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Phosphinoselenothioic Acids and Their Salts: Synthesis, Characterization, and Reaction with Electrophiles

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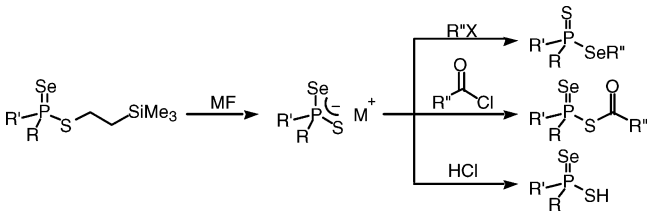
Received March 21, 2005



Phosphinoselenothioic acid ammonium salts were synthesized in good yields by reacting phosphinoselenothioic acid *S*-[2-(trimethylsilyl)ethyl] esters with ammonium fluorides. Phosphinoselenothioic acid alkali metal salts were obtained as 18-crown-6 ether complexes with high efficiency by treating the esters with alkali metal fluorides and 18-crown-6 ether. The salts were stable under air and soluble in water. The structures of the phosphinoselenothioic acid tetramethylammonium salt and *P*-methylseleno-*P*-methylthiophosphonium triflate were determined by X-ray molecular structure analyses. These salts exhibited monomeric structures, and the central phosphorus atoms adopted tetrahedral structures. Alkylation of the ammonium salts selectively gave phosphinoselenothioic acid *Se*-alkyl esters, whereas acylation of the salts preferentially gave *S*-acyl products. Protonation of the salts selectively gave the phosphinoselenothioic *S*-acid. The *S*-acid generated in situ was reacted with α,*β*-unsaturated carbonyl compounds and cyclohexene oxide to give the adducts. Molecular orbital calculations were carried out for the model compound $H_2P(Se)S^-$ to elucidate the electronic structure.

Introduction

The chemistry of phosphinic and phosphinothioic acids and their salts **I** and **II** has been studied in great depth (Figure 1). In contrast, much less attention has been paid to their heavier isologues, i.e., phosphinoselenoic and phosphinotelluroic acids and their salts **III** and **VI**, until recently. The electronic properties of the salts **III** and **IV** are of great interest from the viewpoint of the chemistry of heavy-atom-containing conjugate systems.[1] In addition, these salts are of great importance as key starting materials for phosphinochalcogenoic acid esters[2] and organometallic compounds containing chalcogen−heavy atom bonds, which are used as single-source precursors for semiconducting metal chalcogenides.[3] Recently, phosphinoselenoic, phosphinodiselenoic, phos-

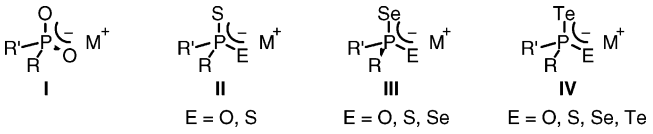


FIGURE 1. Phosphinic acid salts and their heavier isologues.

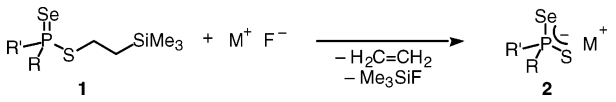
(1) (a) Bildstein, B.; Sladky, F. *Phosphorus, Sulfur Silicon Relat. Elem.* **1990**, *47*, 341. (b) Ebert, K. H.; Cea-Olivares, R.; Garcia-Montalvo, V.; Espinosa-Perez, G.; Estrada, M. R.; Novosad, J.; Woollins, J. D. *Z. Naturforsch., B: Chem. Sci.* **1996**, *51*, 1145. (c) Murai, T.; Kamoto, T.; Kato, S. *J. Am. Chem. Soc.* **2000**, *122*, 9850. (d) Niyomura, O.; Sakai, K.; Murai, T.; Kato, S.; Yamaguchi, S.; Tamao, K. *Chem. Lett.* **2001**, 968. (e) Tani, K.; Murai, T.; Kato, S. *J. Am. Chem. Soc.* **2002**, *124*, 5960. (f) Hernandez-Arganis, M.; Hernandez-Ortega, S.; Toscano, R. A.; Garcia-Montalvo, V.; Cea-Olivares, R. *Chem. Commun.* **2004**, 310.

(2) Kimura, T.; Murai, T. *J. Org. Chem.* **2005**, *70*, 952.

(3) For recent examples, see: (a) Park, J.-H.; Afzaal, M.; Helliwell, M.; Malik, M. A.; O'Brien, P.; Raftery, J. *Chem. Mater.* **2003**, *15*, 4205. (b) Crouch, D. J.; Hatton, P. M.; Helliwell, M.; O'Brien, P.; Raftery, J. *Dalton Trans.* **2003**, 2761. (c) Crouch, D. J.; O'Brien, P.; Malik, M. A.; Skabara, P. J.; Wright, S. P. *Chem. Commun.* **2003**, 1454. (d) Afzaal, M.; Crouch, D.; Malik, M. A.; Motevalli, M.; O'Brien, P.; Park, J.-H. *J. Mater. Chem.* **2003**, *13*, 639. (e) Waters, J.; Crouch, D.; Raftery, J.; O'Brien, P. *Chem. Mater.* **2004**, *16*, 3289. (f) Afzaal, M.; Ellwood, K.; Pickett, N. L.; O'Brien, P.; Raftery, J.; Waters, J. *J. Mater. Chem.* **2004**, *14*, 1310. (g) Afzaal, M.; Crouch, D.; Malik, M. A.; Motevalli, M.; O'Brien, P.; Park, J.-H.; Woollins, J. D. *Eur. J. Inorg. Chem.* **2004**, 171.

10.1021/jo050576c CCC: $30.25
Published on Web 06/03/2005

SCHEME 1



phinoselenotelluroic, and phosphinoditelluroic acid alkali metal salts were synthesized and characterized by X-ray molecular structure analyses.[4] As phosphinoselenothioic acids and their salts, diethylphosphinoselenothioic acid, and sodium salt were synthesized for the first time in 1964,[5] and the synthesis and properties of transition metal complexes of the salts were reported in 1970s.[6] However, there appears to have been no further progress on the syntheses and properties of phosphinoselenothioic acid and their salts **III** (E = S).

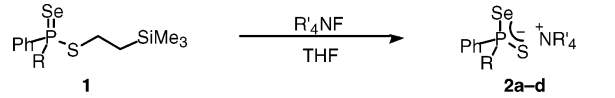
During our studies on phosphinoselenoic acid derivatives,[7] we developed an efficient synthesis of phosphinoselenothioic acid salts.[8] We report here the details of the synthesis, structure, spectroscopic properties, and reactivity of phosphinoselenothioic acids and their salts. Molecular orbital calculations for model compounds are also reported.

