]*. Compound **3** (48 mg, 0.12 mmol, 1.0 equiv.) and tris(pentafluorophenyl)borane (61 mg, 0.12 mmol, 1.0 equiv.) were dissolved in toluene (2 mL) at room temperature. The solution was stirred at room temperature for 2 h. Then, the resulting biphasic solution was fully dried in vacuo and the residue washed with pentane (2×5 mL), yielding compound **4**[HB(C$_6$F$_5$)$_3$] as a white solid (112 mg, 0.12 mmol, 99 %). Colorless crystals of compound **4**[HB(C$_6$F$_5$)$_3$] suitable for single-crystal X-ray diffraction analysis were

obtained by vapor diffusion of pentane into the biphasic mixture of **4**[HB(C$_6$F$_5$)$_3$] and toluene. ^{1}H NMR (400.30 MHz, CD$_2$Cl$_2$, 298 K): δ 1.09 [s, 9H, SiC(CH$_3$)$_3$], 1.22 [d, $^3J_{P-H}=19.0$ Hz, 9H, PC(CH$_3$)$_3$], 1.55 [d, $^3J_{P-H}=19.1$ Hz, 9H, PC(CH$_3$)$_3$], 2.7 [ddd (ABX), $J_1=13.3$ Hz, $J_2=16.0$ Hz, $J_3=29.0$ Hz, 2H, SiCH$_2$P], 3.62 [bq, $^1J_{B-H}=81.0$ Hz, 1H, BH], 7.49–7.52 [m, 2H, H$_{Ph}$], 7.56–7.57 [m, 1H, H$_{Ph}$], 7.61–7.63 [m, 2H, H$_{ar}$]. ^{13}C{^{1}H} NMR (100.66 MHz, CD$_2$Cl$_2$, 298 K): δ 8.5 (d, $^1J_{C-P}=19.2$ Hz, SiCH$_2$P), 22.2 (s, SiC(CH$_3$)$_3$), 25.2 (s, SiC(CH$_3$)$_3$), 26.8 [d, $^2J_{C-P}=2.3$ Hz, PC(CH$_3$)$_3$], 27.0 [d, $^2J_{C-P}=2.3$ Hz, PC(CH$_3$)$_3$], 39.7 [d, $^1J_{C-P}=17.7$ Hz, PC(CH$_3$)$_3$], 41.1 [d, $^1J_{C-P}=15.4$ Hz, PC(CH$_3$)$_3$], 128.4 (s, C$_{Ph}$), 129.3 (s, C$_{Ph}$), 132.3 (s, C$_{Ph}$), 134.0 (s, C$_{Ph}$), 137.1 (bd, $^1J_{C-F}=244.6$ Hz, C$_{Ar}$), 148.6 (bd, $^1J_{C-F}=229.1$ Hz, C$_{Ar}$). ^{29}Si{^{1}H} NMR (79.49 MHz, CD$_2$Cl$_2$, 298 K): δ 7.3 (d, $^2J_{Si-P}=14.3$ Hz; the $^1J_{Si-Se}$ coupling constant could not be determined due to the low signal-to-noise ratio). ^{31}P{^{1}H} NMR (162.04 MHz, CD$_2$Cl$_2$, 298 K): δ 77.8 (s, $^1J_{P-Se}=306.3$ Hz). ^{77}Se{^{1}H} NMR (76.31 MHz, CD$_2$Cl$_2$, 298 K): δ −139.1 (d, $^1J_{Se-P}=306.4$ Hz; the $^1J_{Se-Si}$ coupling constant could not be determined due to the low signal-to-noise ratio). ^{19}F{^{1}H} NMR (376.66 MHz, CD$_2$Cl$_2$, 298 K): δ −167.3 (bs, 6F, CF$_{meta}$), −164.5 (bs, 3F, CF$_{para}$), −133.7 (bs, 6F, CF$_{ortho}$). ^{11}B{^{1}H} NMR (128.43 MHz, CD$_2$Cl$_2$, 298 K): δ −25.6 (bs). HR(FD)-MS: Calcd m/z for C$_{19}$H$_{36}$OPSeSi [Cation]$^+$: 401.1333. Found: 818.2512 [C$_{38}$H$_{68}$OP$_2$Se$_2$Si$_2$]; the compound hydrolyzed during the measurement.

Supporting Information Summary

Original NMR spectra and details on quantum chemical calculations can be found in the Supporting Information.

Conflict of Interests

The corresponding author is member of the Early Career Advisory Board of ChemistrySelect.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

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