

Silyl- and Germyl-Substituted Diorganophosphonites

Thomas D. Hettich,^[a] Richard Rudolf,^[a] Nicholas Birchall,^[a] Martin Nieger,^[b] and Dietrich Gudat*^[a]Dedicated to Professor Rainer Streubel on his 65th birthday.

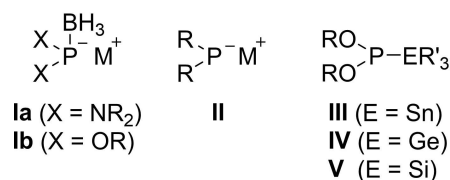
Reactions of metalated diorganophosphonite boranes with triorganosilyl and -germyl halides provided borane adducts of diorgano(teteryl)phosphonites. Further treatment with excess Et₃N or DABCO yielded the borane-free species (RO)₂P-ER'₃ (E = Si, Ge; R, R' = alkyl, aryl). The products of all reactions were characterized by elemental analyses and NMR data, and in selected cases by MS and single-crystal XRD studies.

Reactions of selected ligands with Ni(CO)₄ and selenium were shown to produce Ni(CO)₃-complexes or diorgano(teteryl)phosphonoselenoates (RO)₂(R'₃E)P=Se, respectively, which were identified spectroscopically but could not be isolated. Evaluation of the TEP and ¹J_{PSe} coupling constants were used for a first assessment of the electron donor properties of the new molecules.

Introduction

Borane adducts of phosphides with N- or O-based substituents (**Ia,b**, Scheme 1)^[1,2] were recently introduced as complements to diorganophosphides (**II**), which are well-known as synthetically valuable phosphorus-based nucleophiles.^[3] The possibility to couple **I** with suitable electrophiles and then remove the protecting borane from the product permits using these species in a similar manner as conventional phosphides as synthetic building blocks. In addition, the electronegative substituents in **I** impose some electrophilic character on the phosphorus atom, which makes these species in fact behave as ambiphiles that can also undergo bond forming reactions with nucleophilic reagents.^[2]

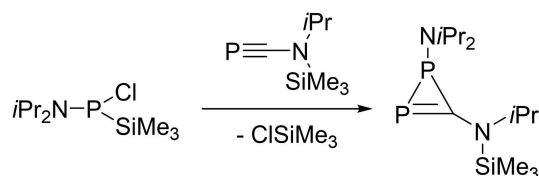
The practical utility of **I** as nucleophilic reagents that can transfer an electrophilic R₂P-fragment to an electrophilic substrate was already demonstrated in the syntheses of new types of functional phosphine derivatives. An instructive example are stannylated diorganophosphonites (**III**, Scheme 1) with their combination of electrofugic and nucleofugic substituents on the phosphorus atom.^[2] Phosphines with this characteristic, or their metal complexes, have long attracted



Scheme 1. Generic molecular structures of phosphide reagents (**I**, **II**) and diorgano(teteryl)phosphonites (**III–V**) (R, R' = alkyl, aryl).

attention due to their potential phosphinidenoid-like reactivity involving formal α -elimination with the prospect of transferring a phosphinidene (RP) unit to a substrate (Scheme 2).^[4,5] Moreover, compounds **III** might also be of interest as tunable ligands with similar properties as phosphites, which are widely used in coordination chemistry and catalysis.^[6]

The use of triorganotin compounds is increasingly deterred because of their toxicity and environmental incompatibility.^[7] In practical applications, stannyl phosphines are by far excelled by silyl phosphines, which display a similar reactivity but lack the disadvantages of their heavier congeners. Seeking therefore to extend our synthetic approach to the lighter homologues of **III**, we report here on trialkylgermyl- (**IV**) and trialkylsilyl-substituted (**V**) phosphonites, as well as a first evaluation of the donor properties of **III–V**, which is of interest for classifying their behavior as ligands.



Scheme 2. Example for the reaction of a phosphine bearing an electrofugic chloro- and a nucleofugic trimethylsilyl substituent as a phosphinidene transfer reagent (according to Ref. [4b]).

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Part of the celebratory collection for Rainer Streubel.

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silyl derivatives, but the products **8 b,c** were only detected by NMR spectroscopy and not isolated.

The unprotected tetrel-substituted diorganophosphonites are, like their borane adducts, moisture sensitive, colorless oils (**2 a'**) or solids which slowly decompose in solution. It should be noted that dialkyl derivatives **2 b,c** could not be isolated free from impurities that could not be identified (see supporting information). Moreover, analysis of ^{31}P NMR spectra of reaction mixtures indicates that the moderate yields of both borane adducts and unprotected diorganophosphonites are not caused by unselective or incomplete transformations, but reflect losses of the products during the work-up procedure originating in their rather high solubility even in unpolar solvents.

Characterization of the borane-free products was accomplished by combustion analyses and NMR data (see Experimental Section), and in several cases by single-crystal XRD studies (see below) and MS. The abstraction of the borane induces a marked deshielding of the ^{31}P nuclei by some 50–85 ppm while the effect on the ^{29}Si NMR chemical shifts of silylated derivatives remains small. The ^{31}P NMR chemical shifts of 209 (**2 c**) to 252 ppm (**8 a**) of the borane-free compounds exceed those of phosphonites and even phosphites bearing three electronegative substituents. The same trend had already been noted for triorganostannyl phosphonites and was interpreted as the result of a rather small HOMO-LUMO gaps and an indication of ambiphilic reactivity.^[2]

Crystallographic Studies

Single crystals of borane adducts **6 a–c**, **6 a'**, **7 a–c** and borane-free diarylphosphonites **2 a** and **8 a** were characterized by XRD studies. The crystals of **6 c**, **6 a'** and **2 a** each contained two crystallographically independent molecules with very similar conformations. Molecular structures obtained are displayed in Figure 1 and

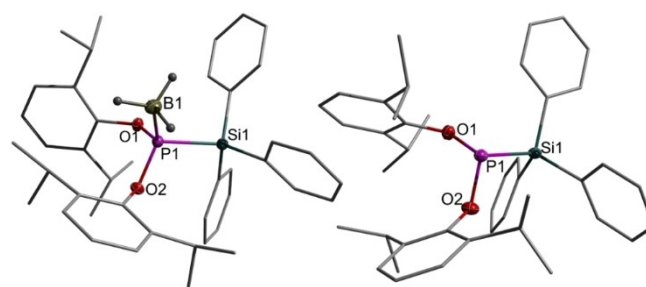


Figure 1. Representation of the molecular structure of **6 a** (left) and one of two crystallographically independent molecules of **2 a** (right) in the crystal. The organic substituents are represented as wire models and their hydrogen atoms omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.

S1–S7 in the Supporting Information, and selected metric parameters for all compounds are listed in Tables 1 and 2.

The general conformational disposition of the molecules as well as individual structural parameters (except P–E distances) are similar as in the analogous P-stannyl derivatives.^[2] The P–O and P–Si/Ge distances are also close to the average distances calculated for appropriate phosphine borane (P–Si 2.299 Å, P–O 1.603 Å) or phosphine derivatives (P–Si 2.268 Å, P–Ge 2.345 Å, P–O 1.651 Å), respectively.^[12] Removal of the borane unit is associated with a lengthening of P–O distances by some 5 pm (cf. Table 1) and enhanced pyramidalization of the phosphine fragment inducing a decrease of the sum of bond angles around phosphorus from 307–318° in borane adducts to 291–294° in boron-free species. Both effects occur also in diorgano(stannyl)-phosphonites^[2] and other trivalent phosphorus compounds, and reflect presumably the rehybridization in the phosphorus valence shell upon abstraction of the borane.^[13]

The notable deformation of bond angles reported for diorgano(stannyl)phosphonites and their borane complexes^[2] is also present in the lighter congeners studied here. The effect

Table 1. Selected distances (in Å) for diorganophosphonites $\text{R}_3\text{E}(\text{R}'\text{O})_2\text{P}$ (**2 a**, **8 a**) and their borane complexes $\text{R}_3\text{E}(\text{R}'\text{O})_2\text{PBH}_3$ (**6 a–c**, **6 a'**, **7 a–c**).