Results and Discussion

Synthesis of Phosphinoselenothioic Acid Salts. To obtain phosphinoselenothioic acid salts **2**, we chose phosphinoselenothioic acid *S*-[(2-trimethylsilyl)ethyl] esters **1** as key precursors. The high affinity of the fluorine atom toward the silicon atom may lead to the formation of salts **2** with the elimination of ethylene and Me_3SiF from the esters **1** (Scheme 1).[1]

As expected, synthesis of phosphinoselenothioic acid ammonium salts **2** was achieved by reacting the esters **1** with ammonium fluorides (Table 1). For example, *P*,*P*-diphenylphosphinoselenothioic acid *S*-[(2-trimethylsilyl)-ethyl] ester (**1a**) was reacted with Bu_4NF in THF at 0 °C for 2 h. The reaction mixture was poured onto water and extracted with CH_2Cl_2. After the solvent was removed, Et_2O was added to the residue. Filtration of the resulting precipitates gave *P*,*P*-diphenylphosphinoselenothioic acid tetrabutylammonium salt (**2a**) in 93% yield (entry 1). A similar reaction of *P*-*tert*-butyl-*P*-phenylphosphinoselenothioic acid *S*-ester (**1d**) with Bu_4NF gave the corresponding salt **2b** in 94% yield (entry 2). The reaction of the esters **1a** and **1d** with Me_4NF also took place under reflux in THF to give phosphinoselenothioic acid tetramethylammonium salts **2c** and **2d** in excellent yields (entries 3 and 4).

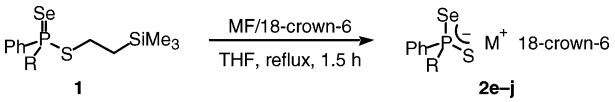
TABLE 1. Synthesis of Phosphinoselenothioic Acid Ammonium Salts



entry	1	R	R_4NF	2	yield (%)[c]
1[a]	**1a**	Ph	Bu_4NF	**2a**	93
2[a]	**1d**	*t*-Bu	Bu_4NF	**2b**	94
3[b]	**1a**	Ph	Me_4NF	**2c**	90
4[b]	**1d**	*t*-Bu	Me_4NF	**2d**	92

[a] Phosphinoselenothioic acid *S*-esters **1** were reacted with Bu_4NF (1.1 equiv) in THF at 0 °C for 2 h. [b] Phosphinoselenothioic acid *S*-esters **1** were reacted with Me_4NF (1 equiv) in THF under reflux for 1.5 h. [c] Isolated yields.

TABLE 2. Synthesis of Phosphinoselenothioic Acid Alkali Metal Salt 18-Crown-6 Ether Complexes



entry	1	R	MF	2	yield (%)[b]
1	**1d**	*t*-Bu	KF	**2e**	94
2	**1a**	Ph	RbF	**2f**	87
3	**1b**	2-$MeOC_6H_4$	RbF	**2g**	92
4	**1c**	*i*-Pr	RbF	**2h**	92
5	**1d**	*t*-Bu	RbF	**2i**	94
6	**1d**	*t*-Bu	CsF	**2j**	91

[a] Phosphinoselenothioic acid *S*-esters **1** were reacted with MF (2 equiv) and 18-crown-6 ether (1 equiv) in THF under reflux for 1.5 h. [b] Isolated yields.

Next, the synthesis of alkali metal salts was examined by reacting the esters **1** with alkali metal fluorides. However, this reaction did not proceed at all, probably because of the insolubility of alkali metal fluorides toward THF. 18-Crown-6 ether was then used as an additive (Table 2). When the ester **1d** was reacted with potassium fluoride in the presence of 1 equiv of 18-crown-6 ether, phosphinoselenothioic acid potassium salt−18-crown-6 ether complex **2e** was formed in 94% yield (entry 1). In addition to potassium fluoride, rubidium fluoride and cesium fluoride could be used as fluorine sources, and phosphinoselenothioic acid rubidium and cesium salt 18-crown-6 ether complexes **2i** and **2j** were obtained with high efficiency (entries 5 and 6). The reaction of esters with various alkyl and aryl substituents on the phosphorus atom **1a**−**d** with rubidium fluoride and 18-crown-6 ether gave the corresponding rubidium salt 18-crown-6 ether complexes **2f**−**i** in high yields (entries 2−5). The salts **2** obtained were stable under air, and no appreciable change was observed upon exposure to air for 1 week. Notably, the salts **2** were soluble not only in organic solvents such as CH_2Cl_2 and THF but also in water.

Spectroscopic Properties. The spectroscopic data for a series of phosphinoselenothioic acid derivatives, i.e., phosphinoselenothioic acid *S*-alkyl ester **1d**, tetrabutylammonium salt **2b**, *P*-methylseleno-*P*-methylthiophosphonium triflate **3**, and phosphinoselenothioic acid *Se*-

(4) (a) Pilkington, M. J.; Slawin, A. M. Z.; Williams, D. J.; Woollins, J. D. *Main Group Chem.* **1995**, 145. (b) Wang, F.; Polavarapu, P. L.; Drabowicz, J.; Kielbasinski, P.; Potrzebowski, M. J.; Mikolajczyk, M.; Wieczorek, M. W.; Majzner, W. W.; Lazewska, I. *J. Phys. Chem. A.* **2004**, *108*, 2072. (c) Davies, R. P.; Martinelli, M. G. *Inorg. Chem.* **2002**, *41*, 348. (d) Davies, R. P.; Martinelli, M. G.; Wheatley, A. E. H.; White, A. J. P.; Williams, D. J. *Eur. J. Inorg. Chem.* **2003**, 3409. (d) Davies, R. P.; Francis, C. V.; Jurd, A. P. S.; Martinelli, M. G.; White, A. J. P.; Williams, D. J. *Inorg. Chem.* **2004**, *43*, 4802.

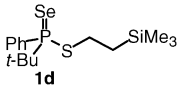
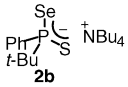
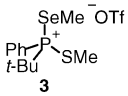
(5) (a) Kuchen, W.; Knop, B. *Angew. Chem.* **1964**, *76*, 496. (b) Kuchen, W.; Knop, B. *Chem. Ber.* **1966**, *99*, 1663.

