Crystal Structure and Chemical Properties of Tris(2,6-dimethoxyphenyl)phosphine Selenide

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The X-ray crystal structure of the title compound, Φ_3PSe [$\Phi = 2,6\text{-}(MeO)_2C_6H_3$], showed that the P=Se bond distance [2.136(2) Å] was the longest among those of the reported triarylphosphine selenides, that the P–C bond distances [av. 1.839 Å] were longer than those of triphenylphosphine selenide, and that all the P···O interatomic distances [2.794—3.189 Å] were shorter than the sum of the van der Waals radii, implying a direct electron-donative interaction from the methoxy oxygen atom to the phosphorus atom. Some chemical evidence also showed that the P=Se bond was weaker than that of triphenylphosphine selenide. Alkyl halides, RX, reacted with Φ_3PSe to give a mixture of alkylselenophosphonium salts, [Φ_3P–SeR]X, and alkylphosphonium salts, [Φ_3P–R]X, while they reacted with $Ph\Phi_2PSe$ to give [$Ph\Phi_2$P-SeR]X almost selectively. Measurements of the reaction rates of $Ph_{3-n}\Phi_nPY$ ($n = 0$—3; Y = none, O, S, Se) with butyl bromide in acetonitrile showed that the rate decreased in the order of Y = none > Se > S > O and $n = 3 > 2 > 1 > 0$. Benzylselenophosphonium salts, [$\Phi_3P\text{–}SeCH_2C_6H_4Z\text{-}4$]Cl (Z = H, Me, Cl) and [$Ph\Phi_2P\text{–}SeCH_2Ph$]Cl, reacted easily with aqueous sodium hydroxide or with aqueous tin(II) chloride to give the diselenides, $(4\text{-}ZC_6H_4CH_2Se)_2$, and most of $Ar\Phi_2P$ [Ar = Φ or Ph] was recovered after these reactions. These properties of [$Ar\Phi_2$P–SeR]X, as well as of $Ar\Phi_2PSe$, were discussed in terms of the electronic effect and/or steric effect of methoxy groups at 2,6-positions.

Triphenylphosphines bearing methoxy substituents at the 2,6-positions of the phenyl groups, such as tris(2,6-dimethoxyphenyl)phosphine, Φ_3P [$\Phi = 2,6\text{-}(MeO)_2C_6H_3$], are highly basic and nucleophilic.[1—4] Its sulfide, Φ_3PS, also is highly nucleophilic, and it reacts with common alkyl halides, RX (X = Cl, Br, I), to form isolable alkylthiophosphonium salts, [Φ_3P–SR]X.[5] Its oxide, Φ_3PO, also is highly nucleophilic.[6] While it reacts easily with RX (X = Br, I), the resultant alkoxyphosphonium halides, [Φ_3P–OR]X, are unstable to decompose reversibly to give Φ_3PO and RX in solutions.[7] The selenide, Φ_3PSe, has been prepared by Allen et al.,[8] who observed the unusual substituent effects of 2,6-dimethoxy groups on ^{31}P and ^{77}Se NMR chemical shifts. However, its chemical properties have not been explored. As an extension of our studies on 2,6-dimethoxyphenylphosphine derivatives, we report here the basic properties of Φ_3PSe including its crystal structure, the reactions of related selenides, $Ph_{3-n}\Phi_nPSe$ ($n = 0$—3), with alkyl halides, the comparison of reaction rates of related compounds, $Ph_{3-n}\Phi_nPY$ (Y = none, O, S, Se), with butyl bromide [Eq. 1], and the properties of alkylselenophosphonium salts, [$Ph_{3-n}\Phi_n$P–SeR]X. Some of the preliminary results have been reported elsewhere.[9]

$$Ph_{3-n}\Phi_nPY + BuBr \longrightarrow [Ph_{3-n}\Phi_nP\text{–}YBu]Br \qquad (1)$$

$$[n = 0\text{—}3;\ Y = \text{none, O, S, Se}]$$

Experimental

General. ^{1}H and ^{13}C NMR spectra were recorded for solutions in $CDCl_3$ using a JEOL model JNM-GX-270 spectrometer operating at 270 and 68 MHz, respectively. IR spectra were recorded for Nujol mull using a Shimadzu FTIR-4200 spectrophotometer. The spectra of perchlorate showed a strong band at 1100 (broad) cm^{-1}, and those of hexafluorophosphate showed a strong band at 840 (broad) cm^{-1}. The ^{1}H and ^{13}C NMR spectral data are summarized in Tables 1 and 2, respectively.

Φ_3P was offered by K. I. Kasei Co. The other triarylphosphines, their oxides, and sulfides were prepared as reported.[1,5—7]

Preparation of Triarylphosphine Selenides, $Ph_{3-n}\Phi_nPSe$. A mixture of Φ_3P (8.85 g, 20 mmol) and elemental selenium (1.89 g, 24 mmol) in acetone (50 ml) was heated at 50—60 °C for 3 h. Unreacted selenium was removed by filtration while the solution was warm. To the filtrate was added methanol (100 ml), and the solution was cooled to 0 °C to precipitate yellow crystals of Φ_3PSe as hydrate; IR 3350 and 1630 cm^{-1} (OH_2). They can be recrystallized from ethanol or toluene to give $\Phi_3PSe\cdot xH_2O$ [x=0.8—2.5 (ethanol) or 1 (toluene)]. The unhydrate can be obtained by heating the crystals at ca. 90 °C for a few hours, and the amounts of crystal water (x) were estimated by the weight loss.

The other selenides were prepared essentially in analogous manners, except water was used in place of methanol as the precipitant. The analytical samples were obtained by recrystallization from ethanol or tetrahydrofuran.

Φ_3PSe, in 70—80% yield, mp 147—148 °C (reported,[8] 148 °C).

$Ph\Phi_2PSe$, in 97% yield, mp 195—195.5 °C. Found: C, 57.20;

