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P-Chiral Phosphinoselenoic Chlorides and Phosphinochalcogenoselenoic Acid Esters: Synthesis, Characterization, and Conformational Studies

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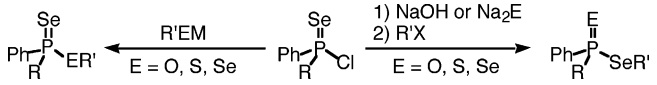

P-Chiral alkyl or aryl phenylphosphinoselenoic chlorides were obtained by reacting $PhPCl_2$ with Grignard reagents and elemental selenium. *P*-Chiral dialkyl chlorides were also obtained by treating PCl_3 with two different Grignard reagents and elemental selenium. The structure of the chloride was determined by X-ray molecular structure analysis. *P*-Chiral phosphinochalcogenoselenoic acid esters bearing a P═Se double bond were synthesized by treating the chlorides with alkali metal alkoxide and chalcogenolates, whereas those bearing a P−Se single bond were obtained by sequential treatment of the chlorides with sodium hydroxide, sulfide or selenide, and alkyl iodides. X-ray molecular structure analyses of esters showed that they adopted gauche conformations. The computational results supported the observed conformational preference. Natural bond orbital analyses of the model compounds showed that two types of nonbonding orbital interactions, $n_{E'} \rightarrow \sigma^*_{P=E}$ and $n_E \rightarrow \sigma^*_{P-E'}$, are important in these compounds. Linear correlations were observed between the experimental ^{77}Se NMR chemical shifts or the coupling constants of P−Se bonds in the esters and the calculated P−Se bond lengths of the model compounds.

Introduction

Studies on *P*-chiral phosphinic-,[1] phosphinothioic-,[2] and phosphinodithioic acid derivatives[3] **I** and **II** have made important contributions to the field of synthetic chemistry. In contrast, much less attention has been paid to selenium-containing *P*-chiral phosphinic acid derivatives, that is, phosphinochalcogenoselenoic acid derivatives **III** and **IV** (Figure 1).

This is mainly due to the lack of the appropriate starting materials leading to these compounds. Nevertheless, compounds **III** are of great interest because the P═Se group exhibits lower polarity and higher affinity toward soft metals than the P═O group. Consequently, derivatives **III** (E = O) have been reported,[4] and their reactions such as isomerization of allyl esters[5] have been disclosed. However, there are scarce examples of the synthesis of *P*-chiral derivatives **III** and **IV** (E = S, Se). Very recently, we reported the synthesis and characterization of *P*-chiral phosphinoselenoic chlorides and their conversion to optically active *P*-chiral phosphinoselenoic amides.[6] We report here the synthesis and spectroscopic, structural, and theoretical studies on a series of *P*-chiral phosphinochalcogenoselenoic acid esters **III** and **IV** along with the detailed synthesis and structure of *P*-chiral phosphinoselenoic chlorides.

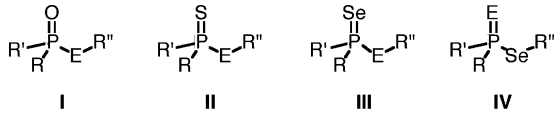

FIGURE 1. *P*-Chiral phosphinochalcogenoselenoic acid derivatives.

Results and Discussion

Synthesis of *P*-Chiral Phosphinoselenoic Chlorides. As we previously reported, *P*-chiral phosphino-

(1) (a) Au-Yeung, T.-L.; Chan, K.-Y.; Chan, W.-K.; Haynes, R. K.; Williams, I. D.; Yeung, L. L. *Tetrahedron Lett.* **2001**, *42*, 453. (b) Horner, L.; Schlotthauer, B. *Phosphorus Sulfur* **1978**, *4*, 155.

(2) Krawiecka, B.; Michalski, J.; Wojna-Tadeusiak, E. *J. Org. Chem.* **1986**, *51*, 4201.

(3) (a) Kawashima, T.; Kojima, S.; Inamoto, N. *Chem. Lett.* **1989**, 849. (b) Omelanczuk, J.; Mikolajczyk, M. *J. Chem. Soc., Chem. Commun.* **1994**, 2223.

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(5) (a) Nuretdinov, I. A.; Buina, N. A.; Bayandina, E. V.; Loginova, E. I.; Gainullina, R. G. *Zh. Obshch. Khim.* **1978**, *48*, 547. (b) Nuretdinov, I. A.; Buina, N. A.; Bayandina, E. V. *Zh. Obshch. Khim.* **1978**, *48*, 1073.

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SCHEME 1

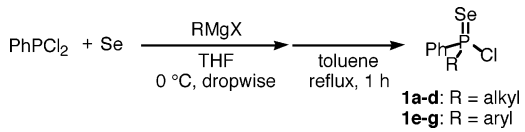
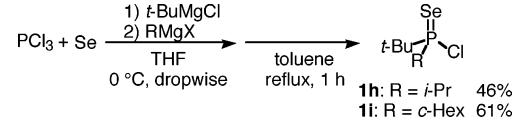


TABLE 1. Synthesis of *P*-Chiral Phosphinoselenoic Chlorides[a]

entry	1	R	yield (%)[b]
1	**1a**	*i*-Pr	91
2	**1b**	*c*-Hex	96
3	**1c**	*sec*-Bu	82
4	**1d**	*t*-Bu	94
5	**1e**	2-$MeOC_6H_4$	61
6	**1f**	4-MeC_6H_4	72
7	**1g**	4-ClC_6H_4	68

[a] The reaction was carried out with 10−30 mmol of $PhPCl_2$ and alkyl (1.0 equiv) or aryl (0.2 equiv) Grignard reagents in the presence of elemental selenium (1.1 equiv) in THF under Ar. [b] Yields of isolated products based on the Grignard reagents.

SCHEME 2



selenoic chlorides were synthesized by reacting $PhPCl_2$ with Grignard reagents and elemental selenium (Scheme 1, Table 1).[6] As Grignard reagents, secondary and tertiary alkyl Grignard reagents were used, and alkyl phenylphosphinoselenoic chlorides **1a**−**d** were obtained in good to high yields (entries 1−4). As for the synthesis of diaryl derivatives **1e**−**g**, excess $PhPCl_2$ was reacted with aryl Grignard reagents (entries 5−7). The method for the synthesis of chlorides bearing two different alkyl groups on the phosphorus atom was developed further (Scheme 2). The sequential addition of two different Grignard reagents to a mixture of PCl_3 and elemental selenium successfully gave dialkyl chlorides **1h** and **1i**. The resulting phosphinoselenoic chlorides were air- and moisture-stable and could easily be handled under air, despite the fact that phosphinic chlorides were prone to be hydrolyzed.

The formation of chlorides **1** was unequivocally demonstrated by X-ray molecular structure analysis (Figure 2). This is the first X-ray molecular structure analysis of phosphinoselenoic chlorides. The phosphorus atom adopts a slightly distorted tetrahedral structure. The P═Se group is located in an equatorial position in the cyclohexyl ring. The P−Cl bond length (2.053 Å) is close to that of the sulfur derivative (2.063 Å)[7] and slightly longer than that of the oxygen derivative (2.017 Å).[8]

Synthesis of *P*-Chiral Phosphinochalcogenoselenoic Acid Esters. Since phosphinoselenoic chlorides **1**, which were key precursors of phosphinoselenoic acid derivatives, were obtained, the synthesis of five different types of phosphinochalcogenoselenoic acid esters was examined by using the chlorides **1** as starting materials.

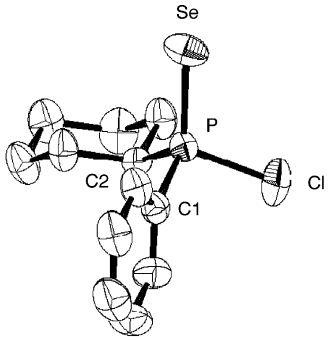


FIGURE 2. ORTEP drawing of phosphinoselenoic chloride **1b** with thermal ellipsoid plot (50% probability). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): P−Se, 2.0812(7); P−Cl, 2.0534(9); P−C1, 1.805(3); P−C2, 1.819(2). Selected bond angles (°): Se−P−Cl, 112.57(4); Se−P−C1, 115.19(8); Se−P−C2, 116.23(8); Cl−P−C1, 101.97(9); Cl−P−C2, 102.53(8); C1−P−C2, 106.7(1).