(6) (a) Hertel, H.; Kuchen, W. *Chem. Ber.* **1971**, *104*, 1735. (b) Hertel, H.; Kuchen, W. *Chem. Ber.* **1971**, *104*, 1740. (c) Christophliemk, P.; Rao, V. V. K.; Tossidis, I.; Mueller, A. *Chem. Ber.* **1972**, *105*, 1736. (d) Mueller, A.; Rao, V. V. K.; Christophliemk, P. *J. Inorg. Nucl. Chem.* **1972**, *34*, 345. (e) Esperås, S.; Husebye, S. *Acta Chem. Scand.* **1973**, *27*, 3355.

(7) (a) Kimura, T.; Murai, T. *Chem. Lett.* **2004**, *33*, 878. (b) Kimura, T.; Murai, T.; Mizuhata, N. *Heteroat. Chem.* **2005**, *16*, 185.

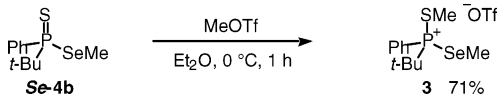
(8) Murai, T.; Kimura, T.; Miwa, A.; Kurachi, D.; Kato, S. *Chem. Lett.* **2002**, 914.

TABLE 3. Selected NMR Spectroscopic Data of Phosphinoselenothioic Acid Derivatives[a]

entry	compounds	^{31}P (ppm)	^{77}Se (ppm)	$^{1}J_{P-Se}$ (Hz)
1	 **1d**	86.1	–311.5	762.2
2	 **2b**	75.3	–125.0	619.4
3	 **3**	97.6	3.2	491.5
4	 ***Se*-4b**	88.3	108.2	366.8

[a] Measured in $CDCl_3$.

SCHEME 2



methyl ester ***Se*-4b**, are listed in Table 3. Phosphonium salt **3** was prepared by alkylation of phosphinoselenothioic acid *Se*-methyl ester ***Se*-4b** with methyl triflate (Scheme 2). In the ^{31}P NMR spectra, the signals of the esters **1d** and ***Se*-4b** were observed at 86.1 and 88.3 ppm, respectively. On the other hand, the signal of the ammonium salt **2b** was observed at a higher field than those of the esters **1d** and ***Se*-4b** by about 12 ppm. The signal of the phosphonium salts **3** was shifted downfield by about 10 ppm compared to those of the esters **1d** and ***Se*-4b**. In the ^{77}Se NMR spectra, the signal of the salt **2b** (−125.0 ppm) was observed midway between those of *S*-ester **1d** (−311.5 ppm) and *Se*-ester ***Se*-4b** (108.2 ppm). The signal of the phosphonium salt **3** (3.2 ppm) was close to that of *Se*-ester ***Se*-4b** rather than that of *S*-ester **1d**. Coupling constants between the phosphorus atom and selenium atom of the phosphinoselenothioic acid derivatives decreased in the order *S*-ester **1d** to ammonium salt **2b**, phosphonium salt **3**, and *Se*-ester ***Se*-4b**, and that of the ammonium salt **2b** was closer to that of *S*-ester **1d** rather than that of *Se*-ester ***Se*-4b**. These results suggested that the phosphorus−selenium bond in the ammonium salt **2b** possesses a double-bond character to some extent.

Structures. The molecular structures of phosphinoselenothioic acid tetramethylammonium salt **2c** and *P*-methylseleno-*P*-methylthiophosphonium triflate **3** were determined by X-ray molecular structure analyses (Figures 2 and 3). The position of the sulfur and selenium atoms in **2c** and **3** could not be determined because they were disordered. The selenium or sulfur atom appears at positions E1 or E2 as shown in Figures 2 and 3. These molecules adopted a monomeric structure in the solid state with a tetrahedral geometry about the phosphorus atom, and no intermolecular interactions were observed. In the ammonium salt **2c**, each benzene ring was almost coplanar with respect to the plane of the P−E group [E1−P−C1−C3 = 2.5(5)°, E2−P−C2−C4 = 7.7(6)°]. There was no interaction between the ammonium cation and the two

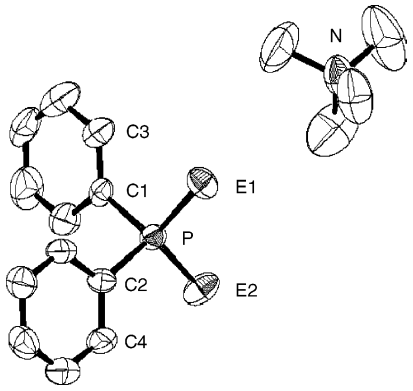


FIGURE 2. ORTEP drawing of phosphinoselenothioic acid tetramethylammonium salt **2c** with a thermal ellipsoid plot (50% probability). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): P−E1, 2.110(2); P−E2, 2.042(2); P−C1, 1.837(6); P−C2, 1.825(6). Selected bond angles and torsion angles (deg): E1−P−E2, 116.40(9); E1−P−C1, 110.8-(2); E1−P−C2, 107.1(2); E2−P−C1, 108.0(2); E2−P−C2, 112.0-(3); C1−P−C2, 101.5(3); E1−P−C1−C3, 2.5(5); E2−P−C2−C4, 7.7(6).

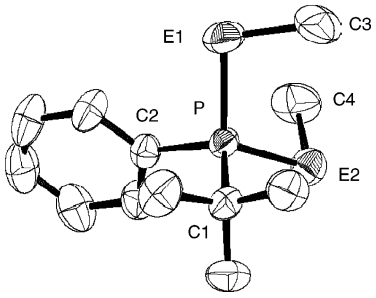
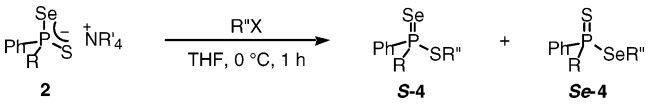


FIGURE 3. ORTEP drawing of *P*-methylseleno-*P*-methylthiophosphonium triflate **3** with a thermal ellipsoid plot (50% probability). Two independent molecules were present in one asymmetric unit, and one of them is shown. Triflate anion and hydrogen atoms are omitted for clarity. Selected bond lengths (Å): P−E1, 2.198(1); P−E2, 2.106(1); P−C1, 1.853(4); P−C2, 1.795(4); E1−C3, 1.901(5); E2−C4, 1.864(5). Selected bond angles and torsion angles (deg): E1−P−E2, 112.76(5); E1−P−C1, 112.8(1); E1−P−C2, 103.9(1); E2−P−C1, 105.4(1); E2−P−C2, 112.5(1); C1−P−C2, 109.6(2); P−E1−C3, 100.6(2); P−E2−C4, 98.9(2); C1−P−E2-C4, 178.0(2); C2−P−E1−C3, −161.0(2).

chalcogen atoms of the phosphinoselenoylthio group. Similarly, no interaction was observed for the triflate anion and the phosphorus atom in **3**.