Table 1. ^{1}H NMR Spectral Data[a] for 2,6-Dimethoxyphenylphosphine Derivatives

Compounds	δ/ppm[b] in $CDCl_3$
Φ_3PSe	7.21, 6.48, 3.55.
$Ph\Phi_2PSe$	7.26, 6.48, 3.48, 8.12 (m, 2H), 7.33 (m, 3H).
$Ph_2\Phi PSe$	—,[c] 6.51, 3.29, 7.98 (m, 4H), 7.36 (m, 7H).
$[\Phi_3P\text{–}SeMe]I$	7.58, 6.67, 3.60, 2.00 (d, J_P=16 Hz, 3H).
$[\Phi_3P\text{–}SeEt]I$	7.55, 6.65, 3.59, 2.52 (dq, J_P=10 Hz, J_H=7 Hz, 2H), 1.29 (dt, J_H=7 Hz, J_P=2 Hz, 3H).
$[\Phi_3P\text{–}SeBu]ClO_4$	7.56, 6.65, 3.59, 2.49 (dt, J_P=10 Hz, J_H=7 Hz, 2H), 1.6 (m, 2H), 1.3 (m, 2H), 0.85 (t, J_H=7 Hz, 3H).
$[\Phi_3P\text{–}SeCH_2Ph]ClO_4$	7.57, 6.68, 3.61, 7.29—7.14 (m, 5H), 3.73 (d, J_P=7 Hz, 2H).
$[\Phi_3P\text{–}SeCH_2C_6H_4Me\text{-}4]ClO_4$	7.57, 6.68, 3.61, 7.08 (A_2B_2 pattern, 4H), 3.69 (d, J_P=6 Hz, 2H), 2.30 (s, 3H).
$[\Phi_3P\text{–}SeCH_2C_6H_4Cl\text{-}4]ClO_4$	7.57, 6.68, 3.61, 7.27—7.10 (m, 4H), 3.70 (d, J_P=7 Hz, 2H).
$[\Phi_3P\text{–}Me]I$[d]	7.51, 6.61, 3.57, 2.56 (d, J_P=15 Hz, 3H).
$[\Phi_3P\text{–}Et]ClO_4$	7.52, 6.62, 3.61, 3.17 (dq, J_P=15 Hz, J_H=7 Hz, 2H), 1.06 (dt, J_P=23 Hz, J_H=7 Hz, 3H).
$[\Phi_3P\text{–}Bu]ClO_4$	7.52, 6.62, 3.62, 3.1 (br, 2H), 1.4 (br, 4H), 0.87 (t, J_H=7 Hz, 3H).
$[\Phi_3P\text{–}CH_2Ph]ClO_4$	7.47, 6.56, 3.63, 7.03 (m, 5H), 4.74 (d, J_P=17 Hz, 2H).
$[\Phi_3P\text{–}CH_2C_6H_4Me\text{-}4]ClO_4$	7.44, 6.54, 3.61, 6.9—6.8 (m, 4H), 4.69 (d, J_P=17 Hz, 2H), 2.15 (d, J_P=1 Hz, 3H).
$[\Phi_3P\text{–}CH_2C_6H_4Cl\text{-}4]ClO_4$	7.46, 6.55, 3.62, 7.00 (br, 4H), 4.73 (d, J_P=18 Hz, 2H).
$[Ph\Phi_2P\text{–}SeMe]I$	7.65, 6.72, 3.61, 7.9—7.5 (m, 5H), 1.97 (d, J_P=16 Hz, 3H).
$[Ph\Phi_2P\text{–}SeEt]ClO_4$	7.64,[c] 6.70, 3.59, 7.9—7.5 (m, 7H), 2.48 (dq, J_P=12 Hz, J_H=7 Hz, 2H), 1.31 (dt, J_H=7 Hz, J_P=2 Hz, 3H).
$[Ph\Phi_2P\text{–}SeBu]ClO_4$	7.64,[c] 6.70, 3.59, 7.9—7.5 (m, 7H), 2.45 (dt, J_P=13 Hz, J_H=7 Hz, 2H), 1.54 (qn, J_H=$J_{H'}$=7 Hz, 2H), 1.26 (hexet, J_H=$J_{H'}$=7 Hz, 2H), 0.79 (t, J_H=7 Hz, 3H).
$[Ph\Phi_2P\text{–}SeCH_2Ph]ClO_4$	7.65,[c] 6.71, 3.58, 7.9—7.5 (m, 5H), 7.3—7.1 (m, 5H), 3.68 (d, J_P=9 Hz, 2H).
$[Ph\Phi_2P\text{–}SeCH_2CH{=}CH_2]ClO_4$	7.65,[c] 6.71, 3.59, 7.9—7.5 (m, 5H), 5.76 (m, 1H), 5.10 (m, 1H), 3.14 (dd, J_P=11 Hz, $J_{H'}$=7 Hz, 2H).
$[Ph\Phi_2P\text{–}SeCH_2CMe{=}CH_2]ClO_4$	7.65,[c] 6.71, 7.9—7.5 (m, 5H), 4.89 (s, 1H), 4.75 (s, 1H), 3.14 (d, J_P=10 Hz, 2H), 1.79 (s, 3H).
$[Ph\Phi_2P\text{–}Me]I$	7.66, 6.72, 3.61, 7.7—7.5 (m, 5H), 2.72 (d, J_P=15 Hz, 3H).
$[Ph\Phi_2P\text{–}Et]ClO_4$	7.63, 6.69, 3.62, 7.6—7.5 (m, 5H), 3.14 (dq, J_P=15 Hz, J_H=7 Hz, 2H), 1.19 (dt, J_P=22 Hz, J_H=7 Hz, 3H).
$[Ph\Phi_2P\text{–}Bu]ClO_4$	7.64, 6.71, 3.62, 7.6—7.5 (m, 5H), 3.04 (br, 2H), 1.47 (br, 4H), 0.90 (t, J_H=7 Hz, 3H).
$[Ph\Phi_2P\text{–}CH_2Ph]ClO_4$	7.62, 6.67, 3.60, 7.6—6.8 (m, 10H), 4.51 (d, J_P=16 Hz, 2H).
$[Ph\Phi_2P\text{–}CH_2CH{=}CH_2]ClO_4$	7.65, 6.70, 3.62, 7.6—7.5 (m, 5H), 5.63 (m, 1H), 5.22 (m, 1H), 3.91 (dd, J_P=17 Hz, J_H=7 Hz, 2H).
$[Ph\Phi_2P\text{–}CH_2CMe{=}CH_2]ClO_4$	7.65, 6.70, 3.62, 7.6—7.5 (m, 5H), 4.89 (d, J_H=5 Hz, 1H), 4.57 (d, J_H=5 Hz, 1H), 3.97 (d, J_P=17 Hz, 2H), 1.63 (s, 3H).
$[Ph\Phi_2P\text{–}OH]ClO_4$	7.58,[c] 6.63, 3.60, 7.8—7.5 (m, 5H).
$[Ph_2\Phi P\text{–}SeEt]ClO_4$	—,[c] 6.78, 3.67, 7.8—7.7 (m, 11H), 2.45 (dq, J_P=11 Hz, J_H=7 Hz, 2H), 1.26 (dt, J_H=7 Hz, J_P=1 Hz, 3H).
$[Ph_2\Phi P\text{–}SeCH_2Ph]ClO_4$	—,[c] 6.77, 3.64, 7.7—7.5 (m, 11H), 7.3—7.1 (m, 5H), 3.63 (d, J_P=10 Hz, 2H).
$[Ph_2\Phi P\text{–}Et]ClO_4$	—,[c] 6.82, 3.71, 7.83—7.66 (m, 11H), 3.26 (dq, J_P=15 Hz, J_H=7 Hz, 2H), 1.24 (dt, J_P=21 Hz, J_P=7 Hz, 3H).
$[Ph_2\Phi P\text{–}CH_2Ph]ClO_4$	7.75, 6.77, 3.67, 7.7—7.4 (m, 10H), 7.2 (m, 1H), 7.1 (m, 2H), 6.7 (m, 2H), 4.59 (d, 16 Hz, 2H).
$(PhCH_2Se)_2$	7.33—7.20 (10H, m), 3.82 (4H, s).
$(4\text{-}MeC_6H_4CH_2Se)_2$	7.10 (8H, s), 3.84 (4H, s), 2.31 (6H, s).
$(4\text{-}ClC_6H_4CH_2Se)_2$	7.26 (4H, d, J_H=8 Hz), 7.12 (4H, d, J_H=8 Hz), 3.80 (4H, s).

a) Φ=2,6-$(MeO)_2C_6H_3$; s=singlet, d=doublet, t=triplet, qn=quintet, m=multiplet, br=broad, dd=double doublets, dt=double triplet, dq=double quartet. b) In the order of 4-H (triplet with J_H=8—9 Hz), 3,5-H (doublet or double doublets with J_H=8—9 Hz and J_P=5—6 Hz), 2,6-MeO (singlet), and others. c) Overlapped. d) Data from Ref. 1.

H, 5.02%. Calcd for $C_{22}H_{23}O_4PSe$: C, 57.28; H, 5.03%.

$Ph_2\Phi PSe$, in 92% yield, mp 153—155 °C. Found: C, 59.85; H, 4.85%. Calcd for $C_{20}H_{19}O_2PSe$: C, 59.86; H, 4.77%.

Reactions of $Ph_{3-n}\Phi_nPSe$ with Acid. To a solution of Φ_3PSe

Table 2. ^{13}C{^{1}H} NMR Spectral Data[a] for 2,6-Dimethoxyphenylphosphine Derivatives

Compounds	δ/ppm[b] in CDCl$_3$
Φ_3PSe	114.7[85], 161.6, 105.0[6], 131.1, 55.7.
PhΦ_2PSe	113.2[82], 161.0, 105.0[6], 129.6, 55.6, 135.6[82], 132.1[12], 127.1[14], 131.9.
Ph$_2\Phi$PSe	108.2[78], 162.0, 105.3[6], 130.0[3], 55.4, 134.7[80], 131.2[11], 127.7[13], 134.1.
[Φ_3P–SeMe]I	100.0[97], 162.4, 104.9[8], 136.1, 56.5, 8.6[6].
[Φ_3P–SeEt]I	100.0[97], 162.4, 104.9[8], 136.1, 56.5, 22.8[6], 8.2[6].
[Φ_3P–SeBu]I	100.0[97], 162.4, 104.9[8], 136.1, 56.5, 31.2[8], 28.7[6], 23.2, 13.6.
[Φ_3P–SeCH$_2$Ph]ClO$_4$	100.1[90], 162.5, 104.9[8], 136.2, 56.5, 135.1[1], 129.3, 129.1, 128.0, 32.9[4].
[Φ_3P–SeCH$_2$C$_6$H$_4$Me-4]ClO$_4$	100.5[90], 162.5, 104.9[6], 136.1, 56.3, 137.9, 131.8[10], 129.7, 129.2, 32.8[6], 21.2.
[Φ_3P–SeCH$_2$C$_6$H$_4$Cl-4]ClO$_4$	100.2[90], 162.5, 104.9[7], 136.2, 56.3, 133.9[10], 133.7, 130.7, 129.1, 32.0[5].
[Φ_3P–Me]ClO$_4$[c]	101.2[103], 162.5, 104.8[7], 135.7, 56.2, 17.4[64].
[Φ_3P–Bu]ClO$_4$	100.3[96], 162.5, 104.6[7], 135.6, 56.0, 27.4[56], 26.0[4], 24.2[21], 13.7.
[Φ_3P–CH$_2$Ph]ClO$_4$	100.3[98], 162.1, 104.2[8], 135.6, 55.9, 132.6[6], 129.2[8], 128.0, 127.2[4], 35.4[55].
[Φ_3P–CH$_2$C$_6$H$_4$Me-4]ClO$_4$	100.6[98], 162.2, 104.3[8], 135.5, 55.9, 136.7[4], 129.4[8], 129.1[8], 128.6, 35.1[53], 20.9.
[Φ_3P–CH$_2$C$_6$H$_4$Cl-4]ClO$_4$	100.2[98], 162.2, 104.4[6], 135.7, 56.0, 132.9[4], 131.5[6], 130.7[8], 128.0, 34.9[55].
[PhΦ_2P–SeMe]I	98.3[88], 161.9, 105.2[7], 133.1[4], 56.6, 137.5, 131.9[13], 129.1[15], 125.7[83], 8.7[5].
[PhΦ_2P–SeEt]ClO$_4$	98.3[88], 162.0, 105.1[7], 133.1[3], 56.3, 137.5, 132.0[13], 129.1[15], 125.7[84], 23.2[5], 15.0[7].
[PhΦ_2P–SeBu]ClO$_4$	98.3[85], 162.0, 105.1[7], 133.1[3], 56.3, 137.5, 132.0[13], 129.1[15], 125.8[84], 32.0[5], 28.8[5], 22.8, 13.3.
[PhΦ_2P–SeCH$_2$Ph]ClO$_4$	98.1[88], 162.1, 105.2[8], 133.2[4], 56.4, 137.7, 134.9[8], 132.1[14], 129.4, 129.2[14], 129.1, 128.2, 125.6[84], 32.8[6].
[PhΦ_2P–SeCH$_2$CH=CH$_2$]ClO$_4$	98.1[97], 162.1, 105.2[7], 133.2[4], 56.4, 137.7, 132.2[12], 131.6[6], 129.2[15], 125.5[83], 120.8, 31.3[5]
[PhΦ_2P–SeCH$_2$CMe=CH$_2$]ClO$_4$	98.1[88], 162.0, 105.2[7], 133.1[3], 56.3, 139.0[6], 137.7, 132.1[12], 129.2[16], 125.7[84], 117.2, 36.1[4], 21.4.
[PhΦ_2P–OH]ClO$_4$	(126.9),[d] 162.9, 104.9[8], 137.6, 56.4, 101.1[115], 128.5[14], 131.2[14], 133.2.
(PhCH$_2$Se)$_2$	139.0, 129.0, 128.4, 127.1, 32.7.
(4-MeC$_6$H$_4$CH$_2$Se)$_2$	136.8, 128.9, 129.1, 136.0, 32.6, 21.2.
(4-ClC$_6$H$_4$CH$_2$Se)$_2$	137.5, 130.2, 128.6, 133.0, 31.7.