	R_3E	$\text{R}'^{[a]}$	P–E	P–O	P–B	
6 a	Ph_3Si	Dipp	2.305(1)	1.616(1)	1.629(1)	1.884(2)
6 b	Ph_3Si	Et	2.279(1)	1.602(1)	1.592(1)	1.895(2)
6 c ^[b]	Ph_3Si	i-Pr	2.270(1)	1.597(2)	1.598(2)	1.909(2)
			2.274(1)	1.598(2)	1.597(2)	1.901(2)
6 a' ^[b]	Me_3Si	Dipp	2.293(1)	1.622(1)	1.615(1)	1.878(2)
			2.291(1)	1.628(1)	1.616(1)	1.882(2)
7 a	Ph_3Ge	Dipp	2.351(1)	1.625(1)	1.616(1)	1.879(2)
7 b	Ph_3Ge	Et	2.331(1)	1.593(2)	1.586(2)	1.890(2)
7 c	Ph_3Ge	i-Pr	2.337(1)	1.597(1)	1.593(1)	1.896(2)
2 a ^[b]	Ph_3Si	Dipp	2.297(2)	1.659(3)	1.660(3)	–
			2.298(2)	1.663(3)	1.660(3)	–
8 a	Ph_3Ge	Dipp	2.364(1)	1.672(1)	1.659(1)	–

[a] Dipp = 2,6-di(isopropyl)phenyl. [b] data for two crystallographically independent molecules.

Table 2. Selected angles (in °) for diorganophosphonites $\text{R}_3\text{E}(\text{R}'\text{O})_2\text{P}$ (**2 a**, **8 a**) and their borane complexes $\text{R}_3\text{E}(\text{R}'\text{O})_2\text{PBH}_3$ (**6 a–c**, **6 a'**, **7 a–c**).

	R_3E	$\text{R}'^{[a]}$	O–P–O	O–P–E	$\Sigma^{[b]}$	
6 a	Ph_3Si	Dipp	104.6(1)	112.0(1)	93.6(1)	310.2(3)
6 b	Ph_3Si	Et	103.3(1)	105.9(1)	100.3(1)	309.5(3)
6 c ^[c]	Ph_3Si	i-Pr	106.7(1)	101.6(1)	100.5(1)	308.8(3)
			107.6(1)	101.4(1)	99.2(1)	308.2(3)
6 a' ^[c]	Me_3Si	Dipp	102.9(1)	110.6(1)	94.0(1)	307.5(3)
			103.2(1)	112.3(1)	94.7(1)	310.2(3)
7 a	Ph_3Ge	Dipp	104.4(1)	112.6(1)	93.5(1)	310.5(3)
7 b	Ph_3Ge	Et	108.5(1)	109.9(1)	98.7(1)	317.1(3)
7 c	Ph_3Ge	i-Pr	107.6(1)	112.3(1)	97.1(1)	317.0(3)
2 a ^[c]	Ph_3Si	Dipp	104.4(2)	97.4(1)	91.9(1)	293.7(4)
			104.8(2)	95.9(2)	93.3(2)	294.0(6)
8 a	Ph_3Ge	Dipp	101.6(1)	102.2(1)	87.8(1)	291.6(3)

[a] Dipp = 2,6-di(isopropyl)phenyl. [b] Sum of O–P–O and O–P–E angles. [c] data for two crystallographically independent molecules.

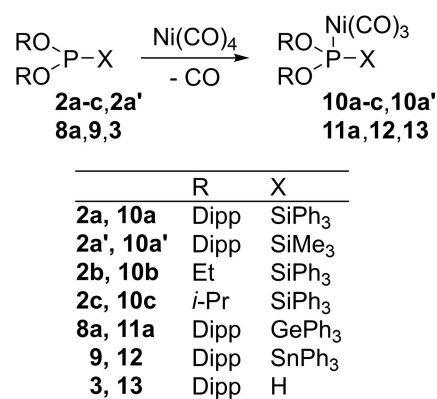
becomes manifest in a marked dissymmetry of the E–P–O angles (E=Si, Ge), one of which usually matches or exceeds the O–P–O angle, while the second one is (with only few exceptions) distinctly (6–19°) smaller and may reach a similar magnitude as in so called ‘constrained geometry’ or ‘non-trigonal’ phosphine derivatives.^[14] A key aspect of these species is that the geometric deformation is considered to affect as well their electronic structure by reducing the size of the HOMO-LUMO gap and instigating thus a highly unusual ambiphilic reactivity.^[14] Still, the ‘constrained geometry’ phosphine derivatives and the phosphonites studied here differ despite all formal similarities because the angular deformation in the former affects all three bond angles, whereas the O–P–O angle in the latter (cf. Table 2) stays close to the average angle in unstrained phosphites (O–P–O 99(4)°) or phosphite boranes (O–P–O 104(3)°), respectively. Given that similar – albeit smaller – deviations from the local trigonal symmetry around the phosphorus atom are even visible for phosphites and their borane adducts,^[12] the structural distortion is most likely attributable to steric interactions between the bulky R₃E- and alkoxy-/phenoxy groups and/or crystal packing effects. Its impact on the electronic structure and reactivity presumably stands back behind the effect induced by the presence of P–O and P–E (E = group-4 element) bonds of opposite polarity.

Exploring Lewis Basicity

The consideration of diorgano(teteryl)phosphonites as tunable ligands with close relations to phosphites stimulated our interest in evaluating the donor behavior of the newly synthesized molecules and comparing it with that of other types of ligands. To this end, we set out to determine the Tolman Electronic Parameter^[15] (TEP) for **2** and **8**, previously reported tin-analogue **9**,^[2] and secondary diarylphosphonite **3**. The TEP of a ligand L equals to the wavenumber of the totally symmetric (a₁) νCO-mode of a complex Ni(CO)₃(L) and is widely acknowledged as a measure of the net electron donating ability of the ligand (i.e. the sum of its σ-donor and π-donor/acceptor strength) and a scale for comparing this property between different ligands.^[16]

The complexes required for the determination of the TEP formed instantaneously upon reacting the ligands with excess Ni(CO)₄ (Scheme 5). Separation of minor amounts of side products and isolation of pure products remained unsuccessful as the samples partially decomposed under liberation of CO, metallic nickel, and some free ligand during crystallization attempts. However, the complexes proved sufficiently stable to allow unequivocal in-situ identification by their characteristic IR data (Table 3 and Experimental Section). Formation of a carbonyl complex with a single phosphorus-containing ligand was also supported by ¹³C NMR data.

The coordination shifts Δδ³¹P associated with the formation of Ni(CO)₃-complexes of **2** and **8** adopt small positive or negative values which are in accord with the approximate empirical relation that Δδ³¹P decreases numerically with



Scheme 5. Formation of diorgano-phosphonite(tricarbonyl)nickel(0) complexes.

Table 3. ³¹P NMR data (chemical shifts δ³¹P for ligands and Ni(CO)₃-complexes and coordination shifts Δδ³¹P) and values of TEP (in cm⁻¹) for diorgano-phosphonites (**2a–c**, **2a'**, **3**, **8a**, **9**) and selected phosphines and phosphites.

L ^[a]	δ ³¹ P(L)	δ ³¹ P(LNi(CO) ₃)	Δδ ³¹ P ^[b]	TEP
(DippO) ₂ PSiPh ₃ (2a)	247.2	248.2	1.0	2072
(EtO) ₂ PSiPh ₃ (2b)	217.7	216.6	–1.1	2069
(<i>i</i> -PrO) ₂ PSiPh ₃ (2c)	209.0	211.9	2.9	2068
(DippO) ₂ PSiMe ₃ (2a')	248.0	244.4	–3.6	2071
(DippO) ₂ PGePh ₃ (8a)	252.1	249.7	–2.4	2073
(DippO) ₂ PSnPh ₃ (9)	273.0	257.2	–15.8	2073
(DippO) ₂ PH (3)	180.0	187.2	7.2	2083
(EtO) ₃ P	140 ^[c]	157 ^[c]	17	2076 ^[d]
Ph ₃ P	–6.6 ^[c]	42.9 ^[c]	49.5	2069 ^[d]
Et ₃ P	–19.1 ^[c]	47.0 ^[c]	66.1	2061 ^[d]
^t Bu ₃ P	62.7 ^[e]	91.0 ^[e]	28.3	2056 ^[d]
(Me ₃ Si) ₃ P	–234.0 ^[e]	–251.0 ^[e]	17.0	2074 ^[e]

[a] Dipp = 2,6-di(isopropyl)phenyl. [b] Δδ³¹P = δ³¹P(LNi(CO)₃) – δ³¹P(L). [c] data from ref. [18]. [d] data from ref. [15]. [e] data from ref. [19].

increasing chemical shift of the free ligand (cf. the data in Table 3).^[17]

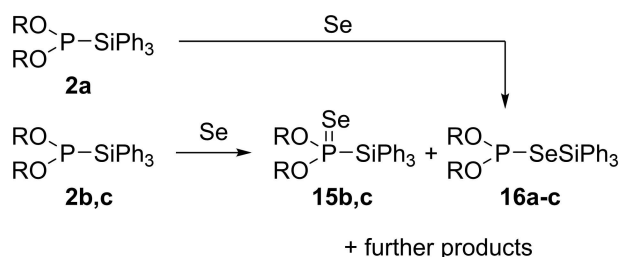
The values of the TEP for dialkyl(teteryl)phosphonites (**2b,c**) are comparable to that of PPh₃ and marginally lower than those for diaryl derivatives (**2a**, **8a**, **9**), which come close to the TEP for P(SiMe₃)₃. The narrow span of the data and their invariance towards variation of the R₃E-moiety in **2a**, **8a** and **9** indicates that substituent effects on the electronic properties of **2** and **8–9** are modest. The TEP for parent diarylphosphonite **3** clearly exceeds those of tetrel-substituted species and falls into the phosphite region (TEP > 2075 cm⁻¹).^[15] When compared with a larger set of P-donors,^[15] diorgano(teteryl)phosphonites are predicted to be better σ-donors and/or weaker π-acceptors than phosphites and analogous diorgano(aryl)phosphonites and seem to have similar properties as electron poor triaryl phosphines.