Reaction with Electrophiles. Initially, phosphinoselenothioic acid ammonium salts **2** were reacted with alkyl halides (Table 4). When the tetrabutylammonium salts **2a** and **2b** were treated with methyl iodide in THF, phosphinoselenothioic acid *Se*-methyl esters ***Se*-4a** and ***Se*-4b** were obtained in high yields (entries 1 and 2). Phosphinoselenothioic acid *S*-methyl esters ***S*-4a** and ***S*-4b** were not observed at all. Similarly, the reaction of tetramethylammonium salt **2d** with methyl iodide selectively gave *Se*-methyl ester ***Se*-4b** in 93% yield (entry 3), although the reaction of the salt **2a** with methyl triflate gave a mixture of phosphinoselenothioic acid *S*-ester ***S*-4a** and *Se*-ester ***Se*-4a** in a ratio of 10:90 (entry 4). In the reaction of the salt **2a** with allyl bromide, phosphinoselenothioic acid *Se*-allyl ester ***Se*-4c** was formed with high selectivity (entry 5).

TABLE 4. Reaction of Phosphinoselenothioic Acid Salts with Alkyl Halides[a]

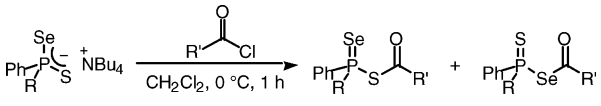


2 ***S*-4** ***Se*-4**

entry	**2**	R	R′	R″X	***S*-4/*Se*-4**	ratio	yield (%)[b]
1	**2a**	Ph	Bu	MeI	***S*-4a/*Se*-4a**	<1:>99	99
2	**2b**	*t*-Bu	Bu	MeI	***S*-4b/*Se*-4b**	<1:>99	91
3	**2d**	*t*-Bu	Me	MeI	***S*-4b/*Se*-4b**	<1:>99	93
4	**2a**	Ph	Bu	MeOTf	***S*-4a/*Se*-4a**	10:90	99
5	**2a**	Ph	Bu	CH_2=$CHCH_2Br$	***S*-4c/*Se*-4c**	<1:>99	88

[a] Phosphinoselenothioic acid ammonium salts **2** were reacted with R″X (1 equiv) in THF at 0 °C for 1 h. [b] Isolated yields.

TABLE 5. Reaction of Phosphinoselenothioic Acid Salts with Acyl Chlorides[a]



2 ***S*-5** ***Se*-5**

entry	**2**	R	R′C(O)Cl	***S*-5/*Se*-5**	ratio	yield (%)[b]
1	**2a**	Ph	PhC(O)Cl	***S*-5a/*Se*-5a**	87:13	60
2	**2a**	Ph	4-$MeOC_6H_4C(O)Cl$	***S*-5b/*Se*-5b**	83:17	42
3	**2a**	Ph	4-$MeC_6H_4C(O)Cl$	***S*-5c/*Se*-5c**	82:18	47
4	**2b**	*t*-Bu	4-$MeC_6H_4C(O)Cl$	***S*-5d/*Se*-5d**	90:10	41
5	**2a**	Ph	4-$ClC_6H_4C(O)Cl$	***S*-5e/*Se*-5e**	85:15	67

[a] Phosphinoselenothioic acid ammonium salts **2** (1 mmol) were reacted with acyl chlorides (1 equiv) at 0 °C for 1 h. [b] Isolated yields.

In contrast to the reaction with alkyl and allyl halides, acylation of the salts **2** gave products in which acyl groups were introduced to the sulfur atom of **2** (Table 5). When the salt **2a** was treated with benzoyl chloride, a mixture of phosphinoselenothioic anhydrosulfide ***S*-5a** and anhydroselenide ***Se*-5a** was obtained in a ratio of 87:13 (entry 1). A similar reaction of the salts **2** with acyl chlorides that had electron-donating and -withdrawing groups at the para position of the benzene ring was also carried out (entries 2−5).[9] In all cases, phosphinoselenothioic anhydrosulfides ***S*-5b**−***S*-5e** were preferentially formed in moderate yields.

The structure of phosphinoselenothioic anhydrosulfide ***S*-5e** was determined by X-ray structure analysis for the first time (Figure 4). The phosphorus atom adopted a tetrahedral structure. The dihedral angle of Se−P−S−C3 was −69°, and the carbonyl group was twisted with respect to the P(Se)S group. The 4-chlorophenyl ring was almost coplanar with respect to the plane of the C(O)S group. The distance between the phosphorus atom and the oxygen atom of the carbonyl group (3.05 Å) was shorter than the sum of their van der Waals radii (3.3 Å).

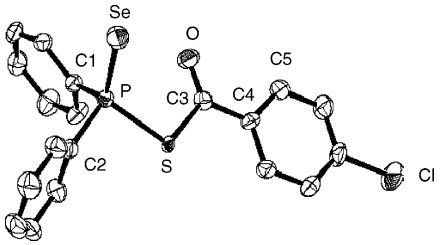
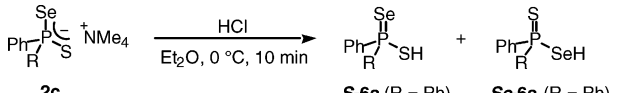


FIGURE 4. ORTEP drawing of $Ph_2P(Se)SC(O)C_6H_4Cl$-4 ***S*-5e** with thermal ellipsoid plot (50% probability). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): P−Se, 2.086(2); P−S, 2.150(2); P−C1, 1.821(6); P−C2, 1.815(6); S−C3, 1.829(6); C3−O, 1.217(7); O···P, 3.05. Selected bond angles and torsion angles (deg): Se−P−S, 117.02(8); Se−P−C1, 115.1(2); Se−P−C2, 113.9(2); S−P−C1, 95.1(2); S−P−C2, 107.6(2); C1−P−C2, 106.1(3); P−S−C3, 106.1(3); S−C3−O, 121.7(4); O···P−C2, 152.4; Se−P−S−C3, −68.5(2); P−S−C3−O, 0.3(5); O−C3−C4−C5, 1.4(9).