a) Φ=2,6-(MeO)$_2$C$_6$H$_3$. b) In the order of C-1 (singlet or doublet), C-2,6, C-3,5 (singlet or doublet), C-4, MeO-2,6 and others, of which the coupling constants J_P (in Hz) are given in square bracket when observed. c) Data from Ref. 2. d) One of the doublet seems to be obscured by the other peaks.

(0.266 g, 0.5 mmol) in methanol (30 ml) was added 6 M hydrochloric acid (0.3 ml) to give red precipitates immediately. Solvents of the filtrate were removed by evaporation under reduced pressure, the residue was dissolved in water (30 ml), and addition of aqueous perchloric acid gave white precipitates of [Φ_3P–H]ClO$_4$[1] in 73% yield.

In an analogous manner as above, PhΦ_2PSe decomposed to give [PhΦ_2P–H]ClO$_4$[1] in 56% yield.

Reactions of Φ_3PSe with Alkyl Halide. A solution of Φ_3PSe was prepared as above from Φ_3P (0.442 g, 1 mmol) and Se (0.119 g, 1.5 mmol) in methanol (10 ml). It was cooled to 0 °C to give precipitates of Φ_3PSe. To this suspension was added benzyl chloride (0.14 ml, 1.2 mmol), and the mixture was kept in the dark with stirring at room temperature for 8 h to give an almost clear solution. A small amount of excess selenium was removed by filtration, and the filtrate was diluted with water (20 ml). An addition of 1 M aqueous perchloric acid (1.5 ml) (1 M=1 mol dm^{-3}) gave white precipitates composed of [Φ_3P–SeCH$_2$Ph]ClO$_4$ and [Φ_3P–CH$_2$Ph]ClO$_4$ in ratios between 80 : 20 and 95 : 5 (by ^{1}H NMR). The mixture was recrystallized from ethanol in the dark to give yellow crystals of [Φ_3P–SeCH$_2$Ph]ClO$_4$ in 90—70% yield; mp 211—212 °C.

When an aqueous methanol solution of [Φ_3P–SeCH$_2$Ph]Cl, prepared as above, was treated with potassium iodide, the iodide [Φ_3P–SeCH$_2$Ph]I was obtained in 61% yield after recrystallization from ethanol in the dark; mp 199—201 °C. Found: C, 50.09; H, 4.72%. Calcd for C$_{31}$H$_{34}$IO$_6$PSe: C, 50.35; H, 4.64%.

In an analogous manner as above, a reaction of Φ_3PSe with 4-methylbenzyl chloride for 3 h gave a mixture composed of [Φ_3P–SeCH$_2$C$_6$H$_4$Me-4]ClO$_4$ and [Φ_3P–CH$_2$C$_6$H$_4$Me-4]ClO$_4$ in 93 : 7 ratio. It was recrystallized from ethanol in the dark to give pure [Φ_3P–SeCH$_2$C$_6$H$_4$Me-4]ClO$_4$ in 87% yield; mp 200—202 °C. Found: C, 52.78; H, 4.99%. Calcd for C$_{32}$H$_{36}$ClO$_{10}$PSe: C, 52.94;

H, 5.00%.

In an analogous manner as above, a reaction of $\mathrm{\Phi_3PSe}$ with 4-chlorobenzyl chloride for 3 h gave a mixture composed of $\mathrm{[\Phi_3P{-}SeCH_2C_6H_4Cl{-}4]ClO_4}$ and $\mathrm{[\Phi_3P{-}CH_2C_6H_4Cl{-}4]ClO_4}$ in 89 : 11 ratio. It was recrystallized from 2-propanol in the dark to give $\mathrm{[\Phi_3P{-}SeCH_2C_6H_4Cl{-}4]ClO_4}$ in 81% yield; mp 199—201 °C. Found: C, 49.66; H, 4.66%. Calcd for $\mathrm{C_{31}H_3Cl_2O_{10}PSe}$: C, 49.88; H, 4.46%.

In analogous manner as above, a reaction with butyl bromide for 18 h at −30 °C, followed by treatment with perchloric acid gave $\mathrm{[\Phi_3P{-}SeBu]ClO_4}$ in 50% yield after recrystallization from ethanol; mp was not observed below 235 °C.

In an analogous manner as above, a reaction with butyl iodide for 4 h at −30 °C gave $\mathrm{[\Phi_3P{-}SeBu]I}$ in 91% yield after recrystallization from water in the dark; mp 209 °C-decomposed. Found: C, 47.79; H, 5.10%. Calcd for $\mathrm{C_{28}H_{36}IO_6PSe}$: C, 47.68; H, 5.14%.

Some other alkyl halides gave mixtures composed of $\mathrm{[\Phi_3P{-}SeR]X}$ and $\mathrm{[\Phi_3P{-}R]X}$ in a variety of ratios, for examples, 84 : 16 (RX= MeI), 34 : 66 (EtBr), and 62 : 38 (EtI). We have not yet succeeded in the pure separations of $\mathrm{[\Phi_3P{-}SeR]X}$, since they often decomposed to give complex mixtures during the procedure.

Reactions of $\mathrm{Ph\Phi_2PSe}$ with Alkyl Halide. Mixtures of $\mathrm{Ph\Phi_2PSe}$ (0.416 g, 1 mmol) and alkyl halides (a slight excess) were treated in analogous manners as above, and the following compounds were obtained.

$\mathrm{[Ph\Phi_2P{-}SeMe]I}$ from methyl iodide in benzene at room temperature for 0.5 h in 83% yield (recrystallized from water in the dark); mp 183 °C, decomposed. Found: C, 45.72; H, 4.30%. Calcd for $\mathrm{C_{23}H_{26}IO_4PSe}$: C, 45.79; H, 4.34%.

$\mathrm{[Ph\Phi_2P{-}SeEt]ClO_4}$ from ethyl bromide in methanol at 50 °C for 5 h in 53% yield (from 2-propanol). **Caution!** The crystals explosively decomposed at a temperature in the region 170—210 °C. Found: C, 49.30; H, 5.17%. Calcd for $\mathrm{C_{24}H_{28}ClO_8PSe}$: C, 48.87; H, 4.78%.

$\mathrm{[Ph\Phi_2P{-}SeBu]ClO_4}$ from butyl bromide in methanol at 50 °C for 5 h in 36% yield (from 2-propanol). **Caution!** The crystals explosively decomposed at a temperature in the region 150—190 °C. Found: C, 50.43; H, 5.38%. Calcd for $\mathrm{C_{26}H_{32}ClO_8PSe}$: C, 50.54; H, 5.22%.

$\mathrm{[Ph\Phi_2P{-}SeCH_2Ph]ClO_4}$ from benzyl chloride in methanol at 50 °C for 5 h in 67% yield (from ethanol); mp 170 °C. Found: C, 53.37; H, 4.63%. Calcd for $\mathrm{C_{29}H_{30}ClO_8PSe}$: C, 53.43; H, 4.64%.

$\mathrm{[Ph\Phi_2P{-}SeCH_2CH{=}CH_2]ClO_4}$ from 3-chloro-1-propene in methanol at 50 °C for 5 h in 74% yield (from 2-propanol); mp 203—204 °C, decomposed. Found: C, 49.72; H, 4.88%. Calcd for $\mathrm{C_{25}H_{28}ClO_8PSe}$: C, 49.89; H, 4.69%.