SCHEME 3

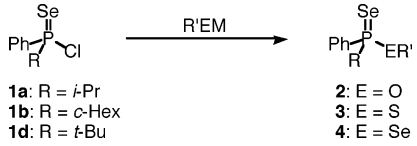


TABLE 2. Synthesis of *P*-Chiral Phosphinochalcogenoselenoic Acid Esters

entry	1	R	ester	R′	E	R′EM	yield (%)[e]
1[a]	**1d**	*t*-Bu	**2a**	Et	O	EtONa	98
2[a]	**1b**	*c*-Hex	**2b**	Et	O	EtONa	93
3[b]	**1d**	*t*-Bu	**3a**	Bu	S	BuSLi	95
4[b]	**1a**	*i*-Pr	**3b**	Bu	S	BuSLi	99
5[b]	**1d**	*t*-Bu	**3c**	Ph	S	PhSLi	79
6[b]	**1d**	*t*-Bu	**3d**	R″[d]	S	R″SLi[d]	93
7[c]	**1d**	*t*-Bu	**4a**	Bu	Se	BuSeLi	96
8[c]	**1d**	*t*-Bu	**4b**	*t*-Bu	Se	*t*-BuSeLi	66
9[c]	**1d**	*t*-Bu	**4c**	Ph	Se	PhSeLi	99

[a] Chloride **1** was treated with EtONa (2 equiv) under reflux in EtOH for 3 h. [b] Chloride **1** was treated with R′SLi (1 equiv) in THF at 0 °C for 1 h. [c] Chloride **1** was treated with R′SeLi (1 equiv) in THF at 0 °C for 15 min. [d] R″ = $Me_3SiCH_2CH_2$. [e] Yields of isolated products.

Initially, the synthesis of *P*-chiral phosphinochalcogenoselenoic acid esters bearing a P═Se double bond **2**−**4** was carried out by treating the chlorides **1** with alkali metal alkoxide and chalcogenolates (Scheme 3, Table 2). The reaction of the chlorides **1b** and **1d** with sodium ethoxide proceeded under reflux in EtOH to give phosphinoselenoic acid *O*-ethyl esters[4] **2a** and **2b** in respective yields of 98 and 93% (entries 1 and 2). Phosphinoselenoic chlorides **1** were then converted to various phosphinoselenothioic acid *S*-esters[9] **3a**−**d** by reacting them with lithium thiolates such as lithium 1-butanethiolate, benzenethiolate, and (2-trimethylsilyl)ethanethiolate (entries 3−6). Furthermore, a similar reaction of chlorides **1** with lithium selenolates gave phosphinodiselenoic acid alkyl and aryl esters[10] **4a**−**c** in moderate to high yields (entries 7−9).

Next, a variety of *P*-chiral phosphinochalcogenoselenoic acid esters bearing a P−Se single bond **8**, **9**, and **4** were

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(8) Kardanov, N. A.; Tkachev, V. V.; Godovikov, N. N.; Kabachnik, M. I. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1984**, *5*, 1052.
(9) Murai, T.; Kimura, T.; Miwa, A.; Kurachi, D.; Kato, S. *Chem. Lett.* **2002**, 914.
(10) Kuchen, W.; Knop, B. *Chem. Ber.* **1966**, *99*, 1663.

SCHEME 4

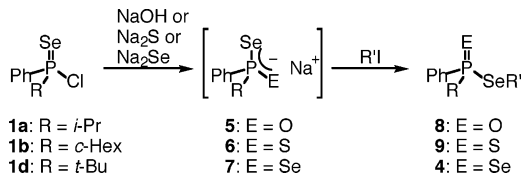


TABLE 3. Synthesis of *P*-Chiral Phosphinochalcogenoselenoic Acid *Se*-Esters

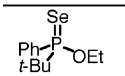
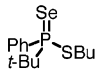
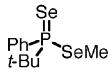
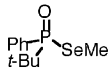
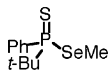
entry	1	R	ester	R′	E	reactants	yield (%)[d]
1[a]	**1d**	*t*-Bu	**8a**	Me	O	NaOH/MeI	98
2[a]	**1b**	*c*-Hex	**8b**	Et	O	NaOH/EtI	95
3[b]	**1d**	*t*-Bu	**9a**	Me	S	Na_2S/MeI	90
4[b]	**1a**	*i*-Pr	**9b**	Bu	S	Na_2S/BuI	93
5[c]	**1d**	*t*-Bu	**4d**	Me	Se	Na_2Se/MeI	94

[a] Chloride **1** was treated with NaOH (10 equiv) in CH_3CN at room temperature for 24 h, and then to the reaction mixture was added alkyl iodide (2 equiv) at room temperature. [b] Chloride **1** was treated with Na_2S (5 equiv) in CH_3CN at room temperature for 6 h, and then to the reaction mixture was added alkyl iodide (2 equiv) at room temperature. [c] Chloride **1a** was treated with Na_2Se (1.1 equiv) in CH_3CN at 0 °C for 4 h, and then to the reaction mixture was added methyl iodide (2 equiv) at 0 °C. [d] Yields of isolated products.

synthesized by alkylation of the phosphinochalcogenoselenoic acid salts **5**−**7** (Scheme 4, Table 3). Phosphinoselenoic acid salts[11] **5** were successfully generated by reacting the chlorides **1b** and **1d** with sodium hydroxide. Alkylation of the salts **5** with alkyl iodides such as methyl iodide and butyl iodide proceeded smoothly at the selenium atom to form phosphinoselenoic acid *Se*-esters[11,12] **8a** and **8b** in high yields (entries 1 and 2). When the chlorides **1** were treated with sodium sulfide, phosphinoselenothioic acid salts[9,10] **6** were generated in situ. The resulting salts **6** were reacted with alkyl iodides to give phosphinoselenothioic acid *Se*-esters[9,10] **9** (entries 3, 4). In this reaction, the alkyl groups were selectively introduced to the selenium atom of the salts **6**. As an alternative method for the synthesis of diselenoic acid esters **4**, the chloride **1a** was reacted with Na_2Se, and the reaction of the resulting phosphinodiselenoic acid salt[13] **7** with methyl iodide gave ester **4d** in 94% yield (entry 5). Notably, all of the esters were stable both as a solid and in solution under air.

Spectroscopic Properties of Phosphinochalcogenoselenoic Acid Esters. The spectroscopic properties of selected alkyl esters **2a**, **3a**, **4d**, **8a**, and **9a** are shown in Table 4. In the ^{31}P NMR spectra, the signals of the esters were observed at 90 ± 22 ppm. The signal of *O*-ester **2a** was observed at a lower field than those of *S*-ester **3a** and *Se*-ester **4d** by about 23−27 ppm, whereas the signal of the ester **8a** was shifted upfield by about 15−20 ppm compared to those of the corresponding sulfur **9a** and selenium derivatives **4d**. In the ^{77}Se NMR spectra, the signals of the selenium atom in the P═Se double bond of **2a**, **3a**, and **4d** were observed in the range of −350 to −280 ppm. On the other hand, the signals of the selenium atom in the P−Se single bond of **8a**, **9a**, and **4d** were observed in the range of 54−113 ppm. On going from the oxygen atom to the selenium atom, the signals **2a**, **3a**, and **4d** were shifted to lower fields, and those of **8a**, **9a**, and **4d** were also shifted to lower fields. The coupling constants between the phosphorus and selenium atoms of **2a**, **3a**, and **4d** were 764−786 Hz, which belonged to typical values for coupling constants between P═Se double bonds. Alternatively, typical coupling constants of P−Se single bonds (366−391 Hz) were detected for the esters **8a**, **9a**, and **4d**. In the former case, the coupling constants decreased in the order **2a** [P(Se)O] to **3a** [P(Se)S] and **4d** [P(Se)Se]. Similarly, the coupling constants of P−Se single bonds decreased in the order **8a** [P(O)Se] to **9a** [P(S)Se] and **4d** [P(Se)Se].

TABLE 4. Selected NMR Spectroscopic Data of Phosphinochalcogenoselenoic Acid Alkyl Esters

ester	^{31}P (δ)[a]	^{77}Se (δ)[a]	J_{PSe} (Hz)[a]
 **2a**	111.0	−350.3	786.3
 **3a**	88.0	−310.8	763.7
 **4d**	82.6	−279.7	762.9
		112.6	366.2
 **8a**	68.2	54.4	390.9
 **9a**	88.3	108.2	366.8

[a] Measured in $CDCl_3$.