SCHEME 3



Finally, protonation of the salts **2** was carried out (Scheme 3). Although the reaction of tetramethylammonium salt **2c** and **2d** with trifluoroacetic acid did not proceed at all, the reaction of the salts **2c** and **2d** with HCl took place smoothly to give phosphinoselenothioic acids **6a** and **6b**. Isolation of *P*,*P*-diphenylphosphinoselenothioic acid (**6a**) was not successful, but *P*-*tert*-butyl-*P*-phenylphosphinoselenothioic acid (**6b**) was isolated in 92% yield. The coupling constant between the phosphorus atom and the selenium atom of the acid **6b** was 750 Hz and was typical for a coupling constant of a P=Se double bond. In addition, the S−H stretching frequency of the acid **6b** was observed at 2397 cm^{-1}. On the basis of these results, the isolated phosphinoselenothioic acid was assigned not as *Se*-acid ***Se*-6** but rather as *S*-acid ***S*-6**. To our knowledge, this is the first identification of phosphinoselenothioic *S*-acid, although the generation of *Se*- or *S*-acids has been noted.[5]

The acid generated in situ was reacted with electrophiles (Scheme 4).[10] When the acid **6a** was reacted with methyl vinyl ketone, phosphinoselenothioic acid *S*- and *Se*-3-oxobutyl esters ***S*-7** and ***Se*-7** were obtained in a ratio of 6:94 in 77% yield. A similar reaction of the acid **6a** with ethyl propiolate gave phosphinoselenothioic acid *S*- and *Se*-alkenyl esters ***S*-8** and ***Se*-8** in a ratio of 7:93. In this reaction, *Z*-isomers were selectively formed. The acid **6a** underwent ring-opening of cyclohexene oxide to give a mixture of *S*- and *Se*-(2-hydoxycyclohexyl) esters ***S*-9** and ***Se*-9** in a ratio of 39:61.

Calculation. To elucidate the electronic structure of phosphinoselenothioic acid salts **2**, geometry optimization and molecular orbital calculations for the model compound $H_2P(Se)S^-$ **2′** were performed at the RHF/6-31+G-

(9) The ratio of ***S*-5** and ***Se*-5** was determined by ^{31}P NMR spectra of the crude products. In acylation, starting materials were recovered in ca. 40% yield along with the formation of ***S*-5** and ***Se*-5**. The reaction at higher temperatures gave complex mixtures due to decomposition of the desired products. The products ***S*-5** and ***Se*-5** were labile upon long-term exposure to water.

(10) Only the reaction of the acid with CH_2N_2 has been reported to give mixtures of *S*-esters and *Se*-esters: (a) Mastryukova, T. A.; Michalski, J.; Uryupin, A. B.; Skrzypczynski, Z.; Kabachnik, M. I. *Zh. Obshch. Khim.* **1978**, *48*, 463. (b) Mastryukova, T. A.; Michalski, J.; Uryupin, A. B.; Skrzypczynski, Z.; Kabachnik, M. I. *Zh. Obshch. Khim.* **1978**, *48*, 1447.

SCHEME 4

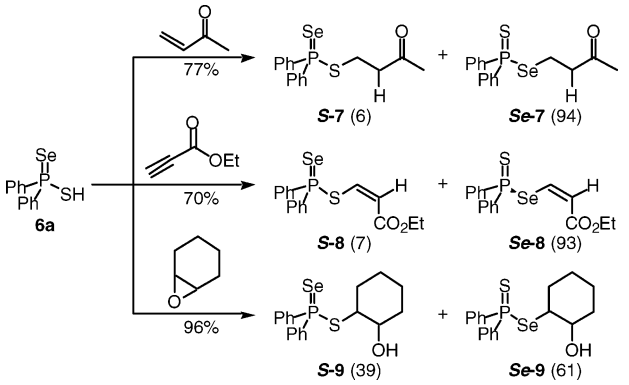


TABLE 6. RHF/6-31+G(d)-Optimized Geometries and Atomic Charges of Model Compounds 1′−4′

		bond length (Å)		atomic charge		
model compound		P−Se	P−S	Se	P	S
$H_2P(Se)SMe$	**1′**	2.103	2.092	−0.565	0.559	0.003
$H_2P(Se)S^-$	**2′**	2.163	2.004	−0.831	0.501	−0.670
$H_2P^+(SeMe)(SMe)$	**3′**	2.201	2.056	−0.100	0.742	0.145
$H_2P(S)SeMe$	**4′**	2.241	1.955	−0.234	0.613	−0.453

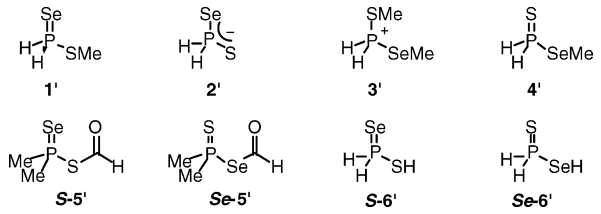


FIGURE 5. Model compounds.

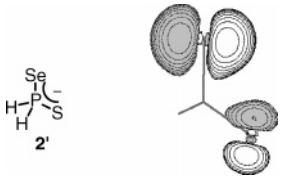
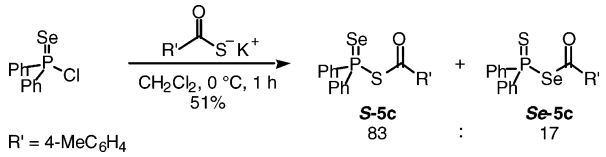


FIGURE 6. MOLDEN plot of HOMO calculated for $H_2P(Se)S^-$.

(d) level with GAUSSIAN 98[11] (Figure 5). For comparison, geometry optimizations of $H_2P(Se)SMe$ **1′**, $H_2P^+(SeMe)(SMe)$ **3′**, and $H_2P(S)SeMe$ **4′** were also carried out. Selected bond lengths and atomic charges are listed in Table 6. The MO plot drawn by the program MOLDEN[12] is shown in Figure 6.

As a result, the negative charge on the phosphinoselenoylthio group in **2′** was delocalized on both the sulfur atom and the selenium atom, but the HOMO of **2′** was the largest at the selenium atom.

