

# Selenophilic Reaction of Organolithium and Magnesium Reagents with Phosphinoselenoic Chlorides

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**ABSTRACT:** The reaction of phosphinoselenoic chlorides **1** with various organolithium and magnesium reagents was studied. Sequential reaction of phosphinoselenoic chlorides **1** with organolithium and magnesium reagents and elemental selenium gave two types of products, phosphine selenides **2** and phosphinodiselenoic acid esters **3**. The esters **3** appeared to be formed via the selenophilic reaction of organolithium and magnesium reagents with the chlorides **1**. Molecular orbital calculations were carried out for model compounds  $H_2P(E)Cl$  ( $E = O, S$  and  $Se$ ) to determine their electronic structures. © 2005 Wiley Periodicals, Inc. *Heteroatom Chem* 16:185–191, 2005; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20091

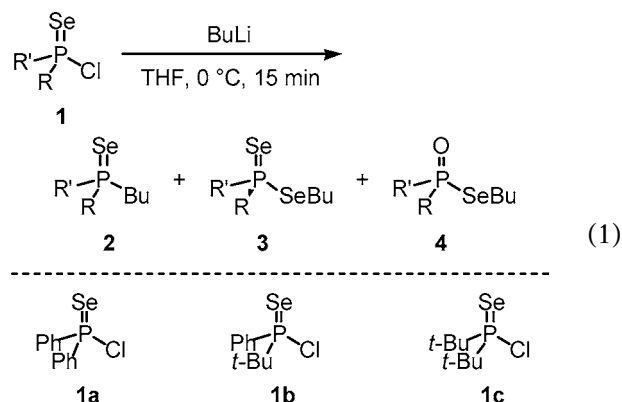
## INTRODUCTION

Phosphinic and phosphinothioic acid derivatives have provided fruitful chemistry. The synthesis and reactions of phosphinic [1] and phosphinothioic halides [2] have been particularly well studied. In contrast, much less attention has been paid to the selenium-isologue, i.e., phosphinoselenoic chlorides, probably because they were predicted to be less stable and had to be handled under an inert

gas [3]. Nevertheless, we recently reported the isolation of phosphinoselenoic chlorides as stable compounds, and their substitution reactions with heteroatom-containing nucleophiles selectively took place at the phosphorus atom [4]. On the other hand, the reaction of these chlorides with organolithium and magnesium reagents gave several types of products. We report here the details of the reaction of phosphinoselenoic chlorides with a variety of organolithium and magnesium reagents. Computational studies on a series of model compounds  $H_2P(E)Cl$  ( $E = O, S$  and  $Se$ ) are also described.

## RESULTS AND DISCUSSION

Initially, diphenylphosphinoselenoic chloride **1a** was treated with BuLi in THF at 0°C for 15 min (Eq. (1), Table 1).



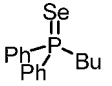
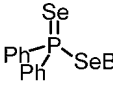
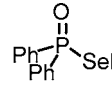
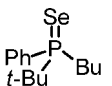
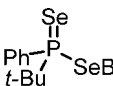
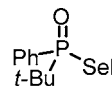
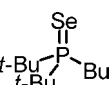
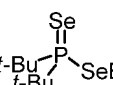
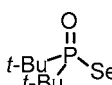
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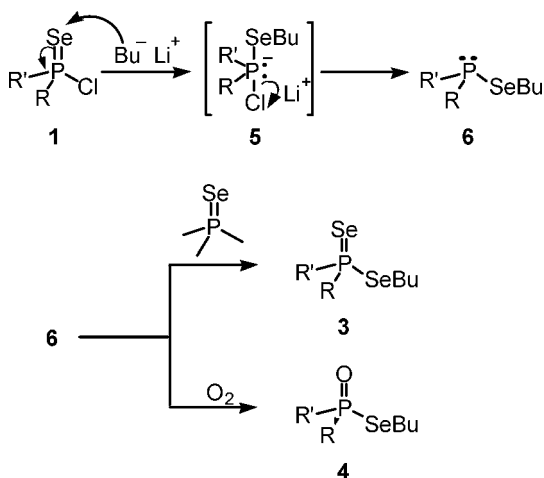
**TABLE 1** Reaction of Phosphinoselenenic Chlorides **1a–c** with BuLi<sup>a</sup>

Entry	1	Yield (%) <sup>b</sup>		
		2	3	4
1	<b>1a</b>	 <b>2a</b> : 19%	 <b>3a</b> : 0%	 <b>4a</b> : 19%
2	<b>1b</b>	 <b>2b</b> : 20%	 <b>3b</b> : 8%	 <b>4b</b> : 36%
3	<b>1c</b>	 <b>2c</b> : 11%	 <b>3c</b> : 17%	 <b>4c</b> : 15%

<sup>a</sup>Phosphinoselenenic chloride **1** was reacted with BuLi (1.1 equiv) at 0°C for 15 min.

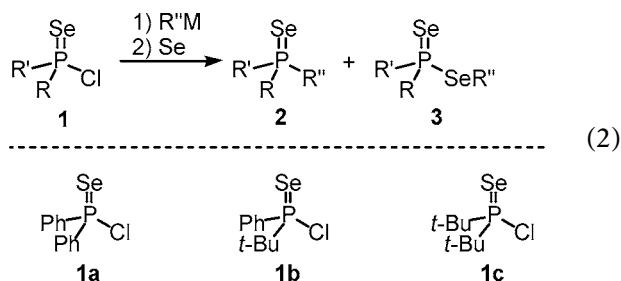
<sup>b</sup>Yields of isolated products.