$\mathrm{[Ph\Phi_2P{-}SeCH_2CMe{=}CH_2]ClO_4}$ from 3-chloro-2-methyl-1-propene in methanol at 50 °C for 5 h in 75% yield (from 2-propanol); mp 197—198 °C, decomposed.

Reactions of $\mathrm{Ph_2\Phi PSe}$ with Alkyl Halide. A mixture of $\mathrm{Ph_2\Phi PSe}$ (0.803 g, 2 mmol) and ethyl bromide (0.17 ml, a slight excess) in methanol (10 ml) was heated at 50 °C for 48 h to give a clear solution. Water (20 ml) was added, and the resultant precipitates of unreacted $\mathrm{Ph_2\Phi PSe}$ (25% recovery) was removed. To the filtrate was added aqueous 1 M sodium perchlorate (3 ml) to give precipitates of $\mathrm{[Ph_2\Phi P{-}SeEt]ClO_4}$ in 60% yield; mp 162—164 °C, decomposed.

In an analogous manner as above, a reaction of $\mathrm{Ph_2\Phi PSe}$ with benzyl chloride gave $\mathrm{[Ph_2\Phi PSe{-}CH_2Ph]ClO_4}$ in 50% yield; mp 131—132 °C, and unreacted $\mathrm{Ph_2\Phi PSe}$ was recovered in 20% yield.

These compounds were characterized only by IR and ^{1}H NMR spectra.

Preparation of Alkyltriarylphosphonium Salts. The following compounds were prepared almost in quantitative yield from $\mathrm{\Phi_3P}$, alkyl halide by analogous methods as reported.[1] Some compounds were characterized only by IR and ^{1}H NMR spectra:

$\mathrm{[\Phi_3P{-}Et]ClO_4}$ from ethyl bromide and perchloric acid, mp was not observed below 235 °C.

$\mathrm{[\Phi_3P{-}Bu]Cl\cdot 0.5H_2O}$ from butyl chloride, mp 201—205 °C. Found: C, 61.60; H, 6.78%. Calcd for $\mathrm{C_{28}H_{36}ClO_6P\cdot 0.5H_2O}$: C, 61.82; H, 6.85%.

$\mathrm{[\Phi_3P{-}Bu]Br\cdot 0.5H_2O}$ from butyl bromide, mp 222—225 °C. Found: C, 56.95; H, 6.22%. Calcd for $\mathrm{C_{28}H_{36}BrO_6P\cdot 0.5H_2O}$: C, 57.15; H, 6.34%.

$\mathrm{[\Phi_3P{-}Bu]I}$ from butyl iodide, mp 225—235 °C. Found: C, 53.42; H, 5.86; I, 20.23%. Calcd for $\mathrm{C_{28}H_{36}IO_6P}$: C, 53.68; H, 5.79; I, 20.26%.

$\mathrm{[\Phi_3P{-}Bu]ClO_4}$ from butyl bromide and perchloric acid, mp was not observed below 235 °C. Found: C, 56.26; H, 6.11; Cl, 6.04%. Calcd for $\mathrm{C_{28}H_{36}ClO_{10}P}$: C, 56.14; H, 6.06; Cl, 5.92%.

$\mathrm{[\Phi_3P{-}CH_2Ph]ClO_4}$ from benzyl chloride and perchloric acid, mp was not observed below 235 °C. Found: C, 58.93; H, 5.37%. Calcd for $\mathrm{C_{31}H_{34}ClO_{10}P}$: C, 58.82; H, 5.41%.

$\mathrm{[\Phi_3P{-}CH_2C_6H_4Me{-}4]ClO_4}$ from 4-methylbenzyl chloride and perchloric acid, mp was not observed below 235 °C. Found: C, 59.09; H, 5.88%. Calcd for $\mathrm{C_{32}H_{36}ClO_{10}P}$: C, 59.40; H, 5.61%.

$\mathrm{[\Phi_3P{-}CH_2C_6H_4Cl{-}4]ClO_4}$ from 4-chlorobenzyl chloride and perchloric acid, mp was not observed below 235 °C. Found: C, 55.47; H, 5.01%. Calcd for $\mathrm{C_{31}H_{33}Cl_2O_{10}P}$: C, 55.78; H, 4.98%.

$\mathrm{[Ph\Phi_2P{-}Me]I}$ from methyl iodide, mp 218—220 °C.

$\mathrm{[Ph\Phi_2P{-}Et]I}$ from ethyl iodide, mp 199—201 °C.

$\mathrm{[Ph\Phi_2P{-}Et]ClO_4}$ from ethyl bromide and perchloric acid, mp 247—252 °C.

$\mathrm{[Ph\Phi_2P{-}Bu]ClO_4}$ from butyl bromide and perchloric acid, mp 186—187 °C.

$\mathrm{[Ph\Phi_2P{-}CH_2Ph]ClO_4}$ from benzyl chloride and perchloric acid, mp 213—214 °C.

$\mathrm{[Ph\Phi_2P{-}CH_2CH{=}CH_2]ClO_4}$ from 3-chloro-1-propene and perchloric acid, mp 220 °C, decomposed.

$\mathrm{[Ph\Phi_2P{-}CH_2CMe{=}CH_2]ClO_4}$ from 3-chloro-2-methyl-1-propene and perchloric acid, mp was not observed below 235 °C.

$\mathrm{[Ph_2\Phi P{-}Et]ClO_4}$ from ethyl bromide and perchloric acid, mp 123—124 °C.

$\mathrm{[Ph_2\Phi P{-}CH_2Ph]ClO_4}$ from benzyl chloride and perchloric acid, mp 232—235 °C.

X-Ray Crystallography. Crystals of $\mathrm{\Phi_3PSe\cdot H_2O}$ suitable for X-ray analysis were obtained by slow cooling of the toluene solution around room temperature. The amount of crystal water was estimated by the weight loss at 80 °C. Crystal data and numerical details of the structural analysis are given in Table 3. The cell parameters and the orientation matrix were identified by 25 Bragg reflections ($17.5° < 2\theta < 25°$). Intensity data were collected on a Rigaku AFC5R diffractometer by ω–2θ mode with scan width= $1.37+0.35\tan\theta$ and ω scan speed $10.0°\ \mathrm{min}^{-1}$, using Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) monochromatized by a pyrolytic graphite. 6308 unique reflections were measured ($4° < 2\theta < 55°$) giving 3151 reflections with $I > 3\sigma(I)$. Crystal decay (ca. 0.26%) was corrected after the measurement. An empirical absorption correction, based on azimuthal scans of some reflections, was applied (max, min transmission factors = 1.00, 0.81). The data were corrected for Lorentz and polarization effects.

The structure was solved by direct methods[10] followed by normal heavy atom procedures,[11] and refined by full-matrix least-square method for 3151 reflections [$I > 3\sigma(I)$]. All the non-hydrogen atoms were refined anisotropically. Aryl and methoxy hydrogen atoms were fixed on the calculated positions, but crystal water hydrogen atoms were not included in the refinement. Final R and R_w values were 0.057 and 0.045 (the weighing scheme $w^{-1}=\sigma^2(F_o)$ with σ^2 (F_o) from counting statistics), respectively, where $R=\sum||F_o|-|F_c||/\sum|F_o|$ and $R_w=[\sum w(|F_o|-|F_c|)^2/\sum w|F_o|^2]^{1/2}$. Maximum shift/error ratio in the final cycle was equal to 0.03. All calculations were made using the TEXSAN of Molecular Structure Corporation.[12] ORTEP II chart[13] with an atom-labeling scheme is given in Fig. 1. Some selected interatomic distances and angles for $\Phi_3PSe\cdot H_2O$ are given in Table 4. Tables of positional and thermal parameters and complete interatomic distances and angles have been deposited as Document No. 69006 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Table 3. Crystal Data for $\Phi_3PSe\cdot H_2O$

Formula	$C_{24}H_{27}O_6PSe\cdot H_2O$
Molecular weight	539.41
Crystal system	Orthorhombic
Space group	*Pbca* (no. 61)
Crystal dimension/mm	0.30 × 0.40 × 0.50
a/Å	17.722(3)
b/Å	18.143(2)
c/Å	15.489(2)
V/Å^3	4980(1)
Z	8
D_c/g cm^{-3}	1.438
D_m/g cm^{-3}	1.45
μ(Mo $K\alpha$)/mm^{-1}	1.588
F(000)	2144
$2\theta_{max}$/°	55
T/K	296
Data with $I_0>3\sigma(I_0)$	3151
R	0.057
R_w	0.045
Largest *shift*/*error*	0.03
Maximum *peak* in D-map/e Å^{-3}	1.13
Minimum *peak* in D-map/e Å^{-3}	−0.50
Goodness of fit S	2.60

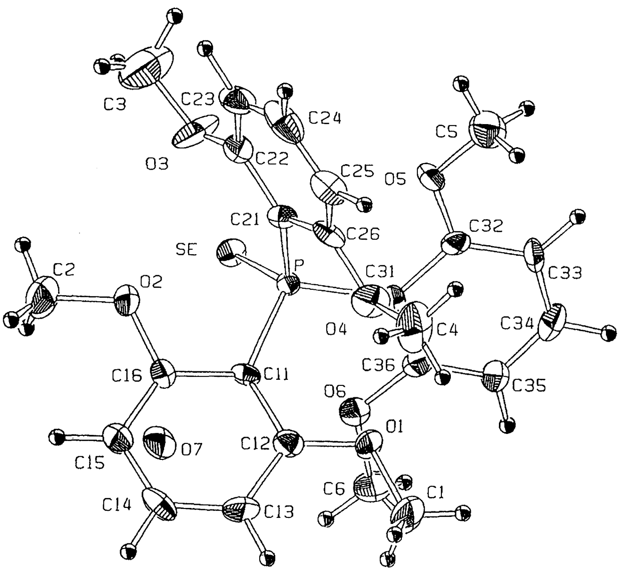


Fig. 1. ORTEP II plot of $\Phi_3PSe\cdot H_2O$.