SCHEME 5



Thus, the reaction of phosphinoselenothioic acid salts with electrophiles is kinetically favorable at the selenium atom compared to the sulfur atom. Indeed, alkylation of the salts **2** selectively gave *Se*-alkyl esters. Nevertheless, acylation and protonation of the salts **2** preferentially gave phosphinoselenothioic anhydrosulfides and phosphinoselenothioic *S*-acid, respectively. The results in Table 5 may be due to the thermodynamic stability of the products. Indeed, the reaction of diphenylphosphinoselenoic chloride with potassium 4-methylbenzenecarbothioate gave a mixture of anhydrosulfide ***S*-5c** and anhydroselenide ***Se*-5c** in a ratio of 83:17 (Scheme 5). This cleanly shows that ***S*-5c** is thermodynamically more stable than ***Se*-5c**, but their energy difference may be less than 1 kcal/mol.

Furthermore, energy calculations for the model compounds $Me_2P(Se)SC(O)H$ ***S*-5′** and $Me_2P(S)SeC(O)H$ ***Se*-5′** at the RHF/6-31+G(d) level indicated that the anhydrosulfide ***S*-5′** was more stable than the anhydroselenide ***Se*-5′** by 0.9 kcal/mol (Figure 5). This value is in good agreement with those calculated on the basis of the results in Table 5 (0.8−1.2 kcal/mol). Similarly, energy calculations for the model compounds $H_2P(Se)SH$ ***S*-6′** and $H_2P(S)SeH$ ***Se*-6′** suggested that *S*-acid ***S*-6′** was more stable than *Se*-acid ***Se*-6′** by 1.8 kcal/mol.

The P−Se bond lengths calculated for the model compounds decreased in the order of **4′** to **3′**, **2′**, and **1′**. The P−Se bond lengths were linearly correlated with the coupling constant between the phosphorus atom and the selenium atom of the phosphinoselenothioic acid derivatives **1d**, **2b**, **3**, and ***Se*-4b** (Figure 7).

In summary, we have demonstrated that phosphinoselenothioic acid ammonium salts and alkali metal salt 18-crown-6 ether complexes can be efficiently synthesized by reacting phosphinoselenothioic acid *S*-[(2-trimethylsilyl)ethyl] esters with ammonium fluorides or alkali metal fluorides and 18-crown-6 ether. X-ray structure analysis of the phosphinoselenothioic acid ammonium

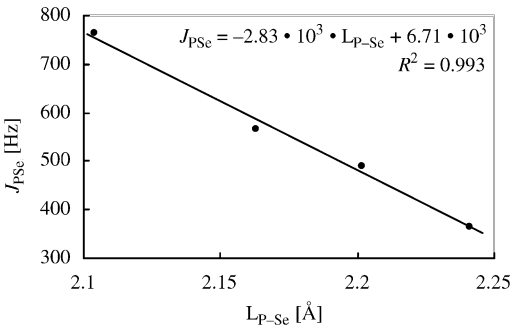


FIGURE 7. Plot of J_{PSe} against calculated P−Se bond lengths.

(11) 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.

(12) Schaftenaar, G.; Noordik, J. H. *J. Comput.-Aided Mol. Des.* **2000**, *14*, 123.

salt showed that the salt was monomeric and the central phosphorus atom was tetrahedral. Alkylation of the salts selectively gave phosphinoselenothioic acid *Se*-esters, whereas acylation of the salts preferentially gave phosphinoselenothioic anhydrosulfides. The phosphinoselenothioic *S*-acids generated by the acidolysis of the salts showed high reactivity toward α,β-unsaturated carbonyl compounds and an oxirane.

Experimental Section

General Procedures. All reactions were carried out under an argon atmosphere. Me_4NF, KF, RbF, and CsF were dried under reduced pressure at 120 °C for 5 h. The silica gel used in column chromatography was silica gel 60 from a commercial supplier.

General Procedure for the Synthesis of Phosphinoselenothioic Acid *S*-[2-(Trimethylsilyl)ethyl] Esters 1. A Representative Procedure for the Synthesis of *P*,*P*-Diphenylphosphinoselenothioic Acid *S*-[2-(Trimethylsilyl)ethyl] Ester (1a). To a THF solution (20 mL) of 2-(trimethylsilyl)ethanethiol (0.32 mL, 2.0 mmol) was added BuLi (1.6 mol/L hexane solution, 1.25 mL, 2.0 mmol) at 0 °C, and the mixture was stirred at that temperature for 10 min. *P*,*P*-Diphenylphosphinoselenoic chloride (0.599 g, 2.0 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 an eluent to give 0.715 g (90%) of *P*,*P*-diphenylphosphinoselenothioic acid *S*-[2-(trimethylsilyl)ethyl] ester (**1a**) as a colorless solid. mp: 65−67 °C (dec). ^{1}H NMR: δ −0.03 (s, 9H), 0.87−0.93 (m, 2H), 2.89−3.00 (m, 2H), 7.40−7.49 (m, 6H), 7.89−7.96 (m, 4H). ^{13}C NMR: δ −1.7, 18.6 (d, J_{CP} = 5.0 Hz), 30.6, 128.5 (d, J_{CP} = 13.2 Hz), 131.8 (d, J_{CP} = 3.3 Hz), 131.8 (d, J_{CP} = 11.6 Hz), 133.9 (d, J_{CP} = 76.1 Hz). ^{31}P NMR: δ 54.0 (J_{PSe} = 774.2 Hz). ^{77}Se NMR: δ −217.9 (d, J_{SeP} = 774.2 Hz). MS (EI) *m*/*z*: 398 (M^+). Anal. Calcd for $C_{17}H_{23}PSSeSi$: C, 51.37; H, 5.83. Found: C, 51.62; H, 5.88.

General Procedure for the Synthesis of Phosphinoselenothioic Acid *N*,*N*,*N*-Tributylbutanaminium Salts 2a and 2b. A Representative Procedure for the Synthesis of *P*,*P*-Diphenylphosphinoselenothioic Acid *N*,*N*,*N*-Tributylbutanaminium Salt (2a). To a THF solution (10 mL) of *P*,*P*-diphenylphosphinoselenothioic acid *S*-[2-(trimethylsilyl)-ethyl] ester (**1a**) (0.397 g, 1.0 mmol) was added Bu_4NF (1.0 mol/L THF solution, 1.1 mL, 1.1 mmol) at 0 °C. The mixture was stirred at that temperature for 2 h. The reaction mixture was extracted with CH_2Cl_2 (50 mL), and the organic layer was washed with water (50 mL × 3). The organic layer was dried over $MgSO_4$, filtered, and concentrated in vacuo. To the residue was added Et_2O (5 mL), and the mixture was stirred for 10 min. The resulting precipitates were collected by filtration to give 0.499 g (93%) of **2a** as a colorless solid. mp: 78−80 °C (dec). ^{1}H NMR: δ 0.94 (t, *J* = 7.3 Hz, 12H), 1.30−1.39 (m, 8H), 1.52−1.59 (m, 8H), 3.20−3.23 (m, 8H), 7.18−7.27 (m, 6H), 8.15−8.21 (m, 4H). ^{13}C NMR: δ 13.7, 19.7, 24.1, 58.7, 127.0 (d, J_{CP} = 11.6 Hz), 128.5 (d, J_{CP} = 3.3 Hz), 131.0 (d, J_{CP} = 11.6 Hz), 144.2 (d, J_{CP} = 66.2 Hz). ^{31}P NMR: δ 44.8 (J_{PSe} = 631.5 Hz). ^{77}Se NMR: δ −5.2 (d, J_{SeP} = 631.5 Hz). Anal. Calcd for $C_{28}H_{46}NPSSe$: C, 62.43; H, 8.61. Found: C, 62.16; H, 8.86.