X-ray Molecular Structure Analyses of Phosphinochalcogenoselenoic Acid Esters. The molecular structures of phosphinoselenothioic **3d** and phosphinodiselenoic acid esters **4c** were determined by X-ray molecular structure analyses. ORTEP drawings of the esters **3d** and **4c** are shown in Figures 3 and 4. The torsion angles in **3d** (Se−P−S−C3) and **4c** (Se1−P−Se2−C3) are −34.8° and −53.0°, respectively, which indicate that these molecules preferred a gauche conformation in the solid state.[14] In each case, the substituents on the chalcogen atoms are located anti to the bulky *tert*-butyl group. The phosphorus atoms adopt a slightly distorted tetrahedral structure, and no significant change in the P−C bond lengths or the angles around the phosphorus atom was observed compared to those in phosphinoselenoic chloride **1b**.

Calculation. To elucidate the conformational preference of the esters, geometry optimizations and energy calculations for model compounds **2′**−**4′**, **8′**, and **9′** were performed using the 6-31+G(d) basis set at the B3LYP level[15] with the Gaussian 98 program[16] (Scheme 5). In each case, three conformations, that is, eclipsed, gauche, and anti conformations, were optimized (Figure 5). The

(11) Kawashima, T.; Iwanaga, H.; Okazaki, R. *Heteroat. Chem.* **1995**, *6*, 235.
(12) Krawiecka, B. *Heteroat. Chem.* **1992**, *3*, 385.
(13) Davies, R. P.; Martinelli, M. G. *Inorg. Chem.* **2002**, *41*, 348.
(14) Lepicard, G.; De Saint-Giniez, D.; Laurent, A.; Rerat, C. *Acta Crystallogr., Sect. B* **1969**, *25*, 617.
(15) Becke's three parameter hybrid method using the LYP correlation functional: Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

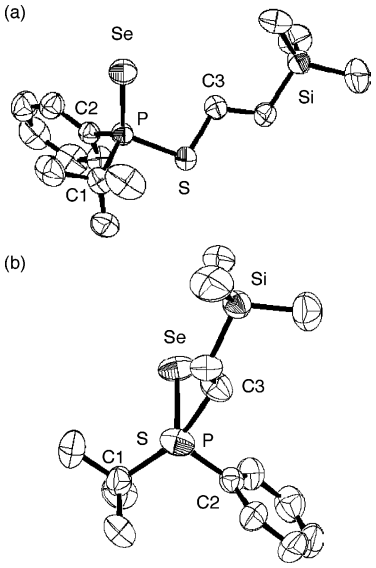


FIGURE 3. (a) ORTEP drawing of phosphinoselenothioic acid *S*-ester **3d** with thermal ellipsoid plot (50% probability). (b) The view of **3d** along the P−S bond. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Se−P, 2.1034(9); P−S, 2.096(1); P−C1, 1.858(3); P−C2, 1.814(3); S−C3, 1.822(3). Selected bond angles and torsion angle (°): Se−P−S, 114.47(5); Se−P−C1, 114.3(1); Se−P−C2, 111.9(1); S−P−C1, 101.8(1); S−P−C2, 107.0(1); C1−P−C2, 106.5(1); P−S−C3, 102.2(1); Se−P−S−C3, −34.8(1).

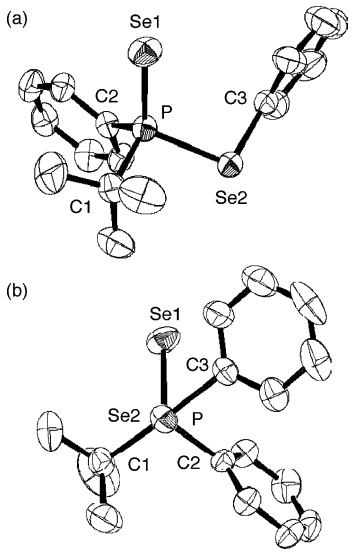


FIGURE 4. (a) ORTEP drawing of phosphinodiselenoic acid ester **4c** with thermal ellipsoid plot (50% probability). (b) The view of **4c** along the P−Se2 bond. Hydrogen atoms are omitted for clarity. Selected bond length (Å): Se1−P, 2.099(1); Se2−P, 2.259(1); P−C1, 1.864(4); P−C2, 1.816(4); Se2−C3, 1.922(3). Selected bond angles and torsion angle (°): Se1−P−Se2, 114.77(5); Se1−P−C1, 114.9(1); Se1−P−C2, 112.6(1); Se2−P−C1, 100.2(1); Se2−P−C2, 107.4(1); C1−P−C2, 105.8(2); P−Se2−C3, 101.1(1); Se1−P−Se2−C3, −53.0(1).

anti conformations were expected to be more stable than the others because of steric considerations. However, the gauche conformations were found to be the most stable in all cases (Table 5). This result is in good agreement with X-ray structure analyses of **3d** and **4c**. Thus, the stereoelectronic effects around the phosphorus atom in

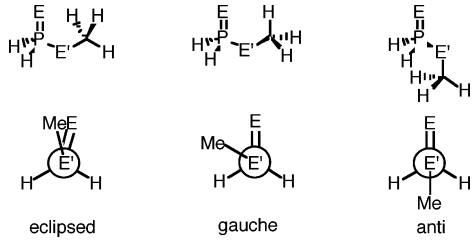


FIGURE 5. Newman projections of $H_2P(E)E'CH_3$ along the P−E′ Bonds.

SCHEME 5

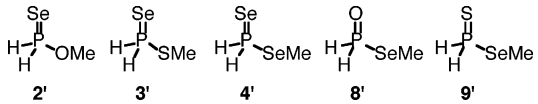


TABLE 5. Relative Conformational Energies (kcal/mol) of Model Compounds $H_2P(E)E'Ch_3$ [B3LYP/6-31+G(d)]

conformation	**2′**	**3′**	**4′**	**8′**	**9′**
anti	+2.580	+1.744	+0.889	+2.477	+1.813
eclipsed	+1.244	+0.827	+0.427	+0.967	+0.516
gauche	0.000	0.000	0.000	0.000	0.000

TABLE 6. NBO Analysis of $H_2P(E)E'Ch_3$ at B3LYP/6-31+G(d) Level (kcal/mol)

	2′	**3′**	**4′**	**8′**	**9′**
$n_{E'} \rightarrow \sigma^*_{P=E}$	6.3	3.5	2.0	6.1	3.0
$n_E \rightarrow \sigma^*_{P-E'}$	19.1	16.5	17.5	27.2	20.8

2′−**4′**, **8′**, and **9′** may be more important than steric effects.

To obtain further information about the stereoelectronic effects, natural bond orbital (NBO) analyses were carried out for model compounds **2′**−**4′**, **8′**, and **9′**, which adopted gauche conformation. The delocalization energies are listed in Table 6. The NBO analyses suggested that two types of nonbonding orbital interactions were important: (1) interaction between the lone pair of chalcogen atoms of P−E′ single bonds and the antibonding orbital of P=E double bonds ($n_{E'} \rightarrow \sigma^*_{P=E}$) and (2) interaction between the lone pair of chalcogen atoms of P=E double bonds and the antibonding orbital of P−E′ single bonds ($n_E \rightarrow \sigma^*_{P-E'}$). The preference for the gauche conformation may be due to the former interactions ($n_{E'} \rightarrow \sigma^*_{P=E}$). The interaction ($n_{E'} \rightarrow \sigma^*_{P=Se}$) in **2′** was greater than those in **3′** and **4′**. Similarly, the energy difference between the gauche and eclipsed conformations in **2′** was greater than those in **3′** and **4′**. Furthermore, among **4′**, **8′**, and **9′**, the interaction ($n_{Se} \rightarrow \sigma^*_{P=E}$) in **8′** was the greatest. This result is consistent with the

(16) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.7; Gaussian, Inc.; Pittsburgh, PA, 1998.

TABLE 7. B3LYP/6-31+G(d)-Optimized Geometries of Model Compounds $H_2P(E)E'Ch_3$

compound	**2′**	**3′**	**4′**	**8′**	**9′**
E	Se	Se	Se	O	S
E′	O	S	Se	Se	Se
		Bond Length (Å)			
P=E	2.092	2.106	2.110	1.499	1.962
P−E′	1.638	2.138	2.287	2.258	2.281
		Angle (deg)			
E−P−E′−C	50.3	41.4	33.1	54.5	41.3

shorter P−Se bond length in **8′** (2.258 Å) compared with those in **4′** (2.287 Å) and **9′** (2.281 Å), as shown in Table 7.

