# Acylthio- and Thioacylthiophosphines [$(RCES)_nPPh_{3-n}$, E = O, S; $n$ = 1—3]: Synthesis and Structural Analysis

**Kazuyasu Tani, Kazuo Matsuyama, Shinzi Kato,* Kohzaburo Yamada,† and Hirotaka Mifune†**

Department of Chemistry, Faculty of Engineering, Gifu University, Yanagido, Gifu 501-1193

†Ashigara Research Laboratories, Fuji Photo Film Co., Ltd., 210, Nakanuma, Minamiashigara, Kanagawa 250-0193

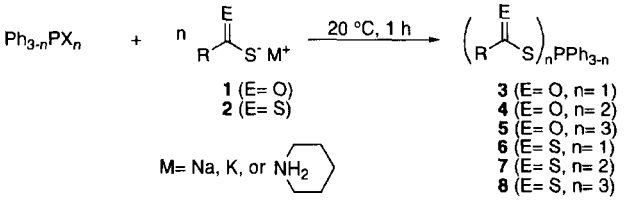
(Received November 8, 1999)

Stoichiometric reactions of alkali metal thio- and dithiocarboxylates with $Ph_2PCl$, $PhPCl_2$, and $PBr_3$ gave the corresponding acylthio- and thioacylthiophosphines [$(RCES)_nPPh_{3-n}$, E = O, S; $n$ = 1—3] **3**—**8** in moderate to good yields. The structures of $(4\text{-}CH_3C_6H_4COS)_nPPh_{3-n}$ (**3d**: $n$ = 1, **4d**: $n$ = 2, **5d**: $n$ = 3) and $(4\text{-}CH_3C_6H_4CS_2)_2PPh$ (**7b**) were analyzed by X-rays. In the thiocarboxylate derivatives **3d**, **4d**, and **5d**, the intramolecular interactions between the carbonyl oxygen and the central phosphorus atoms are weak and the thiocarboxylato ligands act as monodentates through the sulfur atoms. Similarly, in the dithiocarboxylate derivative **7b**, the intramolecular interactions between the thiocarbonyl sulfur and the central phosphorus atoms are weak and the dithiocarboxylato ligands act as monodentates. The covalent phosphorus–sulfur and/or phosphorus–phenyl *ipso*-carbon bonds are nearly at right angles to one another, forming a distorted tetrahedron with the unshared electron pair orbital at the apex. The $^{31}P$ NMR spectra of the thiocarboxylic acid derivatives **3**—**5** show downfield shifts with an increase in the number of thiocarboxylato ligands, whereas those of the dithiocarboxylic acid derivatives **6**—**8** show upfield shifts.

In contrast to the dithiocarbamato-,[1a,1b] dithiophosphinato-,[1b,1c] and dithiocarbonatophosphorus derivatives,[1b] little is known about the chemistry of the thio- and dithiocarboxylic acid derivatives, most likely due to the difficulty of purification. Surprisingly, no structural analyses of thio- and dithiocarboxylatophosphorus compounds except for $(PhCOS)_3P$,[1b] have been reported so far. Previously, we reported the preparation of diphenyl(thioacylthio)phosphines $RCS_2PPh_2$ and diphenyl(thioacylthio)phosphine sulfides $RCS_2P(S)Ph_2$ by reacting piperidinium dithiocarboxylates with $Ph_2PCl$ and $Ph_2P(S)Cl$, respectively.[2] As a part of our studies concerning main group element derivatives of new chalcogenocarboxylic acids, we have focused on the systematic synthesis of group 15 element derivatives of chalcogenocarboxylates. In this paper, we report the full details of the synthesis and structure of the acylthio- and thioacylthiophosphines [$(RCES)_nPPh_{3-n}$, E = O, S; $n$ = 1—3] **3**—**8**.

## Results and Discussion

**Synthesis:** The thiocarboxylatophosphorus derivatives were synthesized first (Eq. 1). Sodium and potassium thiocarboxylates **1** readily reacted with chlorodiphenylphosphine in ether to give the corresponding acylthiodiphenylphosphines $RCOSPPh_2$ **3a**—**g** in good yields (Table 1). In dichloromethane, the reaction of dichlorophenylphosphine with two molar amounts of **1** gave the bis(acylthio)phenylphosphines **4** in 70—90% yields. Similarly, the stoichiometric reaction of tribromophosphine with **1** in dichloromethane gave tris(acylthio)phosphines **5** in 70—90% yields.




| 3–5 | R | 6–8 | R |
|---|---|---|---|
| a | $CH_3$ | a | $C_6H_5$ |
| b | $t\text{-}C_4H_9$ | b | $4\text{-}CH_3C_6H_4$ |
| c | $C_6H_5$ | c | $2\text{-}CH_3OC_6H_4$ |
| d | $4\text{-}CH_3C_6H_4$ | d | $4\text{-}CH_3OC_6H_4$ |
| e | $2\text{-}CH_3OC_6H_4$ | e | $4\text{-}ClC_6H_4$ |
| f | $4\text{-}CH_3OC_6H_4$ | f | $2,4,6\text{-}(CH_3)_3C_6H_2$ |
| g | $4\text{-}ClC_6H_4$ | | |

(1)

Next, dithiocarboxylatophosphorus derivatives were synthesized. Under the conditions used for the synthesis of the thiocarboxylic acid derivatives **3**—**5**, the reactions of piperidinium or sodium dithiocarboxylates with the corresponding halophosphines were examined. As expected, diphenyl(thioacylthio)phosphines **6**, phenylbis(thioacylthio)phosphines **7**, and tris(thioacylthio)phosphines **8** were isolated in yields of 20—90%, 10—70%, and 30—70%, respectively (Table 2). Such low yields are due to the difficulty of purification (loss

Table 1. Yields and Melting Points of Mono-, Bis-, and Tris(acylthio)phosphines **3**—**5**

| No. | $(RCOS)_nPPh_{3-n}$ | | Yield | Mp |
|---|---|---|---|---|
| | R | *n* | % | °C |
| **3a** | $CH_3$ | 1 | 74 | Oil |
| **3b** | *t*-$C_4H_9$ | 1 | 75 | Oil |
| **3c** | $C_6H_5$ | 1 | 95 | Oil |
| **3d** | 4-$CH_3C_6H_4$ | 1 | 93 | 96—97 |
| **3e** | 2-$CH_3OC_6H_4$ | 1 | 80 | 111—114 |
| **3f** | 4-$CH_3OC_6H_4$ | 1 | 93 | Oil |
| **3g** | 4-$ClC_6H_4$ | 1 | 90 | 91—92 |
| **4a** | $CH_3$ | 2 | 74 | Oil |
| **4b** | *t*-$C_4H_9$ | 2 | 75 | Oil |
| **4c** | $C_6H_5$ | 2 | 99 | 103—105 |
| **4d** | 4-$CH_3C_6H_4$ | 2 | 88 | 133—134 |
| **4e** | 2-$CH_3OC_6H_4$ | 2 | 97 | 108—110 |
| **4f** | 4-$CH_3OC_6H_4$ | 2 | 99 | 104—106 |
| **4g** | 4-$ClC_6H_4$ | 2 | 87 | 146—147 |
| **5a** | $CH_3$ | 3 | 82 | Oil |
| **5b** | *t*-$C_4H_9$ | 3 | 82 | Oil |
| **5c** | $C_6H_5$ | 3 | 91 | 98—101 |
| **5d** | 4-$CH_3C_6H_4$ | 3 | 77 | 95—98 |
| **5e** | 2-$CH_3OC_6H_4$ | 3 | 90 | 100—103 |
| **5f** | 4-$CH_3OC_6H_4$ | 3 | 66 | 97—100 |
| **5g** | 4-$ClC_6H_4$ | 3 | 75 | 154—156 |

Table 2. Yields and Melting Points of Mono-, Bis-, and Tris(thioacylthio)phosphines **6**—**8**

| No. | $(RCS_2)_nPPh_{3-n}$ | | Yield | Mp |
|---|---|---|---|---|
| | R | *n* | % | °C |
| **6a** | $C_6H_5$ | 1 | 35 | 74—76 |
| **6b** | 4-$CH_3C_6H_4$ | 1 | 94 | 98—99 |
| **6c** | 2-$CH_3OC_6H_4$ | 1 | 93 | Oil |
| **6d** | 4-$CH_3OC_6H_4$ | 1 | 61 | 95—97 |
| **6e** | 4-$ClC_6H_4$ | 1 | 25 | 75—77 |
| **6f** | 2,4,6-$(CH_3)_3C_6H_2$ | 1 | 54 | 112—117 |
| **7a** | $C_6H_5$ | 2 | 71 | Oil |
| **7b** | 4-$CH_3C_6H_4$ | 2 | 36 | 127—131 |
| **7c** | 2-$CH_3OC_6H_4$ | 2 | 19 | 56—60 |
| **7d** | 4-$CH_3OC_6H_4$ | 2 | 11 | 109—114 |
| **7f** | 2,4,6-$(CH_3)_3C_6H_2$ | 2 | 44 | 126—129 |
| **8b** | 4-$CH_3C_6H_4$ | 3 | 38 | 150—153 |
| **8e** | 4-$ClC_6H_4$ | 3 | 53 | 87—90 |
| **8f** | 2,4,6-$(CH_3)_3C_6H_2$ | 3 | 71 | 169—173 |

during purification).

Thiocarboxylic acid derivatives **3**—**5** are fairly stable thermally and toward oxygen and moisture, and show no appreciable change for 1 week upon exposure to air. In contrast, the dithiocarboxylic acid derivatives **6**—**8** are unstable thermally and are moisture-sensitive. For example, upon exposure to air, the 4-methyl-substituted derivatives were gradually hydrolyzed to the dithiocarboxylic acid. In particular, bis (**4** and **7**) and tris derivatives (**5** and **8**) are readily hydrolyzed even in ether.

**Molecular Structures:** The ORTEP drawing of (4-methylbenzoylthio)diphenylphosphine **3d** is shown in Fig. 1. The crystal data are collected in Table 3. Selected bond distances and angles are shown in Table 4. The compound **3d** crystallizes in a monoclinic system with space group $P2_1/c$ (#14). The dihedral angles suggest that the thiocarboxylato ligand is in approximately same plane as the benzene ring containing C21 atom and is roughly perpendicular to that containing C31 atom. The C–O and C–S bond lengths of **3d** are 1.207(4) and 1.802(4) Å, which reflect C=O double and C–S single bonds, respectively. The P–S bond length [2.136(1) Å] is close to the sum of the single covalent bond radii of both atoms (2.14 Å),[3] and is comparable to the distance observed for $Et_2NCS_2PPh_2$ (2.123 Å).[1b] The distance between the carbonyl oxygen and the phosphorus atom [2.917(3) Å] is considerably longer than the sum of the covalent bond radii of both atoms (1.74 Å),[3] but less than the sum of the van der Waals radii of both atoms (3.28 Å),[4] indicating a weak interaction. The bond angles around the phosphorus atom [S11–P1–C21 = 98.4(1)°, S11–P1–C31 = 102.3(1)°, C21–P1–C31 = 100.7(2)°] are close to right angles, and the phosphorus atom can be considered to exhibit a *p*-type bond, thus forming a distorted tetrahedral structure with the unshared electron pair orbital at the apex.