Measurements of Reaction Rates. Rates for reaction of $Ph_{3-n}\Phi_nPY$ with butyl halides [Eq. 1] were measured by conductimetry for acetonitrile solutions containing $Ph_{3-n}\Phi_nPY$ (0.01 M) and RX (0.10—0.80 M) kept in a boiling chloroform bath at 61.2 °C. Correlation coefficients were >0.9999, except for some very fast or slow reactions (Φ_3P, Ph_3P, $Ph\Phi_2PO$). The second-order reaction rate constants, k_2, obtained are given in Table 5.

Reactions of $[\Phi_3P\text{–}SeCH_2C_6H_4Z\text{-}4]Cl$ (Z=H, Me, Cl) with Aqueous Sodium Hydroxide. A solution of $[\Phi_3P\text{–}SeCH_2Ph]Cl$ was prepared as above from Φ_3P (6 mmol), elemental selenium (7.5 mmol), and benzyl chloride (7 mmol) in methanol (50 ml). A small amount of unreacted selenium was removed by filtration, and the solvent was removed under reduced pressure. The residue was washed well with diethyl ether and was dissolved in water (50 ml). An addition of 5 M aqueous sodium hydroxide (2 ml) gave

Table 4. Some Selected Bond Distances, Interatomic Distances, and Bond Angles for $\Phi_3PSe\cdot H_2O$.

Bond lengths (Å)			
P–C11	1.839(5)	P–Se	2.136(2)
P–C21	1.844(6)		
P–C31	1.834(6)		
Interatomic distances (Å)			
P···O1	3.189(4)	P···O4	2.848(5)
P···O2	2.794(5)	P···O5	3.035(4)
P···O3	3.082(5)	P···O6	2.905(5)
Se···O7	3.461(5)[a]		
Bond angles (°)			
Se–P–C11	112.3(2)	C11–P–C21	101.1(3)
Se–P–C21	118.3(2)	C11–P–C31	111.5(3)
Se–P–C31	104.7(2)	C21–P–C31	109.1(3)

a) The distance between Se and O of crystal water in an asymmetric unit.

Table 5. Reaction Rates[a] for
$Ar_3PY+BuX\xrightarrow{k_2}[Ar_3P\text{–}YBu]X$ (Y=none, O, S, Se)

BuX	Ar_3PY	k_2/dm^3 mol^{-1} sec^{-1}
BuCl	Φ_3P	8.54×10^{-5}
BuBr	Ph_3P	ca. 3.4×10^{-5}
	$Ph_2\Phi P$	4.40×10^{-4}
	$Ph\Phi_2P$	3.39×10^{-3}
	Φ_3P	ca. 2.1×10^{-2}
	Ph_3PO	No reaction
	$Ph_2\Phi PO$	No reaction
	$Ph\Phi_2PO$[b]	ca. 4.4×10^{-6}
	Φ_3PO[b]	4.30×10^{-5}
	Ph_3PS	No reaction
	$Ph_2\Phi PS$[b]	ca. 6.3×10^{-6}
	$Ph\Phi_2PS$	1.15×10^{-4}
	Φ_3PS	2.25×10^{-3}
	Ph_3PSe	No reaction
	$Ph_2\Phi PSe$[b]	4.95×10^{-5}
	$Ph\Phi_2PSe$	1.20×10^{-3}
	Φ_3PSe	Very fast[c]

a) By conductimetry for acetonitrile solutions containing Ar_3PY (0.01 M) and BuX (0.10—0.80 M) at 61.2 °C; $k_2=k_{obsd}/[RX]$. b) The reaction is reversible. c) Not measured precisely due to the instability to release elemental selenium.

precipitates composed of Φ_3P and $(\mathrm{PhCH_2Se})_2$ (by ^{1}H NMR) and the filtrate I. The precipitates were suspended in methanol (20 ml)–water (100 ml), to which aqueous 35% hydrochloric acid (0.8 ml) was added to dissolve Φ_3P as $[\Phi_3\mathrm{P{-}H}]\mathrm{Cl}$. The suspension was filtered to give crystals of dibenzyl diselenide, $(\mathrm{PhCH_2Se})_2$, in 56% yield based on Φ_3P; mp 88—89 °C (reported[14] 90—91 °C). This filtrate was treated with 5 M aqueous sodium hydroxide (3 ml) to give precipitates of Φ_3P in 74% yield. The filtrate I was treated with ammonium hexafluorophosphate (0.324 g, 2 mmol) to give precipitates of $[\Phi_3\mathrm{P{-}CH_2Ph}]\mathrm{PF_6}$ in 18% yield.

In an analogous manner as above, a reaction using Φ_3P, elemental selenium, 4-methylbenzyl chloride, and aqueous sodium hydroxide resulted to give the diselenide, $(4\text{-}\mathrm{MeC_6H_4CH_2Se})_2$, in 63% yield and Φ_3P in 76% yield after separation, and $[\Phi_3\mathrm{P{-}CH_2C_6H_4Me}\text{-}4]\mathrm{PF_6}$ was obtained from the filtrate in 4% yield. $(4\text{-}\mathrm{MeC_6H_4CH_2Se})_2$: mp 57—58 °C (reported[15] 64—65 °C).

In an analogous manner as above, a reaction using Φ_3P, elemental selenium, 4-chlorobenzyl chloride, and aqueous sodium hydroxide resulted to give the diselenide, $(4\text{-}\mathrm{ClC_6H_4CH_2Se})_2$, in 53% yield and Φ_3P in 68% yield after separation, and $[\Phi_3\mathrm{P{-}CH_2C_6H_4Cl}\text{-}4]\mathrm{PF_6}$ was obtained from the filtrate in 4% yield. $(4\text{-}\mathrm{ClC_6H_4CH_2Se})_2$: mp 72—73 °C (reported[16] 77—78 °C).

Reaction of $[\mathrm{Ph}\Phi_2\mathrm{P{-}SeCH_2Ph}]\mathrm{Cl}$ with Aqueous Sodium Hydroxide. A solution of $[\mathrm{Ph}\Phi_2\mathrm{P{-}SeCH_2Ph}]\mathrm{Cl}$ was prepared as above from $\mathrm{Ph}\Phi_2\mathrm{PSe}$ (5 mmol) and benzyl chloride (6 mmol) in methanol (10 ml). The solvent was removed under reduced pressure. The residue was washed with diethyl ether and was dissolved in water (50 ml). Addition of 5 M aqueous sodium hydroxide (2 ml) gave precipitates composed of $\mathrm{Ph}\Phi_2\mathrm{P}$, $\mathrm{Ph}\Phi_2\mathrm{PO}$, and $(\mathrm{PhCH_2Se})_2$ (by ^{1}H NMR) and the filtrate II. The precipitates were suspended in methanol (30 ml)–water (100 ml), to which aqueous 35% hydrochloric acid (1 ml) was added to dissolve $\mathrm{Ph}\Phi_2\mathrm{P}$ and $\mathrm{Ph}\Phi_2\mathrm{PO}$ and to leave the crystals of $(\mathrm{PhCH_2Se})_2$ in 74% yield based on $\mathrm{Ph}\Phi_2\mathrm{PSe}$. This filtrate was neutralized by 5 M aqueous sodium hydroxide to give precipitates of $\mathrm{Ph}\Phi_2\mathrm{P}$ in 69% yield. This filtrate was combined with the filtrate II, and the mixture was treated with aqueous perchloric acid (a slight excess) to give precipitates of $[\mathrm{Ph}\Phi_2\mathrm{P{-}OH}]\mathrm{ClO_4}$ in 14% yield. This filtrate was treated with aqueous tin(II) chloride dihydrate (0.736 g, 3.3 mmol) dissolved in 35% hydrochloric acid (2 ml) to give precipitates of $(\mathrm{PhCH_2Se})_2$ in 12% yield.

$[\mathrm{Ph}\Phi_2\mathrm{P{-}OH}]\mathrm{ClO_4}$ was separately prepared by a reaction of $\mathrm{Ph}\Phi_2\mathrm{PO}$[6] (1 mmol) in ethanol (10 ml) with aqueous perchloric acid (a slight excess), mp 163 °C, decomposed (recrystallized from ethanol). Found: C, 52.90; H, 4.87%. Calcd for $\mathrm{C_{22}H_{24}ClO_9P}$: C, 52.97: H, 4.85%.