Finally, the relationship between spectroscopic properties of the esters and optimized parameters of the model compounds **2′**−**4′**, **8′**, and **9′** was observed (Tables 4 and 7). Although no linear correlation was observed between calculated P−Se bond lengths and ^{31}P NMR chemical shifts of the esters, P−Se bond lengths of model compounds were linearly correlated with the signals of esters in the ^{77}Se NMR spectra: δ (^{77}Se) = 2350 × L (P−Se) − 5255 (R^2 = 0.9980) (Figure 6). Furthermore, a linear correlation was also observed for the calculated P−Se bond lengths of model compounds with the coupling constants between the phosphorus atom and the selenium atom of the esters: J_{PSe} = −2277 × L (P−Se) + 5558 (R^2 = 0.9955) (Figure 7).

In summary, we obtained five different types of *P*-chiral phosphinochalcogenoselenoic acid esters from *P*-chiral phosphinoselenoic chlorides and appropriate oxygen and chalcogen nucleophiles. The gauche effect caused by the stereoelectronic effect was observed for the stable conformations of the esters. Furthermore, linear correlations were observed between the calculated P−Se bond lengths of model compounds and the ^{77}Se NMR chemical shifts or the coupling constants of P−Se bonds.

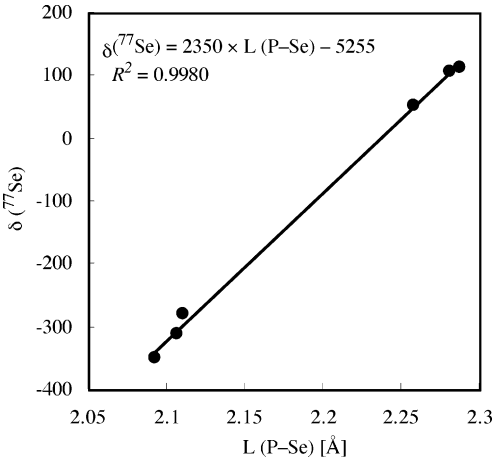


FIGURE 6. Plot of ^{77}Se NMR chemical shifts against calculated P−Se bond lengths.

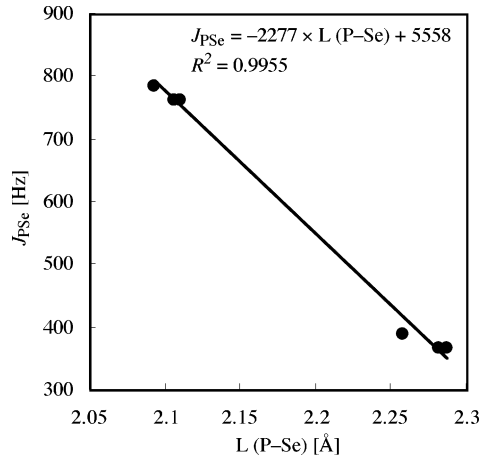


FIGURE 7. Plot of J_{PSe} against calculated P−Se bond lengths.

Experimental Section

General Procedures. All reactions were carried out under an argon atmosphere. Na_2Se was prepared according to the literature.[17] Silica gel used in column chromatography was silica gel 60 from a commercial supplier.

General Procedure for the Synthesis of Alkyl Phenylphosphinoselenoic Chlorides 1a−d. A Representative Procedure for the Synthesis of *P*-(1-Methylethyl)-*P*-phenylphosphinoselenoic Chloride (1a). To a suspension of elemental selenium (0.695 g, 8.80 mmol) in THF (40 mL) was added $PhPCl_2$ (1.09 mL, 8.00 mmol) at room temperature under an Ar atmosphere. To this mixture was added *i*-PrMgCl (2.0 mol/L Et_2O solution, 4.00 mL, 8.0 mmol) in THF (36 mL) dropwise over a period of 1 h at 0 °C with vigorous stirring. After the solvent was removed, toluene (20 mL) was added to the residue. The mixture was stirred under reflux in toluene for 1 h, and the insoluble parts were filtered off. After the solvent was removed, the residue was purified by column chromatography on silica gel using *n*-C_6H_{14}/CH_2Cl_2 as eluent to give 1.927 g (91%) of **1a** as a colorless oil. ^{1}H NMR: δ 0.97 (dd, J = 6.8 Hz, J_{HP} = 24.2 Hz, 3H), 1.36 (dd, J = 6.8 Hz, J_{HP} = 22.9 Hz, 3H), 2.76 (d of heptets, J = 6.8 Hz, J_{HP} = 9.8 Hz, 1H), 7.48−7.58 (m, 3H), 7.99−8.06 (m, 2H); ^{13}C NMR: δ 16.5 (d, J_{CP} = 1.7 Hz), 16.7, 40.0 (d, J_{CP} = 49.6 Hz), 128.6 (d, J_{CP} = 13.2 Hz), 131.8 (d, J_{CP} = 11.6 Hz), 132.0, 132.7 (d, J_{CP} = 3.3 Hz); ^{31}P NMR: δ 100.2 (J_{PSe} = 841.9 Hz); ^{77}Se NMR: δ −219.7 (d, J_{SeP} = 841.9 Hz); MS(EI) *m/z*: 266 (M^+); HRMS calcd for $C_9H_{12}ClPSe$: 265.9530. Found: 265.9537.

***P*-Cyclohexyl-*P*-phenylphosphinoselenoic Chloride (1b).** A colorless solid. mp: 79−81 °C (dec); ^{1}H NMR: δ 1.12−1.38 (m, 4H), 1.50−1.77 (m, 4H), 1.88−1.92 (m, 1H), 2.13−2.17 (m, 1H), 2.39−2.49 (m, 1H), 7.47−7.56 (m, 3H), 7.98−8.03 (m, 2H); ^{13}C NMR: δ 25.4 (d, J_{CP} = 1.7 Hz), 25.7 (d, J_{CP} = 7.4 Hz), 25.8 (d, J_{CP} = 5.6 Hz), 26.0 (d, J_{CP} = 3.3 Hz), 26.3, 49.4 (d, J_{CP} = 47.4 Hz), 128.5 (d, J_{CP} = 13.2 Hz), 131.9 (d, J_{CP} = 11.2 Hz), 132.1 (d, J_{CP} = 71.1 Hz), 132.6 (d, J_{CP} = 3.3 Hz); ^{31}P NMR: δ 95.8 (J_{PSe} = 840.4 Hz); ^{77}Se NMR: δ −196.5 (d, J_{SeP} = 840.4 Hz); MS(EI) *m/z*: 306 (M^+); Anal. Calcd for $C_{12}H_{16}ClPSe$: C, 47.16; H, 5.28. Found: C, 47.33; H, 5.18.

***P*-(1-Methylpropyl)-*P*-phenylphosphinoselenoic Chloride (1c).** A pale-yellow oil. ^{1}H NMR: δ 0.85, 1.04 (d, J = 7.8 Hz, 3H), 0.94, 1.36 (dd, J = 6.8 Hz, J_{HP} = 24.9 Hz, 3H), 1.22−1.58, 2.03−2.17 (m, 2H), 2.44−2.56 (m, 1H), 7.44−7.57 (m, 3H), 7.95−8.01 (m, 2H); ^{13}C NMR: δ 11.6 (d, J_{CP} = 18.2 Hz), 11.8 (d, J_{CP} = 17.4 Hz), 12.8, 13.0, 23.3, 23.5, 46.1 (d, J_{CP} = 48.0 Hz), 46.2 (d, J_{CP} = 48.0 Hz), 128.5 (d, J_{CP} = 13.2 Hz), 128.6 (d, J_{CP} = 13.2 Hz), 131.71 (d, J_{CP} = 11.6 Hz), 131.73 (d, J_{CP} = 11.6 Hz), 132.4 (d, J_{CP} = 71.1 Hz), 132.5 (d, J_{CP} = 72.0 Hz), 132.6 (d, J_{CP} = 3.3 Hz), 132.7 (d, J_{CP} = 3.3 Hz); ^{31}P NMR: δ 98.7 (J_{PSe} = 841.9 Hz); ^{77}Se NMR: δ −206.9 (d, J_{SeP} = 841.9 Hz), −205.0 (d, J_{SeP} = 841.9 Hz); MS(EI) *m/z*: 280 (M^+); Anal. Calcd for $C_{10}H_{14}ClPSe$: C, 42.96; H, 5.05. Found: C, 43.11; H, 4.96.