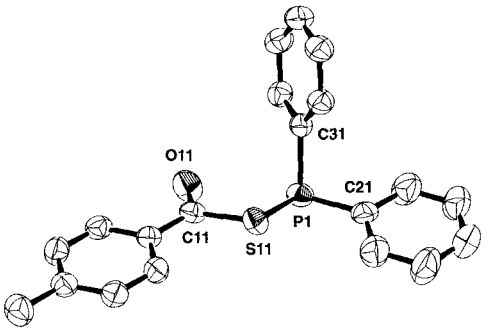



Fig. 1. An ORTEP drawing of 4-$CH_3C_6H_4COSPPh_2$ **3d**.

In bis(4-methylbenzoylthio)phenylphosphine **4d**, the two thiocarboxylato ligands exist in the same plane with the same orientation, where each oxygen atom is located in the same direction (Fig. 2). The phenyl ring is nearly perpendicular to the plane. The C–O and C–S bond lengths of the two thiocarboxylato ligands are av 1.213(5) Å and av 1.787(4) Å, respectively, indicating C=O double and C–S single bonds (Table 5). The two P–S bond lengths [P1–S11 = 2.146(2) Å, P1–S21 = 2.144(2) Å] are close to the sum of the single covalent bond radii of both atoms (2.14 Å),[3] indicating a single bond. The distances between the two carbonyl oxygen and the phosphorus atoms [P1–O11 = 2.784(3) Å, P1–O21 = 2.747(3) Å] are

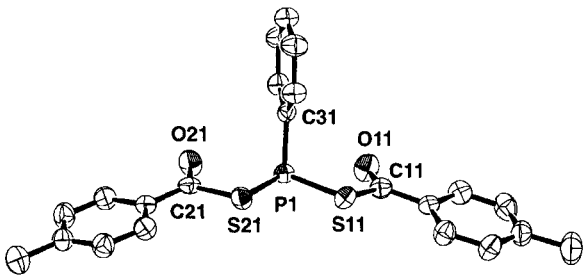



Fig. 2. An ORTEP drawing of $(4\text{-}CH_3C_6H_4COS)_2PPh$ **4d**.

Table 3. Crystal Data, Data Collection, and Refinement Parameters for **3d**, **4d**, **5d**, and **7b**

| | **3d** | **4d** | **5d** | **7b** |
|---|---|---|---|---|
| Empirical formula | $C_{20}H_{17}OPS$ | $C_{22}H_{19}O_2PS_2$ | $C_{24}H_{21}O_3PS_3$ | $C_{22}H_{19}PS_4$ |
| Formula weight | 336.39 | 410.48 | 484.58 | 442.61 |
| Color | Colorless | Colorless | Colorless | Red |
| Crystal system | Monoclinic | Monoclinic | Trigonal | Orthorhonbic |
| $a$/Å | 34.855(2) | 5.906(2) | 13.479(3) | 16.296(2) |
| $b$/Å | 8.318(1) | 16.073(2) | 27.597(3) | 21.708(2) |
| $c$/Å | 5.941(1) | 21.489(2) | | 6.029(1) |
| $\beta$/deg | 89.59(1) | 96.07(2) | | |
| Volume of unit cell/Å$^3$ | 1722.4(4) | 2028.4(6) | 4341(1) | 2132.6(5) |
| Space group | $P2_1/c$ (#14) | $P2_1/c$ (#14) | $R3c$ (#161) | $P2_12_12_1$ (#19) |
| $Z$ value | 4 | 4 | 8 | 4 |
| $D_{calc}$/g cm$^{-3}$ | 1.297 | 1.344 | 1.482 | 1.344 |
| Crystal size /mm | $0.23\times0.23\times0.43$ | $0.23\times0.17\times0.23$ | $0.06\times0.23\times0.31$ | $0.09\times0.14\times0.29$ |
| $\mu$(Mo $K\alpha$)/cm$^{-1}$ | 2.82 | 3.56 | 4.41 | 5.26 |
| Transmission factor for absorption correction | | 0.6834—1.0000 | | 0.6548—1.0000 |
| Temp/°C | 23.0 | 23.0 | 23.0 | 23.0 |
| $2\theta_{max}$/deg. | 55.0 | 55.0 | 55.0 | 55.0 |
| No. of measured reflections | 4018 | 5101 | 2390 | 3221 |
| No. of unique reflections | 3955 | 4659 | 1119 | 2819 |
| $R_{int}$ | 0.033 | 0.063 | 0.132 | 0.043 |
| No. of observations | $2216/I>2.3\sigma(I)$ | $2310/I>1.5\sigma(I)$ | $393/I>2.0\sigma(I)$ | $1865/I>2.0\sigma(I)$ |
| No. of variables | 209 | 245 | 94 | 246 |
| Reflection/parameter ratio | 10.12 | 9.43 | 4.18 | 7.58 |
| Residuals: $R$,[a] $R_w$[b] | 0.049, 0.050 | 0.055, 0.056 | 0.087, 0.287[c] | 0.043, 0.046 |
| $\rho$ value[b] | 0.0230 | 0.0350 | | 0.0350 |
| Max. and min. of residual Electron density/eÅ$^{-3}$ | 0.41, −0.25 | 0.28, −0.31 | 0.92, −0.62 | 0.24, −0.24 |
| Goodness of fit indicator | 1.67 | 1.35 | 1.26 | 1.21 |

a) $R=\sum(|F_o|-|F_c|)/\sum|F_o|$. b) $R_w=[\sum(|F_o|-|F_c|)^2/\sum w|F_o|^2]^{1/2}$, $w=[\sigma^2(F_o)+p^2(F_o)^2/4]^{-1}$. c) $R=\sum(|F_o|-|F_c|)/\sum|F_o|$. $R_w=[\sum w(F_o^2-F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$, $w=[\sigma^2(F_o^2)+(0.1000P)^2+0.0000P]^{-1}$, where $P=(F_o^2+2F_c^2)/3$.

Table 4. Selected Bond Lengths (Å), Angles (deg), Torsion Angles (deg), and Dihedral Angles (deg) of (4-Methylbenzoylthio)diphenylphosphine **3d**

| | | | |
|---|---|---|---|
| | Bond lengths | | |
| P1–S11 | 2.136(1) | P1–C21 | 1.838(4) |
| P1–O11 | 2.917(3) | P1–C31 | 1.828(4) |
| C11–S11 | 1.802(4) | | |
| C11–O11 | 1.207(4) | | |
| | Angles | | |
| S11–P1–O11 | 60.48(6) | S11–P1–C21 | 98.4(1) |
| S11–C11–O11 | 120.8(3) | S11–P1–C31 | 102.3(1) |
| P1–S11–C11 | 97.1(1) | C21–P1–C31 | 100.7(2) |
| P1–O11–C11 | 80.1(2) | | |
| | Torsion angles | | |
| S11–C11–C12–C17 | 6.0(5) | C11–S11–P1–C21 | 171.8(2) |
| | | C11–S11–P1–C31 | 85.2(2) |
| | Dihedral angles | | |
| Plane (S11–C11–O11)–Plane (C21 benzene ring) | | | 164.21 |
| Plane (S11–C11–O11)–Plane (C31 benzene ring) | | | 108.59 |
| Plane (C21 benzene ring)–Plane (C31 benzene ring) | | | 75.39 |

Table 5. Selected Bond Lengths (Å), Angles (deg), and Torsion Angles (deg) of Bis(4-methylbenzoylthio)phenylphosphine **4d**

| | | | |
|---|---|---|---|
| | Bond lengths | | |
| P1–S11 | 2.146(2) | P1–S21 | 2.144(2) |
| P1–O11 | 2.784(3) | P1–O21 | 2.747(3) |
| C11–S11 | 1.785(5) | C21–S21 | 1.788(4) |
| C11–O11 | 1.211(5) | C21–O21 | 1.214(5) |
| P1–C31 | 1.825(4) | | |
| | Angles | | |
| S11–P1–S21 | 91.42(6) | O11–P1–O21 | 142.1(1) |
| S11–P1–O11 | 62.65(8) | S21–P1–O21 | 63.25(8) |
| S11–C11–O11 | 120.8(4) | S21–C21–O21 | 120.0(4) |
| P1–S11–C11 | 93.7(2) | P1–S21–C21 | 92.9(2) |
| P1–O11–C11 | 82.1(3) | P1–O21–C21 | 82.8(3) |
| S11–P1–C31 | 101.4(1) | S21–P1–C31 | 102.3(2) |
| | Torsion angles | | |
| S11–P1–S21–C21 | 172.8(1) | | |
| S11–C11–C12–C17 | 8.8(6) | S21–C21–C22–C27 | 4.4(6) |
| C11–S11–P1–C31 | 87.3(2) | C21–S21–P1–C31 | 85.2(2) |

different, and shorter than that in the monothiocarboxylate **3d** [2.917(3) Å], indicating a strong intramolecular interaction (nonbonding interaction). The bond angles around the phosphorus atom [S11–P1–S21 = 91.42(6)°, S11–P1–C31 = 101.4(1)°, S21–P1–C31 = 102.3(2)°] are nearly right angles,

where the two sulfur and the *ipso*-carbon atoms of the phenyl ring are bound to the 3p orbitals of the central phosphorus atom. The compound **4d** also exists in a distorted tetrahedral structure with unshared pairs of electrons, in analogy with that of **3d**.

The ORTEP drawing of tris(4-methylbenzoylthio)phosphine **5d** is shown in Fig. 3. The principal bond distances and angles and torsion angles are presented in Table 6. The structure of **5d** is essentially comparable to that of tris(benzoylthio)phosphine reported by Russian chemists,[1b] in that the three thiocarboxylato ligands display $C_3$ symmetry [Fig. 3a]. The C–O, C–S, and P–S bond lengths are 1.22(2), 1.79(2), and 2.142(5) Å, respectively, which indicate C=O double and C–S and P–S single bonds. The distance between the carbonyl oxygen and the phosphorus atom [2.82(1) Å] is between those of mono- **3d** [2.917(3) Å] and bis derivatives **4d** [av 2.766(3) Å], indicating a weak interaction. The three covalent phosphorus–sulfur bonds are nearly at right angles [95.4(2)°] to one another, again indicative of a distorted tetrahedron similar to those of **3d** and **4d** [Fig. 3b].