Reactions of $[\Phi_3\mathrm{P{-}SeCH_2C_6H_4Z}\text{-}4]\mathrm{Cl}$ (Z=H, Me, Cl) with Aqueous Tin(II) Chloride. An aqueous solution (50 ml) of $[\Phi_3\mathrm{P{-}SeCH_2Ph}]\mathrm{Cl}$ was prepared as above from Φ_3P (5 mmol). It was acidified by 35% hydrochloric acid (2 ml) and immediately mixed with a solution of tin(II) chloride dihydrate (0.700 g, 3 mmol) dissolved in 35% hydrochloric acid (2 ml) at 0 °C, causing immediate precipitation. The mixture was kept stirred for 2 h at 0 °C. The precipitates were washed well with a mixture of water (70 ml) and methanol (30 ml) and was extracted with diethyl ether (70 ml). On evaporation, yellow crystals of $(\mathrm{PhCH_2Se})_2$ were obtained in 70% yield based on Φ_3P. The aqueous filtrates were combined and was treated with 5 M aqueous sodium hydroxide (14 ml) to give precipitates of Φ_3P in 81% yield. To this filtrates was added ammonium hexafluorophosphate (2 mmol) to give precipitates of $[\Phi_3\mathrm{P{-}CH_2Ph}]\mathrm{PF_6}$ in 13% yield.

In analogous manners as above using 4-methylbenzyl chloride or 4-chlorobenzyl chloride, the diselenides, $(4\text{-}\mathrm{MeC_6H_4CH_2Se})_2$ and $(4\text{-}\mathrm{ClC_6H_4CH_2Se})_2$, were obtained in 72 and 75% yields, respectively. From the aqueous acidic filtrates on neutralization with 5 M aqueous sodium hydroxide, precipitates of Φ_3P were obtained in 70 and 70% yields, respectively. From these filtrates on treatment with ammonium hexafluorophosphate, precipitates of $[\Phi_3\mathrm{P{-}CH_2C_6H_4Z}\text{-}4]\mathrm{PF_6}$ were obtained in 3% (Z=Me) and 2% (Cl) yields, respectively.

Reaction of $[\mathrm{Ph}\Phi_2\mathrm{P{-}SeCH_2Ph}]\mathrm{Cl}$ with Aqueous Tin(II) Chloride. An aqueous solution of $[\mathrm{Ph}\Phi_2\mathrm{P{-}SeCH_2Ph}]\mathrm{Cl}$ was prepared as above from $\mathrm{Ph}\Phi_2\mathrm{PSe}$ (5 mmol). It was treated as above with a solution of tin(II) chloride dihydrate (3 mmol) dissolved in 35% hydrochloric acid (2 ml), and $(\mathrm{PhCH_2Se})_2$ was obtained in 67% yield after purification. From the aqueous filtrates, $\mathrm{Ph}\Phi_2\mathrm{P}$ was obtained in 85%, and the formation of $[\mathrm{Ph}\Phi_2\mathrm{P{-}CH_2Ph}]\mathrm{PF_6}$ was negligible (1% yield).

Results and Discussion

General Properties of 2,6-Dimethoxyphenylphosphine Selenides. Like the sulfide, Φ_3PS,[5] the selenide, Φ_3PSe, crystallizes as hydrates, $\Phi_3\mathrm{PSe}\cdot x\mathrm{H_2O}$ [x=0.8—2.5 (from ethanol) or 1 (from toluene)], and the unhydrate could be obtained on heating the crystals at 90 °C for several hours. On the other hand, the selenides, $\mathrm{Ph}\Phi_2\mathrm{PSe}$ and $\mathrm{PH_2}\Phi\mathrm{PSe}$, were obtained as unhydrated after recrystallization from ethanol. In chloroform-d_1, Φ_3PSe decomposes partly to give a ca. 80 : 20 mixture of Φ_3PSe and Φ_3P during two days, as observed by ^{1}H NMR spectra. Analogous dissociations of elemental chalcogen have been reported for trialkylphosphine telluride[17] and for triphenylarsine selenide.[18] Both Φ_3PS and $\mathrm{Ph_3PSe}$ exist stably under these conditions for a prolonged period, and this observation seems to indicate that the phosphorus-selenium bond of Φ_3PSe is weaker than that of $\mathrm{Ph_3PSe}$ in spite of the much higher basicity of Φ_3P than $\mathrm{Ph_3P}$. In fact, when Φ_3PSe and $\mathrm{Ph_3P}$ were mixed in chloroform-d_1, the mixture immediately changed to that of Φ_3P and $\mathrm{Ph_3PSe}$ [Eq. 2], as observed by ^{1}H NMR spectra. An analogous fast transfer of selenium was observed between $\mathrm{Ph}\Phi_2\mathrm{PSe}$ and $\mathrm{Ph_3P}$, while the reaction between $\mathrm{Ph_2}\Phi\mathrm{PSe}$ and $\mathrm{Ph_3P}$ was very slow and attained to an equilibrium (K=45).

In the presence of acid in polar solvents, both Φ_3PSe and $\mathrm{Ph}\Phi_2\mathrm{PSe}$ decomposed immediately to dissociate elemental selenium, and the tertiary phosphines were recovered as the tertiary phosphonium salts, $[\mathrm{Ar}\Phi_2\mathrm{P{-}H}]\mathrm{X}$. Both $\mathrm{Ph_2}\Phi\mathrm{PSe}$ and $\mathrm{Ph_3PSe}$ were inert under these conditions, and no evidence of deselenization has been observed for $\mathrm{Ph_3PSe}$ even in presence of concentrated acids.[19,20] An analogous desulfurization by acid has been observed for Φ_3PS to occur slowly on heating.[5]

$$\Phi_3\mathrm{PSe} + \mathrm{Ph_3P} \longrightarrow \Phi_3\mathrm{P} + \mathrm{Ph_3PSe} \qquad (2)$$

Crystal Structure of $\Phi_3\mathrm{PSe}\cdot\mathrm{H_2O}$. The crystal structure of $\Phi_3\mathrm{PSe}\cdot\mathrm{H_2O}$ (Fig. 1, Tables 3 and 4) is isomorphous with $\Phi_3\mathrm{PS}\cdot\mathrm{H_2O}$.[21] The relevant structural parameters of related compounds are summarized in Table 6 for comparison. The most characteristic result is that the P=Se bond length of $\Phi_3\mathrm{PSe}\cdot\mathrm{H_2O}$ [2.136(2) Å] is the longest among those found for common triarylphosphine selenides [2.094—2.116 Å] such as $\mathrm{Ph_3PSe}$ [2.106(1) Å].[22,23] This elongation can be

Table 6. Comparison of X-Ray Crystal Structural Data for Triarylphosphine Derivatives

Ar_3PY	av. P–C (Å)	P=Y (Å)	av. C–P–C (°)	O···P (Å)	Refs.
$\Phi_3PS\cdot H_2O$	1.840	1.971(2)	107.1	2.802—3.190	21
Ph_3Ps	1.817	1.950(3)	105.7	—	26
$\Phi_3PSe\cdot H_2O$	1.839	2.136(2)	107.2	2.794—3.189	This work
Ph_3PSe	1.826	2.106(1)	106	—	22
Φ_3P	1.844	—	104.4	2.743—3.193	25
Ph_3P	1.831	—	102.8	—	27

understood by the weaker d_π–p_π double bond character between the phosphorus atom and the selenium atom in Φ_3PSe than that in Ph_3PSe due to the electron donating property of 2,6-dimethoxyphenyl group. As a result, the phosphorus–selenium bond of Φ_3PSe must be highly polarized as shown in Fig. 2. The other possibility for the elongation is owing to the presence of hydrogen bonding with the crystal water. However, the observed distance [3.461(5) Å] between the selenium atom and its nearest water oxygen atom is considerably longer than the sum [3.42 Å] of their van der Waals' radii [1.90 Å (Se) and 1.52 Å (O)], implying the absence of significant hydrogen bonding. Bhattacharyya et al. have recently reported the crystal structure of *N*-(diphenylphosphinoselenoyl)-*P*,*P*-diphenylphosphinoselenoic amide, $(Ph_2PSe)_2NH$, of which molecules exist as dimer pairs in crystals by two N–H···Se hydrogen bonds with a distance of 3.19 Å between the nitrogen and the selenium atoms.$^{24)}$

The average P–C bond length [1.839 Å] of $\Phi_3PSe\cdot H_2O$ is comparable with those of tris(2,6-dimethoxyphenyl)phosphine derivatives: $\Phi_3PS\cdot H_2O$ [1.840 Å]$^{21)}$ and Φ_3P [1.844 Å],$^{25)}$ but it is apparently longer than those of triphenylphosphine derivatives: Ph_3PSe,$^{22)}$ Ph_3PS,$^{26)}$ and $Ph_3P$$^{27)}$ (Table 6). This elongation is unexpected from the viewpoint of the electron-donative properties of the methoxy group to the P–C bonds through the π-orbital system. The C–P–C angle [av. 107.2°] of $\Phi_3PSe\cdot H_2O$ is comparable with that of $\Phi_3PS\cdot H_2O$,$^{21)}$ but it is unfolded in comparison with $\Phi_3P$$^{25)}$ or triphenylphosphine derivatives, Ph_3PSe,$^{22)}$ Ph_3PS,$^{26)}$ and Ph_3P.$^{27)}$

Intramolecular distances between the phosphorus atom of $\Phi_3PSe\cdot H_2O$ and the methoxy oxygen atoms in 2,6-dimethoxyphenyl groups are all shorter than the sum [3.32 Å] of the van der Waals radii of these two atoms [1.80 Å (P) and 1.52 Å (O)]. Especially, one of the two methoxy oxygens in each 2,6-dimethoxyphenyl group is significantly shorter [av. 2.849 Å]. This observation enables us to expect some direct electron-donative interaction from the methoxy oxygen atoms to the phosphorus atom (Fig. 2). This concept has been proposed by Wood, Wilkholm, and McEwen for the crystal structure of benzyl(2-methoxyphenyl)diphenylphosphonium bromide [P···O distance, 2.878(12) Å], and it was supported by energy minimization calculations.$^{28)}$ The presence of this interaction is also consistent with the longer P–C bonds and the longer P=Se bond of Φ_3P-derivatives than those of Ph_3P-derivatives, as mentioned above. The positive charge on the phosphorus atom shown in Fig. 2 must be dispersed among the six methoxy oxygens by such direct interactions.