After the usual work-up, phosphine selenide **2a** and phosphinoselenenic acid *Se*-butyl ester **4a** were obtained in respective yields of 19% and 19% (entry 1). A similar reaction of *tert*-butyl phenyl **1b** and di-*tert*-butylphosphinoselenenic chlorides **1c** with BuLi gave mixtures of phosphine selenides **2**, phosphinodiselenenic acid butyl esters **3**, and phosphinoselenenic acid *Se*-butyl esters **4** (entries 2 and 3). The products **2** may be formed by substitution reaction at the phosphorus atom of **1** with BuLi. On the other hand, **3** and **4** may be formed via selenophilic reaction of BuLi with **1** [5]. A plausible reaction pathway for the present reaction leading to **3** and **4** is shown in Scheme 1.

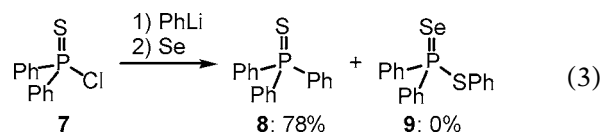
**SCHEME 1**

BuLi initially attacks the selenium atom of the chlorides **1** to form **5**, followed by the elimination of chloride ion from **5** to generate trivalent phosphinoselenenic acid butyl esters **6**. Selenium transfer from other selenium-containing compounds to the resulting esters **6** gives phosphinodiselenenic acid esters **3**. Alternatively, air oxidation of the esters **6** gives phosphinoselenenic acid *Se*-esters **4**. In the reaction of the chloride **1b** with BuLi (entry 2), <sup>31</sup>P NMR spectra of the crude reaction mixture showed the signals due to the deselenated product *t*-BuPhPBU and the ester **6b** at 3.9 ppm and 57.2 ppm (<sup>1</sup>J<sub>PSe</sub> = 234.1 Hz), respectively.

Next, the reaction of phosphinoselenenic chlorides **1a–c** with various organolithium and magnesium reagents was carried out (Eq. (2), Table 2). Elemental selenium was added to the reaction mixture to avoid selenium transfer from selenium-containing compounds to esters **6**. As a result, in all cases, phosphine selenides **2** and phosphinodiselenenic acid esters **3** were obtained.

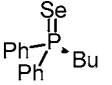
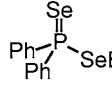
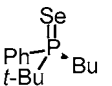
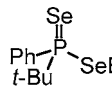
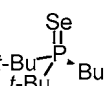
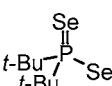
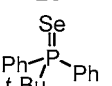
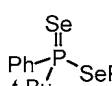
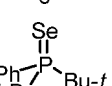
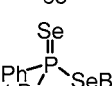
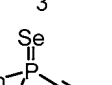
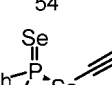


The reaction of diphenylphosphinoselenenic chloride **1a** with BuLi gave a mixture of the phosphine selenide **2a** and the ester **3a** in a ratio of 57:43 (entry 1), whereas the introduction of one *tert*-butyl group to the phosphorus atom gave the ester **3b** in an increased ratio (entry 2). When the chloride **1c** bearing two *tert*-butyl groups was used as a substrate, the ester **3c** was obtained in a higher ratio (entry 3). The use of BuMgCl increased the ratio of the phosphine selenide **2b** (entry 4) [6]. The reaction of **1b** with PhLi preferentially gave phosphinodiselenenic acid ester **3d** (entry 5). Notably, this result is in marked contrast to the reaction of phosphinothioic chloride **7** with PhLi where phosphine sulfide **8** was selectively obtained (Eq. (3)) [7].



The reaction of **1b** with *t*-BuLi afforded the ester **3e** in moderate yield together with a trace amount of phosphine selenide **2e** (entry 6). In this case, <sup>31</sup>P

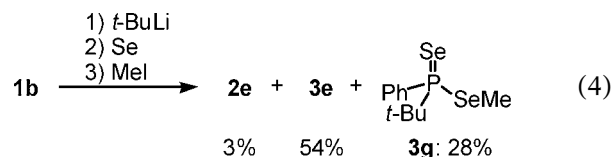
**TABLE 2** Reaction of Phosphinoselenic Chlorides **1a–c** with a Variety of Carbon Nucleophiles<sup>a</sup>

Entry	<b>1</b> <i>R''M</i>	Conv.(%)	Yield (%) <sup>b</sup>	
			<b>2</b>	<b>3</b>
1	<b>1a</b> BuLi	100	 <b>2a</b> 25	 <b>3a</b> 19
2	<b>1b</b> BuLi	100	 <b>2b</b> 24	 <b>3b</b> 37
3	<b>1c</b> BuLi	100	 <b>2c</b> 19	 <b>3c</b> 46
4	<b>1b</b> BuMgCl	98	<b>2b</b> 26	<b>3b</b> 12
5	<b>1b</b> PhLi	95	 <b>2d</b> 6	 <b>3d</b> 63
6	<b>1b</b> <i>t</i> -BuLi	94	 <b>2e</b> 3	 <b>3e</b> 54
7	<b>1b</b> PhC≡CLi	71	 <b>2f</b> 55	 <b>3f</b> 0