On the other hand, the crystallization of dithiocarboxylatophosphorus derivatives is very difficult. After several attempts, single crystals of bis(4-methylthiobenzoylthio)phenylphosphine **7b** were obtained. The ORTEP drawing and selected bond lengths and angles are shown in Fig. 4 and Table 7, respectively. As in **4d**, the two dithiocarboxylato ligands exist in the same plane, where each thiocarbonyl sulfur atom is located in the same direction. The C–S bond lengths of the dithiocarboxylato ligands are different, and can be divided into shorter C–S bond lengths [av 1.632(6) Å] and longer C–S bond lengths [av 1.751(6) Å]. The former is close to the general C=S double bond value (1.61 Å),[3] while the latter is roughly intermediate between C=S double and C–S single bonds.[3] A similar difference in the C–S bonds is found in $(Et_2NCS_2)_2PPh$ (av 1.678 Å and av 1.777 Å).[1b] The P–S bond lengths [P1–S12 = 2.170(3) Å, P1–S22 = 2.158(2) Å] are close to the sum of the single covalent bond radii of both atoms (2.14 Å),[3] indicating a single bond. The distances between the two thiocarbonyl sulfur and the phosphorus atoms [P1–S11 = 2.965(3) Å, P1–S21 = 2.975(3) Å] are longer than the sum of their covalent bond radii,[3] but shorter than the sum of their van der Waals radii (3.66 Å),[4] indicating a weak interaction. The S–P1–C31 angles [av 101.3(2)°] are similar to those in thiocarboxylate derivative **4d**, while the S12–P1–S22 angle [86.20(9)°] is slightly smaller than that of the corresponding thiocarboxylate derivative **4d** [91.42(6)°]. The two phosphorus–sulfur and one phosphorus–benzene

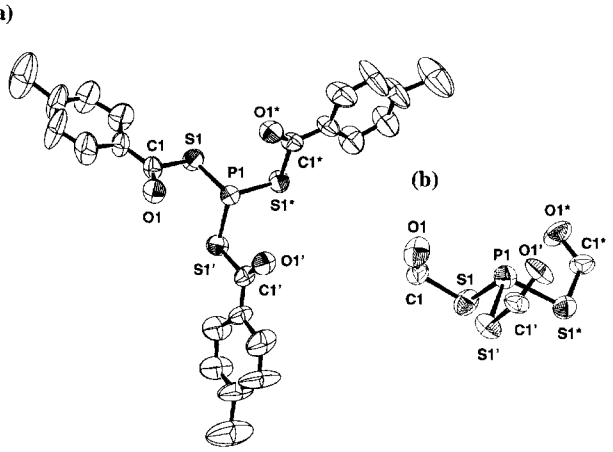



Fig. 3. An ORTEP drawing of $(4\text{-}CH_3C_6H_4COS)_3P$ **5d**. (*) $-Y, X-Y, Z$. (') $-X+Y, -X, Z$.

Table 6. Selected Bond Lengths (Å), Angles (deg), and Torsion Angles (deg) of Tis(4-methylbenzoylthio)phosphine **5d**

| | | | |
|---|---|---|---|
| | Bond lengths | | |
| P1–S1 | 2.142(5) | C1–S1 | 1.79(2) |
| P1–O1 | 2.82(1) | C1–O1 | 1.22(2) |
| | Angles | | |
| S1–P1–O1 | 61.6(3) | P1–S1–C1 | 96.0(5) |
| S1–C1–O1 | 119.3(10) | P1–O1–C1 | 82.8(8) |
| S1–P1–S1* | 95.4(2) | | |
| | Torsion angles | | |
| S1–C1–C2–C7 | 2(2) | S1–P1–S1*–C1* | 89.2(7) |

*) $-Y, X-Y, Z$.

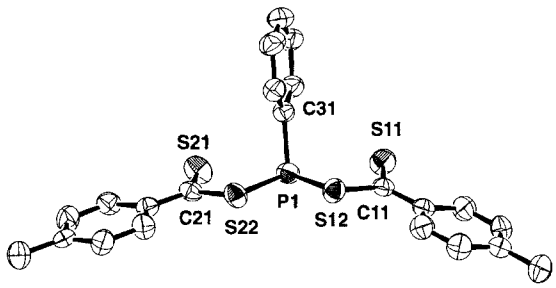



Fig. 4. An ORTEP drawing of $(4\text{-}CH_3C_6H_4CS_2)_2PPh$ **7b**.

Table 7. Selected Bond Lengths (Å), Angles (deg), and Torsion Angles (deg) of Bis(4-methylthiobenzoylthio)-phenylphosphine **7b**

| | | | |
|---|---|---|---|
| | Bond lengths | | |
| P1–S11 | 2.965(3) | P1–S21 | 2.975(3) |
| P1–S12 | 2.170(3) | P1–S22 | 2.158(2) |
| C11–S11 | 1.630(6) | C21–S21 | 1.634(6) |
| C11–S12 | 1.761(6) | C21–S22 | 1.740(6) |
| P1–C31 | 1.836(7) | | |
| | Angles | | |
| S11–P1–S21 | 138.11(8) | S12–P1–S22 | 86.20(9) |
| S11–P1–S12 | 67.73(7) | S21–P1–S22 | 67.45(7) |
| S11–C11–S12 | 120.0(4) | S21–C21–S22 | 120.5(3) |
| P1–S11–C11 | 73.6(2) | P1–S21–C21 | 73.5(2) |
| P1–S12–C11 | 96.8(2) | P1–S22–C21 | 98.3(2) |
| S12–P1–C31 | 101.6(2) | S22–P1–C31 | 101.0(2) |
| | Torsion angles | | |
| S12–P1–S22–C21 | 173.7(2) | | |
| S12–C11–C12–C17 | 2.5(8) | S22–C21–C22–C27 | 3.5(8) |
| C11–S12–P1–C31 | 100.6(3) | C21–S22–P1–C31 | 85.2(3) |

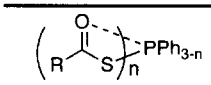
*ipso*-carbon bonds are nearly at right angles to one another, and the structure of **7b** is similar to those of **3d**, **4d**, and **5d**.

**Structural Comparison of Mono-, Bis-, and Tris(arenecarbonylthio)phosphine:** Selected bond lengths and torsion angles of **3d**, **4d**, and **5d** are shown in Tables 8 and 9, respectively. The C–O, C–S, and P–S bond lengths are nearly the same. On the other hand, the distance between the carbonyl oxygen and the phosphorus atoms decrease in the order mono **3d**, tris **5d**, and bis **4d**. Presumably, the greater distance in **3d** may be due to weak interaction, i.e. the interaction of the P–C $\sigma^*$ orbital with the lone-pair electron on the carbonyl oxygen is longer than that of the P–S $\sigma^*$ orbital. The interaction between the carbonyl oxygen and the phosphorus atoms would take an important role in the planarity of the thiocarboxylate moieties with the phosphorus atoms.

**Spectra:** The spectroscopic data of $(RCOS)_nPPh_{3-n}$ (**3**: $n = 1$, **4**: $n = 2$, **5**: $n = 3$) are shown in Table 10. The $\nu_{C=O}$ bands of **3**—**5** appear at about 1690 $cm^{-1}$ for aliphatic derivatives (R = $CH_3$, *t*-$C_4H_9$) and at 1630—1670 $cm^{-1}$ for aromatic derivatives, which is comparable to the corresponding *S*-alkyl esters. The $^{13}C{=}O$ chemical shifts of **3**—**5** appear at $\delta = 188.6\pm1.3$ for aromatic derivatives and $\delta = 198.3\pm5.8$ for aliphatic derivatives, and the coupling constants [$^2J$(CP)] are about 14 Hz. The $^{31}P$ NMR spectra are observed at $\delta$ = 10—14 for **3**, $\delta$ = 25—35 for **4**, and about $\delta$ = 50 for **5**, which indicates a downfield shift with an increase in the number of thiocarboxylato ligands bonded to the phosphorus atom.

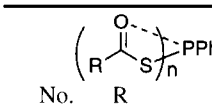
The spectroscopic data of $(RCS_2)_nPPh_{3-n}$ (**6**: $n = 1$, **7**: $n = 2$, **8**: $n = 3$) are tabulated in Table 11. The thiocarbonyl stretching frequencies of **6** appear at 1200—1250 $cm^{-1}$, and that for 2,4,6-trimethylphenyl derivative **6f** is about 30 $cm^{-1}$ lower than those of other aromatic derivatives **6a**—**e**. Those of bis **7** and tris derivatives **8** appear at 1230—1260 $cm^{-1}$.

Table 8. Selected Bond Distances of Mono-, Bis-, and Tris(acylthio)phosphines **3**—**5**




| No. | R | *n* | Bond/Å C–O | C–S | P···O | P–S |
|---|---|---|---|---|---|---|
| **3d** | 4-$CH_3C_6H_4$ | 1 | 1.207(4) | 1.802(4) | 2.917(3) | 2.136(1) |
| **4d** | 4-$CH_3C_6H_4$ | 2 | 1.211(5) | 1.785(5) | 2.784(3) | 2.146(2) |
| | | | 1.214(5) | 1.788(4) | 2.747(3) | 2.144(2) |
| **5d** | 4-$CH_3C_6H_4$ | 3 | 1.22(2) | 1.79(2) | 2.82(1) | 2.142(5) |

Table 9. Selected Torsion Angles of Mono-, Bis-, and Tris(acylthio)phosphines **3**—**5**




| No. | R | *n* | Torsion angles/deg | |
|---|---|---|---|---|
| **3d** | 4-$CH_3C_6H_4$ | 1 | O11–C11–S11–P1 | 14.6(3) |
| **4d** | 4-$CH_3C_6H_4$ | 2 | O11–C11–S11–P1 | 9.2(4) |
| | | | O21–C21–S21–P1 | 11.2(4) |
| **5d** | 4-$CH_3C_6H_4$ | 3 | O11–C11–S11–P1 | 6(1) |

Table 10. Spectroscopic Data of Mono-, Bis-, and Tris(acylthio)phosphines **3**—**5**

| No. | $(RCOS)_nPPh_{3-n}$ R | *n* | IR/$cm^{-1}$ $\nu_{C=O}$ | NMR/$\delta$[c] $^{13}C{=}O$ | $^{31}P$[d] | $^2J_{13C-31P}$/Hz |
|---|---|---|---|---|---|---|
| **3a** | $CH_3$ | 1 | 1694[a] | 193.9 | 14.2 | 15 |
| **3b** | *t*-$C_4H_9$ | 1 | 1682[a] | 198.7 | 10.3 | 15 |
| **3c** | $C_6H_5$ | 1 | 1652[a] | 189.8 | 13.0 | 13 |
| **3d** | 4-$CH_3C_6H_4$ | 1 | 1652[b] | 189.8 | 12.3 | 12 |
| **3e** | 2-$CH_3OC_6H_4$ | 1 | 1630[b] | 189.2 | 11.1 | 12 |
| **3f** | 4-$CH_3OC_6H_4$ | 1 | 1652[a] | 188.3 | 12.3 | 13 |
| **3g** | 4-$ClC_6H_4$ | 1 | 1657[b] | 189.3 | 14.0 | 12 |
| **4a** | $CH_3$ | 2 | 1703[a] | 193.1 | 34.8 | 14 |
| **4b** | *t*-$C_4H_9$ | 2 | 1694[a] | 204.1 | 28.0 | 12 |
| **4c** | $C_6H_5$ | 2 | 1655[b] | 189.8 | 24.5 | 14 |
| **4d** | 4-$CH_3C_6H_4$ | 2 | 1643[b] | 189.3 | 29.3 | 14 |
| **4e** | 2-$CH_3OC_6H_4$ | 2 | 1629[b] | 188.8 | 24.6 | 13 |
| **4f** | 4-$CH_3OC_6H_4$ | 2 | 1654[b] | 188.1 | 29.2 | 14 |
| **4g** | 4-$ClC_6H_4$ | 2 | 1658[b] | 188.6 | 32.0 | 14 |
| **5a** | $CH_3$ | 3 | 1694[a] | 192.5 | 55.1 | 17 |
| **5b** | *t*-$C_4H_9$ | 3 | 1680[a] | 203.6 | 52.3 | 14 |
| **5c** | $C_6H_5$ | 3 | 1648[b] | 189.2 | 51.6 | 16 |
| **5d** | 4-$CH_3C_6H_4$ | 3 | 1647[b] | 188.8 | 51.4 | 16 |
| **5e** | 2-$CH_3OC_6H_4$ | 3 | 1620[b] | 188.6 | 44.7 | 14 |
| **5f** | 4-$CH_3OC_6H_4$ | 3 | 1659[b] | 187.3 | 51.8 | 16 |
| **5g** | 4-$ClC_6H_4$ | 3 | 1677[b] | 188.0 | 52.2 | 17 |

a) Neat. b) KBr. c) NMR spectra recorded in $CDCl_3$. d) Standard in $H_3PO_4$.