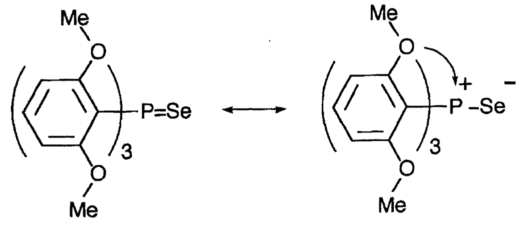
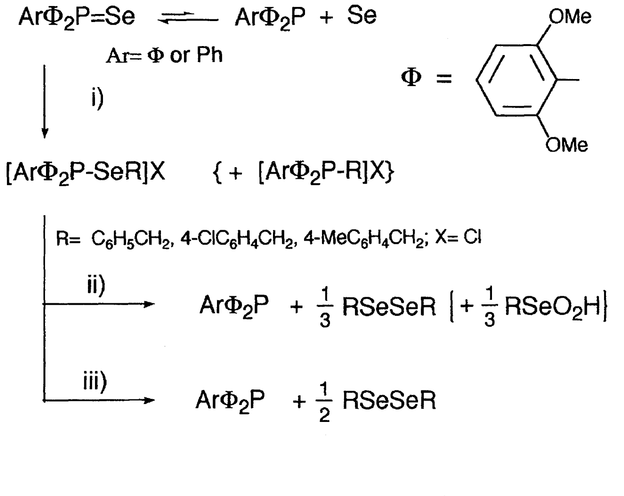


Fig. 2.

Reactions of 2,6-Dimethoxyphenylphosphine Selenides with Alkyl Halides. The reactions studied in this work are summarized in Scheme 1. While Ph_3PSe does not react with alkyl halides, RX, under usual conditions, Φ_3PSe reacted with RX in common organic solvents even at −30 °C (RX=MeI, EtI, EtBr, BuI, BuBr) or at ambient temperature ($RX=PhCH_2Cl$) to give mixtures of an alkylselenophosphonium salt, $[\Phi_3P\text{–}SeR]X$, and an alkylphosphonium salt, $[\Phi_3P\text{–}R]X$, in a variety of ratios. The formation of $[\Phi_3P\text{–}R]X$ can be attributed to the partial decomposition of Φ_3PSe to Φ_3P. When the reaction Φ_3PSe and RX was done in the presence of excess elemental selenium, some salts, $[\Phi_3P\text{–}SeR]X$ ($RX=PhCH_2Cl$, $4\text{-}MeC_6H_4CH_2Cl$, $4\text{-}ClC_6H_4CH_2Cl$, BuI, BuBr), were obtained predominantly. Due to the very high solubility of these chlorides and bromide in polar solvents, they were derived to the perchlorate or iodide for isolation



i) RX in MeOH, C_6H_6, or $CHCl_3$. ii) aq. NaOH.
iii) $SnCl_2$ in aq. HCl; then, aq. NaOH.

Scheme 1.

and characterization in pure form.

The selenide, $\mathrm{Ph\Phi_2PSe}$, also reacted with a variety of RX at ambient temperature (MeI) or on heating (EtBr, BuBr, $\mathrm{CH_2{=}CHCH_2Cl}$, $\mathrm{CH_2{=}CMeCH_2Cl}$, $\mathrm{PhCH_2Cl}$) to give $\mathrm{[Ph\Phi_2P{-}SeR]X}$. In these reactions, the loss of $\mathrm{Ph\Phi_2P}$ by formation of alkylphosphonium salts $\mathrm{[Ph\Phi_2P{-}R]ClO_4}$ was negligible (<2%).

The selenide, $\mathrm{Ph_2\Phi PSe}$, was much less reactive than $\mathrm{Ph\Phi_2PSe}$, and a part of $\mathrm{Ph_2\Phi PSe}$ was recovered after reactions with EtBr or $\mathrm{PhCH_2Cl}$ under analogous conditions used for $\mathrm{Ph\Phi_2PSe}$.

Comparison of Reaction Rates of Triarylphosphine Derivatives. McEwen et al. have found that $\mathrm{Ph_2\Phi P}$ undergoes the quaternization reaction with benzyl chloride 74.7 times faster than $\mathrm{Ph_3P}$,[29] and we have observed that $\mathrm{\Phi_3P}$ reacts with dichloromethane or 1,2-dichloroethane extremely faster than $\mathrm{Ph_3P}$.[1] Such a high reactivity of $\mathrm{\Phi_3P}$ was also observed for reactions with butyl halides in acetonitrile (Table 5). It reacted even with butyl chloride faster than the reaction of $\mathrm{Ph_3P}$ with butyl bromide. While triphenylphosphine oxide, sulfide, and selenide do not react with butyl bromide under normal conditions, $\mathrm{\Phi_3PY}$ [Y=O,[7] S,[5] Se] reacted to give the salts, $\mathrm{[\Phi_3P{-}YBu]Br}$. The reaction of $\mathrm{\Phi_3PO}$ is reversible,[7] while those of $\mathrm{\Phi_3PS}$[5] and $\mathrm{\Phi_3PSe}$ were complete. Although the reaction rate of $\mathrm{\Phi_3PSe}$ was not measured due to instability that released elemental selenium, it must be clear from Table 5 that the reaction rates of $\mathrm{Ph_{3-\mathit{n}}\Phi_{\mathit{n}}PY}$ decrease in the order of Y=none>Se>S>O and $n=3>2>1>0$. The higher nucleophilicity of $\mathrm{Ph_{3-\mathit{n}}\Phi_{\mathit{n}}PSe}$ than $\mathrm{Ph_{3-\mathit{n}}\Phi_{\mathit{n}}PS}$ must originate in the poorer character of selenium element to form double bonds.

Properties of Alkylselenophosphonium Salts. The iodides, $\mathrm{[Ar\Phi_2P{-}SeR]I}$ (Ar=Φ, Ph), are in general sensitive to heat, light, or acid in solutions. During the attempts of their separation from the reaction mixture of $\mathrm{Ar\Phi_2PSe}$ and alkyl iodide, they often decomposed to give complex mixtures containing $\mathrm{[Ar\Phi_2P{-}R]^+}$, $\mathrm{Ar\Phi_2PO}$, $\mathrm{[Ar\Phi_2P{-}H]^+}$, RI, and so on, as detected by the ^{1}H NMR spectrum. The salt, $\mathrm{[\Phi_3P{-}SeBu]I}$, however, exists stably in ethanol in the presence of a base such as triethylamine in the dark for more than 24 h at 60 °C (in a sealed glass tube), and it can be recrystallized from water. The salts, $\mathrm{[Ph\Phi_2P{-}SeMe]I}$, decomposed under analogous conditions or in the absence of a base to give a complex mixture containing $\mathrm{Ph\Phi_2PO}$, $\mathrm{[Ph\Phi_2P{-}Me]^+}$, and $\mathrm{[MeEt_3N]^+}$ species as detected by ^{1}H NMR spectrum. Although we have not analyzed this, it seems that iodide anion acts as catalyst for these complex decompositions. The chlorides, $\mathrm{[Ar\Phi_2P{-}SeCH_2Ph]Cl}$, on the other hand, exist stably in chloroform or in hot methanol (80 °C, 24 h) in the dark even in the presence of trifluoroacetic acid or perchloric acid, although they are also somewhat light-sensitive. Interestingly, these chlorides are soluble and stable even in water in the dark below room temperature. The perchlorates, $\mathrm{[Ar\Phi_2P{-}SeCH_2Ph]ClO_4}$ (Ar=Φ, Ph), also exist stably in methanol (24 h at 80 °C) or in chloroform (7 d at 50 °C), but they are much less soluble in water.