***P*-(1,1-Dimethylethyl)-*P*-phenylphosphinoselenoic Chloride (1d).** A colorless solid. mp: 72−74 °C (dec); ^{1}H NMR: δ

(17) Thompson, D. P.; Boudjouk, P. *J. Org. Chem.* **1988**, *53*, 2109.

1.25 (d, J_{HP} = 21.0 Hz, 9H), 7.45−7.56 (m, 3H), 8.00−8.06 (m, 2H); ^{13}C NMR: δ 24.7 (d, J_{CP} = 2.5 Hz), 42.7 (d, J_{CP} = 43.0 Hz), 128.1 (d, J_{CP} = 12.4 Hz), 130.7 (d, J_{CP} = 67.0 Hz), 132.4 (d, J_{CP} = 2.5 Hz), 133.1 (d, J_{CP} = 10.8 Hz); ^{31}P NMR: δ 111.0 (J_{PSe} = 837.3 Hz); ^{77}Se NMR: δ −171.5 (d, J_{SeP} = 837.3 Hz); MS(EI) *m/z*: 280 (M^+); Anal. Calcd for $C_{10}H_{14}ClPSe$: C, 42.96; H, 5.05. Found: C, 42.95; H, 4.87.

General Procedure for the Synthesis of Aryl Phenylphosphinoselenoic Chlorides 1e−g. A Representative Procedure for the Synthesis of *P*-(2-Methoxyphenyl)-*P*-phenylphosphinoselenoic Chloride (1e). To a suspension of elemental selenium (0.869 g, 11.0 mmol) in THF (20 mL) was added $PhPCl_2$ (1.36 mL, 10.0 mmol) at room temperature under an Ar atmosphere. To this mixture was added *o*-AnisMgBr (1.0 mol/L THF solution, 2.00 mL, 2.0 mmol) in THF (32 mL) dropwise over a period of 1 h at 0 °C with vigorous stirring. After the solvent was removed, toluene (20 mL) was added to the residue. The mixture was stirred under reflux in toluene for 1 h, and the insoluble parts were filtered off. After the solvent was removed, the residue was purified by column chromatography on silica gel using *n*-C_6H_{14}/CH_2Cl_2 as eluent and gel permeation chromatography using $CHCl_3$ as eluent to give 0.402 g (61%) of **1e** as a colorless solid. mp: 90−92 °C (dec); ^{1}H NMR: δ 3.59 (s, 3H), 6.87 (t, *J* = 7.8 Hz, 1H), 7.10−7.15 (m, 1H), 7.40−7.50 (m, 3H), 7.52−7.57 (m, 1H), 7.85−7.91 (m, 2H), 8.14−8.20 (m, 1H); ^{13}C NMR: δ 55.6, 112.2 (d, J_{CP} = 6.6 Hz), 120.8 (d, J_{CP} = 15.7 Hz), 121.7 (d, J_{CP} = 82.7 Hz), 128.1 (d, J_{CP} = 14.9 Hz), 130.3 (d, J_{CP} = 13.2 Hz), 131.8 (d, J_{CP} = 3.3 Hz), 135.3 (d, J_{CP} = 12.4 Hz), 135.4 (d, J_{CP} = 1.7 Hz), 136.5 (d, J_{CP} = 89.3 Hz), 159.7 (d, J_{CP} = 2.5 Hz); ^{31}P NMR: δ 66.3 (J_{PSe} = 840.4 Hz); ^{77}Se NMR: δ −48.4 (d, J_{SeP} = 840.4 Hz); MS(EI) *m/z*: 330 (M^+); HRMS calcd for $C_{13}H_{12}ClOPSe$: 329.9480. Found: 329.9478.

***P*-(4-Methylphenyl)-*P*-phenylphosphinoselenoic Chloride (1f).** A pale-yellow oil. ^{1}H NMR: δ 2.40 (s, 3H), 7.28 (dd, *J* = 8.1 Hz, J_{HP} = 3.9 Hz, 2H), 7.43−7.53 (m, 3H), 7.82 (dd, *J* = 8.1 Hz, J_{HP} = 15.6 Hz, 2H), 7.88−7.95 (m, 2H); ^{13}C NMR: δ 21.5, 128.5 (d, J_{CP} = 14.1 Hz), 129.3 (d, J_{CP} = 14.9 Hz), 131.0 (d, J_{CP} = 13.2 Hz), 131.3 (d, J_{CP} = 13.2 Hz), 131.8 (d, J_{CP} = 86.1 Hz), 132.4 (d, J_{CP} = 3.3 Hz), 135.6 (d, J_{CP} = 84.4 Hz), 143.5 (d, J_{CP} = 3.3 Hz); ^{31}P NMR: δ 72.1 (J_{PSe} = 846.4 Hz); ^{77}Se NMR: δ −68.4 (d, J_{SeP} = 846.4 Hz); MS(EI) *m/z*: 314 (M^+); HRMS calcd for $C_{13}H_{12}ClPSe$: 313.9530. Found: 313.9523.

***P*-(4-Chlorophenyl)-*P*-phenylphosphinoselenoic Chloride (1g).** A pale-yellow oil. ^{1}H NMR: δ 7.43−7.57 (m, 5H), 7.82−7.95 (m, 4H); ^{13}C NMR: δ 128.7 (d, J_{CP} = 13.2 Hz), 128.9 (d, J_{CP} = 14.9 Hz), 131.1 (d, J_{CP} = 13.2 Hz), 132.5 (d, J_{CP} = 14.1 Hz), 132.8 (d, J_{CP} = 3.3 Hz), 133.9 (d, J_{CP} = 86.8 Hz), 134.9 (d, J_{CP} = 85.2 Hz), 139.3 (d, J_{CP} = 3.3 Hz); ^{31}P NMR: δ 69.6 (J_{PSe} = 853.9 Hz); ^{77}Se NMR: δ −67.3 (d, J_{SeP} = 853.9 Hz); MS(EI) *m/z*: 334 (M^+); HRMS calcd for $C_{12}H_9Cl_2PSe$: 333.8984. Found: 333.8988.

General Procedure for the Synthesis of Alkyl (1,1-Dimethylethyl)phosphinoselenoic Chlorides 1h and 1i. A Representative Procedure for the Synthesis of *P*-(1-Methylethyl)-*P*-(1,1-dimethylethyl)phosphinoselenoic Chloride (1h). To a suspension of elemental selenium (0.868 g, 11.0 mmol) in THF (50 mL) was added PCl_3 (0.872 mL, 10.0 mmol) at room temperature under an Ar atmosphere. To this mixture was added *t*-BuMgCl (1.0 M solution in THF, 10.0 mL, 10 mmol) in THF (40 mL) dropwise over a period of 1 h at 0 °C with vigorous stirring. The reaction mixture was stirred at room temperature for 2 h. To this mixture was added *i*-PrMgCl (2.0 M solution in Et_2O, 5.00 mL, 10 mmol) in THF (45 mL) dropwise over a period of 1 h at 0 °C with vigorous stirring. The reaction mixture was stirred at room temperature for 2 h. After the solvent was removed, toluene (25 mL) was added to the residue. The mixture was stirred under reflux in toluene for 1 h, and the insoluble parts were filtered off. After the solvent was removed, the residue was purified by column chromatography on silica gel using *n*-C_6H_{14}/CH_2Cl_2 as eluent and gel permeation chromatography using $CHCl_3$ as eluent to give 1.128 g (46%) of **1h** as a colorless solid. mp: 38−41 °C (dec); ^{1}H NMR: δ 1.22 (dd, *J* = 6.8 Hz, J_{HP} = 21.5 Hz, 3H), 1.36 (dd, *J* = 6.8 Hz, J_{HP} = 20.3 Hz, 3H), 1.38 (d, J_{HP} = 19.0 Hz, 9H), 2.76 (octet, *J* = 6.8 Hz, 1H); ^{13}C NMR: δ 18.8 (d, J_{CP} = 3.3 Hz), 18.9, 26.1, 35.2 (d, J_{CP} = 37.2 Hz), 42.3 (d, J_{CP} = 35.6 Hz); ^{31}P NMR: δ 138.1 (J_{PSe} = 822.4 Hz); ^{77}Se NMR: δ −262.3 (d, J_{SeP} = 822.4 Hz); MS(EI) *m/z*: 246 (M^+); HRMS calcd for $C_7H_{16}ClPSe$: 245.9843. Found: 245.9817.