In addition to the TEP, various alternative schemes for a general assessment of ligand properties have been developed

and are in use today.^[16] Among these, we considered a correlation of the Lewis basicity of P-donor ligands R₃P with the ¹J_{PSe} coupling constants in the corresponding selenides R₃P=Se^[20] a particular interesting case. Synthesis of the selenides by oxidation of the ligands with elemental selenium, which works well for triorganophosphines, is not applicable to silyl phosphines as these react preferably via insertion of a selenium atom into the P–Si bond and conservation of a trivalent phosphorus center.^[21] Although silylphosphine selenides were postulated as elusive intermediates, they were not detected spectroscopically. However, considering that a formal sulfur oxidation product of **2c**, (*i*-PrO)₂P(=S)SiPh₃ (**14**), is known (even if it was not synthesized via **2c**),^[22] we reckoned that selenium homologues might also exist. Anticipating to prove their existence and to deepen our insight into the mechanism of the chalcogenation of silyl phosphine derivatives, we studied the reactions of **2** and **8** with grey selenium. Reaction monitoring by ³¹P NMR spectroscopy indicated that dialkylphosphonites **2b,c** were rapidly converted into mixtures containing the expected phosphonoselenoates **15b,c** as major components along with minor amounts of selenophosphites **16b,c** and further unidentified species (Scheme 6).

Even if attempts to isolate **15b,c** were thwarted by their liability towards slow rearrangement into **16b,c** and further unspecified follow-up reactions, their constitution is unequivocally established by NMR data. Key to the assignment is the observation of ³¹P NMR signals with similar chemical shifts as **14** and large couplings to adjacent ²⁹Si and ⁷⁷Se nuclei (Scheme 6). Both the magnitude of the latter and the corresponding ⁷⁷Se NMR chemical shifts (δ⁷⁷Se –174.9/–174.3 for **15b/15c**) are highly characteristic for a phosphonoselenoate structure and exclude the presence of a product resulting from selenium insertion into the P–Si bond. The identification of the selenophosphite isomers **16b,c** is based on their larger ³¹P NMR chemical shifts and a set of ⁷⁷Se satellites indicative of coupling to a sole singly-bonded selenium atom.

Diarylphosphonite **2a** was rather inert and reacted with selenium only within weeks to produce a mixture containing a



R	δ ³¹ P	¹ J _{PSe} / ¹ J _{PSi}	δ ³¹ P(¹ J _{PSe})
Dipp			16a 227.0 (354 Hz)
Et	15b 109.5	810/166 Hz	16b 198.6 (285 Hz)
<i>i</i> -Pr	15c 105.1	803/173 Hz	16c 197.3 (283 Hz)

Scheme 6. Reactions of dialkyl(triphenylsilyl)phosphonites with selenium and ³¹P NMR data of the resulting phosphonoselenoates and selenophosphites.

component addressed as a selenophosphite **16a** along with species resulting from overoxidation with excess selenium (Scheme 6). Even though **16a** decomposed during work-up and could not be isolated, its identification can safely be derived from the observation of ³¹P NMR signals showing chemical shifts in the expected range^[23] and coupling to a sole, singly-bonded ⁷⁷Se nucleus.

The outcome of the reactions of **2b,c** with selenium strengthens the hypothesis^[21] that silyl phosphines react with chalcogens via initial oxidation at phosphorus and subsequent migratory insertion of the chalcogen into the P–Si bond. Whether the rearrangement proceeds intra- or intermolecularly^[24] remains undecided. The inert behavior of diaryl(teteryl)phosphonites is presumably attributable to a combination of steric screening by the bulky aryl units and reduced basicity. The liability of all initial products towards further oxidation with excess chalcogens as well as other decay processes is in accord with previous findings.^[21]

The magnitude of ¹J_{PSe} for **15b,c** exceeds the value for Ph₃P=Se (736 Hz) but is lower than for the selenides of diorganophosphites (860 Hz for (EtO)₂P(H)=Se) and phosphites (>910 Hz).^[25] Since a numerical decrease of ¹J_{PSe} is associated with increased Lewis basicity,^[20] these results are, apart from the fact that **2b,c** are predicted weaker Lewis bases than PPh₃, qualitatively in accord with the trends derived from evaluation of the TEP.

Conclusions

The approach to the synthesis of diorgano(teteryl)phosphonites via coupling of metalated diorganophosphonite boranes with triorganoteteryl halides and ensuing deprotection was successfully extended to silyl- and germyl-substituted species. The use of DABCO for removal of the borane, which proved crucial for the synthesis of dialkyl(teteryl)phosphonites, was enabled by a protocol permitting the separation of excess amine by addition of a magnesium salt. Studies of reactions with Ni(CO)₄ were used to evaluate the TEP for selected diorgano(teteryl)phosphonites. The values derived are like those of electron poor triaryl phosphines and suggest that the net electron donating ability (aka the sum of σ-donor and π-acceptor contributions) of the ligands is slightly below (OAr-derivatives) or comparable to (OAlkyl-derivatives) that of PPh₃, but exceeds in all cases that of phosphites and parent diorganophosphonites. Investigation of the reactions of dialkyl(silyl)phosphonites with selenium allowed the detection of unprecedented silyl phosphonoselenoates and supports the hypothesis that these species are intermediates in reactions involving insertion of a chalcogen into a P–Si bond.

Experimental Section

All manipulations were carried out under an atmosphere of inert argon inside glove boxes or by using standard vacuum line techniques. Solvents were dried by published procedures.^[26] NMR spectra were recorded on Bruker Avance 250 (¹H 250.0 MHz,

^{11}B 80.2 MHz, ^{13}C 62.9 MHz, ^{29}Si 49.7 MHz, ^{31}P 101.2 MHz) or Avance 400 (^1H 400.1 MHz, ^{11}B 128.3 MHz, ^{13}C 100.5 MHz, ^{29}Si 79.5 MHz, ^{31}P 161.9 MHz) instruments at 293 K if not stated otherwise. ^1H Chemical shifts were referenced to TMS using the signals of the residual protons of the deuterated solvent ($\delta^1\text{H} = 7.24$ (CDCl_3), 7.15 (C_6D_6), 1.73 (THF-D_8)) as secondary reference. Spectra of heteronuclei were referenced using the Ξ -scale^[27] employing TMS ($\Xi = 25.145020/19.867187$ MHz, $^{13}\text{C}/^{29}\text{Si}$), 85% H_3PO_4 ($\Xi = 40.480747$ MHz, ^{31}P) and SnMe_4 ($\Xi = 37.290655$ MHz, ^{119}Sn) as secondary references. Some ^{13}C NMR signals of quaternary carbon atoms were undetectable due to insufficient signal-to-noise ratio and signal broadening effects. ^{29}Si NMR data were extracted from $^1\text{H}/^{29}\text{Si}$ HSQC spectra. Coupling constants are given as absolute values. The FTIR spectra were recorded in ATR (pure substances) or transmission mode (solutions in CaF_2 cells) with a Thermo Scientific/Nicolet iS5 instrument equipped with an iD5 attenuated total reflectance (ATR) accessory. Mass spectra were recorded with Finnigan-MAT MAT95 (EI, 70 eV) or Bruker Daltonics Mikrotrof-Q (ESI) mass spectrometers but proved uninterpretable for most compounds, presumably due to technical limitations (instrument not equipped for sample preparation and submission under inert conditions) and thermally and chemically labile samples decomposing during the ionization process. As far as interpretable spectra were obtained, given masses refer to the peak representing the most abundant isotope combination. Elemental analyses of isolated compounds were determined on a Thermo Micro Cube CHN analyzer. Distinctive deviations between measured and calculated analytical data as well as contaminant signals in NMR spectra that occur in some cases, despite repeated efforts, are due in part to the high thermal and chemical sensitivity of some analytes interfering with sample preparation or causing decomposition during data acquisition, and in part to the presence of impurities. A significant cause for the presence of such impurities is the high solubility of the analytes, which prevents complete removal of adherent solvent residues or by-products by sufficient washing of isolated crystals. Exemplary attempts to determine melting points revealed that the samples exhibited, like the homologous stannyl derivatives **III**,^[2] no well-defined melting points but underwent rather unpecific, and barely reproducible, thermal decomposition. Synthesis and metalation of diorganophosphonite boranes (**5a–c**) was carried out as reported elsewhere.^[2]