The inertness of $\mathrm{[Ar\Phi_2P{-}SeCH_2Ph]Cl}$ in hot alcohols or water is astonishing, since organoselenophosphonium salts have been assumed to be versatile intermediates during the organic synthesis,[30—34] and they were converted by aqueous sodium hydroxide to the phosphine oxide and sodium areneselenolate.[33,34] There are four reaction sites expected in $\mathrm{[Ar\Phi_2P{-}SeCH_2Ph]Cl}$: (i) the cationic phosphorus atom, (ii) the selenium atom, (iii) the benzyl carbon atom, and (iv) the benzylic protons. The hydrolysis at the cationic phosphorus atom must be protected by 2,6-dimethoxyphenyl groups both sterically and electronically, especially when Ar=Φ. This electronic effect of methoxy groups must also decrease the reactivity at the benzyl carbon and the benzylic protons by the decrease of cationic character around these atoms.

The alkylselenotriphenylphosphonium salts, $\mathrm{[Ph_3P{-}SeR]BF_4}$ (R=Me, Et), have been prepared by the reaction of $\mathrm{Ph_3PSe}$ with trialkyloxionium salts, and their ^{31}P NMR chemical shifts have been compared with alkoxy- and alkylthiophosphonium salts.[19,35] The ^{31}P and ^{77}Se NMR of $\mathrm{\Phi_3PSe}$ have been discussed by Allen et al.[8] The ^{1}H NMR spectra of these 2,6-dimethoxyphenylphosphine derivatives (Table 1) show a triplet due to 4-protons, double doublets due to 3,5-protons and a sharp singlet due to 2,6-dimethoxy protons. Because of the sharpness of the methoxy proton resonance, the ^{1}H NMR spectrum is quite useful for the characterization of these compounds and of their decomposition products. The spectral data of alkylphosphonium salts, $\mathrm{[Ar\Phi_2P{-}R]X}$, are also shown in Table 1 for comparison. **Caution!** We have recently found that alkylthiophosphonium salts $\mathrm{[\Phi_3P{-}SR]X}$ are highly toxic: $\mathrm{LD_{50}}$=ca. 5 mg kg^{-1} (venous injection to mouse) for R,X=Bu,Cl; Bu,Br; $\mathrm{CH_2Ph}$,Cl. Although we have no experimental evidence for alkylselenophosphonium salts at present, there is a possibility that these related compounds reported here are also highly toxic.

Reactions of Benzylseleno-2,6-dimethoxyphenylphosphonium Salts with Aqueous Sodium Hydroxide. On prolonged heating the aqueous solution, $\mathrm{[\Phi_3P{-}SeCH_2Ph]Cl}$ decomposed slowly to give diselenide, $\mathrm{(PhCH_2Se)_2}$, which must be the hydrolysis product at the selenium atom followed by disproportionation [Eq. 3][36] of tolueneselenenic acid, thus formed. In aqueous sodium hydroxide, it decomposed fast even at room temperature to give a mixture of $\mathrm{\Phi_3P}$ and $\mathrm{(PhCH_2Se)_2}$. This means that we have constructed a sequential process for a new synthetic method of $\mathrm{(PhCH_2Se)_2}$ from benzyl chloride, elemental selenium, and sodium hydroxide using $\mathrm{\Phi_3P}$ as a reproducible reagent. Since $\mathrm{\Phi_3P}$ dissolves in aqueous hydrochloric acid forming the tertiary phosphonium salt, $\mathrm{[\Phi_3P{-}H]Cl}$, $\mathrm{(PhCH_2Se)_2}$ could easily be separated from the mixture with $\mathrm{\Phi_3P}$. The isolated yield of $\mathrm{(PhCH_2Se)_2}$ was 56% based on the starting $\mathrm{\Phi_3P}$, and a treatment of the aqueous solution of $\mathrm{[\Phi_3P{-}H]Cl}$ with aqueous sodium hydroxide deposited $\mathrm{\Phi_3P}$ in 74% recovery. From the first filtrate treated with aqueous sodium hydroxide, a considerable amount of $\mathrm{[\Phi_3P{-}CH_2Ph]PF_6}$ (18% yield) was obtained, but the formation of the oxide $\mathrm{\Phi_3PO}$ or its derivatives was negligible (2—3%). Using 4-methylbenzyl chloride or 4-chlorobenzyl chloride, the diselenides, $\mathrm{(4\text{-}MeC_6H_4CH_2Se)_2}$ and $\mathrm{(4\text{-}ClC_6H_4CH_2Se)_2}$, were obtained in 63 and 53% yields, respectively, and Φ_3P was recovered in 76 and 68% yields, respectively.

$$3RSeOH \longrightarrow RSeSeR + RSeO_2H + H_2O \qquad (3)$$

An analogous treatment of $[Ph\Phi_2P\text{–}SeCH_2Ph]Cl$ in water with aqueous sodium hydroxide as above gave a mixture of $(PhCH_2Se)_2$, $Ph\Phi_2P$, and a small amount of $Ph\Phi_2PO$. The yields of $(PhCH_2Se)_2$ and $Ph\Phi_2P$ were 74% and 69% after separation, respectively, and $Ph\Phi_2PO$ was separated in the form of $[Ph\Phi_2P\text{–}OH]ClO_4$ in 14% yield. To confirm the formation of tolueneseleninic acid by disproportionation of toluene–selenenic acid intermediate, the aqueous filtrate was further treated with a variety of reducing reagents. Among them, we found that tin(II) chloride was the most effective to produce an additional $(PhCH_2Se)_2$ in 12% yield.

There are two reaction paths considered for the formation of $Ph\Phi_2PO$; (1) the hydrolysis of $[Ph\Phi_2P\text{–}SeCH_2Ph]^+$ cation at the phosphorus atom, and (2) the oxidation of $Ph\Phi_2P$ by tolueneseleninic acid. Since the formation of Φ_3PO was negligible in the reaction of $[\Phi_3P\text{–}SeCH_2Ph]Cl$, we may assume that the path (1) worked for $[Ph\Phi_2P\text{–}SeCH_2Ph]^+$, where the phosphorus atom is less protected from the attack of hydroxide ion than that in $[\Phi_3P\text{–}SeCH_2Ph]^+$, although the second path still cannot be excluded.

It is worth noting here that hexafluorophosphates of these phosphonium cations are in general quite insoluble in water, and they are suitable for quantitative isolation of phosphonium cations. Perchlorates are slightly soluble in water, and they are suitable for elemental analysis or spectral measurements after recrystallization. Hexafluorophosphates are often not suitable for elemental analysis due probably to the incomplete combustion character.

Reactions of Benzylseleno-2,6-dimethoxyphenylphosphonium Salt with Aqueous Tin(II) Chloride. In the previous reactions, part of the benzylseleno moiety in $[Ar\Phi_2P\text{–}SeCH_2Ph]Cl$ must be lost by the formation of tolueneseleninic acid. In addition, there still is a possibility that the seleninic acid thus formed oxidized $Ar\Phi_2P$ to decrease its recovery yield. To improve the yield of diselenides and the recovery of $Ar\Phi_2P$, the hydrolysis was attempted in the presence of a reducing reagent. Thus, $[\Phi_3P\text{–}SeCH_2Ph]Cl$, prepared as above, was treated with tin(II) chloride in aqueous hydrochloric acid, and immediate precipitation of a mixture containing $(PhCH_2Se)_2$ and a small amount of inorganic impurity resulted. From this precipitates, $(PhCH_2Se)_2$ was separated in 70% yield (based on Φ_3P). The acidic filtrate was neutralized by aqueous sodium hydroxide to reproduce Φ_3P in 81% yield. Again, $[\Phi_3P\text{–}CH_2Ph]PF_6$ was obtained in 13% yield. The mechanism, or the role of the tin(II) chloride, is not clear.

Analogous results were obtained for $4\text{-}MeC_6H_4CH_2Cl$ and $4\text{-}ClC_6H_4CH_2Cl$; the diselenides, $(4\text{-}MeC_6H_4CH_2Se)_2$ and $(4\text{-}ClC_6H_4CH_2Se)_2$, were obtained in 72 and 75% yields (based on Φ_3P), respectively, and Φ_3P was recovered in 70% yield.

The salt, $[Ph\Phi_2P\text{–}SeCH_2Ph]Cl$, also reacted with tin(II) chloride in aqueous hydrochloric acid in an analogous manner, and $(PhCH_2Se)_2$ was obtained in 67% yield after purification. The formations of $[Ph\Phi_2P\text{–}CH_2Ph]X$ and $Ph\Phi_2PO$ were negligible, and the recovery yield of $Ph\Phi_2P$ reached 85%. While the yield of $Ph\Phi_2P$ increased, as expected, the cause of poor yield of $(PhCH_2Se)_2$ is unknown.

Dibenzyl diselenides, $(ArCH_2Se)_2$, have been prepared (a) by the reaction of benzaldehyde with hydrogen selenide in tertiary amines,[37)] (b) by the reaction of benzyl chloride with alkali metal diselenide,[14—16)] (c) by the reaction of triphenylphosphine, selenocyanogen and benzyl alcohol,[38)] or (d) by the reaction of samarium diiodide, elemental selenium, and benzyl halide.[39)] Although all of these methods have their own merits, they suffer from one or more disadvantages including the use of expensive reagents, relatively severe reaction conditions, and troublesome alkali metals. This method uses unique tertiary phosphines, Φ_3P or $Ph\Phi_2P$, but most of them are recovered after the reaction. Hence, $(PhCH_2Se)_2$ can be prepared from elemental selenium, benzyl chloride, and sodium hydroxide or tin(II) chloride under mild conditions.

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