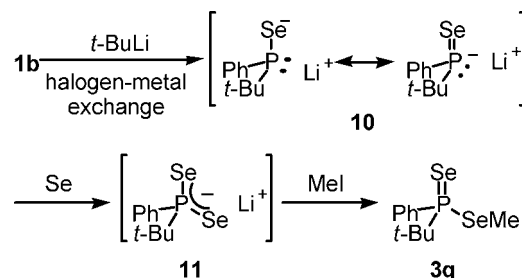
<sup>a</sup>Phosphinoselenic chloride **1** was reacted with organometallic reagent (1 equiv) at 0°C (organolithium reagents) or room temperature (BuMgCl) in THF (10 ml) for 15 min. After elemental selenium (2 equiv) was added to the reaction mixture, the mixture was stirred at room temperature for 1 h.

<sup>b</sup>Yields of isolated products.

NMR spectra of the crude reaction mixture showed an unidentified signal (58.1 ppm) with relatively high intensity. Methyl iodide was then added to the reaction mixture to give phosphinodiselenic acid methyl ester **3g** in 28% yield along with **2e** and **3e** (Eq. (4)) [8]. A plausible reaction pathway leading to the methyl ester **3g** may involve a halogen–metal exchange reaction to generate phosphinoselenous acid lithium salt **10**, followed by the insertion of elemental selenium to form phosphinodiselenic acid lithium salt **11** (Scheme 2) [9]. Methylation of the



salt **11** may give phosphinodiselenic acid methyl ester **3g** [4b].



#### SCHEME 2

Finally, lithium phenylethynylide was reacted with the chloride **1b** (entry 7). In contrast to the reaction with alkyl and phenyllithiums, selective introduction of a phenylethynyl group to the phosphorus atom took place to give **2f** in 55% yield.

To determine the electronic structure of phosphinoselenic chlorides, geometry optimization and molecular orbital calculations for the model compounds  $\text{H}_2\text{P}(\text{O})\text{Cl}$  **12'**,  $\text{H}_2\text{P}(\text{S})\text{Cl}$  **7'**, and  $\text{H}_2\text{P}(\text{Se})\text{Cl}$  **1'** were performed at the RHF/6-31G(d) level with the GAUSSIAN 98 programs [10]. Selected bond lengths, atomic charges, and energies of LUMO and LUMO+1 are listed in Table 3. The MO plots drawn by the MOLDEN program [11] are shown in Figure 1.

No significant change in the P–Cl bond lengths was observed for these compounds, whereas the positive charge on the phosphorus atom of phosphinoselenic chloride **1'** was much smaller than that of phosphinic chloride **12'**. The LUMOs of **1'**, **7'**, and **12'** were mainly P–Cl antibonding orbitals. Notably,

**TABLE 3** RHF/6-31G(d) Optimized Bond Lengths, Atomic Charges and Orbital Energies of Model Compounds  $\text{H}_2\text{P}(\text{E})\text{Cl}$ 

$\text{H}_2\text{P}(\text{E})\text{Cl}$	<b>12'</b> (E = O)	<b>7'</b> (E = S)	<b>1'</b> (E = Se)
Bond length (Å)			
P=E	1.454	1.926	2.706
P–Cl	2.023	2.036	2.038
Atomic charge			
E	–0.729	–0.371	–0.467
P	0.980	0.524	0.620
Cl	–0.202	–0.153	–0.154
Orbital energy (eV)			
LUMO	3.833	2.383	2.206
LUMO+1	4.412	3.860	3.569

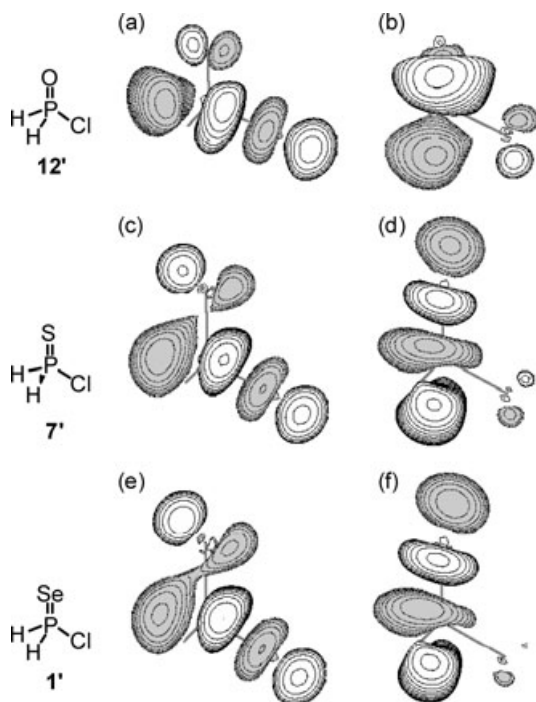


FIGURE 1 MOLDEN plots of orbitals calculated for model compounds: (a) LUMO and (b) LUMO + 1 of  $\text{H}_2\text{P}(\text{O})\text{Cl}$  **12'**; (c) LUMO and (d) LUMO + 1 of  $\text{H}_2\text{P}(\text{S})\text{Cl}$  **7'**; (e) LUMO and (f) LUMO + 1 of  $\text{H}_2\text{P}(\text{Se})\text{Cl}$  **1'**.