Crystallographic Studies. Single-crystal X-ray diffraction data were measured on a Bruker Kappa APEX2 Duo diffractometer at 140(2) K using $\text{MoK}\alpha$ radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods or heavy atom methods (SHELXS^[28]) and refined with a full-matrix-least-squares scheme on F^2 (SHELXL-2014^[28]). Semi-empirical absorption corrections were applied. For **6a**, an extinction correction was applied. Non-hydrogen atoms were refined anisotropically. One O-dipp group of **6a'**, one alkyl group of **6b**, **6c** and two alkyl groups for **7b** were disordered. Disordered atoms were refined anisotropically (see cif-files for details). The absolute structure of **2a** could not be determined reliably and a refinement as an inversion twin failed (see cif-file for details). Further crystallographic data and details on the structure refinement are given in the Supporting Information. Deposition Numbers 2265645 (for **6c**), 2265655 (for **6b**), 2265656 (for **7a**), 2265657 (for **8a**), 2265658 (for **2a**), 2265659 (for **6a'**), 2265660 (for **6a**), 2265661 (for **7b**), 2265662 (for **7c**) 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.

Bis-(2,6-diisopropylphenyl)(triphenylsilyl)phosphonite borane **6a**: **4a** (200 mg, 0.50 mmol) and KHMDS (100 mg, 0.50 mmol) were

dissolved at -78°C in toluene (10 mL). A solution of Ph_3SiOTf (204 mg, 0.50 mmol) in toluene (5 mL) was added dropwise. The mixture was kept at -78°C for 15 min, then warmed to RT, and filtered. The residue was washed with toluene (10 mL). The combined filtrates were evaporated to dryness and the resulting solid washed once more with pentane (20 mL) to produce **6a** as a colorless solid (yield 134 mg, 0.20 mmol, 41%). Single crystals suitable for XRD studies were obtained from a concentrated solution in toluene. ^1H NMR: $\delta = 8.04$ (m, 6 H, *o*-Ph), 7.15–7.12 (m, 9 H, *m/p*-Ph), 6.99 (b, 6 H, C_6H_3), 3.31 (sept, $^3J_{\text{HH}} = 6.8$ Hz, 4 H, CH), 1.05 (d, $^3J_{\text{HH}} = 6.8$ Hz, 12 H, CH_3), 0.84 (d, $^3J_{\text{HH}} = 6.8$ Hz, 12 H, CH_3). ^{31}P NMR: $\delta = 182.3$ (b). $^{11}\text{B}\{^1\text{H}\}$ NMR: $\delta = -34.9$ (b). $^{13}\text{C}\{^1\text{H}\}$ NMR: $\delta = 147.4$ (d, $^2J_{\text{PC}} = 13$ Hz, *i*- C_6H_3), 141.2 (d, $^3J_{\text{PC}} = 3$ Hz, *o*- C_6H_3), 137.3 (d, $^3J_{\text{PC}} = 2$ Hz, *o*-Ph), 130.6 (s, *p*-Ph), 130.3 (d, $^2J_{\text{PC}} = 13$ Hz, *i*-Ph), 128.2 (s, *m*-Ph), 124.5 (d, $^5J_{\text{PC}} = 2$ Hz, *p*- C_6H_3), 124.3 (d, $^4J_{\text{PC}} = 2$ Hz, *m*- C_6H_3), 27.4 (s, CH), 24.0 (s, CH_3), 23.4 (s, CH_3). $^{29}\text{Si}\{^1\text{H}\}$ NMR: $\delta = -18.3$ ($^1J_{\text{PSi}} = 78$ Hz). IR (pure): $\tilde{\nu}$ (cm^{-1}) = 2445, 2383 (vBH). $-\text{C}_{42}\text{H}_{52}\text{BO}_2\text{PSi}$ (658.74 g mol^{-1}): calcd. C 76.58 H 7.96, found C 76.66 H 7.94.

Bis-(2,6-Diisopropylphenyl)(trimethylsilyl)phosphonite borane **6a'**: **4a** (950 mg, 2.37 mmol) and KHMDS (520 mg, 2.61 mmol) were dissolved under stirring at -78°C in toluene (50 mL). The solution was allowed to warm to RT, stirred for 1 h, and then re-cooled to -78°C . Me_3SiCl (309 mg, 2.85 mmol, 360 μL) was added dropwise, and the mixture then once again allowed to warm to RT, stirred for 1 h, and filtered. Evaporation of the filtrate to dryness produced a colorless oil which upon scratching crystallized within a few days at RT (yield 876 mg, 1.85 mmol, 78%). ^1H NMR: $\delta = 7.02$ (b, 6 H, C_6H_3), 3.52 (sept, $^3J_{\text{HH}} = 7$ Hz, 4 H, CH), 1.20 (d, $^3J_{\text{HH}} = 7.0$ Hz, 12 H, CH_3), 1.17 (d, $^3J_{\text{HH}} = 7.0$ Hz, 12 H, CH_3), 0.38 (d, $^2J_{\text{PH}} = 6.2$ Hz, 9 H, SiMe_3). ^{31}P NMR: $\delta = 184.0$ (b). ^{11}B NMR: $\delta = -35.9$ (b). $^{13}\text{C}\{^1\text{H}\}$ NMR: $\delta = 148.3$ (d, $^2J_{\text{PC}} = 13$ Hz, *i*- C_6H_3), 140.7 (d, $^3J_{\text{PC}} = 3$ Hz, *m*- C_6H_3), 125.6 (d, $^5J_{\text{PC}} = 2$ Hz, *p*- C_6H_3), 124.1 (d, $^4J_{\text{PC}} = 2$ Hz, *o*- C_6H_3), 27.4 (s, CH), 23.6 (s, CH_3), 23.2 (s, CH_3), -2.5 (d, $^2J_{\text{PC}} = 10.1$ Hz, SiMe_3). $^{29}\text{Si}\{^1\text{H}\}$ NMR: $\delta = 4.4$ ($^1J_{\text{PSi}} = 65$ Hz). IR (pure): $\tilde{\nu}$ (cm^{-1}) = 2424, 2352 (vBH). $-\text{C}_{27}\text{H}_{46}\text{BO}_2\text{PSi}$ (472.53 g mol^{-1}): calcd. C 68.63 H 9.81, found C 67.12 H 9.84.

Diethyl(triphenylsilyl)phosphonite borane **6b**: Toluene (20 mL) was added at 0°C to a mixture of **5b** (500 mg, 2.87 mmol) and Ph_3SiCl (847 mg, 2.87 mmol). The mixture was stirred for 20 h, filtered over Celite, and the residue washed with toluene (10 mL). The combined filtrates were evaporated and the residue suspended in pentane (20 mL). The resulting mixture was filtered and the filtration residue extracted several times with pentane (4×20 mL). The filtrate was concentrated to a volume of approx. 5 mL. Storage at -25°C produced a colorless crystalline solid which was separated by decantation and dried in vacuum (yield 750 mg, 1.90 mmol, 66%). ^1H NMR (CDCl_3): $\delta = 7.68$ (m, 6 H, *o*-Ph), 7.52–7.32 (m, 9 H, *m/p*-Ph), 4.16–3.90 (m, 4 H, CH_2), 1.16 (t, $^3J_{\text{HH}} = 7.0$ Hz, 6 H, CH_3), 1.51 to -0.10 (b, 3 H, BH_3). ^{31}P NMR (CDCl_3): $\delta = 162.9$ (b). $^{11}\text{B}\{^1\text{H}\}$ NMR (CDCl_3): $\delta = -40.4$ (d, $^1J_{\text{PB}} = 50$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): $\delta = 136.6$ (d, $^3J_{\text{PC}} = 2.3$ Hz, *o*-Ph), 130.6 (d, $^5J_{\text{PC}} = 1$ Hz, *p*-Ph), 129.4 (d, $^2J_{\text{PC}} = 13.3$ Hz, *i*-Ph), 128.1 (s, *m*-Ph), 64.3 (d, $^2J_{\text{PC}} = 8.2$ Hz, CH_2), 16.7 (d, $^3J_{\text{PC}} = 5.4$ Hz, CH_3). $^{29}\text{Si}\{^1\text{H}\}$ NMR (CDCl_3): $\delta = -19.3$ ($^1J_{\text{PSi}} = 71$ Hz). IR (pure): $\tilde{\nu}$ (cm^{-1}) = 2386, 2352 (vBH). $-\text{C}_{22}\text{H}_{28}\text{BO}_2\text{PSi}$ (394.33 g mol^{-1}): calcd. C 67.01 H 7.16, found C 68.48, H 6.87.