***P*-Cyclohexyl-*P*-(1,1-dimethylethyl)phosphinoselenoic Chloride (1i).** A colorless solid. mp: 61−63 °C (dec); ^{1}H NMR: δ 1.17−1.43 (m, 3H), 1.37 (d, J_{HP} = 19.0 Hz, 9H), 1.46−1.75 (m, 3H), 1.80−1.95 (m, 3H), 2.07−2.13 (m, 1H), 2.37−2.46 (m, 1H); ^{13}C NMR: δ 25.3, 25.8, 26.0 (d, J_{CP} = 6.6 Hz), 26.2, 27.3 (d, J_{CP} = 4.1 Hz), 28.6, 42.4 (d, J_{CP} = 35.6 Hz), 45.0 (d, J_{CP} = 35.6 Hz); ^{31}P NMR: δ 133.3 (J_{PSe} = 817.8 Hz); ^{77}Se NMR: δ −233.5 (d, J_{SeP} = 817.8 Hz); MS(EI) *m/z*: 286 (M^+); Anal. Calcd for $C_{10}H_{20}ClPSe$: C, 42.05; H, 7.06. Found: C, 42.22; H, 6.77.

General Procedure for the Synthesis of Phosphinoselenoic Acid *O*-Esters 2. A Representative Procedure for the Synthesis of *P*-(1,1-Dimethylethyl)-*P*-phenylphosphinoselenoic Acid *O*-Ethyl Ester (2a). To a EtOH solution (5 mL) of EtONa (0.137 g, 2.00 mmol) was added *P*-(1,1-dimethylethyl)-*P*-phenylphosphinoselenoic chloride (**1d**) (0.280 g, 1.00 mmol) at room temperature, and the mixture was stirred under reflux for 3 h. The reaction mixture was poured onto water and extracted with Et_2O (20 mL). The organic layer was dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by column chromatography on silica gel using *n*-C_6H_{14}/Et_2O as eluent to give 0.283 g (98%) of **2a** as a pale-yellow oil. ^{1}H NMR: δ 1.13 (d, J_{HP} = 18.1 Hz, 9H), 1.32 (t, *J* = 7.0 Hz, 3H), 3.81−3.91 (m, 1H), 4.17−4.27 (m, 1H), 7.40−7.49 (m, 3H), 7.79−7.84 (m, 2H); ^{13}C NMR: δ 16.1 (d, J_{CP} = 7.4 Hz), 24.5, 36.9 (d, J_{CP} = 65.3 Hz), 62.9 (d, J_{CP} = 7.4 Hz), 127.9 (d, J_{CP} = 11.6 Hz), 131.6 (d, J_{CP} = 77.8 Hz), 131.7 (d, J_{CP} = 3.3 Hz), 132.7 (d, J_{CP} = 9.9 Hz); ^{31}P NMR: δ 111.0 (J_{PSe} = 786.3 Hz); ^{77}Se NMR: δ −350.3 (d, J_{SeP} = 786.3 Hz); MS(EI) *m/z*: 290 (M^+); Anal. Calcd for $C_{12}H_{19}OPSe$: C, 49.83; H, 6.62. Found: C, 49.78; H, 6.68.

***P*-Cyclohexyl-*P*-phenylphosphinoselenoic Acid *O*-Ethyl Ester (2b).** A pale-yellow oil. ^{1}H NMR: δ 1.11−1.50 (m, 5H), 1.28 (t, *J* = 6.8 Hz, 3H), 1.54−1.85 (m, 4H), 2.00−2.12 (m, 2H), 3.73−3.83 (m, 1H), 4.10−4.21 (m, 1H), 7.45−7.54 (m, 3H), 7.85−7.90 (m, 2H); ^{13}C NMR: δ 16.0 (d, J_{CP} = 8.3 Hz), 25.3, 25.6, 25.7, 25.8 (d, J_{CP} = 5.0 Hz), 25.9 (d, J_{CP} = 6.6 Hz), 44.0 (d, J_{CP} = 68.7 Hz), 62.0 (d, J_{CP} = 6.6 Hz), 128.1 (d, J_{CP} = 12.4 Hz), 131.8, 131.9 (d, J_{CP} = 6.6 Hz), 132.7; ^{31}P NMR: δ 102.9 (J_{PSe} = 781.7 Hz); ^{77}Se NMR: δ −359.3 (d, J_{SeP} = 781.7 Hz); MS(EI) *m/z*: 316 (M^+); Anal. Calcd for $C_{14}H_{21}OPSe$: C, 53.34; H, 6.71. Found: C, 53.36; H, 6.51.

General Procedure for the Synthesis of Phosphinoselenothioic Acid *S*-Esters 3. A Representative Procedure for the Synthesis of *P*-(1,1-Dimethylethyl)-*P*-phenylphosphinoselenothioic Acid *S*-Butyl Ester (3a). To a THF solution (5 mL) of 1-butanethiol (118 μL, 1.10 mmol) was added *n*-BuLi (1.6 mol/L hexane solution, 0.625 mL, 1.0 mmol) at 0 °C, and the mixture was stirred at that temperature for 10 min. *P*-(1,1-Dimethylethyl)-*P*-phenylphosphinoselenoic chloride (**1d**) (0.280 g, 1.00 mmol) was then added at 0 °C, and the mixture was stirred at that temperature for 1 h. The reaction mixture was poured onto water and extracted with Et_2O (20 mL). The organic layer was dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by column chromatography on silica gel using *n*-C_6H_{14}/Et_2O as eluent to give 0.317 g (95%) of **3a** as a colorless oil. ^{1}H NMR: δ 0.82 (t, *J* = 7.3 Hz, 3H), 1.21 (d, J_{HP} = 19.0 Hz, 9H), 1.35 (sextet, *J* = 7.3 Hz, 2H), 1.48−1.56 (m, 2H), 2.73−2.94 (m, 2H), 7.40−7.48 (m, 3H), 8.05−8.10 (m, 2H); ^{13}C NMR: δ 13.5, 21.8, 25.2, 32.1 (d, J_{CP} = 5.0 Hz), 33.0 (d, J_{CP} = 2.5 Hz), 38.1 (d, J_{CP} = 43.0 Hz), 127.9 (d, J_{CP} = 11.6 Hz), 130.8 (d, J_{CP} = 58.7 Hz), 131.5 (d, J_{CP} = 3.3 Hz), 133.5 (d, J_{CP} = 9.1 Hz); ^{31}P NMR: δ 88.0 (J_{PSe} = 763.7 Hz); ^{77}Se NMR: δ −310.8 (d, J_{SeP} = 763.7 Hz);

MS(EI) *m/z* 334 (M^+); Anal. Calcd for $C_{14}H_{23}PSSe$: C, 50.45; H, 6.95. Found: C, 50.17; H, 7.04.

***P*-(1-Methylethyl)-*P*-phenylphosphinoselenothioic Acid *S*-Butyl Ester (3b)**. A colorless oil. ^{1}H NMR: δ 0.82 (t, J = 7.3 Hz, 3H), 1.00 (dd, J = 6.8 Hz, J_{HP} = 21.5 Hz, 3H), 1.30 (dd, J = 6.8 Hz, J_{HP} = 21.0 Hz, 3H), 1.29−1.39 (m, 2H), 1.47−1.54 (m, 2H), 2.43−2.55 (m, 1H), 2.73−2.92 (m, 2H), 7.44−7.52 (m, 3H), 8.01−8.07 (m, 2H); ^{13}C NMR: δ 13.5, 16.7, 17.1, 21.7, 32.1 (d, J_{CP} = 4.1 Hz), 32.5 (d, J_{CP} = 2.5 Hz), 35.5 (d, J_{CP} = 48.0 Hz), 128.3 (d, J_{CP} = 12.4 Hz), 131.7 (d, J_{CP} = 2.5 Hz), 132.1 (d, J_{CP} = 10.8 Hz), 132.2 (d, J_{CP} = 63.7 Hz); ^{31}P NMR: δ 77.5 (J_{PSe} = 768.2 Hz); ^{77}Se NMR: δ −355.0 (d, J_{SeP} = 768.2 Hz); MS(EI) *m/z* 320 (M^+); Anal. Calcd for $C_{13}H_{21}PSSe$: C, 48.90; H, 6.63. Found: C, 48.88; H, 6.64.