LUMO of **1'** spread not only along the P–Cl bond but also on the selenium atom. In addition, LUMO+1s of **1'** and **7'** were in essence P–E antibonding orbitals, and LUMO+1 of **1'** had a large back lobe of a P–E antibonding orbital at the selenium atom. Furthermore, the LUMO+1 energy of **1'** was the lowest and the energy gap between the LUMO and LUMO+1 of **1'** was the smallest among the model compounds. These results are consistent with the experimental results that a selenophilic reaction occurred between organolithium and magnesium reagents and phosphinoselenoic chlorides.

## CONCLUSION

Phosphinoselenoic chlorides reacted with a variety of organolithium and magnesium reagents. This reaction may involve the selenophilic reaction of organolithium and magnesium reagents with the chlorides.

## EXPERIMENTAL

### General

Melting points were measured by a Yanagimoto micro-melting point apparatus and are uncorrected.

NMR spectra were measured with  $\text{CDCl}_3$  on a JEOL  $\alpha$ -400 spectrometer. Mass spectra were taken on SHIMADZU GCMS QP1000 (EI mode). High-resolution mass spectra were measured on a JEOL JMS-GC mate II. Elemental analyses were performed at the Elemental Analysis Center of Kyoto University.

### Synthesis of *P,P*-bis(1,1-dimethylethyl)phosphinoselenoic Chloride (**1c**)

In a 50-mL two-necked flask, elemental selenium (1.579 g, 20.0 mmol) was added to a toluene solution (20 mL) of *t*- $\text{Bu}_2\text{P}(\text{Cl})$  (3.80 mL, 20.0 mmol) at room temperature, and the mixture was stirred under reflux for 15 min. The reaction mixture was concentrated in vacuo. The residue was purified by column chromatography on silica gel using hexane- $\text{CH}_2\text{Cl}_2$  as eluent to give *P,P*-bis(1,1-dimethylethyl)phosphinoselenoic chloride (**1c**) (5.115 g, 99%) as a colorless solid. mp (dec.) 131–132°C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.46 (d,  $^3J_{\text{HP}} = 18.5$  Hz, 18H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  27.8 (d,  $^2J_{\text{CP}} = 2.5$  Hz), 45.5 (d,  $^1J_{\text{CP}} = 29.8$  Hz);  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ )  $\delta$  145.8 ( $^1J_{\text{PSe}} = 816.3$  Hz);  $^{77}\text{Se}$  NMR ( $\text{CDCl}_3$ )  $\delta$  -205.0 (d,  $^1J_{\text{SeP}} = 816.3$  Hz); EIMS ( $m/z$ ) 260 ( $\text{M}^+$ ); Anal. Calcd for  $\text{C}_8\text{H}_{18}\text{ClPSe}$ : C, 37.01; H, 6.99. Found: C, 36.81; H, 6.86.

### Reaction of *P*-(1,1-Dimethylethyl)-*P*-phenylphosphinoselenoic Chloride (**1b**) with BuLi

In a 20-mL two-necked flask, BuLi (1.6 mol/L hexane solution, 1.4 mL, 2.2 mmol) was added to a THF solution (5 mL) of *P*-(1,1-dimethylethyl)-*P*-phenylphosphinoselenoic chloride (**1b**) (0.559 g, 2.0 mmol) at 0°C, and the mixture was stirred at that temperature for 15 min. The reaction mixture was poured into water and extracted with  $\text{CH}_2\text{Cl}_2$  (50 mL). The organic layer was dried over  $\text{MgSO}_4$  and concentrated in vacuo. The residue was purified by column chromatography on silica gel using hexane- $\text{CH}_2\text{Cl}_2$  and  $\text{CHCl}_3$ -MeOH as eluent to give *P*-butyl-*P*-(1,1-dimethylethyl)-*P*-phenylphosphine selenide (**2b**) (0.121 g, 20%) as a pale-yellow solid, *P*-(1,1-dimethylethyl)-*P*-phenylphosphinodiselenoic acid butyl ester (**3b**) (0.059 g, 8%) as a pale-yellow oil and *P*-(1,1-dimethylethyl)-*P*-phenylphosphinoselenoic acid *Se*-butyl ester (**4b**) (0.226 g, 36%) as a pale-yellow oil. **2b**: mp (dec.) 87–89°C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.88 (t,  $J = 7.3$  Hz, 3H), 1.14 (d,  $^3J_{\text{HP}} = 16.6$  Hz, 9H), 1.22–1.32 (m, 1H), 1.41 (sex,  $J = 7.3$  Hz, 2H), 1.77–1.91 (m, 1H), 1.96–2.07 (m, 1H), 2.52–2.62 (m, 1H), 7.40–7.49 (m, 3H), 7.83–7.88 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  13.7, 23.9, 24.1 (d,  $^1J_{\text{CP}} = 25.6$  Hz), 25.2 (d,  $^2J_{\text{CP}} = 1.7$  Hz), 25.3 (d,  $J_{\text{CP}} = 2.5$  Hz), 33.8 (d,  $^1J_{\text{CP}} = 42.2$  Hz), 127.0 (d,  $^1J_{\text{CP}} = 61.2$  Hz), 128.1 (d,  $J_{\text{CP}} = 10.8$  Hz), 131.3 (d,  $^4J_{\text{CP}} = 2.5$  Hz),