General Procedure for the Synthesis of Phosphinoselenothioic Acid *N*,*N*,*N*-Trimethylmethanaminium Salts 2c and 2d. A Representative Procedure for the Synthesis of *P*,*P*-Diphenylphosphinoselenothioic Acid *N*,*N*,*N*-Trimethylmethanaminium Salt (2c). To a THF suspension (10 mL) of Me_4NF (0.093 g, 1.0 mmol) was added *P*,*P*-diphenylphosphinoselenothioic acid *S*-[2-(trimethylsilyl)ethyl] ester (**1a**) (0.397 g, 1.0 mmol) at room temperature. The mixture was stirred under reflux for 1.5 h. After THF (40 mL) was added to the reaction mixture, the insoluble parts were filtered, and the filtrate was concentrated in vacuo. To the residue was added Et_2O (5 mL), and the mixture was stirred for 10 min. The resulting precipitates were collected by filtration to give 0.333 g (90%) of **2c** as a colorless solid. mp: 165−167 °C (dec). ^{1}H NMR: δ 3.17 (s, 12H), 7.21−7.29 (m, 6H), 8.10−8.16 (m, 4H). ^{13}C NMR: δ 56.1, 127.4 (d, J_{CP} = 11.5 Hz), 129.0, 130.9 (d, J_{CP} = 11.6 Hz), 143.7 (d, J_{CP} = 69.4 Hz). ^{31}P NMR: δ 44.3 (J_{PSe} = 616.3 Hz); ^{77}Se NMR (DMSO-d_6): δ −7.0 (d, J_{SeP} = 646.4 Hz).

General Procedure for the Synthesis of Phosphinoselenothioic Acid Alkali Metal Salt 18-Crown-6 Ether Complexes 2e−j. A Representative Procedure for the Synthesis of *P*-(1,1-Dimethylethyl)-*P*-phenylphosphinoselenothioic Acid Potassium Salt 18-Crown-6 Ether Complex (2e). To a THF suspension (5 mL) of potassium fluoride (0.116 g, 2.0 mmol) and 18-crown-6 ether (0.264 g, 1.0 mmol) was added *P*-(1,1-dimethylethyl)-*P*-phenylphosphinoselenothioic acid *S*-[2-(trimethylsilyl)ethyl] ester (**1d**) (0.377 g, 1.0 mmol) at room temperature. The mixture was stirred under reflux for 1.5 h. After THF (20 mL) was added to the reaction mixture, the insoluble parts were filtered, and the filtrate was concentrated in vacuo. To the residue was added Et_2O (5 mL), and the mixture was stirred for 10 min. The resulting precipitates were collected by filtration to give 0.544 g (94%) of **2e** as a colorless solid. mp: 220−222 °C (dec). ^{1}H NMR: δ 1.21 (d, J_{HP} = 17.1 Hz, 9H), 3.60 (s, 24H), 7.26−7.48 (m, 3H), 8.39−8.44 (m, 2H). ^{13}C NMR: δ 25.4 (d, J_{CP} = 3.3 Hz), 37.8 (d, J_{CP} = 44.7 Hz), 70.0, 126.1 (d, J_{CP} = 11.6 Hz), 128.6, 133.7 (d, J_{CP} = 9.9 Hz), 138.4 (d, J_{CP} = 56.2 Hz). ^{31}P NMR: δ 74.8 (J_{PSe} = 607.4 Hz). ^{77}Se NMR: δ −128.4 (d, J_{SeP} = 607.4 Hz). Anal. Calcd for $C_{22}H_{38}KO_6PSSe$: C, 45.59; H, 6.61. Found: C, 45.31; H, 6.56.

Synthesis of *P*-(1,1-Dimethylethyl)-*P*-methylseleno-*P*-methylthio-*P*-phenylphosphonium Trifluoromethanesulfonate (3). To an Et_2O solution (5 mL) of *P*-(1,1-dimethylethyl)-*P*-phenylphosphinoselenothioic acid *Se*-methyl ester (***Se*-4b**) (0.291 g, 1.0 mmol) was added methyl trifluoromethanesulfonate (113 μL, 1.0 mmol) at 0 °C. The mixture was stirred at that temperature for 1 h. After the solvent was removed, the residue was recrystallized from THF/Et_2O to give 0.323 g (71%) of **3** as a colorless solid. mp: 145−147 °C (dec). ^{1}H NMR: δ 1.40 (d, J_{HP} = 21.0 Hz, 9H), 2.55 (d, J_{HP} = 14.6 Hz, 3H), 2.57 (d, J_{HP} = 13.2 Hz, 3H), 7.75−7.91 (m, 5H). ^{13}C NMR: δ 9.2 (d, J_{CP} = 4.1 Hz), 14.9 (d, J_{CP} = 5.0 Hz), 25.7, 41.9 (d, J_{CP} = 29.0 Hz), 117.2 (d, J_{CP} = 62.9 Hz), 130.8 (d, J_{CP} = 12.4 Hz), 133.0 (d, J_{CP} = 9.1 Hz), 135.8 (d, J_{CP} = 3.3 Hz). ^{31}P NMR: δ 97.6 (J_{PSe} = 491.5 Hz). ^{77}Se NMR: δ 3.2 (d, J_{SeP} = 491.5 Hz). Anal. Calcd for $C_{13}H_{20}F_3O_3PS_2Se$: C, 34.29; H, 4.43. Found: C, 34.12; H, 4.15.