The $^{13}C{=}S$ chemical shifts appear in the narrow region $\delta$ = 223—227, excluding the 2,4,6-trimethylphenyl derivatives **6f**, **7f**, and **8f** (about $\delta$ = 237). Steric hindrance of the mesityl group would reduce $\pi$ conjugation between the aromatic ring and C=S moiety, resulting in downfield shift of $^{13}C{=}S$ chemical shifts. On the other hand, the $^{31}P$ NMR spectra are observed at about $\delta$ = 20 for **6**, $\delta$ = 9—15 for **7**, and about $\delta = -4$ for **8**, which indicate upfield shifts with an increase in the number of dithiocarboxylato ligands bonded to the phosphorus atom. The spectroscopic data of the (4-methylbenzoylthio)phosphines **3d**, **4d**, and **5d** are shown in Table 12. The $\nu_{C=O}$ bands show high wavenumber shifts in the order **4d**, **5d**, and **3d**. In X-ray structural analyses, the C=O double bond lengths are nearly the same, while the distances between the carbonyl oxygen and the phosphorus atoms follow this same order. Therefore, a high wavenumber shift of the $\nu_{C=O}$ may be related to interaction between the carbonyl oxygen and the phosphorus atoms. The $^{13}C{=}O$ chemical shifts show upfield shifts in the order **3d**, **4d**, and **5d**. On the other hand, the $^{31}P$ NMR chemical shifts show downfield shifts in the order **3d**, **4d**, and **5d**, which may be due to the electron-withdrawing effect of the thiocarboxylato ligands. In the dithiocarboxylate derivatives, the $\nu_{C=S}$ bands show high wavenumber shifts in the order **6b**, **7b**, and **8b**. However, the $^{13}C{=}S$ chemical shifts show downfield shifts and the $^{31}P$ NMR chemical shifts show upfield shifts in the order **6b**, **7b**, and **8b**, which are opposite to the trends seen with the corresponding thiocarboxylic acid derivatives. Presumably, the electron on the dithiocarboxylate groups

Table 11. Spectroscopic Data of Mono-, Bis-, and Tris(thioacylthio)phosphines **6**—**8**

| No. | $(RCS_2)_nPPh_{3-n}$ | | IR/$cm^{-1}$ a) | NMR/$\delta$ c) | | |
|---|---|---|---|---|---|---|
| | R | $n$ | $\nu_{C=S}$ | $^{13}C{=}S$ | $^{31}P$ d) | $^2J_{13C-31P}$/Hz |
| **6a** | $C_6H_5$ | 1 | 1222 | 225.7 | 21.3 | 21 |
| **6b** | 4-$CH_3C_6H_4$ | 1 | 1231 | 225.5 | 20.2 | 20 |
| **6c** | 2-$CH_3OC_6H_4$ | 1 | 1252 b) | 222.7 | 22.1 | 17 |
| **6d** | 4-$CH_3OC_6H_4$ | 1 | 1241 | 223.5 | 19.4 | 19 |
| **6e** | 4-$ClC_6H_4$ | 1 | 1242 | 224.2 | 22.8 | 21 |
| **6f** | 2,4,6-$(CH_3)_3C_6H_2$ | 1 | 1195 | 236.3 | 22.0 | 19 |
| **7a** | $C_6H_5$ | 2 | 1239 b) | 226.9 | 12.5 | 23 |
| **7b** | 4-$CH_3C_6H_4$ | 2 | 1244 | 226.3 | 11.0 | 22 |
| **7c** | 2-$CH_3OC_6H_4$ | 2 | 1250 | 227.9 | 14.9 | 24 |
| **7d** | 4-$CH_3OC_6H_4$ | 2 | 1249 | 224.2 | 8.73 | 24 |
| **7f** | 2,4,6-$(CH_3)_3C_6H_2$ | 2 | 1261 | 236.5 | 12.7 | 22 |
| **8b** | 4-$CH_3C_6H_4$ | 3 | 1251 | 227.6 | −3.99 | 25 |
| **8e** | 4-$ClC_6H_4$ | 3 | 1231 | 227.0 | −3.46 | 26 |
| **8f** | 2,4,6-$(CH_3)_3C_6H_2$ | 3 | 1243 | 238.9 | −3.96 | 25 |

a) KBr. b) Neat. c) NMR spectra recorded in $CDCl_3$. d) Standard in $H_3PO_4$.

Table 12. Selected Feature in Spectra of 4-Methylbenzoylthio- and 4-Methyl(thiobenzoylthio)phosphine Derivatives

| No. | $(RCES)_nPPh_{3-n}$ | | | IR/$cm^{-1}$ a) | NMR/$\delta$ b) | | |
|---|---|---|---|---|---|---|---|
| | R | E | $n$ | $\nu_{C=E}$ | $^{13}C{=}E$ | $^{31}P$ c) | $^2J_{13C-31P}$/Hz |
| **3d** | 4-$CH_3C_6H_4$ | O | 1 | 1652 | 189.8 | 12.3 | 12 |
| **4d** | | O | 2 | 1643 | 189.3 | 29.3 | 14 |
| **5d** | | O | 3 | 1647 | 188.8 | 51.4 | 16 |
| **6b** | | S | 1 | 1231 | 225.5 | 20.2 | 20 |
| **7b** | | S | 2 | 1244 | 226.3 | 11.0 | 22 |
| **8b** | | S | 3 | 1251 | 227.6 | −3.99 | 25 |

a) KBr. b) NMR spectra recorded in $CDCl_3$. c) Standard in $H_3PO_4$.

may be backdonated through the thiocarbonyl sulfur atoms.

## Conclusion

A series of thio- and dithiocarboxylatophosphorus derivatives were synthesized and their X-ray structural analyses were obtained. The crystal structures of these compounds show intramolecular-nonbonding interactions between the carbonyl oxygen or thiocarbonyl sulfur and the central phosphorus atoms. However, these intramolecular interactions are weak, and the covalent phosphorus–sulfur and/or phosphorus–benzene *ipso*-carbon bonds are nearly at right angles to one another, forming essentially distorted tetrahedral structures with the unshared electron pair orbital at the apex. In the bis-derivatives $[(RCES)_2PPh$, E = O, S], the two thio- and dithiocarboxylato ligands exist in the same plane with the same orientation, where each carbonyl oxygen or thiocarbonyl sulfur atom is located in the same direction.

## Experimental

Melting points were determined by a Yanagimoto micromelting point apparatus and are uncorrected. The IR spectra were measured on a Perkin–Elmer FT-IR 1640 spectrophotometer. The $^1H$ NMR spectra were recorded on a JEOL JNM-$\alpha$400 (400 MHz); the following abbreviations were used; s: singlet, d: doublet, t: triplet, m: multiplet. The $^{13}C$ NMR were recorded on a JEOL JNM-$\alpha$400 (100 MHz). The $^{31}P$ NMR were recorded on a JEOL JNM-$\alpha$400 (162 MHz) with phosphoric acid as an external standard. Elemental analyses were performed by the Elemental Analysis Center of Kyoto University.

**Materials.** The following solvents were purified under argon and dried as indicated: Diethyl ether and hexane were refluxed with sodium metal using benzophenone as an indicator and distilled before use: Dichloromethane was distilled over diphosphorus pentaoxide, after refluxing for 4 h. Chlorodiphenylphosphine, dichlorophenylphosphine, and tribromophosphine/dichloromethane (1.0 M solution, 1 M = 1 mol $dm^{-3}$) were obtained from Aldrich.

**X-Ray Structure Analysis.** Measurements were carried out on a Rigaku AFC7R four-circle diffractometer with graphite-monochromated Mo$K\alpha$ radiation ($\lambda$ = 0.71069 Å). All the structures were solved and refined using the teXsan® crystallographic software package on an IRIS Indigo computer. Crystal samples were cut from grown crystals and mounted on a glass fiber. Since (4-methylbenzoylthio)diphenylphosphine (**3d**), bis(4-methylbenzoylthio)phenylphosphine (**4d**), tris(4-methylbenzoylthio)phosphine (**5d**), and bis(4-methylthiobenzoylthio)phenylphosphine (**7b**) were unstable in air, the crystals of **3d**, **4d**, **5d**, and **7b** were coated with an epoxy resin. The cell dimensions were determined from a least-squares refinement of the setting diffractometer angles for 25 automatically centered reflections. Three standard reflections were measured every 150 reflections and showed no significant intensity variations during data collection. Lorentz and polarization corrections were applied to the data, and empirical absorption corrections [DIFABS[5] (**4d** and **7b**) and $\Psi$-scans[6] (**3d** and **5d**)] were also applied. The structures were solved by a di-

rect method using SHELXS86[7] for **3d**, **4d**, **7b**, and **5d** and expanded using DIRDIF94.[8] Scattering factors for neutral atoms were obtained from Cromer and Waber[9] and anomalous dispersion[10] was used. The function minimized was $\sum w(|F_{obs}|-|F_{calc}|)^2$, and the weighting scheme used was $w=[\sigma^2(F_o)+p^2(F_o)^2/4]^{-1}$ for **3d**, **4d**, and **7b**, while $[\sum w(|F_{obs}|-|F_{calc}|)^2/(N_o-N_v)]^{1/2}$ and $[\sigma^2(F_o)+(0.1000P)^2+0.0000P]^{-1}$, $P=(F_o^2+2F_c^2)/3$ were used for **5d**. A full-matrix least-squares refinement was executed, with non-hydrogen atoms being anisotropic for **3d**, **4d**, and **7b**, and using SHELXL93 for **5d**.[11] The final least-square cycle included fixed hydrogen atoms at calculated positions, for which each isotropic thermal parameter was set to 1.2 times that of the connecting atom. Crystal data and a description of the measurement are summarized in Table 3.