Diethyl(trimethylsilyl)phosphonite borane **6b'**: A solution of Me_3SiCl (375 mg, 3.45 mmol, 0.45 mL) in THF (20 mL) was cooled to -78°C . A pre-cooled (-78°C) solution of **5b** (500 mg, 2.87 mmol) in THF (10 mL) was slowly added dropwise. The mixture was stirred for 15 min at -78°C and then 1 h at RT. The resulting suspension was filtered. Evaporation of the filtrate in vacuum furnished a colorless oil (255 mg) containing **6b'** along with some **4b**. ^1H NMR: $\delta = 4.04$ (m, 2 H, CH_2), 3.88 (m, 2 H, CH_2),

1.25 (dq, 3 H, $^1J_{\text{BH}}=96$ Hz, $^2J_{\text{PH}}=9$ Hz, BH₃), 1.04 (t, 6 H, $^3J_{\text{HH}}=7.0$ Hz, CH₃), 0.20 (d, 9 H, $^3J_{\text{PH}}=7.2$ Hz, SiMe₃). – ^{31}P NMR: $\delta=168.5$ (q, $^1J_{\text{PB}}=57$ Hz). – ^{11}B NMR: $\delta=-38.5$ (dq, $^1J_{\text{PB}}=57$ Hz, $^1J_{\text{BH}}=96$ Hz). – $^{13}\text{C}\{^1\text{H}\}$ NMR: $\delta=62.6$ (d, $^2J_{\text{PC}}=8.0$ Hz, CH₂), 15.5 (d, $^3J_{\text{PC}}=5.5$ Hz, CH₃), -5.5 (d, $^2J_{\text{PC}}=12.5$ Hz, $^1J_{\text{CSi}}=51.4$ Hz, SiMe₃). – ^{29}Si NMR: $\delta=-0.9$ ($^1J_{\text{PSi}}=89$ Hz).

Diisopropyl(triphenylsilyl)phosphonite borane **6c**: Toluene (20 mL) was added at 0 °C to a mixture of **5c** (500 mg, 2.47 mmol) and Ph₃SiCl (729 mg, 2.47 mmol). The mixture was stirred for 24 h, filtered over Celite, and the residue washed with toluene (20 mL). The combined filtrates were evaporated and the residue suspended in pentane (20 mL). The resulting mixture was filtered and the filtration residue extracted several times with pentane (5 × 20 mL). The filtrate was concentrated to a volume of approx. 10 mL. Storage at -25 °C produced a colorless crystalline solid which was separated by decantation and dried in vacuum (yield 365 mg, 0.86 mmol, 35%). – ^1H NMR: $\delta=7.93$ (m, 6 H, *o*-Ph), 7.20–7.15 (m, 9 H, *m/p*-Ph), 4.74 (dsept, $^3J_{\text{PH}}=9.6$ Hz, $^3J_{\text{HH}}=6.1$ Hz, 2 H, CH), 1.05 (d, $^3J_{\text{HH}}=6.1$ Hz, 6 H, CH₃), 0.95 (d, $^3J_{\text{HH}}=6.1$ Hz, 6 H, CH₃). – ^{31}P NMR: $\delta=161.2$ (b). – $^{11}\text{B}\{^1\text{H}\}$ NMR: $\delta=-39.4$ (d, $^1J_{\text{PB}}=47$ Hz). – d $^{13}\text{C}\{^1\text{H}\}$ MR: $\delta=136.0$ (d, $^2J_{\text{PC}}=2$ Hz, *o*-Ph), 129.5 (d, $^5J_{\text{PC}}=1$ Hz, *p*-Ph), 129.2 (d, $^2J_{\text{PC}}=13$ Hz, *i*-Ph), 127.2 (s, *m*-Ph), 71.6 (d, $^2J_{\text{PC}}=7.2$ Hz, CH), 23.1 (d, $^3J_{\text{PC}}=3$ Hz, CH₃), 22.7 (d, $^3J_{\text{PC}}=5$ Hz, CH₃). – ^{29}Si NMR: $\delta=-20.2$ ($^1J_{\text{PSi}}=101$ Hz). – IR (pure): $\tilde{\nu}$ (cm⁻¹)=2382, 2349 (νBH). – C₂₄H₃₂BO₂PSi (422.39 g mol⁻¹): calcd. C 68.25 H 7.64, found C 69.11 H 7.31.

Bis-(2,6-diisopropylphenyl)(triphenylgermyl)phosphonite borane **7a**: Toluene (15 mL) was added at -78 °C to a mixture of **4a** (400 mg, 1.0 mmol) and KHMDS (200 mg, 1.0 mmol). The resulting suspension was then allowed to warm to RT. The clear solution formed was re-cooled to -78 °C, and a solution of Ph₃GeBr (380 mg, 1.00 mmol) in toluene (5 mL) was added. The solution was allowed to warm up, stirred for 18 h at RT, and filtered. The filtrate was evaporated to dryness and the residue taken up in hexane (20 mL). The resulting suspension was filtered and the solid residue washed several times with hexane (3 × 20 mL), and dried in vacuum (yield 416 mg, 0.59 mmol, 59%). Single crystals suitable for XRD studies were obtained from a saturated hexane solution. – ^1H NMR: $\delta=7.93$ (m, 6 H, *o*-Ph), 7.15–7.09 (m, 9 H, *m/p*-Ph), 7.06–6.95 (m, 6 H, C₆H₃), 3.36 (sept, $^3J_{\text{HH}}=6.7$ Hz, 2 H, CH), 2.37–1.12 (b, 3 H, BH₃), 1.07 (d, $^3J_{\text{HH}}=6.7$ Hz, 6 H, CH₃), 0.85 (d, $^3J_{\text{HH}}=6.7$ Hz, 6 H, CH₃). – ^{31}P NMR: $\delta=187.5$ (b). – $^{11}\text{B}\{^1\text{H}\}$ NMR: $\delta=-34.0$ (b). – $^{13}\text{C}\{^1\text{H}\}$ NMR: $\delta=147.5$ (d, $^2J_{\text{PC}}=13.2$ Hz, *i*-C₆H₃), 141.1 (d, $^3J_{\text{PC}}=3$ Hz, *o*-C₆H₃), 136.0 (d, $^3J_{\text{PC}}=2$ Hz, *o*-Ph), 133.7 (d, $^2J_{\text{PC}}=13$ Hz, *i*-Ph), 129.8 (s, *p*-Ph), 128.6 (s, *m*-Ph), 125.8 (d, $^5J_{\text{PC}}=2$ Hz, *p*-C₆H₃), 124.3 (d, $^4J_{\text{PC}}=2$ Hz, *m*-C₆H₃), 27.5 (s, CH), 24.0 (s, CH₃), 23.2 (s, CH₃). – IR (pure): $\tilde{\nu}$ (cm⁻¹)=2449, 2383, 2345 (νBH). – C₄₂H₅₂BGeO₂P (703.29 g mol⁻¹): calcd. C 71.73 H 7.45, found C 70.27 H 6.55.

Diethyl(triphenylgermyl)phosphonite borane **7b**: A solution of Ph₃GeBr (309 mg, 0.80 mmol) in toluene (5 mL) was added dropwise at 0 °C to a solution of **5b** (139 mg, 0.80 mmol) in toluene (10 mL). The mixture was stirred overnight, and filtered. The filtrate was evaporated to dryness and the residue suspended in hexane (20 mL). The resulting suspension was filtered and the solid residue washed with hexane (20 mL). The combined filtrates were concentrated to a volume of 5 mL. Crystallization at -25 °C furnished **7b** as a colorless solid (yield 145 mg, 0.43 mmol, 53%). – ^1H NMR: $\delta=7.82$ (m, 6 H, *o*-Ph), 7.19–7.12 (m, 9 H, *m/p*-Ph), 3.99 (dq, 2 H, $^3J_{\text{HH}}=7.0$ Hz, $^3J_{\text{PH}}=10$ Hz CH₂), 3.82 (dq, 2 H, $^3J_{\text{HH}}=7.0$ Hz, $^3J_{\text{PH}}=10$ Hz, CH₂), 2.36–0.95 (b, 3 H, BH₃), 0.89 (t, $^3J_{\text{HH}}=7.0$ Hz, 6 H, CH₃). – ^{31}P NMR: $\delta=171.9$ (b). – $^{11}\text{B}\{^1\text{H}\}$ NMR: $\delta=-38.6$ (d, $^1J_{\text{PB}}=31$ Hz). – $^{13}\text{C}\{^1\text{H}\}$ NMR: $\delta=135.7$ (d, $^3J_{\text{PC}}=2$ Hz, *o*-Ph), 133.1 (d, $^2J_{\text{PC}}=13$ Hz, *i*-Ph), 129.7 (d, $^5J_{\text{PC}}=1$ Hz, *p*-Ph), 128.5 (s, *m*-Ph), 64.3 (d, $^2J_{\text{PC}}=8$ Hz, CH₂), 16.3 (d, $^3J_{\text{PC}}=5$ Hz, CH₃). – IR (pure): $\tilde{\nu}$ (cm⁻¹)=

2399, 2351 (νBH). – C₂₂H₂₈BGeO₂P (438.88 g mol⁻¹): calcd. C 60.21 H 6.43, found C 60.19 H 6.40.