***P*-(1,1-Dimethylethyl)-*P*-phenylphosphinoselenothioic Acid *S*-Phenyl Ester (3c).** A colorless solid. mp: 120−125 °C (dec); ^{1}H NMR: δ 1.31 (d, J_{HP} = 18.5 Hz, 9H), 7.22−7.51 (m, 8H), 8.16−8.21 (m, 2H); ^{13}C NMR: δ 25.7, 39.1 (d, J_{CP} = 40.5 Hz), 127.2 (d, J_{CP} = 5.0 Hz), 127.9 (d, J_{CP} = 11.6 Hz), 128.9 (d, J_{CP} = 2.5 Hz), 129.6 (d, J_{CP} = 2.5 Hz), 130.1 (d, J_{CP} = 57.1 Hz), 131.6 (d, J_{CP} = 3.3 Hz), 134.1 (d, J_{CP} = 9.9 Hz), 136.8 (d, J_{CP} = 4.1 Hz); ^{31}P NMR: δ 93.5 (J_{PSe} = 783.2 Hz); ^{77}Se NMR: δ −279.3 (d, J_{SeP} = 783.2 Hz); MS(EI) *m/z*: 354 (M^+); HRMS calcd for $C_{16}H_{19}PSSe$: 354.0110. Found: 354.0087.

***P*-(1,1-Dimethylethyl)-*P*-phenylphosphinoselenothioic Acid *S*-[2-(Trimethylsilyl)ethyl] Ester (3d).** A colorless solid. mp: 45−47 °C (dec); ^{1}H NMR: δ −0.05 (s, 9H), 0.81−0.96 (m, 2H), 1.20 (d, J_{HP} = 19.0 Hz, 9H), 2.75−2.84 (m, 1H), 2.93−3.04 (m, 1H), 7.40−7.48 (m, 3H), 8.05−8.11 (m, 2H); ^{13}C NMR: δ −1.7, 18.8 (d, J_{CP} = 5.0 Hz), 25.2, 30.3 (d, J_{CP} = 3.3 Hz), 38.1 (d, J_{CP} = 41.4 Hz), 128.9 (d, J_{CP} = 11.6 Hz), 130.9 (d, J_{CP} = 57.9 Hz), 131.4 (d, J_{CP} = 3.3 Hz), 133.5 (d, J_{CP} = 9.9 Hz); ^{31}P NMR: δ 86.1 (J_{PSe} = 762.2 Hz); ^{77}Se NMR: δ −311.5 (d, J_{SeP} = 762.2 Hz); MS(EI) *m/z*: 378 (M^+); Anal. Calcd for $C_{15}H_{27}PSSeSi$: C, 47.73; H, 7.21. Found: C, 47.45; H, 6.91.

General Procedure for the Synthesis of Phosphinodiselenoic Acid Esters 4. A Representative Procedure for the Synthesis of *P*-(1,1-Dimethylethyl)-*P*-phenylphosphinodiselenoic Acid Butyl Ester (4a). To a THF suspension (5 mL) of elemental selenium (0.079 g, 1.0 mmol) was added *n*-BuLi (1.6 mol/L hexane solution, 0.625 mL, 1.0 mmol) at 0 °C, and the mixture was stirred at that temperature for 10 min. *P*-(1,1-Dimethylethyl)-*P*-phenylphosphinoselenoic chloride (**1d**) (0.252 g, 0.90 mmol) was then added, and the mixture was stirred at that temperature for 15 min. The reaction mixture was poured onto water and extracted with Et_2O (20 mL). The organic layer was dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by column chromatography on silica gel using *n*-C_6H_{14}/Et_2O as eluent to give 0.330 g (96%) of **4a** as a pale-yellow oil. ^{1}H NMR: δ 0.81 (t, J = 6.8 Hz, 3H), 1.21 (d, J_{HP} = 18.5 Hz, 9H), 1.34 (sextet, J = 7.3 Hz, 2H), 1.52−1.60 (m, 2H), 2.91−2.97 (m, 2H), 7.38−7.46 (m, 3H), 8.06−8.11 (m, 2H); ^{13}C NMR: δ 13.5, 22.9, 25.5 (d, J_{CP} = 2.5 Hz), 31.1 (d, J_{CP} = 2.5 Hz), 32.4 (d, J_{CP} = 3.3 Hz), 38.7 (d, J_{CP} = 37.2 Hz), 127.8 (d, J_{CP} = 11.6 Hz), 130.8 (d, J_{CP} = 52.1 Hz), 131.4 (d, J_{CP} = 2.5 Hz), 133.7 (d, J_{CP} = 9.9 Hz); ^{31}P NMR: δ 79.9 (J_{PSe} = 381.9, 756.2 Hz); ^{77}Se NMR: δ −277.8 (d, J_{SeP} = 756.2 Hz), 181.4 (d, J_{SeP} = 381.9 Hz); MS(EI) *m/z*: 382 (M^+); Anal. Calcd for $C_{14}H_{23}PSe_2$: C, 44.22; H, 6.10. Found: C, 44.41; H, 6.16.

***P*-(1,1-Dimethylethyl)-*P*-phenylphosphinodiselenoic Acid 1,1-Dimethylethyl Ester (4b).** A pale-yellow solid. mp: 102−105 °C (dec); ^{1}H NMR: δ 1.17 (d, J_{HP} = 19.0 Hz, 9H), 1.51 (d, J_{HP} = 1.0 Hz, 9H), 7.41−7.44 (m, 3H), 8.19−8.25 (m, 2H); ^{13}C NMR: δ 25.5, 33.1, 39.4 (d, J_{CP} = 37.2 Hz), 53.1 (d, J_{CP} = 4.1 Hz), 127.6 (d, J_{CP} = 11.6 Hz), 130.8 (d, J_{CP} = 50.5 Hz), 131.2 (d, J_{CP} = 2.5 Hz), 134.2 (d, J_{CP} = 9.9 Hz); ^{31}P NMR: δ 65.8 (J_{PSe} = 420.9, 745.6 Hz); ^{77}Se NMR: δ −237.8 (d, J_{SeP} = 745.6 Hz), 385.2 (d, J_{SeP} = 420.9 Hz); MS(EI) *m/z*: 382 (M^+); Anal. Calcd for $C_{14}H_{23}PSe_2$: C, 44.22; H, 6.10. Found: C, 44.22; H, 5.97.

***P*-(1,1-Dimethylethyl)-*P*-phenylphosphinodiselenoic Acid Phenyl Ester (4c)**. A pale-yellow solid. mp: 95−98 °C (dec); ^{1}H NMR: δ 1.33 (d, J_{HP} = 19.0 Hz, 9H), 7.22−7.28 (m, 2H), 7.32−7.41 (m, 1H), 7.44−7.51 (m, 5H), 8.16−8.21 (m, 2H); ^{13}C NMR: δ 25.9 (d, J_{CP} = 1.7 Hz), 39.6 (d, J_{CP} = 34.7 Hz), 125.0 (d, J_{CP} = 5.8 Hz), 127.9 (d, J_{CP} = 11.6 Hz), 128.9 (d, J_{CP} = 1.7 Hz), 129.4 (d, J_{CP} = 1.7 Hz), 129.8 (d, J_{CP} = 52.1 Hz), 131.5 (d, J_{CP} = 2.5 Hz), 134.1 (d, J_{CP} = 9.1 Hz), 137.4 (d, J_{CP} = 3.3 Hz); ^{31}P NMR: δ 85.7 (J_{PSe} = 371.4, 774.2 Hz); ^{77}Se NMR: δ −239.6 (d, J_{SeP} = 774.2 Hz), 365.4 (d, J_{SeP} = 371.4 Hz); MS(EI) *m/z*: 402 (M^+); Anal. Calcd for $C_{16}H_{19}PSe_2$: C, 48.02; H, 4.79. Found: C, 47.76; H, 4.69.