**Preparation of Single Crystals.** (4-Methylbenzoylthio)diphenylphosphine (**3d**) (0.090 g) was single-crystallized from dichloromethane (1.0 mL) and hexane (1.0 mL) at 25 °C for 5 d. Bis(4-methylbenzoylthio)phenylphosphine (**4d**) (0.150 g) was single-crystallized from dichloromethane (1.2 mL) and hexane (1.0 mL) at 25 °C for 1 week. Tris(4-methylbenzoylthio)phosphine (**5d**) (0.109 g) was single-crystallized from dichloromethane (3.0 mL) and hexane (4.0 mL) at 25 °C for 1 week. Bis(4-methylthiobenzoylthio)phenylphosphine (**7b**) (0.065 g) was single-crystallized from dichloromethane (0.5 mL) and hexane (0.6 mL) at 25 °C for 4 d.

**Acetylthiodiphenylphosphine (3a).** To a solution of chlorodiphenylphosphine (0.225 g, 1.02 mmol) in ether (10 mL), sodium thioacetate (0.114 g, 1.16 mmol) was added. The mixture was stirred at 20 °C for 1 h. The insoluble parts (NaCl) were filtered off by glass filter (G4) in vacuo. The solvents were removed under reduced pressure (23 °C/53 Pa) to give acetylthiodiphenylphosphine (**3a**) as colorless oil (0.199 g, 74%). $^1$H NMR ($CDCl_3$) $\delta$ = 2.42 (s, 3H, $CH_3$), 7.30—7.32 (m, 6H), 7.47—7.50 (m, 4H). $^{13}$C NMR ($CDCl_3$) $\delta$ = 32.1 ($CH_3$), 128.4 ($^3J_{13C-31P}$ = 6.8 Hz), 129.4, 132.8 ($^2J_{13C-31P}$ = 21 Hz), 135.5 ($^1J_{13C-31P}$ = 24 Hz), 193.9 ($^2J_{13C-31P}$ = 14 Hz, C=O).

**(2,2-Dimethylpropionylthio)diphenylphosphine (3b).** As with **3a**, the reaction of chlorodiphenylphosphine (0.220 g, 1.00 mmol) with sodium 2,2-dimethylthiopropionate (0.150 g, 1.07 mmol) gave (2,2-dimethylpropionylthio)diphenylphosphine (**3b**) as colorless oil (0.226 g, 75%). $^1$H NMR ($CDCl_3$) $\delta$ = 1.16 (s, 9H, $CH_3$), 7.19—7.21 (m, 6H), 7.37—7.41 (m, 4H). $^{13}$C NMR ($CDCl_3$) $\delta$ = 26.4 ($CH_3$), 47.4 [$C(CH_3)$], 128.3 ($^3J_{13C-31P}$ = 6.8 Hz), 129.3, 132.7 ($^2J_{13C-31P}$ = 21 Hz), 135.8 ($^1J_{13C-31P}$ = 24 Hz), 198.7 ($^2J_{13C-31P}$ = 15 Hz, C=O).

**Benzoylthiodiphenylphosphine (3c).** As with **3d**, the reaction of chlorodiphenylphosphine (0.226 g, 1.02 mmol) with potassium thiobenzoate (0.185 g, 1.06 mmol) gave benzoylthiodiphenylphosphine (**3c**) as yellow oil (0.312 g, 95%). $^1$H NMR ($CDCl_3$) $\delta$ = 7.28—7.39 (m, 9H), 7.55—7.59 (m, 4H), 7.97—7.99 (m, 2H). $^{13}$C NMR ($CDCl_3$) $\delta$ = 127.9, 128.1, 128.4 ($^3J_{13C-31P}$ = 5.9 Hz), 129.4, 132.8 ($^2J_{13C-31P}$ = 22 Hz), 135.4 ($^1J_{13C-31P}$ = 24 Hz), 134.2, 136.7, 189.8 ($^2J_{13C-31P}$ = 13 Hz, C=O).

**(4-Methylbenzoylthio)diphenylphosphine (3d).** To a solution of chlorodiphenylphosphine (0.221 g, 1.00 mmol) in ether (10 mL) was added potassium 4-methylthiobenzoate (0.198 g, 1.04 mmol), and the mixture was stirred at 20 °C for 1 h. The insoluble parts (KCl) were filtered off by glass filter (G4) in vacuo. The solvents were removed under reduced pressure (23 °C/53 Pa). Dichloromethane (0.5 mL), ether (1.0 mL), and then hexane (1.3 mL) were added and this mixture was allowed to stand at −20 °C for 24 h. Filtration of the resulting crystals gave (4-methylbenzoylthio)diphenylphosphine (**3d**) as colorless crystals (0.312 g, 93%). $^1$H NMR ($CDCl_3$) $\delta$ = 2.31 (s, 3H, $CH_3$), 7.15 (d, $J$ = 8.2 Hz, 2H), 7.27—7.29 (m, 6H), 7.48—7.52 (m, 4H), 7.86 (d, $J$ = 8.2 Hz, 2H). $^{13}$C NMR ($CDCl_3$) $\delta$ = 21.7 ($CH_3$), 128.3, 128.6 ($^3J_{13C-31P}$ = 6.8 Hz), 129.3, 129.6, 130.8, 133.1 ($^2J_{13C-31P}$ = 21 Hz), 135.8 ($^1J_{13C-31P}$ = 24 Hz), 144.7, 189.8 ($^2J_{13C-31P}$ = 12 Hz, C=O). Found: C, 71.46; H, 5.11%. Calcd for $C_{20}H_{17}OPS$: C, 71.41; H, 5.09%.

**(2-Methoxybenzoylthio)diphenylphosphine (3e).** As with **3d**, the reaction of chlorodiphenylphosphine (0.223 g, 1.01 mmol) with potassium 2-methoxythiobenzoate (0.210 g, 1.02 mmol), followed by recrystallization from a mixed solvent of dichloromethane (1.0 mL), ether (0.5 mL), and then hexane (2.0 mL) gave (2-methoxybenzoylthio)diphenylphosphine (**3e**) as colorless crystals (0.282 g, 80%). $^1$H NMR ($CDCl_3$) $\delta$ = 3.88 (s, 3H, $CH_3O$), 6.87—6.91 (m, 2H), 7.26—7.28 (m, 6H), 7.48—7.52 (m, 4H), 7.62—7.67 (m, 1H), 7.73—7.75 (m, 1H). $^{13}$C NMR ($CDCl_3$) $\delta$ = 55.8 ($CH_3O$), 112.1, 120.4, 126.9, 128.5 ($^3J_{13C-31P}$ = 6.8 Hz), 129.4, 130.4, 133.2 ($^2J_{13C-31P}$ = 21 Hz), 134.1, 136.0 ($^1J_{13C-31P}$ = 24 Hz), 158.2, 189.2 ($^2J_{13C-31P}$ = 12 Hz, C=O). Found: C, 68.20; H, 4.92%. Calcd for $C_{20}H_{17}O_2PS$: C, 68.17; H, 4.86%.

**(4-Methoxybenzoylthio)diphenylphosphine (3f).** As with **3d**, the reaction of chlorodiphenylphosphine (0.228 g, 1.03 mmol) with potassium 4-methoxythiobenzoate (0.218 g, 1.06 mmol) gave (4-methoxybenzoylthio)diphenylphosphine (**3f**) as yellow oil (0.337 g, 93%). $^1$H NMR ($CDCl_3$) $\delta$ = 3.80 (s, 3H, $CH_3O$), 6.90 (d, $J$ = 8.8 Hz, 2H), 7.35—7.37 (m, 6H), 7.60—7.64 (m, 4H), 8.04 (d, $J$ = 8.8 Hz, 2H). $^{13}$C NMR ($CDCl_3$) $\delta$ = 55.4 ($CH_3O$), 113.6, 128.4 ($^3J_{13C-31P}$ = 6.8 Hz), 129.4, 130.3, 131.5, 132.9 ($^2J_{13C-31P}$ = 22 Hz), 135.7 ($^1J_{13C-31P}$ = 24 Hz), 163.9, 188.3 ($^2J_{13C-31P}$ = 13 Hz, C=O).

**(4-Chlorobenzoylthio)diphenylphosphine (3g).** As with **3d**, the reaction of chlorodiphenylphosphine (0.224 g, 1.02 mmol) with potassium 4-chlorothiobenzoate (0.244 g, 1.06 mmol), followed by recrystallization from a mixed solvent of dichloromethane (1.0 mL), ether (1.0 mL), and then hexane (2.0 mL) gave (4-chlorobenzoylthio)diphenylphosphine (**3g**) as colorless crystals (0.329 g, 90%). $^1$H NMR ($CDCl_3$) $\delta$ = 7.29—7.36 (m, 8H), 7.48—7.52 (m, 4H), 7.97—7.99 (m, 2H); $^{13}$C NMR ($CDCl_3$) $\delta$ = 128.7 ($^3J_{13C-31P}$ = 6.8 Hz), 129.0, 129.6, 129.8, 132.7, 133.1 ($^2J_{13C-31P}$ = 21 Hz), 135.4 ($^1J_{13C-31P}$ = 24 Hz), 140.2, 189.3 ($^2J_{13C-31P}$ = 12 Hz, C=O). Found: C, 64.01; H, 4.02%. Calcd for $C_{19}H_{14}ClOPS$: C, 63.96; H, 3.95%.

**Bis(acetylthio)phenylphosphine (4a).** To a solution of dichlorophenylphosphine (0.180 g, 1.01 mmol) in dichloromethane (10 mL) was added sodium thioacetate (0.201 g, 2.05 mmol), and the mixture was stirred at 20 °C for 1 h. The insoluble parts (NaCl) were filtered off by glass filter (G4) in vacuo. The solvents were removed under reduced pressure (23 °C/53 Pa) to give bis(acetylthio)phenylphosphine (**4a**) as pale yellow oil (0.203 g, 74%). $^1$H NMR ($CDCl_3$) $\delta$ = 2.29 (s, 6H, $CH_3$), 7.20—7.77 (m, 5H). $^{13}$C NMR ($CDCl_3$) $\delta$ = 31.9 ($CH_3$), 128.2, 128.6, 130.5, 132.1 ($^1J_{13C-31P}$ = 24 Hz), 193.1 ($^2J_{13C-31P}$ = 14 Hz, C=O).

**Bis(2,2-dimethylpropionylthio)phenylphosphine (4b).** As with **4a**, the reaction of dichlorophenylphosphine (0.185 g, 1.03 mmol) with sodium 2,2-dimethylthiopropionate (0.295 g, 2.10 mmol) gave bis(2,2-dimethylpropionylthio)phenylphosphine (**4b**) as colorless oil (0.251 g, 75%). $^1$H NMR ($CDCl_3$) $\delta$ = 1.13 (s, 18H, $CH_3$), 7.24—7.90 (m, 5H). $^{13}$C NMR ($CDCl_3$) $\delta$ = 27.2 ($CH_3$), 47.6 [$C(CH_3)$], 128.1, 128.4, 130.3, 132.2 ($^1J_{13C-31P}$ = 25 Hz), 204.1 ($^2J_{13C-31P}$ = 12 Hz, C=O).