Diisopropyl(triphenylgermyl)phosphonite borane **7c**: The preparation was carried out as described for **7b** from **5c** (70 mg, 0.35 mmol) and Ph₃GeBr (133 mg, 0.35 mmol). Yield 56 mg (0.12 mmol, 34%) of colorless crystals. – ^1H NMR: $\delta=7.84$ (m, 6 H, *o*-Ph), 7.23–7.16 (m, 9 H, *m/p*-Ph), 4.72 (dsept, $^3J_{\text{PH}}=9.8$ Hz, $^3J_{\text{HH}}=6.1$ Hz, 2 H, CH), 2.43–1.06 (b, 3 H, BH₃), 1.03 (d, $^3J_{\text{HH}}=6.1$ Hz, CH₃), 0.96 (d, $^3J_{\text{HH}}=6.1$ Hz, CH₃). – $^{31}\text{P}\{^1\text{H}\}$ NMR: $\delta=167.5$ (b). – $^{11}\text{B}\{^1\text{H}\}$ NMR: $\delta=-38.3$ (d, $^1J_{\text{PB}}=38$ Hz). – $^{13}\text{C}\{^1\text{H}\}$ NMR: $\delta=135.8$ (d, $^3J_{\text{PC}}=2$ Hz, *o*-Ph), 133.3 (d, $^2J_{\text{PC}}=13$ Hz, *i*-Ph), 129.6 (d, $^3J_{\text{PC}}=1$ Hz, *p*-Ph), 128.4 (s, *m*-Ph), 72.8 (d, $^2J_{\text{PC}}=8$ Hz, CH), 23.9 (d, $^3J_{\text{PC}}=2$ Hz, CH₃), 23.6 (d, $^3J_{\text{PC}}=5$ Hz, CH₃). – (+)-ESI-MS: *m/z*=491.133(7) (MNA⁺, calcd. 491.1346). – C₂₄H₃₂BGeO₂P (466.93 g mol⁻¹): calcd. C 61.74 H 6.91, found C 61.65 H 6.82.

Bis-(2,6-diisopropylphenyl)(triphenylsilyl)phosphonite **2a**: **6a** (75 mg, 0.11 mmol) was dissolved in toluene (5 mL) and NEt₃ (230 mg, 2.28 mmol, 0.32 mL) and the resulting mixture stirred for 20 h at RT. Volatiles were evaporated in vacuum, hexane (10 mL) was added, the resulting mixture filtered, and the filtration residue washed with additional hexane (5 mL). The combined filtrates were concentrated to a volume of 3 mL. The resulting suspension was allowed to settle and the liquid phase decanted off. Drying of the residual solid produced **2a** as a colorless solid (57 mg, 88 μmol, 80%). – ^1H NMR: $\delta=7.92$ (m, 6 H, *o*-Ph), 7.15–7.09 (m, 9 H, *m/p*-Ph), 7.00 (b, 6 H, C₆H₃), 3.31 (dsept, $^3J_{\text{HH}}=7$ Hz, $^5J_{\text{PH}}=2$ Hz, CH, 0.99 (d, $^3J_{\text{HH}}=7$ Hz, 12 H, CH₃), 0.95 (d, $^3J_{\text{HH}}=7$ Hz, 12 H, CH₃). – ^{31}P NMR: $\delta=247.2$ (s). – $^{13}\text{C}\{^1\text{H}\}$ NMR: $\delta=151.1$ (d, $^2J_{\text{PC}}=2$ Hz, *i*-C₆H₃), 140.3 (d, $^3J_{\text{PC}}=2$ Hz, *o*-C₆H₃), 136.6 (d, $^3J_{\text{PC}}=3$ Hz, *o*-Ph), 132.8 (d, $^2J_{\text{PC}}=10$ Hz, *i*-Ph), 129.9 (s, *p*-Ph), 128.1 (s, *m*-Ph), 124.4 (d, $^4J_{\text{PC}}=1$ Hz, *p*-C₆H₃), 124.1 (d, $^4J_{\text{PC}}=1$ Hz, *m*-C₆H₃), 27.3 (d, $^4J_{\text{PC}}=5$ Hz, CH), 23.9 (d, $^5J_{\text{PC}}=1$ Hz, CH₃), 23.4 (d, $^5J_{\text{PC}}=1$ Hz, CH₃). – ^{29}Si NMR: $\delta=-21.5$ ($^1J_{\text{PSi}}=34$ Hz, $^3J_{\text{SiH}}=10$ Hz). – (+)EI-MS: *m/z*=644.32(1) (M⁺, calcd. 644.3234). – C₄₂H₄₉O₂PSi (644.91 g mol⁻¹): calcd. C 78.22 H 7.66, found C 78.37 H 7.87.

Bis-(2,6-diisopropylphenyl)(trimethylsilyl)phosphonite **2a'**: **6a'** was freshly prepared from **4a** (550 mg, 1.37 mmol), KHMDS (302 mg, 1.51 mmol), and Me₃SiCl (179 mg, 1.65 mol) in toluene (20 mL) as described above. NEt₃ (1.9 g, 19 mmol, 2.6 mL) was added to the crude reaction mixture and the resulting blend then refluxed for 2 h. The residue obtained after cooling to RT and evaporation of volatiles was extracted with hexane, and the resulting suspension filtered. The solvent was removed from the filtrate under reduced pressure and the residue purified by trap-to trap distillation in vacuum (0.1 mbar). The first fraction boiling at 70–110 °C contained Et₃NBH₃ and was discarded. Collection of the higher boiling fraction yielded 80 mg of a colorless oil consisting of a mixture of **2a'** and **3**. – Data for **2a'**: ^1H NMR (toluene-*d*₈) $\delta=7.07$ –6.97 (m, 6 H, C₆H₃), 3.43 (dsept, $^3J_{\text{HH}}=7$ Hz, $^5J_{\text{PH}}=2$ Hz, 4 H, CH), 1.13 (d, $^3J_{\text{HH}}=7$ Hz, 12 H, CH₃), 1.08 (d, $^3J_{\text{HH}}=7$ Hz, 12 H, CH₃), 0.39 (d, $^3J_{\text{PH}}=4$ Hz, 9 H, SiMe₃). – ^{31}P NMR (toluene-*d*₈): $\delta=248.0$ (b). – $^{29}\text{Si}\{^1\text{H}\}$ NMR (toluene-*d*₈): $\delta=-0.34$ ($^1J_{\text{PSi}}=16$ Hz). – $^{13}\text{C}\{^1\text{H}\}$ NMR (toluene-*d*₈): $\delta=151.7$ (d, $^2J_{\text{PC}}=2$ Hz, *i*-C₆H₃), 139.6 (d, $^3J_{\text{PC}}=2$ Hz, *o*-C₆H₃), 123.9 (d, $^5J_{\text{PC}}=1$ Hz, *p*-C₆H₃), 123.8 (d, $^4J_{\text{PC}}=1$ Hz, *m*-C₆H₃), 27.2 (d, $^4J_{\text{PC}}=7$ Hz, CH), 23.6 (s, CH₃), 23.4 (d, $^5J_{\text{PC}}=1$ Hz, CH₃), -3.7 (d, $^2J_{\text{PC}}=10$ Hz, SiMe₃).