Synthesis of *P*-(1,1-Dimethylethyl)-*P*-phenylphosphinodiselenoic Acid Methyl Ester (4d). To a CH_3CN suspension (5 mL) of Na_2Se (0.069 g, 0.55 mmol) was added *P*-(1,1-dimethylethyl)-*P*-phenylphosphinoselenoic chloride (**1d**) (0.140 g, 0.50 mmol) at 0 °C, and the mixture was stirred at that temperature for 4 h. After the insoluble parts were filtered off, MeI (62 μL, 1.0 mmol) was added to the filtrate at 0 °C, and the mixture was stirred at that temperature for 1 h. The reaction mixture was poured onto water and extracted with Et_2O (20 mL). The organic layer was dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by column chromatography on silica gel using *n*-C_6H_{14}/Et_2O as eluent to give 0.159 g (94%) of **4d** as a pale-yellow oil. ^{1}H NMR: δ 1.23 (d, J_{HP} = 19.5 Hz, 9H), 2.18 (d, J_{HP} = 12.2 Hz, 3H), 7.40−7.48 (m, 3H), 8.05−8.11 (m, 2H); ^{13}C NMR: δ 9.2 (d, J_{CP} = 2.5 Hz), 25.6 (d, J_{CP} = 2.5 Hz), 39.0 (d, J_{CP} = 36.4 Hz), 128.0 (d, J_{CP} = 11.6 Hz), 129.8 (d, J_{CP} = 52.9 Hz), 131.6 (d, J_{CP} = 3.3 Hz), 133.7 (d, J_{CP} = 9.1 Hz); ^{31}P NMR: δ 82.6 (J_{PSe} = 366.2, 762.9 Hz); ^{77}Se NMR: δ −279.7 (d, J_{SeP} = 762.9 Hz), 112.6 (d, J_{SeP} = 366.2 Hz); MS(EI) *m/z*: 340 (M^+); Anal. Calcd for $C_{11}H_{17}PSe_2$: C, 39.07; H, 5.07. Found: C, 39.28; H, 4.91.

General Procedure for the Synthesis of Phosphinoselenoic Acid *Se*-Esters 8. A Representative Procedure for the Synthesis of *P*-(1,1-Dimethylethyl)-*P*-phenylphosphinoselenoic Acid *Se*-Methyl Ester (8a). To a CH_3CN suspension (5 mL) of NaOH (0.389 g, 9.7 mmol) was added *P*-(1,1-dimethylethyl)-*P*-phenylphosphinoselenoic chloride (**1d**) (0.280 g, 1.00 mmol) at room temperature, and the mixture was stirred at that temperature for 24 h. After the insoluble parts were filtered off, MeI (125 μL, 2.0 mmol) was added to the filtrate at room temperature, and the mixture was stirred at that temperature for 1 h. The reaction mixture was poured onto water and extracted with CH_2Cl_2 (20 mL). The organic layer was dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by column chromatography on silica gel using $CHCl_3$/MeOH as eluent to give 0.270 g (98%) of **8a** as a pale-yellow oil. ^{1}H NMR: δ 1.13 (d, J_{HP} = 17.6 Hz, 9H), 1.97 (d, J_{HP} = 9.3 Hz, 3H), 7.39−7.49 (m, 3H), 7.80−7.87 (m, 2H); ^{13}C NMR: δ 2.1 (d, J_{CP} = 2.5 Hz), 24.7, 37.7 (d, J_{CP} = 62.9 Hz), 128.1 (d, J_{CP} = 12.4 Hz), 131.4 (d, J_{CP} = 81.9 Hz), 131.9 (d, J_{CP} = 3.3 Hz), 132.6 (d, J_{CP} = 9.1 Hz); ^{31}P NMR: δ 68.2 (J_{PSe} = 390.9 Hz); ^{77}Se NMR: δ 54.4 (d, J_{SeP} = 390.9 Hz); MS (EI) *m/z*: 276 (M^+); Anal. Calcd for $C_{11}H_{17}OPSe$: C, 48.01; H, 6.23. Found: C, 47.84; H, 6.23.

***P*-Cyclohexyl-*P*-phenylphosphinoselenoic Acid *Se*-Ethyl Ester (8b)**. A colorless solid. ^{1}H NMR: δ 1.11−1.52 (m, 5H), 1.34 (t, J = 7.3 Hz, 3H), 1.68−1.86 (m, 4H), 1.99−2.07 (m, 2H), 2.68−2.84 (m, 2H), 7.47−7.55 (m, 3H), 7.82−7.87 (m, 2H); ^{13}C NMR: δ 16.6 (d, J_{CP} = 3.3 Hz), 17.6 (d, J_{CP} = 1.7 Hz), 25.5, 25.6 (d, J_{CP} = 2.5 Hz), 25.7 (d, J_{CP} = 2.5 Hz), 25.9, 26.0, 44.0 (d, J_{CP} = 64.5 Hz), 128.2 (d, J_{CP} = 12.4 Hz), 131.3 (d, J_{CP} = 9.9 Hz), 131.6 (d, J_{CP} = 2.5 Hz), 133.1 (d, J_{CP} = 85.2 Hz); ^{31}P NMR: δ 55.9 (J_{PSe} = 387.8 Hz); ^{77}Se NMR: δ 199.3 (d, J_{SeP} = 387.8 Hz); MS(EI) *m/z*: 316 (M^+); Anal. Calcd for $C_{14}H_{21}OPSe$: C, 53.34; H, 6.71. Found: C, 53.25; H, 6.69.

General Procedure for the Synthesis of Phosphinoselenothioic Acid *Se*-Esters 9. A Representative Procedure for the Synthesis of *P*-(1,1-Dimethylethyl)-*P*-phenylphosphinoselenothioic Acid *Se*-Methyl Ester (9a). To a CH_3CN suspension (5 mL) of Na_2S (0.390 g, 5.0 mmol) was

added *P*-(1,1-dimethylethyl)-*P*-phenylphosphinoselenoic chloride (**1d**) (0.280 g, 1.00 mmol) at room temperature, and the mixture was stirred at that temperature for 6 h. After the insoluble parts were filtered off, MeI (125 μL, 2.0 mmol) was added to the filtrate at room temperature, and the mixture was stirred at that temperature for 1 h. The reaction mixture was poured onto water and extracted with Et_2O (20 mL). The organic layer was dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by column chromatography on silica gel using n-C_6H_{14}/Et_2O as eluent to give 0.261 g (90%) of **9a** as a pale-yellow oil. ^{1}H NMR: δ 1.23 (d, J_{HP} = 19.0 Hz, 9H), 2.19 (d, J_{HP} = 11.2 Hz, 3H), 7.43−7.52 (m, 3H), 8.03−8.09 (m, 2H); ^{13}C NMR: δ 6.7 (d, J_{CP} = 3.3 Hz), 25.3, 39.6 (d, J_{CP} = 44.6 Hz), 128.0 (d, J_{CP} = 11.6 Hz), 131.1 (d, J_{CP} = 62.9 Hz), 131.6 (d, J_{CP} = 3.1 Hz), 133.2 (d, J_{CP} = 8.3 Hz); ^{31}P NMR: δ 88.3 (J_{PSe} = 366.8 Hz); ^{77}Se NMR: δ 108.2 (d, J_{SeP} = 366.8 Hz); MS(EI) *m*/*z*: 292 (M^+); HRMS calcd for $C_{11}H_{17}PSSe$: 291.9954. Found: 291.9928.

***P*-(1-Methylethyl)-*P*-phenylphosphinoselenothioic Acid *Se*-Butyl Ester (9b)**. A colorless oil. ^{1}H NMR: δ 0.83 (t, J = 7.6 Hz, 3H), 1.03 (dd, J = 6.8 Hz, J_{HP} = 21.0 Hz, 3H), 1.26−1.38 (m, 2H), 1.32 (dd, J = 6.8 Hz, J_{HP} = 21.5 Hz, 3H), 1.55−1.62 (m, 2H), 2.49 (sextet, J = 6.8 Hz, 1H), 2.86−2.99 (m, 2H), 7.44−7.52 (m, 3H), 7.96−8.02 (m, 2H); ^{13}C NMR: δ 13.5, 16.4, 16.8, 22.9, 28.3 (d, J_{CP} = 2.5 Hz), 32.7 (d, J_{CP} = 3.3 Hz), 36.6 (d, J_{CP} = 49.6 Hz), 128.4 (d, J_{CP} = 12.4 Hz), 131.4 (d, J_{CP} = 9.9 Hz), 131.5 (d, J_{CP} = 3.3 Hz), 133.6 (d, J_{CP} = 67.0 Hz); ^{31}P NMR: δ 72.5 (J_{PSe} = 366.8 Hz); ^{77}Se NMR: δ 234.5 (d, J_{SeP} = 366.8 Hz); MS(EI) *m*/*z*: 320 (M^+); Anal. Calcd for $C_{13}H_{21}PSSe$: C, 48.90; H, 6.63. Found: C, 49.15; H, 6.41.

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Supporting Information Available: Copies of ^{1}H and ^{13}C NMR spectra for compounds **1a**, **1e**−**h**, **3c**, and **9a**, tables of crystallographic data including atomic positional and thermal parameters for **1b**, **3d**, and **4c**, *Z* matrixes of optimized structures for **2′**−**4′**, **8′**, and **9′**. This material is available free of charge via the Internet at http://pubs.acs.org.

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