**Bis(benzoylthio)phenylphosphine (4c).** As with **4d**, the reaction of dichlorophenylphosphine (0.200 g, 1.12 mmol) with potassium thiobenzoate (0.403 g, 2.30 mmol), followed by recrystallization from a mixed solvent of dichloromethane (1.0 mL) and then hexane (2.0 mL), gave bis(benzoylthio)phenylphosphine

(**4c**) as colorless crystals (0.423 g, 99%). $^1$H NMR ($CDCl_3$) $\delta$ = 7.41—7.48 (m, 6H), 7.56—7.62 (m, 3H), 7.89—7.93 (m, 2H), 7.98—8.01 (m, 4H). $^{13}$C NMR ($CDCl_3$) $\delta$ = 127.9, 128.3, 128.7, 128.8, 130.8, 132.7 ($^1J_{13C-31P}$ = 25 Hz), 134.0, 136.6, 189.8 ($^2J_{13C-31P}$ = 14 Hz, C=O). Found: C, 62.93; H, 4.06%. Calcd for $C_{20}H_{15}O_2PS_2$: C, 62.81; H, 3.95%.

**Bis(4-methylbenzoylthio)phenylphosphine (4d).** To a solution of dichlorophenylphosphine (0.187 g, 1.04 mmol) in dichloromethane (10 mL) was added potassium 4-methylthiobenzoate (0.409 g, 2.15 mmol), and the mixture was stirred at 20 °C for 1 h. The insoluble parts (KCl) were filtered off by glass filter (G4) in vacuo. The solvents were removed under reduced pressure (23 °C/53 Pa). Dichloromethane (1.0 mL) and then hexane (2.0 mL) were added and this mixture was allowed to stand at −20 °C for 24 h. Filtration of the resulting crystals gave bis(4-methylbenzoylthio)phenylphosphine (**4d**) as colorless crystals (0.376 g, 88%). $^1$H NMR ($CDCl_3$) $\delta$ = 2.39 (s, 6H, $CH_3$), 7.23 (d, $J$ = 8.2 Hz, 4H), 7.40—7.42 (m, 3H), 7.87—7.89 (m, 2H), 7.89 (d, $J$ = 8.2 Hz, 4H). $^{13}$C NMR ($CDCl_3$) $\delta$ = 21.7 ($CH_3$), 128.4, 128.6, 128.7, 129.4, 130.6, 132.7 ($^1J_{13C-31P}$ = 24 Hz), 134.1, 145.1, 189.3 ($^2J_{13C-31P}$ = 14 Hz, C=O). Found: C, 64.09; H, 5.14%. Calcd for $C_{22}H_{19}O_2PS_2$: C, 64.37; H, 4.67%.

**Bis(2-methoxybenzoylthio)phenylphosphine (4e).** As with **4d**, the reaction of dichlorophenylphosphine (0.180 g, 1.01 mmol) with potassium 2-methoxythiobenzoate (0.426 g, 2.06 mmol), followed by recrystallization from a mixed solvent of dichloromethane (1.5 mL) and then hexane (3.0 mL), gave bis(2-methoxybenzoylthio)phenylphosphine (**4e**) as colorless crystals (0.434 g, 97%). $^1$H NMR ($CDCl_3$) $\delta$ = 3.90 (s, 6H, $CH_3O$), 6.95—7.03 (m, 8H), 7.36—7.38 (m, 3H), 7.85—7.90 (m, 2H). $^{13}$C NMR ($CDCl_3$) $\delta$ = 55.8 ($CH_3O$), 112.1, 120.4, 128.5, 128.6, 130.0, 130.2, 130.5, 132.7 ($^1J_{13C-31P}$ = 24 Hz), 134.5, 158.6, 188.8 ($^2J_{13C-31P}$ = 13 Hz, C=O). Found: C, 59.58; H, 4.82%. Calcd for $C_{22}H_{19}O_4PS_2$: C, 59.72; H, 4.33%.

**Bis(4-methoxybenzoylthio)phenylphosphine (4f).** As with **4d**, the reaction of dichlorophenylphosphine (0.356 g, 1.99 mmol) with potassium 4-methoxythiobenzoate (0.826 g, 4.00 mmol), followed by recrystallization from a mixed solvent of dichloromethane (1.0 mL) and then hexane (1.0 mL), gave bis(4-methoxybenzoylthio)phenylphosphine (**4f**) as pale yellow crystals (0.871 g, 99%). $^1$H NMR ($CDCl_3$) $\delta$ = 3.84 (s, 6H, $CH_3O$), 6.90 (d, $J$ = 8.7 Hz, 4H), 7.39—7.41 (m, 3H), 7.85—7.90 (m, 2H), 7.97 (d, $J$ = 8.7 Hz, 4H). $^{13}$C NMR ($CDCl_3$) $\delta$ = 55.6 ($CH_3O$), 113.9, 128.6, 128.7, 130.2, 130.5, 130.6, 132.6 ($^1J_{13C-31P}$ = 25 Hz), 164.3, 188.1 ($^2J_{13C-31P}$ = 14 Hz, C=O). Found: C, 59.62; H, 4.83%. Calcd for $C_{22}H_{19}O_4PS_2$: C, 59.72; H, 4.33%.

**Bis(4-chlorobenzoylthio)phenylphosphine (4g).** As with **4d**, the reaction of dichlorophenylphosphine (0.173 g, 0.97 mmol) with potassium 4-chlorothiobenzoate (0.410 g, 1.95 mmol), followed by recrystallization from a mixed solvent of dichloromethane (2.0 mL) and then hexane (2.0 mL), gave bis(4-chlorobenzoylthio)phenylphosphine (**4g**) as colorless crystals (0.381 g, 87%). $^1$H NMR ($CDCl_3$) $\delta$ = 7.42 (d, $J$ = 8.8 Hz, 4H), 7.42—7.44 (m, 3H), 7.88—7.92 (m, 2H), 7.94 (d, $J$ = 8.8 Hz, 4H). $^{13}$C NMR ($CDCl_3$) $\delta$ = 128.8, 128.9, 129.1, 129.6, 131.0, 132.8 ($^1J_{13C-31P}$ = 25 Hz), 134.9, 140.7, 188.6 ($^2J_{13C-31P}$ = 14 Hz, C=O). Found: C, 53.02; H, 3.36%. Calcd for $C_{20}H_{13}Cl_2O_2PS_2$: C, 53.22; H, 2.90%.

**Tris(acetylthio)phosphine (5a).** To a suspension of sodium thioacetate (0.272 g, 2.77 mmol) in dichloromethane (10 mL) was added tribromophosphine/dichloromethane 1.0 M solution (0.8 mL, 0.80 mmol), and the mixture was stirred at 20 °C for 1 h. The insoluble parts (NaBr) were filtered off by glass filter (G4) in vacuo. The solvents were removed under reduced pressure (23 °C/53 Pa) to give tris(acetylthio)phosphine (**5a**) as yellow oil (0.168 g, 82%). $^1$H NMR ($CDCl_3$) $\delta$ = 2.29 (s, 9H, $CH_3$). $^{13}$C NMR ($CDCl_3$) $\delta$ = 32.0 ($CH_3$), 192.5 ($^2J_{13C-31P}$ = 17 Hz, C=O).

**Tris(2,2-dimethylpropionylthio)phosphine (5b).** As with **5a**, the reaction of tribromophosphine/dichloromethane 1.0 M solution (0.8 mL, 0.80 mmol) with sodium 2,2-dimethylthiopropionate (0.420 g, 3.00 mmol) gave tris(2,2-dimethylpropionylthio)phosphine (**5b**) as yellow oil (0.250 g, 82%). $^1$H NMR ($CDCl_3$) $\delta$ = 1.19 (s, 27H, $CH_3$). $^{13}$C NMR ($CDCl_3$) $\delta$ = 27.2 ($CH_3$), 47.9 [$C(CH_3)$], 203.6 ($^2J_{13C-31P}$ = 14 Hz, C=O).

**Tris(benzoylthio)phosphine (5c).** As with **5d**, the reaction of tribromophosphine/dichloromethane 1.0 M solution (0.8 mL, 0.80 mmol) with potassium thiobenzoate (0.530 g, 3.02 mmol), followed by recrystallization from a mixed solvent of dichloromethane (2.0 mL) and then hexane (2.0 mL), gave tris(benzoylthio)phosphine (**5c**) as colorless crystals (0.320 g, 91%). $^1$H NMR ($CDCl_3$) $\delta$ = 7.46 (t, $J$ = 7.4 Hz, 6H), 7.60 (t, $J$ = 7.4 Hz, 3H), 8.00 (d, $J$ = 7.4 Hz, 6H). $^{13}$C NMR ($CDCl_3$) $\delta$ = 128.4, 128.8, 134.3, 136.2, 189.2 ($^2J_{13C-31P}$ = 16 Hz, C=O). Found: C, 57.08; H, 3.57%. Calcd for $C_{21}H_{15}O_3PS_3$: C, 57.00; H, 3.42%.

**Tris(4-methylbenzoylthio)phosphine (5d).** To a suspension of potassium 4-methylthiobenzoate (0.574 g, 3.02 mmol) in dichloromethane (10 mL) was added tribromophosphine/dichloromethane 1.0 M solution (0.8 mL, 0.80 mmol), and the mixture was stirred at 20 °C for 1 h. The insoluble parts (KBr) were filtered off by glass filter (G4) in vacuo. The solvents were removed under reduced pressure (23 °C/53 Pa). Dichloromethane (6.0 mL) and then hexane (4.0 mL) were added and this mixture was allowed to stand at −20 °C for 24 h. Filtration of the resulting crystals gave tris(4-methylbenzoylthio)phosphine (**5d**) as colorless crystals (0.299 g, 77%). $^1$H NMR ($CDCl_3$) $\delta$ = 2.39 (s, 9H, $CH_3$), 7.22 (d, $J$ = 8.2 Hz, 6H), 7.87 (d, $J$ = 8.2 Hz, 6H). $^{13}$C NMR ($CDCl_3$) $\delta$ = 21.8 ($CH_3$), 128.4, 129.4, 133.7, 145.4, 188.8 ($^2J_{13C-31P}$ = 16 Hz, C=O). Found: C, 59.52; H, 4.40%. Calcd for $C_{24}H_{21}O_3PS_3$: C, 59.49; H, 4.37%.

**Tris(2-methoxybenzoylthio)phosphine (5e).** As with **5d**, the reaction of tribromophosphine/dichloromethane 1.0 M solution (0.8 mL, 0.80 mmol) with potassium 2-methoxythiobenzoate (0.609 g, 2.95 mmol), followed by recrystallization from a mixed solvent of dichloromethane (2.0 mL) and then hexane (4.0 mL), gave tris(2-methoxybenzoylthio)phosphine (**5e**) as colorless crystals (0.382 g, 90%). $^1$H NMR ($CDCl_3$) $\delta$ = 3.90 (s, 9H, $CH_3O$), 6.95 (d, $J$ = 7.9 Hz, 3H), 6.97 (t, $J$ = 7.9 Hz, 3H), 7.47 (t, $J$ = 7.9 Hz, 3H), 7.86 (d, $J$ = 7.9 Hz, 3H). $^{13}$C NMR ($CDCl_3$) $\delta$ = 55.8 ($CH_3O$), 112.0, 120.5, 125.6, 130.6, 134.8, 158.9, 188.6 ($^2J_{13C-31P}$ = 14 Hz, C=O). Found: C, 54.29; H, 4.09%. Calcd for $C_{24}H_{21}O_6PS_3$: C, 54.13; H, 3.97%.