133.1 (d,  $J_{CP} = 8.3$  Hz);  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ )  $\delta$  59.1 ( $^1J_{PSe} = 708.1$  Hz);  $^{77}\text{Se}$  NMR ( $\text{CDCl}_3$ )  $\delta$  -436.7 (d,  $^1J_{SeP} = 708.1$  Hz); EIMS ( $m/z$ ) 302 ( $\text{M}^+$ ); Anal. Calcd for  $\text{C}_{14}\text{H}_{23}\text{PSe}$ : C, 55.81; H, 7.70. Found: C, 55.59; H, 7.58. **3b**:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.81 (t,  $J = 6.8$  Hz, 3H), 1.21 (d,  $^3J_{HP} = 18.5$  Hz, 9H), 1.34 (sex,  $J = 7.3$  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);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  13.5, 22.9, 25.5 (d,  $^2J_{CP} = 2.5$  Hz), 31.1 (d,  $J_{CP} = 2.5$  Hz), 32.4 (d,  $J_{CP} = 3.3$  Hz), 38.7 (d,  $^1J_{CP} = 37.2$  Hz), 127.8 (d,  $J_{CP} = 11.6$  Hz), 130.8 (d,  $^1J_{CP} = 52.1$  Hz), 131.4 (d,  $^4J_{CP} = 2.5$  Hz), 133.7 (d,  $J_{CP} = 9.9$  Hz);  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ )  $\delta$  79.9 ( $^1J_{PSe} = 381.9$ , 756.2 Hz);  $^{77}\text{Se}$  NMR ( $\text{CDCl}_3$ )  $\delta$  -277.8 (d,  $^1J_{SeP} = 756.2$  Hz), 181.4 (d,  $^1J_{SeP} = 381.9$  Hz); EIMS ( $m/z$ ) 382 ( $\text{M}^+$ ); Anal. Calcd for  $\text{C}_{14}\text{H}_{23}\text{PSe}_2$ : C, 44.22; H, 6.10. Found: C, 44.41; H, 6.16. **4b**:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.69 (t,  $J = 7.3$  Hz, 3H), 1.06 (d,  $^3J_{HP} = 17.6$  Hz, 9H), 1.20 (sex,  $J = 7.3$  Hz, 2H), 1.48 (quint,  $J = 7.3$  Hz, 2H), 2.58–2.74 (m, 2H), 7.33–7.42 (m, 3H), 7.76–7.80 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  13.2, 22.6, 23.6 (d,  $J_{CP} = 2.5$  Hz), 24.5, 32.8 (d,  $J_{CP} = 3.3$  Hz), 37.4 (d,  $^1J_{CP} = 62.9$  Hz), 127.9 (d,  $J_{CP} = 11.6$  Hz), 131.6 (d,  $^4J_{CP} = 2.5$  Hz), 131.7, 132.5 (d,  $J_{CP} = 9.9$  Hz);  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ )  $\delta$  67.3 ( $^1J_{PSe} = 398.4$  Hz);  $^{77}\text{Se}$  NMR ( $\text{CDCl}_3$ )  $\delta$  129.5 (d,  $^1J_{SeP} = 398.4$  Hz); EIMS ( $m/z$ ) 318 ( $\text{M}^+$ ); Anal. Calcd for  $\text{C}_{14}\text{H}_{23}\text{OPSe}$ : C, 53.00; H, 7.31. Found: C, 53.19; H, 7.44.

*P,P*-Diphenylphosphinoselenic Acid *Se*-Butyl Ester (**4a**). Pale-yellow oil;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.75 (t,  $J = 7.3$  Hz, 3H), 1.25 (sex,  $J = 7.3$  Hz, 2H), 1.54–1.61 (m, 2H), 2.73–2.79 (m, 2H), 7.37–7.47 (m, 6H), 7.79–7.84 (m, 4H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  13.2, 22.6, 25.1 (d,  $J_{CP} = 2.5$  Hz), 32.6, 128.5 (d,  $J_{CP} = 13.2$  Hz), 131.1 (d,  $J_{CP} = 10.8$  Hz), 132.0 (d,  $^4J_{CP} = 2.5$  Hz), 134.2 (d,  $^1J_{CP} = 97.6$  Hz);  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ )  $\delta$  39.9 ( $^1J_{PSe} = 395.4$  Hz);  $^{77}\text{Se}$  NMR ( $\text{CDCl}_3$ )  $\delta$  211.9 (d,  $^1J_{SeP} = 395.4$  Hz); EIMS ( $m/z$ ) 338 ( $\text{M}^+$ ); HRMS Calcd for  $\text{C}_{16}\text{H}_{19}\text{OPSe}$ : 338.0339. Found: 338.0312.