Diethyl(triphenylsilyl)phosphonite **2b**: **6b** (300 mg, 0.76 mmol) and DABCO (341 mg, 3.04 mmol) were dissolved in hexane (20 mL) and the solution heated for 4 h to 66 °C. The resulting mixture was allowed to cool to RT and a solution of MgBr₂·OEt₂ (786 mg, 3.94 mmol) in Et₂O (10 mL) added. A colorless precipitate formed, and the resulting suspension was stirred for 1 h and then filtered over Celite. The residue was washed with hexane (2 × 20 mL), and the combined filtrates evaporated to dryness. The

residue was dissolved in pure hexane (20 mL), the resulting solution concentrated to a volume of 3 mL and stored at -25°C . Any precipitated solid was separated and discarded and the supernatant solution evaporated to dryness to give **2b** as a colorless solid (yield 58 mg, 0.15 mmol, 20%). ^1H NMR: $\delta = 7.97$ (m, 6 H, *o*-Ph), 7.23–7.16 (m, 9 H, *m/p*-Ph), 3.91–3.67 (m, 4 H, CH_2), 0.98 (dt, $^3J_{\text{HH}} = 7.0$ Hz, $^5J_{\text{PH}} = 0.6$ Hz, 6 H, CH_3). ^{31}P NMR: $\delta = 217.7$ (quint, $^3J_{\text{PH}} = 9$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR: $\delta = 136.6$ (d, $^3J_{\text{PC}} = 3$ Hz, *o*-Ph), 133.4 (d, $^2J_{\text{PC}} = 11$ Hz, *i*-Ph), 129.6 (d, $^5J_{\text{PC}} = 1$ Hz, *p*-Ph), 128.0 (s, *m*-Ph), 69.4 (d, $^2J_{\text{PC}} = 15$ Hz, CH_2), 17.0 (d, $^3J_{\text{PC}} = 5$ Hz, CH_3). ^{29}Si NMR: $\delta = -23.6$ ($^1J_{\text{PSi}} = 26$ Hz). $\text{C}_{22}\text{H}_{25}\text{O}_2\text{PSi}$ (380.14 g mol^{-1}): calcd. C 69.45 H 6.62, found C 68.94 H 5.36.

Diisopropyl(triphenylsilyl)phosphonite 2c: The preparation was carried out as described for **2b** from **6c** (187 mg, 0.44 mmol) and DABCO (199 mg, 1.76 mmol). Yield 33 mg (81 μmol , 18%) of a colorless solid. ^1H NMR: $\delta = 7.92$ (m, 6 H, *o*-Ph), 7.23–7.18 (m, 9 H, *m/p*-Ph), 3.79 (dsept, $^3J_{\text{HH}} = 8.8$ Hz, $^3J_{\text{HH}} = 6.1$ Hz, 2 H, CH), 1.14 (d, $^3J_{\text{HH}} = 6.1$ Hz, 6 H, CH_3), 0.99 (d, $^3J_{\text{HH}} = 6.1$ Hz, 6 H, CH_3). ^{31}P NMR: $\delta = 209.0$ (t, $^3J_{\text{PH}} = 9$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR: $\delta = 136.7$ (d, $^3J_{\text{PC}} = 3$ Hz, *o*-Ph), 133.4 (d, $^2J_{\text{PC}} = 11$ Hz, *i*-Ph), 129.5 (d, $^5J_{\text{PC}} = 1$ Hz, *p*-Ph), 127.9 (s, *m*-Ph), 77.0 (d, $^2J_{\text{PC}} = 16$ Hz, CH), 24.3 (d, $^3J_{\text{PC}} = 3$ Hz, CH_3), 24.1 (d, $^3J_{\text{PC}} = 3$ Hz, CH_3). $^{29}\text{Si}\{^1\text{H}\}$ NMR: $\delta = -22.9$ ($^1J_{\text{PSi}} = 19$ Hz). $\text{C}_{24}\text{H}_{29}\text{O}_2\text{PSi}$ (408.55 g mol^{-1}): calcd. C 70.56 H 7.16, found C 68.06 H 7.61.

Bis-(2,6-diisopropylphenyl)(triphenylgermyl)phosphonite 8a: A solution of **7a** (195 mg, 0.41 mmol) in toluene (10 mL) and NEt_3 (418 mg, 0.57 mL, 4.1 mmol) was stirred for 18 h at RT. Volatiles were evaporated under reduced pressure and the residue taken up in hexane (20 mL). The mixture was filtered over Celite. The product was eluted from the filter cake with hexane (2×20 mL). Removal of the solvent from the eluate under reduced pressure produced 56 mg (81 μmol , 20%) of **8a** as colorless solid. ^1H NMR: $\delta = 8.01$ (m, 6 H, *o*-Ph), 7.33–7.27 (m, 12 H, *m/p*-Ph and C_6H_3), 3.52 (dsept, $^3J_{\text{HH}} = 7.0$ Hz, $^5J_{\text{PH}} = 1.5$ Hz, 4 H, CH), 1.16 (d, $^3J_{\text{HH}} = 7.0$ Hz, 12 H, CH_3), 1.11 (d, $^3J_{\text{HH}} = 7.0$ Hz, 12 H, CH_3). ^{31}P NMR: $\delta = 252.1$ (s). $^{13}\text{C}\{^1\text{H}\}$ NMR: $\delta = 151.0$ (d, $^2J_{\text{PC}} = 2$ Hz, *i*- C_6H_3), 140.4 (d, $^3J_{\text{PC}} = 3$ Hz, *o*- C_6H_3), 136.5 (d, $^2J_{\text{PC}} = 7$ Hz, *i*-Ph), 135.9 (d, $^3J_{\text{PC}} = 2$ Hz, *o*-Ph), 129.3 (s, *m*-Ph), 128.6 (s, *p*-Ph), 124.7 (d, $^5J_{\text{PC}} = 2$ Hz, *p*- C_6H_3), 124.3 (d, $^4J_{\text{PC}} = 1$ Hz, *m*- C_6H_3), 27.7 (d, $^4J_{\text{PC}} = 5$ Hz, CH), 23.9 (d, $^5J_{\text{PC}} = 1$ Hz, CH_3), 23.5 (d, $^5J_{\text{PC}} = 1$ Hz, CH_3). $\text{C}_{42}\text{H}_{49}\text{GeO}_2\text{P}$ (689.46 g mol^{-1}): calcd. C 73.17 H 7.16, found C 72.78 H 7.20.

General procedure for the in-situ preparation of phosphonite-nickeltricarboxylates: The appropriate phosphonite (8.5 μmol) was dissolved in a 0.085 M stock solution of $\text{Ni}(\text{CO})_4$ in toluene (2.0 mL of solution, 0.17 mmol of $\text{Ni}(\text{CO})_4$) and the solution stirred for 2 h at RT. A portion (0.6 mL) of this solution was transferred to an NMR tube, volatiles were removed under reduced pressure, the residue dissolved in C_6D_6 (0.5 mL) and characterized by NMR spectroscopy. The remaining reaction mixture was evaporated to dryness, the residue dissolved in CH_2Cl_2 (0.3 mL) and the solution analyzed by IR spectroscopy.

{Bis-(2,6-diisopropylphenyl)(triphenylsilyl)phosphonite} tricarboxyl nickel(0) 10a: ^1H NMR: $\delta = 8.04$ (m, 6 H, *o*-Ph), 7.17 (b, 9 H, *m/p*-Ph), 7.01 (b, 6 H, C_6H_3), 3.40 (sept, 4 H, $^3J_{\text{HH}} = 6.8$ Hz, CH), 1.06 (d, 12 H, $^3J_{\text{HH}} = 6.8$ Hz, CH_3), 0.82 (d, 12 H, $^3J_{\text{HH}} = 6.8$ Hz, CH_3). $^{31}\text{P}\{^1\text{H}\}$ NMR: $\delta = 248.2$ (s). $^{29}\text{Si}\{^1\text{H}\}$ NMR: $\delta = -18.5$ ($^1J_{\text{PSi}} = 38$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR: $\delta = 194.6$ (d, $^2J_{\text{PC}} = 5$ Hz, CO), 149.8 (d, $^3J_{\text{PC}} = 9$ Hz, *i*- C_6H_3), 141.7 (d, $^3J_{\text{PC}} = 3$ Hz, *o*- C_6H_3), 137.6 (d, $^2J_{\text{PC}} = 2$ Hz, *o*-Ph), 135.3 (s, *i*-Ph), 132.0 (s, *p*-Ph), 130.3 (s, *m*-Ph), 125.5 (d, $^5J_{\text{PC}} = 2$ Hz, *p*- C_6H_3), 123.8 (d, $^4J_{\text{PC}} = 2$ Hz, *m*- C_6H_3), 27.9 (d, $^3J_{\text{PC}} = 1$ Hz, CH), 23.7 (s, CH_3), 23.0 (s, CH_3). ^1H NMR: $\delta = 2072$ (a_1), 2005 (e) (νCO).

{Bis-(2,6-Diisopropylphenyl)(trimethylsilyl)phosphonite} tricarboxyl nickel(0) 10a': $^{31}\text{P}\{^1\text{H}\}$ NMR: $\delta = 244.4$ (s). ^1H NMR: $\delta = 2071$ (a_1), 2006 (e) (νCO).