**Tris(4-methoxybenzoylthio)phosphine (5f).** As with **5d**, the reaction of tribromophosphine/dichloromethane 1.0 M solution (0.8 mL, 0.80 mmol) with potassium 4-methoxythiobenzoate (0.630 g, 3.05 mmol), followed by recrystallization from a mixed solvent of dichloromethane (2.0 mL) and then hexane (4.0 mL), gave tris(4-methoxybenzoylthio)phosphine (**5f**) as colorless crystals (0.280 g, 66%). $^1$H NMR ($CDCl_3$) $\delta$ = 3.78 (s, 9H, $CH_3O$), 6.84 (d, $J$ = 8.9 Hz, 6H), 7.89 (d, $J$ = 8.9 Hz, 6H). $^{13}$C NMR ($CDCl_3$) $\delta$ = 55.5 ($CH_3O$), 113.8, 128.7, 130.5, 164.3, 187.3 ($^2J_{13C-31P}$ = 16 Hz, C=O). Found: C, 54.25; H, 3.98%. Calcd for $C_{24}H_{21}O_6PS_3$: C, 54.13; H, 3.97%.

**Tris(4-chlorobenzoylthio)phosphine (5g).** As with **5d**, the reaction of tribromophosphine/dichloromethane 1.0 M solution (0.8 mL, 0.80 mmol) with potassium 4-chlorothiobenzoate (0.617 g, 2.93 mmol), followed by recrystallization from a mixed solvent of

dichloromethane (3.0 mL) and then hexane (3.0 mL), gave tris(4-chlorobenzoylthio)phosphine (**5g**) as colorless crystals (0.328 g, 75%). $^1$H NMR ($CDCl_3$) $\delta$ = 7.42 (d, $J$ = 8.5 Hz, 6H), 7.91 (d, $J$ = 8.5 Hz, 6H). $^{13}$C NMR ($CDCl_3$) $\delta$ = 129.2, 129.7, 134.4, 141.1, 188.0 ($^2J_{13C-31P}$ = 17 Hz, C=O). Found: C, 46.38; H, 2.45%. Calcd for $C_{21}H_{12}Cl_3O_3PS_3$: C, 46.21; H, 2.22%.

**Diphenyl(thiobenzoylthio)phosphine (6a).** As with **6b**, the reaction of chlorodiphenylphosphine (0.218 g, 0.99 mmol) with piperidinium dithiobenzoate (0.241 g, 1.01 mmol), followed by recrystallization from a solvent of ether (3.0 mL), gave diphenyl(thiobenzoylthio)phosphine (**6a**) as purple crystals (0.117 g, 35%). $^1$H NMR ($CDCl_3$) $\delta$ = 7.32—8.14 (m, 15H). $^{13}$C NMR ($CDCl_3$) $\delta$ = 127.3, 128.6 ($^3J_{13C-31P}$ = 6.8 Hz), 128.8, 129.5, 129.7, 130.8, 133.2 ($^2J_{13C-31P}$ = 21 Hz), 134.8 ($^1J_{13C-31P}$ = 24 Hz), 225.7 ($^2J_{13C-31P}$ = 21 Hz, C=S). Found: C, 67.47; H, 4.50%. Calcd for $C_{19}H_{15}PS_2$: C, 67.43; H, 4.47%.

**(4-Methylthiobenzoylthio)diphenylphosphine (6b).** To a solution of chlorodiphenylphosphine (0.212 g, 0.96 mmol) in ether (10 mL) was added piperidinium 4-methyldithiobenzoate (0.247 g, 0.98 mmol), and the mixture was stirred at 20 °C for 1 h. The insoluble parts were filtered off by glass filter (G4) in vacuo. The solvents were removed under reduced pressure (23 °C/53 Pa). Ether (1.6 mL) was added and this mixture was allowed to stand at −20 °C for 24 h. Filtration of the resulting crystals gave (4-methylthiobenzoylthio)diphenylphosphine (**6b**) as red crystals (0.318 g, 94%). $^1$H NMR ($CDCl_3$) $\delta$ = 2.35 (s, 3H, $CH_3$), 7.15 (d, $J$ = 8.4 Hz, 2H), 7.33—7.39 (m, 6H), 7.54—7.58 (m, 4H), 8.06 (d, $J$ = 8.4 Hz, 2H). $^{13}$C NMR ($CDCl_3$) $\delta$ = 21.6 ($CH_3$), 127.3, 128.6 ($^3J_{13C-31P}$ = 6.8 Hz), 128.9, 129.7, 133.2 ($^2J_{13C-31P}$ = 21 Hz), 134.8 ($^1J_{13C-31P}$ = 24 Hz), 142.1, 143.9, 225.5 ($^2J_{13C-31P}$ = 20 Hz, C=S). Found: C, 68.20; H, 4.88%. Calcd for $C_{20}H_{17}PS_2$: C, 68.16; H, 4.86%.

**(2-Methoxythiobenzoylthio)diphenylphosphine (6c).** As with **6b**, the reaction of chlorodiphenylphosphine (0.244 g, 1.11 mmol) with piperidinium 2-methoxydithiobenzoate (0.305 g, 1.13 mmol) gave (2-methoxythiobenzoylthio)diphenylphosphine (**6c**) as red oil (0.377 g, 93%). $^1$H NMR ($CDCl_3$) $\delta$ = 3.83 (s, 3H, $CH_3O$), 6.89—6.95 (m, 2H), 7.36—7.94 (m, 12H). $^{13}$C NMR ($CDCl_3$) $\delta$ = 56.0 ($CH_3O$), 111.8, 120.4, 128.4, 128.6 ($^3J_{13C-31P}$ = 6.8 Hz), 129.4, 129.6, 131.8, 133.1 ($^2J_{13C-31P}$ = 21 Hz), 134.8 ($^1J_{13C-31P}$ = 25 Hz), 155.0, 222.7 ($^2J_{13C-31P}$ = 17 Hz, C=S).

**(4-Methoxythiobenzoylthio)diphenylphosphine (6d).** As with **6b**, the reaction of chlorodiphenylphosphine (0.106 g, 0.45 mmol) with sodium 4-methoxydithiobenzoate (0.108 g, 0.52 mmol), followed by recrystallization from a solvent of ether (3.0 mL), gave (4-methoxythiobenzoylthio)diphenylphosphine (**6d**) as vermilion crystals (0.098 g, 61%). $^1$H NMR ($CDCl_3$) $\delta$ = 3.84 (s, 3H, $CH_3O$), 6.83 (d, $J$ = 8.8 Hz, 2H), 7.36—7.38 (m, 6H), 7.50—7.56 (m, 4H), 8.20 (d, $J$ = 8.8 Hz, 2H). $^{13}$C NMR ($CDCl_3$) $\delta$ = 55.6 ($CH_3O$), 113.4, 128.6 ($^3J_{13C-31P}$ = 6.4 Hz), 129.6, 129.7, 131.9, 133.2 ($^2J_{13C-31P}$ = 21 Hz), 134.9, 164.0, 223.5 ($^2J_{13C-31P}$ = 19 Hz, C=S). Found: C, 65.44; H, 4.74%. Calcd for $C_{20}H_{17}OPS_2$: C, 65.20; H, 4.65%.

**(4-Chlorothiobenzoylthio)diphenylphosphine (6e).** As with **6b**, the reaction of chlorodiphenylphosphine (0.213 g, 0.97 mmol) with piperidinium 4-chlorodithiobenzoate (0.268 g, 0.98 mmol), followed by recrystallization from a solvent of ether (2.0 mL), gave (4-chlorothiobenzoylthio)diphenylphosphine (**6e**) as red crystals (0.090 g, 25%). $^1$H NMR ($CDCl_3$) $\delta$ = 7.32—7.55 (m, 12H). $^{13}$C NMR ($CDCl_3$) $\delta$ = 128.1, 128.5, 128.6 ($^3J_{13C-31P}$ = 6.8 Hz), 129.7, 133.2 ($^2J_{13C-31P}$ = 21 Hz), 134.8 ($^1J_{13C-31P}$ = 25 Hz), 139.0, 141.6, 224.2 ($^2J_{13C-31P}$ = 21 Hz, C=S). Found: C, 61.24; H, 3.81%. Calcd for $C_{19}H_{14}ClPS_2$: C, 61.21; H, 3.78%.

**(2, 4, 6- Trimethylthiobenzoylthio)diphenylphosphine (6f).** As with **6b**, the reaction of chlorodiphenylphosphine (0.123 g, 0.56 mmol) with sodium 2,4,6-trimethyldithiobenzoate (0.131 g, 0.60 mmol), followed by recrystallization from a solvent of ether (2.0 mL), gave (2,4,6-trimethylthiobenzoylthio)diphenylphosphine (**6f**) as pink crystals (0.114 g, 54%). $^1$H NMR ($CDCl_3$) $\delta$ = 2.24 (s, 3H, $CH_3$), 2.25 (s, 6H, $CH_3$), 6.82 (s, 2H), 7.34—7.39 (m, 6H), 7.66—7.73 (m, 4H). $^{13}$C NMR ($CDCl_3$) $\delta$ = 19.3 ($CH_3$), 21.1 ($CH_3$), 128.5, 128.7 ($^3J_{13C-31P}$ = 6.4 Hz), 129.9, 130.8, 132.2, 133.2 ($^2J_{13C-31P}$ = 21 Hz), 138.0, 144.9, 236.3 ($^2J_{13C-31P}$ = 19 Hz, C=S). Found: C, 69.72; H, 5.58%. Calcd for $C_{22}H_{21}PS_2$: C, 69.45; H, 5.56%.

**Phenylbis(thiobenzoylthio)phosphine (7a).** As with **7b**, the reaction of dichlorophenylphosphine (0.065 mL, 0.48 mmol) with sodium dithiobenzoate (0.180 g, 1.02 mmol) gave phenylbis(thiobenzoylthio)phosphine (**7a**) as reddish purple oil (0.142 g, 71%). $^1$H NMR ($CDCl_3$) $\delta$ = 7.40—7.43 (m, 6H), 7.55—7.64 (m, 3H), 7.92—7.97 (m, 2H), 8.15—8.17 (m, 4H). $^{13}$C NMR ($CDCl_3$) $\delta$ = 127.0, 128.4 ($^3J_{13C-31P}$ = 6.8 Hz), 128.8, 129.1, 130.5, 133.3 ($^1J_{13C-31P}$ = 21 Hz), 133.7, 143.7, 226.9 ($^2J_{13C-31P}$ = 23 Hz, C=S).