*P*-Butyl-*P,P*-bis(1,1-dimethylethyl)phosphine Selenide (**2c**). Pale-yellow solid; mp (dec.) 106–109°C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.87 (t,  $J = 7.3$  Hz, 3H), 1.27 (d,  $^3J_{HP} = 14.6$  Hz, 18H), 1.27–1.41 (m, 2H), 1.58–1.67 (m, 2H), 1.74–1.81 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  13.7, 22.2 (d,  $^1J_{CP} = 36.4$  Hz), 24.4 (d,  $J_{CP} = 14.1$  Hz), 27.9, 28.3 (d,  $J_{CP} = 3.3$  Hz), 36.9 (d,  $^1J_{CP} = 33.9$  Hz);  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ )  $\delta$  76.9 ( $^1J_{PSe} = 688.5$  Hz);  $^{77}\text{Se}$  NMR ( $\text{CDCl}_3$ )  $\delta$  -464.2 (d,  $^1J_{SeP} = 688.5$  Hz); EIMS ( $m/z$ ) 282 ( $\text{M}^+$ ); Anal. Calcd for  $\text{C}_{12}\text{H}_{27}\text{PSe}$ : C, 51.24; H, 9.68. Found: C, 51.07; H, 9.87.

*P,P*-Bis(1,1-dimethylethyl)phosphinodiselenic Acid Butyl Ester (**3c**). Pale-yellow oil;  $^1\text{H}$  NMR

( $\text{CDCl}_3$ )  $\delta$  0.89 (t,  $J = 7.3$  Hz, 3H), 1.20–1.56 (m, 2H), 1.38 (d,  $^3J_{HP} = 17.6$  Hz, 18H), 1.67 (quint,  $J = 7.3$  Hz, 2H), 2.85–2.91 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  13.7, 23.1, 28.1, 32.6 (d,  $J_{CP} = 2.5$  Hz), 32.8 (d,  $J_{CP} = 2.5$  Hz), 42.1 (d,  $^1J_{CP} = 25.6$  Hz);  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ )  $\delta$  112.7 ( $^1J_{PSe} = 370.9$  Hz, 742.4 Hz);  $^{77}\text{Se}$  NMR ( $\text{CDCl}_3$ )  $\delta$  -317.2 (d,  $^1J_{SeP} = 742.4$  Hz), 120.9 (d,  $^1J_{SeP} = 370.9$  Hz.); EIMS ( $m/z$ ) 362 ( $\text{M}^+$ ); Anal. Calcd for  $\text{C}_{12}\text{H}_{27}\text{PSe}_2$ : C, 40.01; H, 7.55. Found: C, 40.28; H, 7.29.

*P,P*-Bis(1,1-dimethylethyl)phosphinoselenic Acid *Se*-Butyl Ester (**4c**). Pale-yellow oil;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.87 (t,  $J = 7.3$  Hz, 3H), 1.28 (d,  $^3J_{HP} = 15.6$  Hz, 18H), 1.33–1.42 (m, 2H), 1.61–1.72 (m, 2H), 2.78–2.85 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  13.6, 23.0, 24.3 (d,  $J_{CP} = 2.5$  Hz), 26.6, 33.6 (d,  $J_{CP} = 2.5$  Hz), 40.7 (d,  $^1J_{CP} = 49.6$  Hz);  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ )  $\delta$  87.6 ( $^1J_{PSe} = 377.4$  Hz);  $^{77}\text{Se}$  NMR ( $\text{CDCl}_3$ )  $\delta$  63.2 (d,  $^1J_{SeP} = 377.4$  Hz); EIMS ( $m/z$ ) 298 ( $\text{M}^+$ ); Anal. Calcd for  $\text{C}_{12}\text{H}_{27}\text{OPSe}$ : C, 48.48; H, 9.15. Found: C, 48.68; H, 9.42.

#### Reaction of *P*-(1,1-Dimethylethyl)-*P*-phenylphosphinoselenic Chloride (**1b**) with BuLi and Elemental Selenium

In a 20-mL two-necked flask, BuLi (1.6 mol/L hexane solution, 0.63 mL, 1.0 mmol) was added to a THF solution (10 mL) of **1b** (0.280 g, 1.0 mmol) at 0°C, and the mixture was stirred at that temperature for 15 min. To the reaction mixture was added elemental selenium (0.158 g, 2.0 mmol), and the mixture was stirred at room temperature for 1 h. The reaction mixture was poured into water and extracted with  $\text{CH}_2\text{Cl}_2$  (50 mL). The organic layer was dried over  $\text{MgSO}_4$  and concentrated in vacuo. The residue was purified by column chromatography on silica gel using hexane- $\text{CH}_2\text{Cl}_2$  as eluent to give **2b** (0.071 g, 24%) and **3b** (0.141 g, 37%).