{Diethyl(triphenylsilyl)phosphonite} tricarboxyl nickel(0) 10b: ^1H NMR: $\delta = 7.89$ (b, 6 H, *o*-Ph), 7.19 (b, 9 H, *m/p*-Ph), 3.72 (b, 4 H, CH_2), 0.92 (b, 6 H, CH_3). ^{31}P NMR: $\delta = 216.6$ (quint, $^3J_{\text{PH}} = 10$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR: $\delta = 136.7$ (s, *o*-Ph), 135.3 (s, *i*-Ph), 130.2 (s, *p*-Ph), 129.8 (s, *m*-Ph), 65.5 (s, CH_2), 16.2 (s, CH_3). ^1H NMR: $\delta = 2069$ (a_1), 1998 (e) (νCO).

{Diisopropyl(triphenylsilyl)phosphonite} tricarboxyl nickel(0) 10c: ^1H NMR: $\delta = 7.92$ (m, 6 H, *o*-Ph), 7.24–7.19 (m, 9 H, *m/p*-Ph), 4.26 (sept, $^3J_{\text{HH}} = 6.0$ Hz, 2 H, CH), 1.09 (d, $^3J_{\text{HH}} = 6.0$ Hz, 6 H, CH_3), 0.90 (d, $^3J_{\text{HH}} = 6.0$ Hz, 6 H, CH_3). ^{31}P NMR: $\delta = 211.9$ (t, $^3J_{\text{PH}} = 12$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR: $\delta = 196.4$ (d, $^2J_{\text{PC}} = 3$ Hz, CO), 136.8 (d, $^2J_{\text{PC}} = 2$ Hz, *o*-Ph), 135.1 (s, *i*-Ph), 131.2 (s, *p*-Ph), 130.1 (s, *m*-Ph), 74.4 (s, CH), 23.9 (d, $^3J_{\text{PC}} = 2$ Hz, CH_3), 23.6 (d, $^3J_{\text{PC}} = 2$ Hz, CH_3). ^1H NMR: $\delta = 2068$ (a_1), 1998 (e) (νCO).

{Bis-(2,6-diisopropylphenyl)(triphenylgermyl)phosphonite} tricarboxyl nickel(0) 11a: ^1H NMR: $\delta = 7.93$ (m, 6 H, *o*-Ph), 7.16 (m, *m/p*-Ph), 7.06 (b, 6 H, C_6H_3), 3.46 (sept, $^3J_{\text{HH}} = 6.4$ Hz, 4 H, CH), 1.09 (d, $^3J_{\text{HH}} = 6.4$ Hz, 12 H, CH_3), 0.83 (d, $^3J_{\text{HH}} = 6.4$ Hz, 12 H, CH_3). ^{31}P NMR: $\delta = 249.7$ (s). $^{13}\text{C}\{^1\text{H}\}$ NMR: $\delta = 141.6$ (d, $^3J_{\text{PC}} = 3$ Hz, *o*- C_6H_3), 136.4 (d, $^2J_{\text{PC}} = 2$ Hz, *o*-Ph), 135.4 (s, *i*-Ph), 129.6 (s, *m*-Ph), 128.4 (s, *p*-Ph), 125.6 (d, $^5J_{\text{PC}} = 2$ Hz, *p*- C_6H_3), 123.9 (d, $^4J_{\text{PC}} = 2$ Hz, *m*- C_6H_3), 28.2 (d, $^3J_{\text{PC}} = 1$ Hz, CH), 23.7 (s, CH_3), 23.1 (s, CH_3). ^1H NMR: $\delta = 2073$ (a_1), 2005 (e) (νCO).

{Bis-(2,6-diisopropylphenyl)(triphenylstannyl)phosphonite} tricarboxyl nickel(0) 12: ^1H NMR: $\delta = 7.67$ (m, 6 H, *o*-Ph), 7.12–7.08 (m, 9 H, *m/p*-Ph), 7.00 (b, 6 H, C_6H_3), 3.64 (sept, $^3J_{\text{HH}} = 7$ Hz, 4 H, CH), 1.12 (d, $^3J_{\text{HH}} = 7$ Hz, 12 H, CH_3), 0.91 (d, $^3J_{\text{HH}} = 7$ Hz, CH_3). ^{31}P NMR: $\delta = 257.2$ (s). $^{13}\text{C}\{^1\text{H}\}$ NMR: $\delta = 141.4$ (d, $^3J_{\text{PC}} = 4$ Hz, *o*- C_6H_3), 137.7 (d, $^2J_{\text{PC}} = 1$ Hz, *o*-Ph), 137.5 (s, *i*-Ph), 129.2 (s, *m*-Ph), 128.7 (s, *p*-Ph), 125.9 (s, *p*- C_6H_3), 124.4 (d, $^4J_{\text{PC}} = 2$ Hz, *m*- C_6H_3), 28.5 (s, CH), 23.6 (s, CH_3), 23.1 (s, CH_3). ^1H NMR: $\delta = 2073$ (a_1), 2007 (e) (νCO).

{Bis-(2,6-diisopropylphenyl)phosphonite} tricarboxyl nickel(0) 13: ^1H NMR: $\delta = 7.93$ (d, $^1J_{\text{PH}} = 344.2$ Hz, 1 H, PH), 7.05 (b, 6 H, C_6H_3), 3.57 (sept, $^3J_{\text{HH}} = 6.8$ Hz, 4 H, CH), 1.24 (d, $^3J_{\text{HH}} = 6.8$ Hz, 6 H, CH_3), 1.21 (d, $^3J_{\text{HH}} = 6.8$ Hz, CH_3). ^{31}P NMR: $\delta = 187.2$ (d, $^1J_{\text{PH}} = 344$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR: $\delta = 193.8$ (d, $^2J_{\text{PC}} = 3$ Hz, CO), 152.0 (d, $^3J_{\text{PC}} = 10$ Hz, *i*- C_6H_3), 140.4 (d, $^3J_{\text{PC}} = 4$ Hz, *o*- C_6H_3), 126.0 (d, $^5J_{\text{PC}} = 2$ Hz, *p*- C_6H_3), 124.4 (d, $^4J_{\text{PC}} = 2$ Hz, *m*- C_6H_3), 27.9 (d, $^4J_{\text{PC}} = 1$ Hz, CH), 23.7 (s, CH_3), 23.0 (s, CH_3). ^1H NMR: $\delta = 2083$ (a_1), 2016 (e) (νCO).

General procedure for the reactions of diorgano(triphenylsilyl)phosphonite with selenium: A NMR tube was charged with the appropriate phosphonite and grey selenium. C_6D_6 (0.6 mL) was added, the mixture homogenized until the phosphonite had completely dissolved, and the sample immediately characterized by ^{31}P and ^{77}Se NMR spectroscopy.

Selenation of **2b**: **2b** (5 mg, 13 μmol) and Se (2 mg, 25 μmol) were reacted as described. Selenophosphonate **15b** was identified as main product. ^{31}P NMR: $\delta = 109.5$ (q, $^3J_{\text{PH}} = 11$ Hz, $^1J_{\text{PSe}} = 166$ Hz, $^1J_{\text{PSe}} = 810$ Hz, **15b**), 198.6 ($^3J_{\text{PH}} = 8$ Hz, $^1J_{\text{PSe}} = 285$ Hz, **16b**). $^{77}\text{Se}\{^1\text{H}\}$ NMR: $\delta = -174.9$ (d, $^1J_{\text{PSe}} = 810$ Hz, **15b**).

Selenation of **2c**: **2c** (5 mg, 12 μmol) and Se (2 mg, 25 μmol) were reacted as described to afford a mixture of selenophosphonate **15c** (77%), unreacted **2c** (18%), and a further species attributed as **16c**, (5%). ^{31}P NMR: $\delta = 105.1$ (t, $^3J_{\text{PH}} = 14$ Hz, $^1J_{\text{PSe}} = 173$ Hz, $^1J_{\text{PSe}} = 803$ Hz, **15c**), 197.3 ($^3J_{\text{PH}} = 11$ Hz, **16c**). $^{77}\text{Se}\{^1\text{H}\}$ NMR: $\delta = -174.3$ (d, $^1J_{\text{PSe}} = 803$ Hz, **15c**).

Selenation of **2a**: **2a** (30 mg, 46.5 μmol) and Se (7 mg, 93.0 μmol) were dissolved in toluene (2 mL) and stirred at RT. Reaction

monitoring by NMR spectroscopy revealed that conversion of **2a** was complete after 4 weeks. The NMR spectrum of the reaction mixture and afforded a mixture containing a product attributed as **16a** beside further species arising from overoxidation. **16a** decomposed during attempted work-up. $^{-31}\text{P}\{^1\text{H}\}$ NMR: $\delta = 227.0$ (s, $^1J_{\text{PSe}} = 354$ Hz, **16a**).

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Conflict of Interests

The authors declare no conflict of interest.

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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