**Bis(4-methylthiobenzoylthio)phenylphosphine (7b).** To a solution of dichlorophenylphosphine (0.070 mL, 0.52 mmol) in dichloromethane (10 mL) was added sodium 4-methyldithiobenzoate (0.247 g, 1.31 mmol), and the mixture was stirred at 20 °C for 1 h. The insoluble parts (NaCl) were filtered off by glass filter (G4) in vacuo. The solvents were removed under reduced pressure (23 °C/53 Pa). Dichloromethane (6.0 mL) and then hexane (5.0 mL) were added and this mixture was allowed to stand at −20 °C for 24 h. Filtration of the resulting crystals gave bis(4-methylthiobenzoylthio)phenylphosphine (**7b**) as red crystals (0.079 g, 36%). $^1$H NMR ($CDCl_3$) $\delta$ = 2.36 (s, 6H, $CH_3$), 7.16 (d, $J$ = 8.2 Hz, 4H), 7.36—7.38 (m, 3H), 7.86—7.90 (m, 2H), 8.04 (d, $J$ = 8.2 Hz, 4H). $^{13}$C NMR ($CDCl_3$) $\delta$ = 21.6 ($CH_3$), 127.1, 127.2, 128.4 ($^3J_{13C-31P}$ = 6.8 Hz), 129.1, 130.4, 133.7 ($^1J_{13C-31P}$ = 20 Hz), 141.4, 144.5, 226.3 ($^2J_{13C-31P}$ = 22 Hz, C=S). Found: C, 59.92; H, 4.47%. Calcd for $C_{22}H_{19}PS_4$: C, 59.70; H, 4.33%.

**Bis(2-methoxythiobenzoylthio)phenylphosphine (7c).** As with **7b**, the reaction of dichlorophenylphosphine (0.070 mL, 0.52 mmol) with sodium 2-methoxydithiobenzoate (0.213 g, 1.04 mmol), followed by recrystallization from a mixed solvent of dichloromethane (3.0 mL) and then hexane (2.0 mL), gave bis(2-methoxythiobenzoylthio)phenylphosphine (**7c**) as red crystals (0.046 g, 19%). $^1$H NMR ($CDCl_3$) $\delta$ = 3.86 (s, 6H, $CH_3O$), 6.90—6.94 (m, 8H), 7.37—7.42 (m, 3H), 7.78—7.85 (m, 2H). $^{13}$C NMR ($CDCl_3$) $\delta$ = 55.9 ($CH_3O$), 112.0, 120.6, 128.6, 128.8 ($^3J_{13C-31P}$ = 6.8 Hz), 130.1, 130.5, 132.7, 133.3 ($^1J_{13C-31P}$ = 22 Hz), 135.6, 155.7, 227.9 ($^2J_{13C-31P}$ = 24 Hz, C=S). Found: C, 55.69; H, 4.09%. Calcd for $C_{22}H_{19}O_2PS_4$: C, 55.68; H, 4.03%.

**Bis(4-methoxythiobenzoylthio)phenylphosphine (7d).** As with **7b**, the reaction of dichlorophenylphosphine (0.100 mL, 0.74 mmol) with sodium 4-methoxydithiobenzoate (0.331 g, 1.60 mmol), followed by recrystallization from a mixed solvent of dichloromethane (3.0 mL) and then hexane (1.0 mL), gave bis(4-methoxythiobenzoylthio)phenylphosphine (**7d**) as red crystals (0.038 g, 11%). $^1$H NMR ($CDCl_3$) $\delta$ = 3.84 (s, 6H, $CH_3O$), 6.83 (d, $J$ = 7.6 Hz, 4H), 7.35—7.36 (m, 3H), 7.87—7.90 (m, 2H), 8.17 (d, $J$ = 7.6 Hz, 4H). $^{13}$C NMR ($CDCl_3$) $\delta$ = 55.6 ($CH_3O$), 113.5, 128.3 ($^3J_{13C-31P}$ = 6.3 Hz), 129.4, 129.5, 130.3, 133.7 ($^1J_{13C-31P}$ = 21 Hz), 137.2, 164.4, 224.2 ($^2J_{13C-31P}$ = 24 Hz, C=S). Found: C, 55.74; H, 4.06%. Calcd for $C_{22}H_{19}O_2PS_4$: C, 55.68; H, 4.03%.

**Bis(2, 4, 6- trimethylthiobenzoylthio)phenylphosphine (7f).** As with **7b**, the reaction of dichlorophenylphosphine (0.060 mL, 0.44 mmol) with sodium 2,4,6-trimethyldithiobenzoate (0.216 g,

0.99 mmol), followed by recrystallization from a mixed solvent of dichloromethane (2.0 mL) and then hexane (1.0 mL), gave bis-(2,4,6-trimethylthiobenzoylthio)phenylphosphine (**7f**) as vermilion crystals (0.192 g, 44%). $^1$H NMR ($CDCl_3$) $\delta$ = 2.23 (s, 6H, $CH_3$), 2.27 (s, 12H, $CH_3$), 6.85 (s, 4H), 7.38—7.41 (m, 3H), 7.78—7.85 (m, 2H). $^{13}$C NMR ($CDCl_3$) $\delta$ = 19.2 ($CH_3$), 21.1 ($CH_3$), 128.5, 128.6, 130.9, 132.0, 132.5, 133.7 ($^1J_{13C-31P}$ = 21 Hz), 138.4, 144.1, 236.5 ($^2J_{13C-31P}$ = 22 Hz, C=S). Found: C, 62.79; H, 5.51%. Calcd for $C_{26}H_{27}PS_4$: C, 62.62; H, 5.46%.

**Tris(4-methylthiobenzoylthio)phosphine (8b).** To a suspension of sodium 4-methyldithiobenzoate (0.202 g, 1.06 mmol) in dichloromethane (10 mL) was added tribromophosphine/dichloromethane 1.0 M solution (0.3 mL, 0.30 mmol), and the mixture was stirred at 20 °C for 1 h. The insoluble parts (NaBr) were filtered off by glass filter (G4) in vacuo. The solvents were removed under reduced pressure (23 °C/53 Pa). Dichloromethane (2.0 mL) and then hexane (3.0 mL) were added and this mixture was allowed to stand at −20 °C for 24 h. Filtration of the resulting crystals gave tris(4-methylthiobenzoylthio)phosphine (**8b**) as red crystals (0.061 g, 38%). $^1$H NMR ($CDCl_3$) $\delta$ = 2.38 (s, 9H, $CH_3$), 7.19 (d, $J$ = 7.3 Hz, 6H), 8.02 (d, $J$ = 7.3 Hz, 6H). $^{13}$C NMR ($CDCl_3$) $\delta$ = 21.8 ($CH_3$), 127.1, 129.3, 134.8, 145.8, 227.6 ($^2J_{13C-31P}$ = 25 Hz, C=S). Found: C, 54.27; H, 3.99%. Calcd for $C_{24}H_{21}PS_6$: C, 54.11; H, 3.97%.

**Tris(4-chlorothiobenzoylthio)phosphine (8e).** As with **8b**, the reaction of tribromophosphine/dichloromethane 1.0 M solution (0.4 mL, 0.40 mmol) with sodium 4-chlorodithiobenzoate (0.320 g, 1.52 mmol), followed by recrystallization from a mixed solvent of dichloromethane (2.0 mL) and then hexane (2.0 mL), gave tris-(4-chlorothiobenzoylthio)phosphine (**8e**) as red crystals (0.125 g, 53%). $^1$H NMR ($CDCl_3$) $\delta$ = 7.41 (d, $J$ = 8.8 Hz, 6H), 8.06 (d, $J$ = 8.8 Hz, 6H). $^{13}$C NMR ($CDCl_3$) $\delta$ = 128.3, 128.8, 140.6, 141.3, 227.0 ($^2J_{13C-31P}$ = 26 Hz, C=S). Found: C, 42.52; H, 2.08%. Calcd for $C_{21}H_{12}Cl_3PS_6$: C, 42.46; H, 2.04%.

**Tris(2,4,6-trimethylthiobenzoylthio)phosphine (8f).** As with **8b**, the reaction of tribromophosphine/dichloromethane 1.0 M solution (0.4 mL, 0.40 mmol) with sodium 2,4,6-trimethyldithiobenzoate (0.325 g, 1.40 mmol), followed by recrystallization from a mixed solvent of dichloromethane (2.0 mL) and then hexane (3.0 mL), gave tris(2,4,6-trimethylthiobenzoylthio)phosphine (**8f**) as vermilion crystals (0.176 g, 71%). $^1$H NMR ($CDCl_3$) $\delta$ = 2.29 (s, 9H, $CH_3$), 2.31 (s, 18H, $CH_3$), 6.88 (s, 6H). $^{13}$C NMR ($CDCl_3$) $\delta$ = 19.4 ($CH_3$), 21.1 ($CH_3$), 128.6, 132.6, 138.8, 143.8, 238.9 ($^2J_{13C-31P}$ = 25 Hz, C=S). Found: C, 58.51; H, 5.44%. Calcd for $C_{30}H_{33}PS_6$: C, 58.41; H, 5.39%.

This research was supported by a Grant-in-Aid for Scientific Research on Priority Areas No. 09239220 and by a Grant-in-Aid for Scientific Research No. 09355032 from the Ministry of Education, Science, Sports and Culture. We thank Prof. Takashi Kawamura and Associate Prof. Masahiro Ebihara of Gifu University for their invaluable assistance with X-ray crystallography.

## References

1 a) R. W. Light, L. D. Hutchins, R. T. Paine, and C. F. Campana, *Inorg. Chem.*, **19**, 3597 (1980). b) I. A. Litvinov, M. B. Zuev, O. N. Kataeva, and V. A. Naumov, *Zh. Obshch. Khim.*, **61**, 1017 (1991) (Engl. Trans.). c) V. A. Al'fonsov, I. A. Litvinov, O. N. Kataeva, D. A. Pudovik, and S. A. Katsyuba, *Rus. J. Gen. Chem.*, **65**, 1029 (1995).

2 a) S. Kato, M. Goto, R. Hattori, K. Nishiwaki, M. Mizuta, and M. Ishida, *Chem. Ber.*, **118**, 1668 (1985). b) S. Min, H. Ishihara, T. Murai, and S. Kato, *Z. Naturforsch., B*, **44b**, 153 (1989).

3 A. F. Wells, "Structural Inorganic Chemistry," 4th ed, Clarendon Press, Oxford, England (1975).

4 A. Bondi, *J. Phys. Chem.*, **68**, 441 (1964).

5 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, **A39**, 158 (1983).

6 G. M. Sheldrick, "Crystallographic Computing 3," ed by G. M. Sheldrick, C. Kruger, and R. Goddard, Oxford University Press, Oxford (1985), pp. 175—189.

7 A. C. T. North, D. C. Phillips, and F. S. Mathews, *Acta Crystallogr., Sect. A*, **A24**, 351 (1968).

8 The DIRDIF-94 program system was used: P. T. Beukskens, G. Admiraal, G. Beurskiens, W. P. Bosman, R.de Gelder, R. Israel, and J. M. M. Smits, "Technical Report of the Crystallography Laboratory," University of Nijmegen, The Netherlands (1994).

9 D. T. Cromer and J. T. Waber, "International Tables for X-Ray Crystallography," The Kynoch Press, Birmingham, England (1974), Vol. IV, Table 2.2A.

10 D. C. Creagh and W. J. Mcauley, "International Tables for X-Ray Crystallography," ed by A. J. C. Wilson and K. Creagh, Academic Publishers, Boston (1992), Vol. C, Table 4.2.6.8, pp. 219—222.

11 G. M. Sheldrick, "Program for the Refinement of Crystal Structure," University of Goettingen, Germany (1993).