*P,P*-Diphenylphosphinodiselenic Acid Butyl Ester (**3a**). Pale-yellow oil;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.81 (t,  $J = 7.3$  Hz, 3H), 1.33 (sex,  $J = 7.3$  Hz, 2H), 1.60 (quint,  $J = 7.3$  Hz, 2H), 2.99 (td,  $J = 7.3$  Hz,  $^3J_{HP} = 12.7$  Hz), 7.38–7.47 (m, 6H), 7.89–7.96 (m, 4H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  13.5, 22.8, 31.5 (d,  $J_{CP} = 1.7$  Hz), 32.1 (d,  $J_{CP} = 4.1$  Hz), 128.4 (d,  $J_{CP} = 12.4$  Hz), 131.7 (d,  $^4J_{CP} = 3.3$  Hz), 131.8 (d,  $J_{CP} = 11.6$  Hz), 133.9 (d,  $^1J_{CP} = 68.6$  Hz);  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ )  $\delta$  40.3 ( $^1J_{PSe} = 371.3$ , 765.2 Hz);  $^{77}\text{Se}$  NMR ( $\text{CDCl}_3$ )  $\delta$  -176.5 (d,  $^1J_{SeP} = 765.2$  Hz), 289.0 (d,  $^1J_{SeP} = 371.3$  Hz); EIMS ( $m/z$ ) 402 ( $\text{M}^+$ ); HRMS Calcd for  $\text{C}_{16}\text{H}_{19}\text{PSe}_2$ : 401.9555. Found: 401.9579.

*P*-(1,1-Dimethylethyl)-*P*-phenylphosphinodiselenoic Acid Phenyl Ester (**3d**). Pale-yellow solid; mp (dec.) 95–98°C; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.33 (d, <sup>3</sup>J<sub>HP</sub> = 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); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 25.9 (d, <sup>2</sup>J<sub>CP</sub> = 1.7 Hz), 39.6 (d, <sup>1</sup>J<sub>CP</sub> = 34.7 Hz), 125.0 (d, <sup>1</sup>J<sub>CP</sub> = 5.8 Hz), 127.9 (d, <sup>1</sup>J<sub>CP</sub> = 11.6 Hz), 128.9 (d, <sup>1</sup>J<sub>CP</sub> = 1.7 Hz), 129.4 (d, <sup>1</sup>J<sub>CP</sub> = 1.7 Hz), 129.8 (d, <sup>1</sup>J<sub>CP</sub> = 52.1 Hz), 131.5 (d, <sup>1</sup>J<sub>CP</sub> = 2.5 Hz), 134.1 (d, <sup>1</sup>J<sub>CP</sub> = 9.1 Hz), 137.4 (d, <sup>1</sup>J<sub>CP</sub> = 3.3 Hz); <sup>31</sup>P NMR (CDCl<sub>3</sub>) δ 85.7 (<sup>1</sup>J<sub>PSe</sub> = 371.4, 774.2 Hz); <sup>77</sup>Se NMR (CDCl<sub>3</sub>) δ -239.6 (d, <sup>1</sup>J<sub>SeP</sub> = 774.2 Hz), 365.4 (d, <sup>1</sup>J<sub>SeP</sub> = 371.4 Hz); EIMS (*m/z*) 402 (M<sup>+</sup>); Anal. Calcd for C<sub>16</sub>H<sub>19</sub>PSe<sub>2</sub>: C, 48.02; H, 4.79. Found: C, 47.76; H, 4.69.

*P,P*-Bis(1,1-dimethylethyl)-*P*-phenylphosphine Selenide (**2e**). Pale-yellow solid; mp (dec.) 140–145°C; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.39 (d, <sup>3</sup>J<sub>HP</sub> = 15.6 Hz, 18H), 7.40–7.48 (m, 3H), 8.20–8.30 (m, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 28.8, 38.1 (d, <sup>1</sup>J<sub>CP</sub> = 33.9 Hz), 127.6 (d, <sup>1</sup>J<sub>CP</sub> = 54.2 Hz), 127.7 (d, <sup>1</sup>J<sub>CP</sub> = 10.8 Hz), 131.1 (d, <sup>4</sup>J<sub>CP</sub> = 2.5 Hz), 134.8; <sup>31</sup>P NMR (CDCl<sub>3</sub>) δ 79.5 (<sup>1</sup>J<sub>PSe</sub> = 708.1 Hz); <sup>77</sup>Se NMR (CDCl<sub>3</sub>) δ -423.9 (d, <sup>1</sup>J<sub>SeP</sub> = 708.1 Hz); EIMS (*m/z*) 302 (M<sup>+</sup>); Anal. Calcd for C<sub>14</sub>H<sub>23</sub>PSe: C, 55.81; H, 7.70. Found: C, 55.81; H, 7.88.

*P*-(1,1-Dimethylethyl)-*P*-phenylphosphinodiselenoic Acid 1,1-Dimethylethyl Ester (**3e**). Pale-yellow solid; mp (dec.) 102–105°C; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.17 (d, <sup>3</sup>J<sub>HP</sub> = 19.0 Hz, 9H), 1.51 (d, <sup>4</sup>J<sub>HP</sub> = 1.0 Hz, 9H), 7.41–7.44 (m, 3H), 8.19–8.25 (m, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 25.5, 33.1, 39.4 (d, <sup>1</sup>J<sub>CP</sub> = 37.2 Hz), 53.1 (d, <sup>2</sup>J<sub>CP</sub> = 4.1 Hz), 127.6 (d, <sup>1</sup>J<sub>CP</sub> = 11.6 Hz), 130.8 (d, <sup>1</sup>J<sub>CP</sub> = 50.5 Hz), 131.2 (d, <sup>4</sup>J<sub>CP</sub> = 2.5 Hz), 134.2 (d, <sup>1</sup>J<sub>CP</sub> = 9.9 Hz); <sup>31</sup>P NMR (CDCl<sub>3</sub>) δ 65.8 (<sup>1</sup>J<sub>PSe</sub> = 420.9, 745.6 Hz); <sup>77</sup>Se NMR (CDCl<sub>3</sub>) δ -237.8 (d, <sup>1</sup>J<sub>SeP</sub> = 745.6 Hz), 385.2 (d, <sup>1</sup>J<sub>SeP</sub> = 420.9 Hz); EIMS (*m/z*) 382 (M<sup>+</sup>); Anal. Calcd for C<sub>14</sub>H<sub>23</sub>PSe<sub>2</sub>: C, 44.22; H, 6.10. Found: C, 44.22; H, 5.97.