General Procedure for the Reaction of Phosphinoselenothioic Acid Salts 2 with Alkyl Halides. A Representative Procedure for the Reaction of *P*,*P*-Diphenylphosphinoselenothioic Acid *N*,*N*,*N*-Tributylbutanaminium Salt (2a) with Methyl Trifluoromethanesulfonate. To a THF solution (5 mL) of *P*,*P*-diphenylphosphinoselenothioic acid *N*,*N*,*N*-tributylbutanaminium salt (**2a**) (0.539 g, 1.0 mmol) was added methyl trifluoromethanesulfonate (113 μL, 1.0 mmol) 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 (50 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified by column chromatography on silica gel using *n*-C_6H_{14}/Et_2O as an eluent to give 0.308 g (99%) of a mixture of *P*,*P*-diphenylphosphinoselenothioic acid *S*-methyl ester (***S*-4a**) and *P*,*P*-diphenylphosphinoselenothioic acid *Se*-methyl ester (***Se*-4a**) in a ratio of 10:90 as a colorless oil. ***S*-4a**: ^{31}P NMR: δ 58.0 (J_{PSe} = 780.2 Hz). ^{77}Se NMR: δ −225.6 (d, J_{SeP} = 780.2 Hz). ***Se*-4a**: A colorless oil. ^{1}H NMR: δ 2.22 (d, J_{HP} = 18.0 Hz, 3H), 7.24−7.51 (m, 6H), 7.90−7.96 (m, 4H). ^{13}C NMR: δ 7.4, 128.7 (d, J_{CP} = 12.4 Hz), 131.5 (d, J_{CP} = 3.3 Hz), 131.9 (d, J_{CP} = 11.6 Hz), 134.3 (d, J_{CP} = 80.3 Hz). ^{31}P NMR: δ 53.9

(J_{PSe} = 359.5 Hz). ^{77}Se NMR: δ 209.3 (d, J_{SeP} = 359.5 Hz). MS (EI) *m/z*: 312 (M^+). Anal. Calcd for $C_{13}H_{13}PSSe$: C, 50.17; H, 4.21. Found: C, 50.03; H, 4.03.

General Procedure for the Reaction of Phosphinoselenothioic Acid Salts 2 with Acyl Chlorides. A Representative Procedure for the Reaction of *P*,*P*-Diphenylphosphinoselenothioic Acid *N*,*N*,*N*-Tributylbutanaminium Salt (2a) with 4-Chlorobenzoyl Chloride. To a CH_2Cl_2 solution (5 mL) of *P*,*P*-diphenylphosphinoselenothioic acid *N*,*N*,*N*-tributylbutanaminium salt (**2a**) (0.539 g, 1.0 mmol) was added a CH_2Cl_2 solution (5 mL) of 4-chlorobenzoyl chloride (0.263 g, 1.5 mmol) at 0 °C, and the mixture was stirred at that temperature for 1 h. The reaction mixture was poured onto water and extracted with CH_2Cl_2 (50 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was recrystallized from CH_2Cl_2/hexane to give 0.292 g (67%) of a mixture of 4-chlorobenzenecarbothioic acid (anhydrosulfide) with phosphinoselenothioic acid (***S*-5e**) and 4-chlorobenzenecarboselenoic acid (anhydroselenide) with phosphinoselenothioic acid (***Se*-5e**) in a ratio of 85:15 as a pale-yellow solid. IR (KBr): 1677 cm^{-1} (C=O). ^{1}H NMR: δ 7.40 (d, *J* = 8.6 Hz, 2H), 7.47−7.54 (m, 6H), 7.85 (d, *J* = 8.6 Hz, 2H), 7.99−8.05 (m, 4H). ^{13}C NMR: δ 128.7 (d, J_{CP} = 13.7 Hz), 129.2, 129.6, 131.7 (d, J_{CP} = 47.3 Hz), 132.1 (d, J_{CP} = 12.2 Hz), 132.3 (d, J_{CP} = 3.4 Hz), 134.6, 141.2, 185.1 (d, J_{CP} = 3.4 Hz). ^{31}P NMR: δ 48.4 (J_{PSe} = 799.8 Hz, ***S*-5e**), 55.3 (J_{PSe} = 339.8 Hz, ***Se*-5e**). ^{77}Se NMR: δ −151.9 (d, J_{SeP} = 799.8 Hz, ***S*-5e**); 685.6 (d, J_{SeP} = 339.8 Hz, ***Se*-5e**). MS (EI) *m/z*: 436 (M^+). HRMS calcd for $C_{19}H_{14}ClOPSSe$: 435.9357. Found: 435.9360.

Synthesis of *P*-(1,1-Dimethylethyl)-*P*-phenylphosphinoselenothioic *S*-Acid (*S*-6b). To an Et_2O suspension (5 mL) of *P*-(1,1-dimethylethyl)-*P*-phenylphosphinoselenothioic acid *N*,*N*,*N*-trimethylmethanaminium salt (**2d**) (0.350 g, 1.0 mmol) was added hydrogen chloride (1.0 mol/L Et_2O solution, 1.0 mL, 1.0 mmol) at 0 °C. The mixture was stirred at that temperature for 10 min. The insoluble parts were filtered. Removal of the solvent from the filtrate under reduced pressure gave 0.255 g (92%) of ***S*-6b** as a pale-yellow solid. mp: 58−60 °C (dec); IR (KBr): 2397 cm^{-1} (SH). ^{1}H NMR: δ 1.26 (d, J_{HP} = 19.5 Hz, 9H), 2.45 (s, 1H), 7.46−7.54 (m, 3H), 8.04−8.11 (m, 2H). ^{13}C NMR: δ 24.8, 39.1 (d, J_{CP} = 39.7 Hz), 128.0 (d, J_{CP} = 11.6 Hz), 131.0 (d, J_{CP} = 62.9 Hz), 131.7, 133.1 (d, J_{CP} = 9.9 Hz). ^{31}P NMR: δ 74.9 (J_{PSe} = 749.6 Hz). ^{77}Se NMR: δ −161.4 (d, J_{SeP} = 749.6 Hz). MS (EI) *m/z*: 278 (M^+). HRMS calcd for $C_{10}H_{15}PSSe$: 277.9797. Found: 277.9776.

Acknowledgment. This was supported by a Grant-in-Aid for Scientific Research on Priority Area (No. 16033224, "Reaction Control of Dynamic Complexes") from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

Supporting Information Available: Spectroscopic and analytical data for **1**, **2**, **4**, **5**, **7**−**9**; copies of ^{1}H and ^{13}C NMR spectra for compounds **2b**−**d**, **5**−**9**; tables of crystallographic data including atomic positional and thermal parameters for **2c**, **3**, and ***S*-5e**; Z matrixes of optimized structures for **1′**−**6′**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO050576C