*P*-(1,1-Dimethylethyl)-*P*-phenyl-*P*-phenylethynylphosphine Selenide (**2f**). Pale-yellow oil; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.26 (d, <sup>3</sup>J<sub>HP</sub> = 19.5 Hz, 9H), 7.35–7.51 (m, 6H), 7.58 (d, *J* = 7.8 Hz, 2H), 8.04–8.09 (m, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 24.5 (d, <sup>2</sup>J<sub>CP</sub> = 3.3 Hz), 36.1 (d, <sup>1</sup>J<sub>CP</sub> = 50.5 Hz), 78.4 (d, <sup>1</sup>J<sub>CP</sub> = 128.2 Hz), 106.4 (d, <sup>2</sup>J<sub>CP</sub> = 19.0 Hz), 120.3 (d, <sup>1</sup>J<sub>CP</sub> = 4.1 Hz), 128.1 (d, <sup>1</sup>J<sub>CP</sub> = 13.2 Hz), 128.3 (d, <sup>1</sup>J<sub>CP</sub> = 77.7 Hz), 128.6, 130.5, 131.8 (d, <sup>1</sup>J<sub>CP</sub> = 3.3 Hz), 132.4 (d, <sup>1</sup>J<sub>CP</sub> = 1.7 Hz), 132.7 (d, <sup>1</sup>J<sub>CP</sub> = 10.8 Hz); <sup>31</sup>P NMR (CDCl<sub>3</sub>) δ 34.3 (<sup>1</sup>J<sub>PSe</sub> = 742.7 Hz); <sup>77</sup>Se NMR (CDCl<sub>3</sub>) δ -316.3 (d, <sup>1</sup>J<sub>SeP</sub> = 742.7 Hz); EIMS (*m/z*) 346 (M<sup>+</sup>); HRMS Calcd for C<sub>18</sub>H<sub>19</sub>PSe: 346.0390. Found: 346.0395.

### Reaction of *P,P*-Diphenylphosphinothioic Chloride (**7**) with PhLi and Elemental Selenium

In a 20-mL two-necked flask, PhLi (0.94 mol/L cyclohexane-Et<sub>2</sub>O solution, 1.05 mL, 1.0 mmol) was added to a THF solution (10 mL) of *P,P*-diphenylphosphinothioic chloride (**7**) (0.253 g, 1.0 mmol) at 0°C, and the mixture was stirred at that temperature for 15 min. To the reaction mixture was added elemental selenium (0.087 g, 1.1 mmol), and the mixture was stirred at room temperature for 1 h. The reaction mixture was poured into water and extracted with Et<sub>2</sub>O (50 mL). The organic layer was dried over MgSO<sub>4</sub> and concentrated in vacuo. The residue was purified by column chromatography on silica gel using hexane-Et<sub>2</sub>O as eluent to give triphenylphosphine sulfide (**8**) (0.230 g, 78%) as a colorless solid.

*P*-(1,1-Dimethylethyl)-*P*-phenylphosphinodiselenoic Acid Methyl Ester (**3g**). Pale-yellow oil; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.23 (d, <sup>3</sup>J<sub>HP</sub> = 19.5 Hz, 9H), 2.18 (d, <sup>3</sup>J<sub>HP</sub> = 12.2 Hz, 3H), 7.40–7.48 (m, 3H), 8.05–8.11 (m, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 9.2 (d, <sup>1</sup>J<sub>CP</sub> = 2.5 Hz), 25.6 (d, <sup>1</sup>J<sub>CP</sub> = 2.5 Hz), 39.0 (d, <sup>1</sup>J<sub>CP</sub> = 36.4 Hz), 128.0 (d, <sup>1</sup>J<sub>CP</sub> = 11.6 Hz), 129.8 (d, <sup>1</sup>J<sub>CP</sub> = 52.9 Hz), 131.6 (d, <sup>1</sup>J<sub>CP</sub> = 3.3 Hz), 133.7 (d, <sup>1</sup>J<sub>CP</sub> = 9.1 Hz); <sup>31</sup>P NMR (CDCl<sub>3</sub>) δ 82.6 (<sup>1</sup>J<sub>PSe</sub> = 366.2, 762.9 Hz); <sup>77</sup>Se NMR (CDCl<sub>3</sub>) δ -279.7 (d, <sup>1</sup>J<sub>SeP</sub> = 762.9 Hz), 112.6 (d, <sup>1</sup>J<sub>SeP</sub> = 366.2 Hz); EIMS (*m/z*) 340 (M<sup>+</sup>); Anal. Calcd for C<sub>11</sub>H<sub>17</sub>PSe<sub>2</sub>: C, 39.07; H, 5.07. Found: C, 39.28; H, 4.91.

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